UNCLASSIFIED

ORNL-2366 cy. 4
Technology-Raw Materials

PROGRESS REPORT ON RAW MATERIALS

FOR MAY, 1957

K. B. Brown
C. F. Coleman
D. J. Crouse
A. D. Ryon

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide and Carbon Corporation
UCC
POST OFFICE BOX X · OAK RIDGE, TENNESSEE

UNCLASSIFIED

Printed in USA, Price 25 cents. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

Report Number: ORNL-2366

Contract No. W-7405, eng 26

CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT ON RAW MATERIALS

FOR MAY, 1957

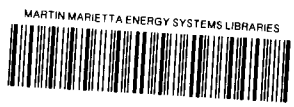
Chemical Development Section C
K. B. Brown, Section Chief

K. B. Brown
C. F. Coleman
D. J. Crouse
A. D. Ryon

DATE ISSUED

SEP 4 1957

OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box X
Oak Ridge, Tennessee



INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-26. Laboratory Records Department
27. Laboratory Records, ORNL R.C.
28. A. M. Weinberg
29. L. B. Emlet (K-25)
30. J. P. Murray (Y-12)
31. J. A. Swartout
32. E. H. Taylor
33. E. D. Shipley
34-35. F. L. Culler
36. M. L. Nelson
37. W. H. Jordan
38. C. P. Keim
39. J. H. Frye, Jr.
40. S. C. Lind
41. A. H. Snell
42. A. Hollaender
43. K. Z. Morgan
44. M. T. Kelley
45. T. A. Lincoln
46. R. S. Livingston
47. A. S. Householder
48. C. S. Harrill
49. C. E. Winters
50. D. W. Cardwell
51. D. Phillips
52. W. K. Eister
53. F. R. Bruce
54. D. E. Ferguson
55. R. B. Lindauer
56. H. E. Goeller
57. R. A. Charpie
58. J. A. Lane
59. M. J. Skinner
60. R. E. Blanco
61. G. E. Boyd
62. W. E. Unger
63. R. R. Dickison
64. A. T. Gresky
65. E. D. Arnold
66. C. E. Guthrie
67. J. W. Ullmann
68. K. B. Brown
69. K. O. Johnsson
70. H. M. McLeod
71. C. W. Hancher
72. J. C. Bresee
73. J. S. Drury
74. K. A. Allen
75. W. D. Arnold
76. C. F. Baes
77. C. A. Blake
78. C. F. Coleman
79. D. J. Crouse
80. F. L. Daley
81. D. E. Horner
82. F. J. Hurst
83. J. X. Khym
84. B. B. Klima
85. R. S. Lowrie
86. W. J. McDowell
87. J. G. Moore
88. J. M. Schmitt
89. F. G. Seeley
90. A. D. Ryon
91. J. C. White
92. W. W. Weinrich (consultant)
93. M. D. Peterson (consultant)
94. G. T. Seaborg (consultant)
95. M. Benedict (consultant)
96. D. L. Katz (consultant)
97. C. E. Larson (consultant)
98. L. Squires (consultant)
99. J. H. Rushton (consultant)
100. ORNL - Y-12 Technical Library, Document Reference Section

EXTERNAL DISTRIBUTION

101. R. F. Bacher, California Institute of Technology
102. John Breitenstein, National Lead Company, Inc., Winchester
103. E. C. Van Blarcom, Division of Raw Materials, Washington
104. Division of Research and Development, AEC, ORO
105-596. Given distribution as shown in TID-4500 (13th ed.) under Technology-Raw Materials category (100 copies - OTS)

CONTENTS

		Page
1.0	Systematic Studies	4
2.0	Process Development Studies	22
3.0	Engineering Studies	27

All studies reported here are preliminary and conclusions are subject to change. The information is published as a formal report only to permit ready dissemination of data to interested persons.

OTHER REPORTS IN THIS SERIES

Preliminary,	ORNL-2268	(20¢)
February,	ORNL-2269	(25¢)
March,	ORNL-2306	(25¢)
April,	ORNL-2346	(25¢)

ABSTRACT

Systematic Studies. A mixed n-octyl-n-decyl tertiary amine, commercially available in development quantities, appeared promising for process use. Its uranium extraction power was similar to that of tri-n-octylamine, and loss by distribution to a sulfate liquor was lower. A corresponding secondary amine was similar in extraction behavior to di-n-decylamine, but loss by distribution was higher.

Screening tests of uranium extraction power from dilute acid test solutions are summarized for various organophosphorus compounds, with principal attention to dialkylphosphinic acids, monoalkylphosphonic acids, and some polymeric compounds. Unusually high uranium extraction power was shown by an α-hydroxy phosphinic acid, phenyl(1-hydroxy-2-ethylhexyl)phosphinic acid.

Uranium(IV) was extracted strongly from dilute acidic sulfate solution by a primary and a secondary amine, but not by a tertiary amine. It was extracted more strongly than uranium(VI) from hydrochloric acid solutions by di(2-ethylhexyl)phosphoric acid (D2EHPA). In contrast to uranium(VI), uranium(IV) extraction by D2EHPA was enhanced little if any by the presence of TBP.

Process Development. In tests with tri-iso-octylamine, a number of diluent additives were tested for ability to prevent separation of amine heteropolymolybdate precipitates from the usual kerosene-alcohol diluent during the chloride stripping cycle. Addition of nitrobenzene at 100 g/liter was effective for this purpose. In other tests, several of the molybdenum precipitates were separated and analyzed for amine, molybdenum, phosphate, and vanadium content.

The amount of molybdenum reporting to uranium products from the Dapex process varied with the method and conditions by which uranium was precipitated from the sodium carbonate strip solution.

Direct caustic precipitation of the uranium gave products essentially free of molybdenum although filtration characteristics of the precipitate were poor. When the uranium was recovered by first acidifying with sulfuric acid and then precipitating with ammonia, most of the molybdenum remained in the product even when an excess of ammonia was used. Recovery by acidification and precipitation with caustic resulted in better molybdenum decontamination, particularly when an appreciable excess of caustic was added.

Engineering Studies. The rate of uranium extraction from a synthetic sulfuric acid leach liquor by a Dapex-type organic was proportional to the cube root of power input and was slightly faster in a 12-in. than in a 6-in. mixer at the same power input per unit volume. At a given power input the rate increased with decreased turbine diameter. Location of the turbine at one diameter from the bottom of the mixer tank provided only slightly faster extraction than at a center location.

1.0 SYSTEMATIC STUDIES

In addition to the studies described below, systematic studies during the month have included (1) preliminary study and preparation of laboratory facilities for examining the applicability of amine and organophosphorus extractants to separations in fuel reprocessing and waste disposal, (2) testing of new alkyl dialkylphosphonates as uranium extractants and as synergistic components in Dapex extraction, (3) preparation and purification of long-chain monoalkylphosphoric acids, (4) measurement of solubility loss rates of amines and of monoalkylphosphates, and (5) re-evaluation of the quantitative determination of primary, secondary, and tertiary amines by differential titration.

1.1 Examination of Mixed Alkyl Amines (J. G. Moore)

A tertiary amine prepared from a mixture of straight-chain alkyls, principally octyl and decyl,* was tested in the expectation that it should be similar to tri-n-octylamine but with decreased aqueous solubility. It showed good uranium extraction power in preliminary tests from acidic sulfate solutions and very low loss by distribution to the aqueous phase, warranting interest in further testing for process use.

A sample of secondary amine prepared from the same alkyl mixture was also tested, mainly because it is likely to be representative of a minor contaminant in the tertiary amine (Table 1.1). It was not expected to be of particular interest for process use, since the straight-chain secondaries have been less versatile than tertiaries or branched secondaries, and in addition it was found to be lost to aqueous solution at a fairly high rate.

---

*Supplied by General Mills, Inc., Chemical Division, Kankakee, Ill.

Table 1.1 Assay of Mixed Octyl-Decyl Amines

Amine	Neutral Equivalent		Differential Analysis, %		
	Theo.[a]	Found	Vendor[b]	ORNL[c]	
RC-3749 (tertiary)	392	387	0.8	3	Primary
			8.3	12	Secondary
			87.5	85	Tertiary
			(~3)		(Inert)
RC-3748 (secondary)	255	253	2.0	4	Primary
			97.0	95	Secondary
			1.0	1	Tertiary

[a]Theoretical neutral equivalent for pure secondary or pure tertiary amine at 55/45 octyl/decyl mole ratio.

[b]Analytical method not stated.

[c]Mole % of the titratable base content only, by the differential titration method described in ORNL-1922, p. 85.

The alkyl mixture from which these amines were prepared was reported to contain n-octyl and n-decyl at a ratio of approximately 55/45, plus possibly a small amount of lauryl (n-dodecyl). The equivalent weights found (Table 1.1) were close to the theoretical calculated on the basis of a 55/45 mole ratio, and the purities found with respect to amine class were close to those reported by the vendor. The analytical method used by the vendor was not stated. The method used in this laboratory was the differential titration described in ORNL-1922, p. 85. (Since the method of preparation of these amines and the possible presence of basic compounds other than simple amines was not reported, the fractions of primary, secondary, and tertiary amine shown in Table 1.1 might actually contain some other constituents.)

Both amines extracted uranium well from 1 M sulfate solution at pH ~1. The extractions varied with choice of diluent in the same way as was previously found with the symmetrical secondary and tertiary n-octyl, n-decyl, and lauryl amines (Table 1.2; cf. ORNL-2269, p. 7, and references cited there). The sulfate-bisulfate salts of the mixed secondary amine formed a third phase when used in unmodified kerosene. The salts of the mixed tertiary appeared to be close to the miscibility limit, since a third phase separated from the unmodified kerosene in some tests, but not in others, when contacted with dilute sulfate solution at pH near 1. This is similar to the behavior of tri-n-octylamine (ORNL-1922, p. 35).

The extractions after prewashing of the benzene solutions (last column of Table 1.2) indicated little loss of the mixed tertiary amine to the aqueous phase but considerable loss of the mixed secondary amine. This was confirmed by direct measurement

Table 1.2 Uranium Extraction by Mixed Octyl-Decyl Amines

Initial aqueous composition: 0.004 M U(VI), 1 M SO_4, pH 0.9; extraction at room temperature; phase ratio 1/1.

Amine Concn. M	U Extracted, % of initial, and U E_o^a									
	Kerosene		Kerosene--Tricecanol		Chloroform		Benzene		Benzene Prewashed[a]	
	%	E	%	E	%	E	%	E	%	E
RC-3749										
0.1 M	98	40	98[b]	60[b]	82	5	99	130	99	75
0.01 M	35	--	--	--	5	-	45	-	47	--
Tri-n-octyl-amine										
0.1 M	30[d]	--	--	--	76[e]	3[e]	99[e]	110[e]	99[e]	95[e]
0.01 M	--	--	--	--	5[e]	-	40[e]	-	43[e]	--
RC-3748										
0.1 M	[f]		95[c]	20[c]	99	130	92	12	39	0.6
0.01 M		[f]	--	--	39	-	42	--	14	--

[a] Reagent adjusted to stated concentration and then scrubbed with a dilute sulfate solution. A resulting decrease of uranium extraction power indicates significant loss of reagent to the aqueous phase.

[b] 97% kerosene--3% tridecanol.

[c] 95% kerosene--5% tridecanol.

[d] From ORNL-1734, p. 27.

[e] From ORNL-1734, p. 14.

[f] Third phase formed on contact with the acidic sulfate solution.

of the losses to a synthetic sulfate leach liquor containing, in g/liter, 5.8 Fe(III), 3.3 Al, 50 SO_4, 2 PO_4, and 1.7 F at pH 0.9 (cf. ORNL-2269 p. 12, -2306 p. 6). The mixed tertiary amine, RC-3749, 0.1 M in 97% kerosene--3% tridecanol, showed no rapid initial loss* and a steady-state loss of less than 5 mg per liter of aqueous solution. Since the corresponding loss rate of tri-

*Many amine samples have been found to show rapid loss of certain fraction of titratable base to the first relatively small volume of aqueous solution contacted, which is usually ascribed to components of significantly lower molecular weight than the principal component.

n-octylamine was about 10 mg/liter (ORNL-2099 p. 42), the incorporation of 45% decyl amine appears to have improved the aqueous insolubility significantly. It is noteworthy that the loss rate was <5 mg/liter at the lowest a/o phase ratio tested (100/1) as well as at the highest (500/1, where the total loss amounted to ~20%) instead of showing some loss at first at a rate closer to that of tri-n-octylamine, as might have been expected from a mixture.

Loss of the mixed secondary amine RC-3748, 0.1 M in 95% kerosene--5% tridecanol, was fairly high and there was a change in loss rate at "steady-state": ~15% rapid initial loss; average ~55 mg per liter of aqueous up to a/o = 200/1, where the total loss amounted to ~55%; and average ~25 mg per liter of aqueous from a/o = 200/1 to 400/1, where the total loss amounted to ~75%.

Availability. The mixed n-octyl-n-decyl tertiary amine is reported* to be immediately available in preliminary development quantities at $2.00 per pound, with semicommercial quantities, competitively priced, to be available in September or October, and commercial quantities available thereafter.

1.2 Examination of Organophosphorus Compounds for Uranium Extraction Ability (C. A. Blake, D. E. Horner, J. M. Schmitt)

In the course of the systematic study of uranium solvent extraction during the last several years, compounds of a wide range of types were tested for uranium extraction power. Extraction was measured from dilute acidic sulfate, phosphate, and nitrate solutions (in contrast to highly salted nitrate solutions) as an approximation to potential effectiveness for extraction from ore leach liquors and possibly other process liquors. Such initial "screening" tests results for many of the compounds were reported in ORNL-1220, -1308, -1384, and -1480, and the results for some compounds most recently tested were reported in ORNL-2269.

The results obtained with a number of other organophosphorus compounds not reported previously are summarized in the following sections. Some of the compounds were strong uranium extractants but were not studied past the initial screening tests because of doubtful availability (phosphinic acids) or because of instability (phosphoramides). Others were ineffective under the conditions of interest although they might be useful for somewhat different applications. A few compounds, especially a phenyl(α-hydroxyalkyl)phosphinic acid which showed unusually high uranium extraction power, are of interest for further investigation.

Test Conditions. Carbon tetrachloride was used as the diluent in nearly all the following tests, since it has been found to dissolve a great variety of test compounds to a usable extent. Although extraction by some types of reagents is known to be significantly lower in carbon tetrachloride than in hydrocarbon diluents, it is not likely to be so much lower that a promising extractant would fail to be recognized.

*Letter from Owen A. Moe, Manager, Market Development Dept., Chemical Div., General Mills, Inc., to K. B. Brown, May 22, 1957.

Equilibrations were made at room temperature, which varied from 20 to 30°C, with agitation either by hand or by a Burrell wrist-action shaker, for a minimum of 2 min. The phase ratio was 1/1, usually 10 ml each of 0.1 M reagent in CCl_4 and of the aqueous test solution. Uranium was analyzed fluorometrically, in at least the phase containing less uranium, and usually in both phases to provide a check by material balance.

Aqueous solutions were chosen so as to represent various types of potential process liquors, involving varying degrees of ease of extraction, and most of the compounds were tested with one or more of the following solutions:

Anion	M	pH
NO_3	0.1	1-2
SO_4	0.5-1.5	1
PO_4	0.4-1.4	1-2
SO_4 + NO_3	0.5 + 0.3	1
PO_4 + NO_3	0.4 + 0.3	1

The initial uranium concentration was 1 g/liter (~0.004 M) in each.

The purity of the compounds available for testing varied widely, and was often difficult to assess. However, the test results were considered to be useful even when contamination was considerable, on the basis that high extraction power was not likely to be completely hidden by impurities, while extraction due to a contaminant instead of the nominal compound would be recognized on further testing and hence would not be a serious error at this stage.

Phosphinic Acids. The structure of the dialkylphosphinic acids is analogous to that of the dialkylphosphoric acids, differing in having the alkyls attached by carbon-phosphorus bonds instead of through oxygen atoms. The compounds have greater stability toward hydrolysis than the phosphoric acid esters, and were expected to show stronger uranium extraction power by virtue of the effect of the C-P bonds on the basicity of the phosphoryl group. The uranium extraction power was indeed found to be generally greater than the dialkyl (and alkyl-aryl-) phosphinic acids than with the dialkylphosphoric acids. At the same time, as suggested by similarities in structure, the variation of extraction power with structure of alkyl groups and with aqueous composition was similar to the variations found with dialkylphosphoric acids (ORNL-1903 and -2172).

Extraction was tested from 0.5 and 1.5 M sulfate solutions, pH 1, and 0.4 and 1.4 M phosphate solutions, pH 1 to 2 (Table 1.3). The phosphinic acids extracted best from dilute

Table 1.3 Acid Assay, Relative Acidity, and Uranium Extraction Power of Phosphinic Acids

Phosphinic Acid	Batch No.	Acid, meq/g Theo.	Acid, meq/g Found	Rel. Acidity "pKa"[b]	U Extraction Coefficient,[c] o/a 0.5 M $SO_4^=$ pH 1	1.5 M $SO_4^=$ pH 1	0.4 M $PO_4^=$ pH 1	1.4 M $PO_4^=$ pH 1.4	1.4 M $PO_4^=$ pH 2
Di-n-butyl	OP-36	5.62	5.56	4.7	75	20	20	0.7	2.5
Di-n-amyl	OP-301	5.45	--	-	--	--	--	0.5	1.5
Di-n-hexyl	OP-32	4.27	4.21	4.8	--	--	--	0.4	2
Di-n-octyl	OP-33	3.45	3.35	5.2	160	20	20	1.0	2
Di-n-decyl	OP-40	2.89	2.77	5.2	80	15	20	0.4	1.5
Di(3,5,5-trimethyl-hexyl)	OP-28	3.14	2.97	5.1	120	--	12	0.4	1.0
Di(2-ethylhexyl)	OP-13	3.45	3.41	5.6	30	5	5	0.2	0.4
Di(β-cyclohexylethyl)	OP-149	3.50	3.49	4.8	ppt	--	ppt	0.6	1.3
Dicyclohexyl	OP-37	4.35	4.35	4.2	ppt	ppt	ppt	ppt	ppt
Di-β-phenylethyl	OP-35	3.65	3.56	3.8	--	--	0.04	0.1	0.2
Di-γ-phenylpropyl	OP-30	3.31	3.28	4.6	300	--	--	0.9	5
Phenyl(2-ethylhexyl)	OP-208[a]	3.94	3.95	5.1	300	15	15	0.5	1.5
Phenyl(1-hydroxy-2-ethylhexyl)	OP-177[a]	3.70	3.75	4.4	--	1000	1000	130	370

[a] Source: Virginia-Carolina Chemical Corp., Richmond, Va. All others prepared at ORNL.

[b] "pKa" is the apparent pH at half-neutralization in 70% ethanol.

[c] Initial uranium concentration ~1 g/liter (0.004 M), 0.1 M phosphoric acid in CCl_4, a/o phase ratio 1/1, room temperature.

sulfate solution, showed a decrease of coefficient when the anionic concentration was raised, extracted better as the pH was raised, and extracted less well from phosphate solutions than from sulfate solutions of the same anionic concentration. The extraction power was somewhat higher with kerosene than with carbon tetrachloride as the diluent in a single set of extractions with 0.06 M di(2-ethylhexyl)phosphinic acid from 0.4 M phosphate solution at pH 1:

Diluent:	Kerosene	n-dodecane	CCl_4	Benzene	$CHCl_3$
E_a^o	5	5	2	2	0.5

This difference is in the same direction, but not so large, as was found with di(2-ethylhexyl)phosphoric acid in extraction from sulfate solution (ORNL-1903 p. 7).

The straight-chain alkyl compounds (Table 1.3) showed little if any systematic variation with change of chain length from four to ten carbons. While the higher extraction by the octyl compound than by the butyl and decyl compounds from 0.5 M sulfate might indicate a maximum at an intermediate chain length, it is more likely to be fortuitous, possibly the effect of a contaminant.

Three of the compounds provide a comparison of alkyl branching. The extractions by bis(3,5,5-trimethylhexyl)phosphinic acid, with branching no closer than the third carbon atom, were only slightly lower than those by the straight-chain compounds (lower than octyl but higher than butyl or decyl from the 0.5 M sulfate solution). In contrast, the extractions by di(2-ethylhexyl)phosphinic acid were lower by a factor of about 4. The bis(β-cyclohexylethyl)phosphinic acid was tested to see whether the restricted movement of the branches at the second carbon (i.e., by being closed into a ring) would decrease the effect of branching and increase the extraction. The extraction coefficients obtained from the 1.4 M phosphate solutions appear to bear this out, being close to those obtained with the straight chain compounds. This compound precipitated uranium from the 0.5 M sulfate and 0.4 M phosphate solutions, and dicyclohexylphosphinic acid precipitated it from all five test solutions.

Extraction by di(β-phenylethyl)phosphinic acid was low, perhaps because of direct effects of the phenyl groups attached to the second carbons, or perhaps because of increased aqueous solubility (not measured) due to the short chains and aromatic nature. Di(2-phenylpropyl)phosphinic acid gave higher extractions than the straight-chain compounds.

Extraction by one of the two unsymmetrical alkyl-arylphosphinic acids examined (i.e., compounds with a phenyl group directly bonded to the phosphorus atom), phenyl(2-ethylhexyl)-phosphinic acid, was about the same as with the straight-chain compounds. In contrast, the extraction power was several orders of magnitude higher with phenyl(1-hydroxy-2-ethylhexyl)phosphinic

acid, which differs from the preceding compound only by the α-hydroxy group on the alkyl. This compound has the highest uranium extraction power yet observed in this laboratory with a monofunctional organophosphorus compound (that is, excluding the pyro- and polyphosphoric acid esters and some of the synergistic extractant combinations). Extraction from 30% P_2O_5 phosphoric acid (Table 1.4) was high enough to raise interest in the possibility that extraction could be further enhanced by means of some additive or some variation in structure, or possibly by incorporation into a resin. The extraction could not be increased by increasing the reagent concentration in these tests, since the solubility is limited to about 0.1 M in toluene and in carbon tetrachloride. It is somewhat higher in benzene (at least 0.2 M), but lower in the aromatic mineral spirits Amsco D-95 and Solvesso 100, and it is essentially insoluble in kerosene. The only other α-hydroxy phosphinic acid so far obtained, di(α-hydroxy-n-heptyl)phosphinic acid, was too insoluble in either carbon tetrachloride or kerosene to be tested. The α-hydroxy group may contribute to the low solubility (e.g., through increased hydrogen bonding between molecules) as well as to the extraction power; this possibility increases the interest in its possible use in a resin where solubility would not be a limitation.

Table 1.4 Uranium Extraction from Phosphoric Acid with 0.1 M Phenyl(1-hydroxy-2-ethylhexyl)phosphinic Acid

Initial uranium concentration: 0.1 g/liter (0.0004 M)
Phase ratio, o/a: 2/1
Room temperature

H_3PO_4 Concentration			U E_a^o	
M	% P_2O_5	Diluent	U(IV)	U(VI)
3.3	21	CCl_4	10	16
		Toluene	6	8
5.3	30	Toluene	-	0.75

The phosphinic acids tested were appreciably weaker acids* than the corresponding dialkylphosphoric acids, as well as considerable stronger uranium extractants. As with the dialkylphosphoric acids, the uranium extraction power within the group of phosphinic acids decreased as the acid strength decreased (Fig. 1.1). There is considerable scatter, but only the β-phenylethyl compound was far out of line, with higher acidity and lower extraction power. The curves included in Fig. 1.1 represent the previously reported results with dialkylphosphoric acid (in

*Relative acidities in 70% ethanol solution as indicated by "pKa", the apparent pH at half neutralization measured by glass electrode in that medium, the lower pKa values corresponding to higher acidity.

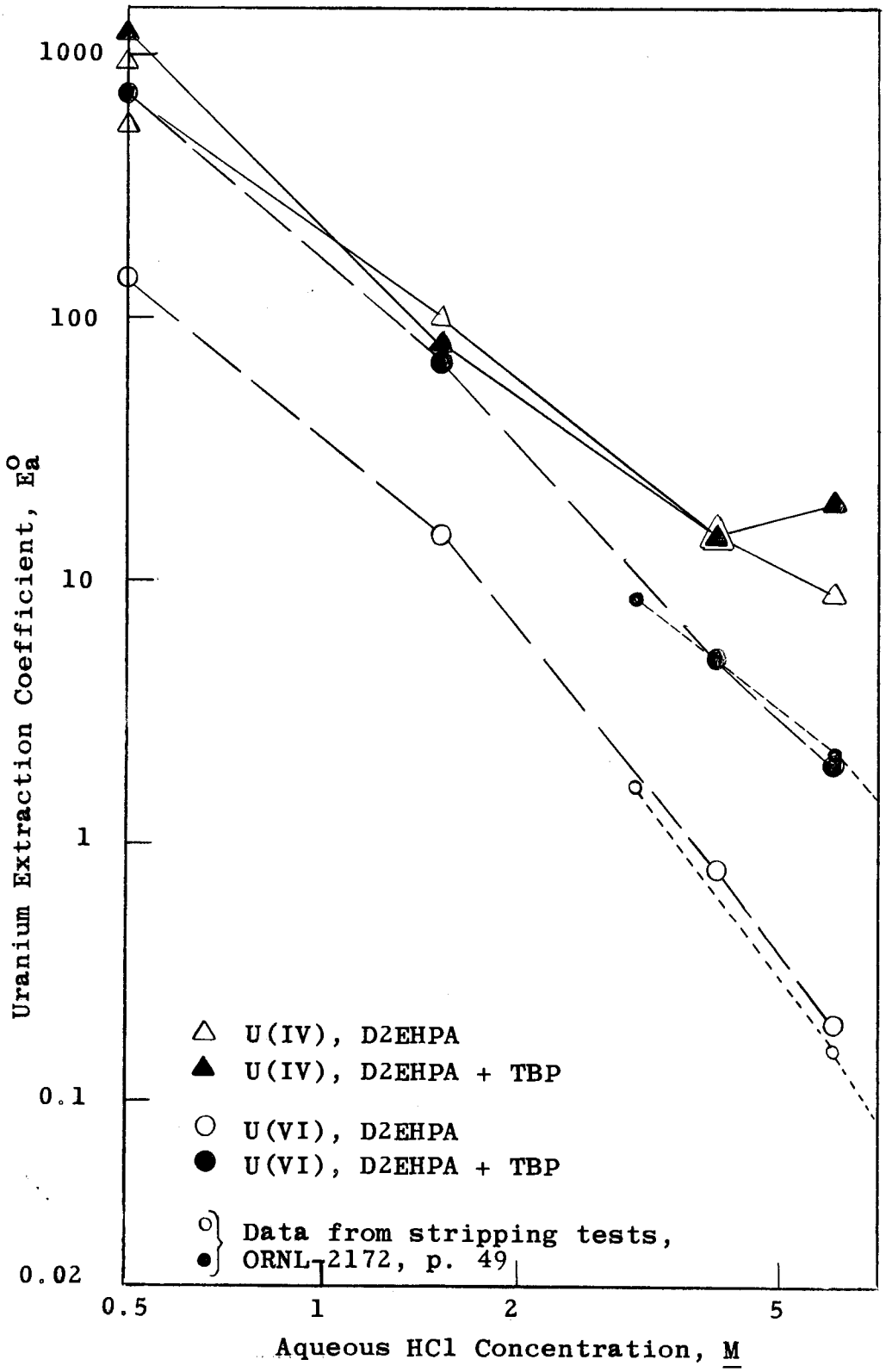


Fig. 1.3. Dependence of uranium extraction by D2EHPA on hydrochloric acid concentration; 0.1 M D2EHPA with or without addition of 0.11 M TBP, initial uranium concentration 1-2 g/liter, phase ratio 1/1.

kerosene) from the same aqueous solutions (ORNL-2172 p. 86). The extraction coefficients with the latter in kerosene are of about the same magnitude as those with the phosphinic acids in carbon tetrachloride, facilitating comparison of the relative effects.

Phosphonic Acids. The alkylphosphonic acids are analogous to the monoalkylphosphoric acids, differing by having a direct C-P bond instead of the C-O-P ester linkage. The uranium extraction power from phosphate solutions (Table 1.5) was generally a little higher than that of the corresponding monoalkylphosphoric acids (ORNL-2172 p. 84), both used in carbon tetrachloride diluent, but decreased a little more than the latter with decreasing pH. The relative acidities (apparent pH at half-neutralization in 70% ethanol) were lower than those of the corresponding monoalkylphosphoric acids (ORNL-1903 p. 104). The relative acidity appeared to decrease slightly with increasing length of straight alkyl chain, and more with branching, and to increase on incorporation of an α-hydroxy group.

Some other phosphonic acids were examined but not tested for extraction. Benzylphosphonic acid was too water soluble, while lauryl-, cetyl-, 2,4- and 3,4-dichlorobenzyl-, and β-cyclohexylethylphosphonic acids were insufficiently soluble in either carbon tetrachloride or kerosene.

Neutral Compounds. The esters of phosphorus acids are of interest as synergistic modifiers in the Dapex extraction process, as reported in ORNL-2172 and -2307. Most of the compounds tested for that purpose were also tested alone as simple neutral extractants. None of the trialkylphosphites, trialkylphosphates, dialkyl alkylphosphonates, or alkyl dialkylphosphinates (0.1 M in carbon tetrachloride) were able to extract uranium effectively from dilute sulfate or phosphate solutions, and of these only the phosphinates extracted to a significant extent from dilute nitrate solution. However, some of the phosphonates, and phosphinates if they became commercially available, might still prove useful in different applications which may require extraction powers intermediate between those of TBP and the phosphine oxides.

Some samples of dialkylhydrogenphosphites gave high uranium extraction from dilute nitrate solutions, while some nominally similar compounds were ineffective. These compounds were not examined further, because they appeared in the initial tests to be too unstable for practical use. The samples which gave high extraction were from one source, and the extraction might have been due to a contaminant characteristically present in those samples, or the dialkylphosphites may actually comprise more than one type of compound.

Bifunctional Compounds. Since the extracted uranium appears generally to be combined with at least two molecules of an organophosphorus reagent, various compounds were examined that combine two potentially-extracting groups in the same molecule, in hope of obtaining enhanced extraction power by chelation.

Table 1.5 Acid Assay, Relative Acidity, and Uranium Extraction Power of Phosphonic Acids

Phosphonic Acid	Batch No.	Acid Assay, meq/g: Theo. Strong or Weak	Acid Assay, meq/g: Found Strong	Acid Assay, meq/g: Found Weak	Relative Acidity[b]: "pKa_1"	Relative Acidity[b]: "pKa_2"	U Extraction Coefficient,[c] o/a: 0.4 M PO_4 pH 1	U Extraction Coefficient,[c] o/a: 1.4 M PO_4 pH 1.3	U Extraction Coefficient,[c] o/a: 1.4 M PO_4 pH 2
n-Hexyl	OP-47	6.02	5.89	5.99	3.9	9.2	--	9	60
n-Octyl	OP-50	5.16	5.19	5.36	4.1	9.2	--	20	100
n-Decyl	OP-54	4.50	4.44	4.56	4.2	9.3	--	15	70
2-Ethylhexyl	OP-232	5.16	4.69	4.88	4.7	9.7	100	20	60
1-Hydroxy-2-ethylhexyl	OP-170[a]	4.76	4.73	4.79	4.0	9.2	300	40	60

[a]Source: Virginia-Carolina Chemical Corp., Richmond, Va. Others prepared at ORNL.

[b]"pKa" is the apparent pH at half-neutralization in 70% ethanol.

[c]Initial uranium concentration in ~1 g/liter (0.004 M), 0.1 M phosphoric acid in CCl_4, a/o phase ratio 1/1, room temperature.

None of the bifunctional compounds so far tested has been significantly better than the corresponding simple reagent; however, some of the possibilities are probably worth further consideration.

Ethylene-, trimethylene-, and hexamethylenediphosphonic acids, although highly soluble in water, distributed sufficiently to carbon tetrachloride to permit extraction tests. The methylene and ethylene compounds extracted uranium with about the same degree of extraction power as shown by the simple phosphonic acids. The hexamethylene compound precipitated most of the uranium from dilute nitrate, sulfate, and phosphate solutions, and might be worth consideration as a precipitant.

Dioctyl ethylenediphosphinic acid and diphenyl ethylenediphosphinic acid were insoluble in all the diluents tested, presumably because of chain formation by chelation between acid groups. A mono-ester of such an acid, which could form dimers but not chains, was sought but has not been obtained.

All attempts to prepare and isolate pure alkyl acid pyrophosphates failed. Some neutral pyrophosphate esters were obtained, including tetraoctylpyrophosphate; however, these extracted little uranium from sulfate or phosphate solution. Like the simple phosphate esters, the diphosphate and diphosphonate $[(RO)_2P\text{-}R\text{-}P(OR)_2]$ ester samples that were essentially free from acid contaminants extracted little if any uranium from dilute (i.e., unsalted nitrate solutions).

Polyphosphates prepared by reaction of a dialkylphosphoric acid with P_2O_5 extracted both uranium(IV) and uranium(VI) from 5 M phosphoric acid. Hydrolysis of the extractant appeared to be slow, even when the extracted uranium was stripped with sodium carbonate solution. A brief study of the preparation and extraction performance of this type of extractant will be reported later.

Polymeric Compounds. Several organic polymers containing either neutral or acid phosphate ester groups were obtained for preliminary scouting tests of solid or resinous extraction. The advantages sought were high extraction power from the high concentration of reagent groups possible within a polymer, and vanishingly small loss by aqueous solubility, both of which would aid in extending the applicability of extraction to more dilute uranium solutions.

The uranium sorptions (Table 1.6) appeared high enough to warrant further consideration of such reagents, especially since two of the neutral esters were much more effective than has been found with simple monomeric phosphate esters. However, these particular neutral compounds did not have good physical properties. The two polyvinyl acid phosphates were crystalline-appearing, easily handled solids, but the other polymers were gummy and spread on the surfaces of the glass vessels.

Table 1.6 Uranium Sorption by Solid Polymers

Compound[a]	Batch No.	U Removed from Aqueous, % of initial[b] 0.1 M NO_3 pH 1.5	0.4 M PO_4 pH 1
Polyvinyl alcohol-polyvinyl acid phosphate copolymer[c]	OP-265	99	81
Polyvinyl alcohol-polyvinyl acid phosphate copolymer[c]	OP-264	56	63
Cellulose acid phosphate	OP-262	99	84
Polyvinyl alcohol-polyvinyl-dioctylphosphate copolymer	OP-259	31	2
Polyvinyl alcohol-polyvinyl-dibutylphosphate copolymer	OP-258	--	84
Cellulose-dibutylphosphate	OP-267	99	98

[a] Supplied by Virginia-Carolina Chemical Corp., Richmond, Va.

[b] Two millimoles of reagent (based on molecular weight of monomeric unit) contacted with 40 ml of aqueous phase for 1.5 hr at room temperature. Initial uranium concentration ~1 g/liter (0.004 M).

[c] Mole ratio ester/alcohol ≈1/6 in OP-264 and ≈1/20 in OP-265.

Two other polymeric reagents were soluble in carbon tetrachloride and were tested at 0.1 M, based on the molecular weight of the nominal monomeric unit. The ethylcellulose derivative extracted strongly even from the dilute phosphate solution:

	$U E_a^o$			
	0.5 M SO_4 pH 1	0.4 M PO_4 pH 1	0.5 M SO_4 0.3 M NO_3 pH 1	0.4 M PO_4 0.3 M NO_3 pH 1
Polymerization product of dioctyl-β-hydroxyethylphosphate (OP-239)	1	--	2	1
Ethylcellulose-di(2-ethylhexyl)phosphate (OP-263)	20	30	25	--

However, the organic phase gelled in each test with this compound. Extraction by the β-hydroxyethylphosphate compound, while relatively low, was still much higher than has been found with simple monomeric phosphate esters.

Phosphorus-Nitrogen Compounds. The phosphoryl group in the phosphoramides (phosphoryl triamides), especially those formed from secondary amines, are reported* to display a pronounced hydrogen bonding tendency, and also to withstand rather drastic hydrolytic media, both acid and alkaline. Hence, several phosphoramides were obtained for testing as uranium extractants in the hope of achieving improved extraction power over even the phosphine oxides, and particularly in the hope of obtaining useful extractants like the phosphine oxides but more likely to be commercially available.

As shown in Table 1.7, some of the phosphoramides tested did show stronger extraction than tri-n-octylphosphine oxide from sulfate and phosphate solutions. However, all the phosphoramides tested hydrolyzed more readily than had been expected, and apparently too readily for consideration as practical extractants, at least in raw materials applications. For example, decomposition of 0.2 M reagents (in kerosene) amounted to 3-4% in 16 hr contact with 0.5 M sulfate or chloride solution, pH 1, at room temperature. Decomposition was much more rapid in contact with 6 M acid solutions.

Other Compounds. In a single test, 5-ethyl-4-propyl-2-oxo-2-hydroxy-1,3-dioxa-2-phosphorinane** at 0.1 M concentration

*G. M. Kosolapoff, Organophosphorus Compounds, John Wiley and Sons, Inc., New York, 1950, p. 299.

**$CH_2CHRCHROP(=O)(OH)O$, essentially a cyclic dialkylphosphoric acid.

Table 1.7 Uranium Extraction with Amido-Phosphorus Compounds

Initial uranium concentration ~1 g/liter (0.004 M), phase ratio 1/1, room temperature

Compound, 0.1 M, in CCl_4	Structure	Batch No.	Uranium Extraction, % of initial: 0.1 M NO_3 pH 2	0.5 M SO_4 pH 1	0.4 M PO_4 pH 1	0.5 M SO_4 0.3 M NO_3 pH 1	0.4 M PO_4 0.3 M NO_3 pH 1
Tri-n-butylphosphoramide	$(RHN)_3PO$	OP-219	99.6[b]	95[b]	26[b]	99.8[b]	99[b]
Tri-n-octylphosphoramide	$(RHN)_3PO$	OP-245	96	87	44	94	85
Tri(2-ethylhexyl)phosphoramide	$(RHN)_3PO$	OP-218	99.4	47	38	99	89
Di-n-octylphosphenimidic amide	$RHN-\overset{O}{P}=NR$	OP-240	--	29	--	41	29
Hexa-n-butylphosphoramide	$(R_2N)_3PO$	OP-268	96	<1	<1	67	9
n-Octyl bis(dimethylamido)phosphate	$(R_2N)_2\overset{O}{P}OR$	OP-336	--	<1	--	--	--
Tridecyl bis(dimethylamido)phosphate	$(R_2N)_2\overset{O}{P}OR$	OP-337	--	<1	--	47	14
Di-n-butyl di-n-butylphosphinamide	$R_2N\overset{O}{P}R_2$	OP-270[a]	--	<1	<1	88	--
Tetra-n-butylphosphorodiamidic chloride	$(R_2N)_2\overset{O}{P}Cl$	OP-220	3	--	--	--	--
Octamethylpyrophosphoramide	$(R_2N)_2\overset{O}{P}O\overset{O}{P}(NR_2)_2$	OP-22	98	--	--	--	--
Octa-n-butylpyrophosphoramide	$(R_2N)_2\overset{O}{P}O\overset{O}{P}(NR_2)_2$	OP-260	33	17	--	29	17
Hexa-n-butylphosphorous triamide	$(R_2N)_3P$	OP-266	(decomposed in CCl_4 solution)				
(Tri-n-octylphosphine oxide, ORNL-1964)			99.7	<10[c]	<10[c]	95	70

[a] Prepared at ORNL. All others supplied by Virginia-Carolina Chemical Corp., Richmond, Va.

[b] Some of the uranium (10-30%) was precipitated; percent shown is that removed from the aqueous phase.

[c] Estimated from extraction tests made under somewhat different conditions.

in carbon tetrachloride gave a uranium extraction coefficient of 3 from 0.4 M phosphate solution, pH 1, which is the same as was given by di(2-ethylhexyl)phosphoric acid from this solution (ORNL-2172 p. 84).

Triphenylphosphine $(C_6H_5)_3P$, extracted essentially no uranium from dilute nitrate solution.

Salts of two phosphorus bases, tri-n-butyl-n-octylphosphonium iodide in either benzene or chloroform and tri-n-butylbenzylphosphonium chloride in chloroform, extracted little uranium from either 1 M sulfate solution at pH 1 or 0.5 M Na_2CO_3 solution. As with many of the quaternary ammonium compounds tested (ORNL-1922 p. 27), the compatibility with diluents was poor.

1.3 Extraction of Uranium(IV) (F. G. Seeley, J. M. Schmitt)

Some cursory tests have been made of uranium(IV) extraction by amines and by di(2-ethylhexyl)phosphoric acid.

Extraction with Amines from Sulfate Solutions. Strong extraction of uranium(IV) by primary amines and by secondary amines not branched close to the nitrogen, in contrast to weak extraction by tertiary amines, was previously noted in ORNL-1734 p. 38 and -2099 p. 36. This has been corroborated over a wider range of uranium concentrations (Fig. 1.2) by extraction isotherms with Primene JM-T, di(tridecyl P)amine, and tri-n-octylamine. All three amines were used at a concentration of 0.1 M, the first two in kerosene and the third in 97% kerosene--3% tridecanol. The aqueous solution was 0.5 M sulfate, pH 1.1, containing initially ~1 g of uranium(IV) per liter. The initial slopes of the primary and secondary amine extraction isotherms (from 0 to ~2 g/liter in the organic phase), which appear essentially vertical on the scale used in Fig. 1.2, correspond to extraction coefficients of ~10,000 with Primene JM-T and ~1000 with di(tridecyl P)amine. The extraction coefficient with tri-n-octylamine was <1.

After the initial steep rise, the extraction isotherm with the primary amine leveled off, approaching about 3 g/liter organic in equilibrium with 1 g/liter aqueous. This corresponds to a uranium/amine mole ratio of about 1/8. The curve for the secondary amine was higher, approaching about 4 g/liter organic, or a mole ratio of about 1/6.

Extractions with D2EHPA from HCl Solutions. The extraction of uranium(IV) from 0.5-6 M HCl by 0.1 M D2EHPA in unmodified kerosene (Fig. 1.3) was considerably higher than that of uranium(VI). The addition of ~0.1 M TBP had little if any effect on the extraction power of uranium(IV), in contrast to the marked synergistic enhancement of the uranium(VI) extraction (cf. ORNL-2346, sec. 1.1). With the 0.1 M TBP added, the extraction of uranium(VI) was nearly the same as that of uranium(IV) at 0.5 and 1.5 M HCl, but still somewhat lower at higher HCl concentrations.

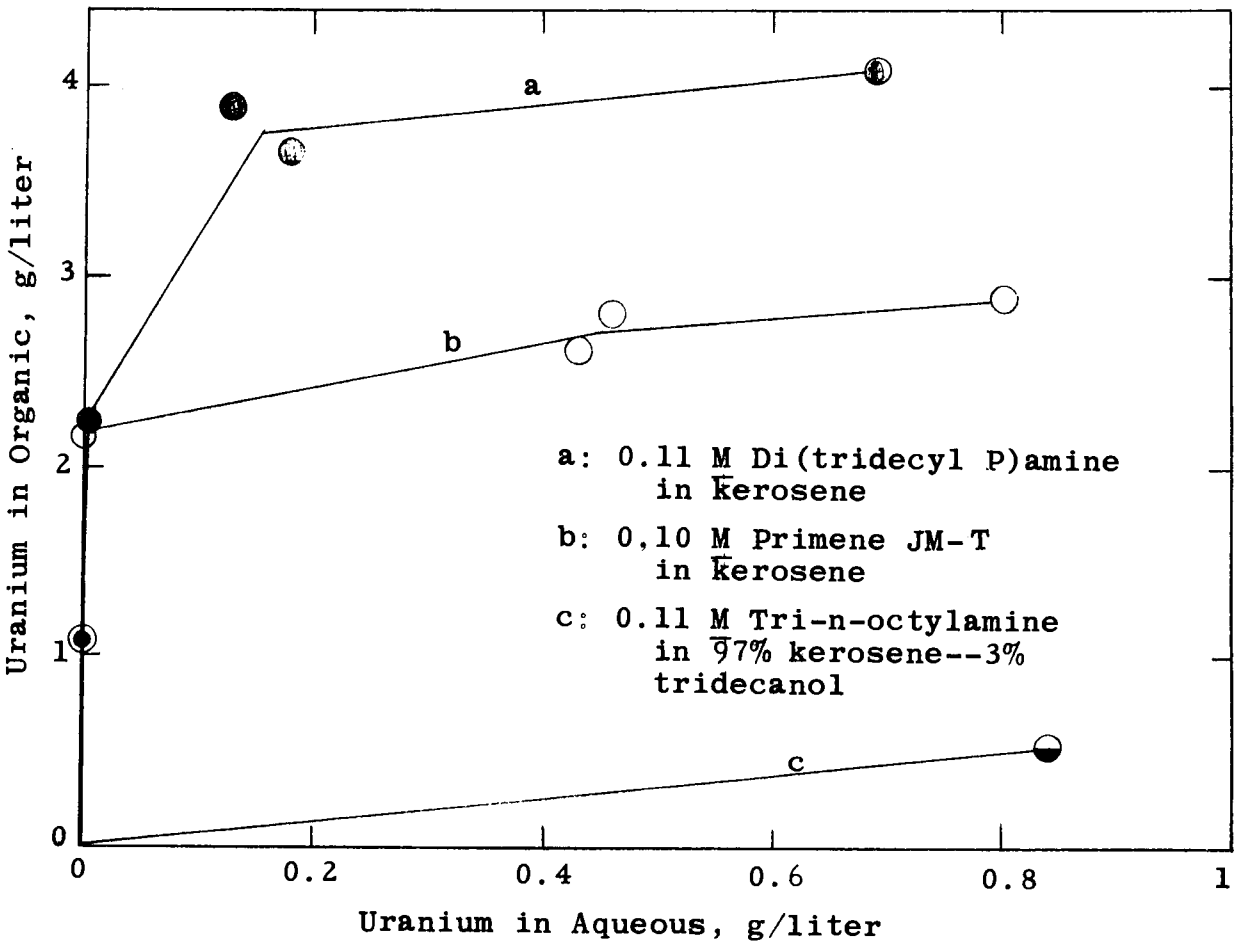


Fig. 1.2. Extraction isotherms of uranium(IV) from 0.5 M sulfate solution, pH 1.1; contact time 15 min at 22-24°C, phase ratio aqueous/organic 1/1 to 10/1.

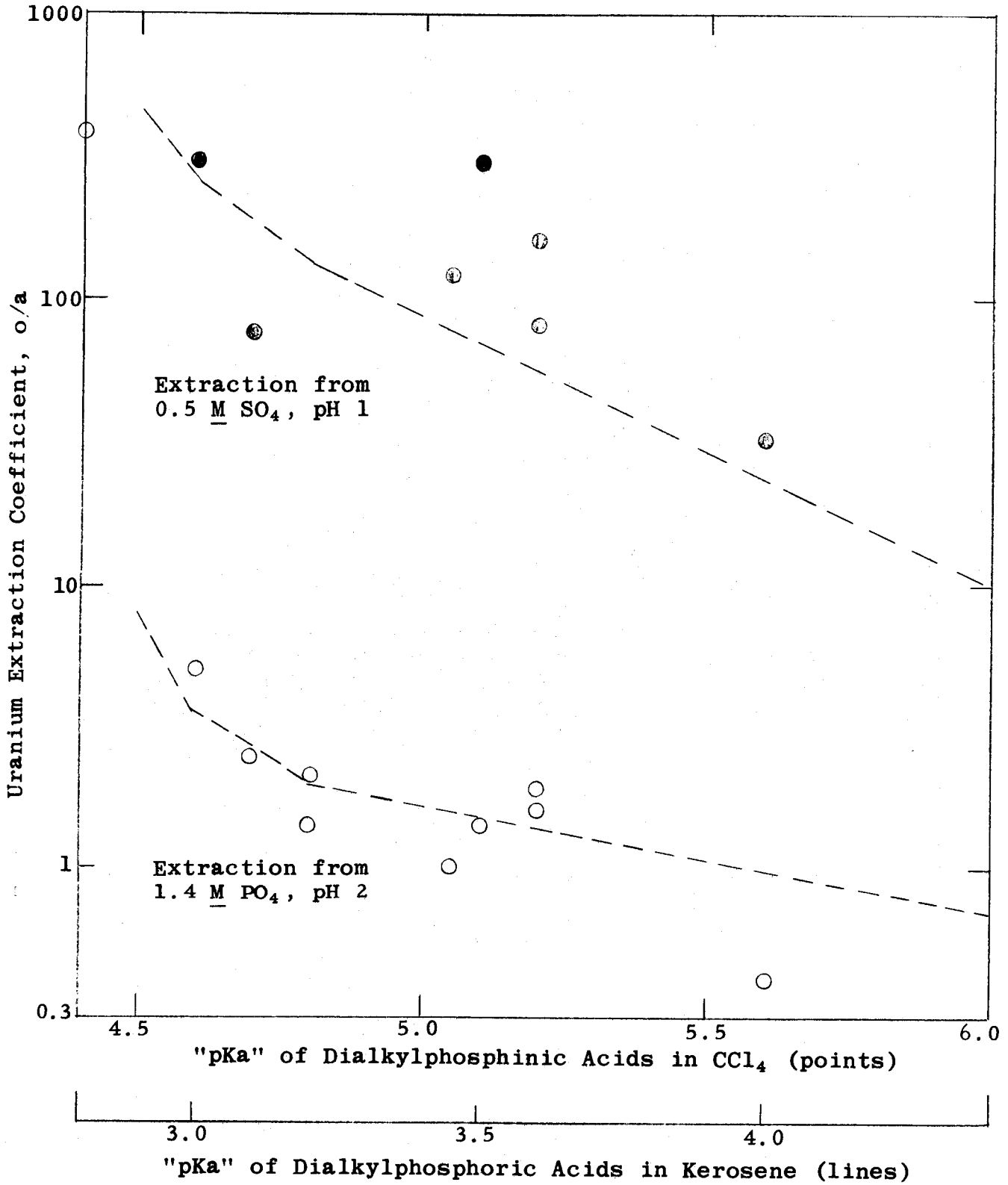


Fig. 1.1. Extraction Ability of Dialkylphosphinic Acids vs. Relative Acidity, "pKa", i.e., the Apparent pH at Half-neutralization in 70% Ethanol, compared with Extraction Ability of Dialkylphosphoric Acids (ORNL-2172, p. 86). The dialkylphosphinic acids are identified in Table 1.3.

The slope, $\Delta \log E_a^o / \Delta \log [HCl]$, of the extraction curves for uranium(IV) was close to -2, whereas a slope of about -4 was expected on the basis of the expected exchange of four hydrogen ions for each uranous ion. No tests have yet been made to attempt to account for the lower slope. One possibility to be considered is the extraction of a uranyl chloride complex.

In addition to the uranium(VI) extractions, Fig. 1.3 includes points calculated (using the relation $E_a^o = 1/S_o^a$) from earlier HCl stripping tests (ORNL-2172 p. 49). The close agreement in the overlapping region serves to confirm that true equilibrium was reached in both extraction and stripping.

Three points on an isotherm for extraction of uranium(IV) by 0.1 M D2EHPA from 1.5 M hydrochloric acid solution showed an extraction coefficient of about 100 at a uranium loading of 1 g/liter, and suggested approach toward a D2EHPA/U mole ratio of 4/1 at high loading:

g of U/liter aqueous:	0.01	0.32	2.6
g of U/liter organic:	0.93	2.8	5.2
D2EHPA/U mole ratio:	25	8.5	4.6

The initial aqueous uranium concentration was ~3 g/liter, and the diluent was unmodified kerosene. These points are not well fitted by any curve based on $E \propto (M\ D2EHPA - 4\ M\ U)^4$, which is the simplest relation suggested by a 4/1 mole ratio. In this regard, it is of interest to compare the behavior of uranium(VI) in previous extraction studies.* While the D2EHPA/U mole ratio was 2/1 at high loading, the extraction at low loading did not conform to the expected relation $E \propto (M\ D2EHPA - 2\ M\ U)^2$, but instead to $E \propto (M\ D2EHPA - 4\ M\ U)^2$. This behavior was accounted for by establishing that the D2EHPA was dimerized in the hydrocarbon solution used, and by assuming that each uranyl ion extracted was complexed (at low loading only) with two singly-ionized dimers. The present three points are not sufficient to test whether complexing with the reagent dimers also occur at low loading in the extraction of uranium(IV), but the failure of the expected relation to fit the points is in the direction to suggest that it may be.

2.0 PROCESS DEVELOPMENT STUDIES

In addition to the studies described below, process development projects during the month have included (1) control of the phosphate content of vanadium products from the Dapex and Amex processes, (2) evaluation of several new amine samples as uranium extractants, (3) the effect on thorium extraction by amines of small amounts of nitrate or chloride in the sulfate liquors,

---

*C. F. Baes, Jr. et al., "The Extraction of Uranium(VI) from Acid Perchlorate Solutions by Di(2-ethylhexyl)phosphoric Acid," presented at Am. Chem. Soc. Meeting, Miami, April 12, 1957.

(4) extraction of nitrate from ion-exchange barren liquors with amines, and (5) recovery of thorium from pregnant carbonate strip solutions.

2.1 Compatibility of Amines with Liquors Containing Molybdenum (W. D. Arnold, A. D. Kelmers)

In continued studies on the compatibility of amines with liquors containing molybdenum, a number of different organic compounds were tested as diluent modifiers in an attempt to find an additive that would prevent precipitation of amine from the organic diluent. In other tests a number of these precipitates, formed under various contacting conditions, were collected and analyzed. The tests reported here were confined to tri-iso-octylamine, this compound having shown poor compatibility with molybdenum, particularly in processes using a chloride strip (ORNL-2099, -2269).

2.1.1 Comparison of Diluent Modifiers

The test procedure was similar to that described previously (ORNL-2269) and involved contacting the organic solvent with a uranium-molybdenum liquor at $3^a/1^o$, stripping the extract with three successive volumes of 1.0 M NaCl-0.05 M H_2SO_4 at $1^a/2^o$, and, finally, regenerating the amine solution with 3% Na_2CO_3 at $1^a/4^o$. Each contact was for 5 min, with 20 min allowed between contacts during which observations were made for precipitate formation.

The composition of the aqueous liquor, in g/liter, was 1.0 U, 0.4 Mo, 1.07 V(IV), 2.2 Fe(III), 2.1 Al, 2.0 PO_4, and 51 SO_4 at pH 1. Each solvent contained 0.10 M tri-iso-octylamine in 95% kerosene--5% tridecanol plus one of the following modifiers at concentrations of 20 and 100 g/liter:

tributyl phosphate
dibutyl butylphosphonate
di(2-ethylhexyl)phosphoric acid (D2EHPA
oleic acid
n-caprylic acid
nonylphenol
benzyl alcohol
methyl-n-hexyl ketone
di-isobutyl ketone
cyclohexanone
trichloroethylene
benzyl chloride
2-ethylhexyl chloride
nitrobenzene
o-nitrotoluene
α-nitronaphthalene
nitromesitylene
2-nitro-p-cymene
sec-amyl benzene
2-ethylhexyl acetate
xylene
Esso Heavy Aromatic Naphtha
naphthalene
d-limonene
2-ethyl butyraldehyde
Arneed T

Nearly all the molybdenum in the aqueous liquor was extracted in each test so that the molybdenum loading of the solvent was nearly uniform at 1 g/liter.

With no additive in the system, precipitation did not occur during extraction but did occur in the first chloride

strip. Similar performance was ordinarily noted with modifiers present, although in a few cases precipitates were noted during the extraction step. In all cases the precipitates were of the characteristic green color.

None of the compounds tested was effective in preventing precipitates except nitrobenzene. When this compound was present at 100 g/liter, no precipitates were observed during extraction, stripping, or regeneration.

The uranium extraction coefficient was lower by a factor of 3 with nitrobenzene present. This effect, along with high aqueous solubility, high toxicity, and other objectional characteristics, seems to eliminate this compound as a practical additive for process application. However, the successful results obtained suggest the possibility of finding other more suitable additives.

2.1.2 Composition of Precipitates

A series of four tests was performed with 0.10 M tri-iso-octylamine in 95% kerosene--5% tridecanol wherein molybdenum concentrations were adjusted to give precipitation in the extraction, chloride stripping, or regeneration steps. The precipitates formed were washed with kerosene and water and then dissolved in acetone for analysis. Washing was difficult owing to the gummy, waxy nature of the precipitates. Except molybdenum, the composition of the liquor used in the tests, in g/liter, was 1 U, 1.8 PO_4, 2.1 Fe, 2.1 Al, 1.0 V(IV), and 52 SO_4 at pH 1. The molybdenum content was varied from 0.063 to 1 g/liter.

Experiment 1: (0.063 g Mo/liter in head liquor) No precipitation was noted during extraction at $3^a/1^o$ or during the first two chloride strips ($1^o/2^a$). The organic became turbid in the third strip contact and a very small amount of precipitate, too little for analysis, was obtained by filtration. During subsequent regeneration with 3% Na_2CO_3 ($1^a/4^o$) a small amount of a light green precipitate formed. Analysis of this precipitate showed the main constituent to be amine. The molybdenum/amine mole ratio was 0.12/1 and the molybdenum/phosphate ratio 2.9/1.

Experiment 2: (0.23 g Mo/liter in head liquor) No precipitation was observed during extraction or in the first chloride strip. A trace of precipitate formed in the first chloride strip and a much larger amount in the third chloride strip. Analysis of this precipitate showed a molybdenum/amine ratio of 11/1 and a molybdenum/phosphate ratio of 12/1. Vanadium was also present, the vanadium/phosphate ratio being approximately 1/1.

Experiment 3: (0.38 g Mo/liter in the head liquor) A very small amount of precipitate formed during extraction. In the first chloride strip, a considerable amount of green precipitate formed which was determined to have a molybdenum/amine ratio of 8.3/1 and a molybdenum/phosphate ratio of 9/1. The vanadium/phosphate ratio was 1.4/1.

Experiment 4: (1 g Mo/liter in the head liquor) A yellowish-green precipitate formed during the extraction step. The molybdenum/amine ratio in this precipitate was 90/1 and the molybdenum/phosphate ratio was 9/1. The vanadium/phosphate ratio was 1.2/1.

2.2 Molybdenum in Dapex Process Uranium Products (F. J. Hurst)

In the Dapex uranium extraction process, a major part of any molybdenum in the sulfuric acid leach liquor is extracted into the solvent along with the uranium. In the sodium carbonate stripping cycle, both elements report to the strip solution in a soluble form. Leach liquors from most ores contain unimportant amounts of molybdenum. However, in some cases sufficient amounts are present that the uranium product specification of a 0.5% molybdenum content (U_3O_8 basis) can be exceeded unless some provision is made for molybdenum separation during the process sequence.

The studies described here have been made to determine the degree of separation that can be obtained in different precipitation methods for recovering uranium from the pregnant sodium carbonate strip solution. The strip solution used in the tests was prepared by contacting a di(2-ethylhexyl)phosphoric acid (D2EHPA) extract containing uranium and molybdenum with 10% Na_2CO_3 solution. The resulting liquor contained 45 g of U_3O_8 and 3.6 g of molybdenum per liter. Three uranium precipitation methods were examined: direct precipitation with caustic, destruction of the carbonate with sulfuric acid followed by precipitation with caustic, and destruction of carbonate followed by precipitation with ammonia.

2.2.1 Direct Caustic Precipitation

Two tests of direct precipitation were made by adding 20% NaOH to the strip liquor. Total sodium hydroxide addition amounted to 0.85 lb/lb U_3O_8. In the first test the precipitate was filtered immediately after caustic addition. The second precipitate was digested 3 hr at 60°C and filtered hot. In both cases filtration was difficult and there was a noticeable tendency toward peptization. Repeated filtration was necessary to obtain a clear filtrate. After filtration, the precipitates were washed with water and dried at 110°C.

Analyses (Table 2.1) showed that in both tests the molybdenum content of the uranium product was negligible, i.e., <0.05%. Precipitation of uranium was not complete although presumably the recovery would have been improved by adding a larger excess of caustic. Other tests (results not reported) have shown nearly complete (>99.8%) uranium recovery from similar strip solutions with sodium hydroxide additions of 1.1 lb/lb U_3O_8. Deficiency of caustic might also have contributed to the poor physical properties of the precipitate. This possibility is being checked.

Table 2.1 Molybdenum Contamination of Uranium Precipitated from Carbonate Strip Solutions

Pregnant strip solution: 45 g U_3O_8 and 3.6 g Mo per liter

Precipitation Method	Precipitant, lb/lb U_3O_8	pH	Uranium Recovery, %	Dried Product (110°C) U_3O_8, %	Dried Product (110°C) Mo, %	% of Original Mo in Product
Direct NaOH addition[a]	0.85 NaOH	11.6	98.4	82.2	0.02	0.2
Direct NaOH addition[b]	0.85 NaOH	11.8	99.0	85.1	0.03	0.4
Acidification, addition of NaOH[c]	0.43 NaOH	8.0	>99.8	81.0	4.6	57
Acidification, addition of NaOH[c]	0.51 NaOH	10.5	>99.8	78.5	1.3	17
Acidification, addition of NH_4OH[c]	0.20 NH_3	8.0	>99.8	78.6	8.0	94
Acidification, addition of NH_4OH[c]	0.24 NH_3	8.7	>99.8	77.4	6.1	74

[a]Precipitate slurry filtered immediately, washed on the filter with water.

[b]Precipitate digested 3 hr at 60°C prior to filtration, washed on the filter with water.

[c]Precipitate digested 3 hr at 60°C prior to centrifugation, washed by reslurrying three times with hot 1% NH_3--1% NH_4NO_3 solution.

2.2.2 Acidification, Hydroxide Precipitation

A series of four tests was made in which the pregnant strip solution was acidified to pH 2.0 with sulfuric acid and boiled to drive off carbon dioxide, and the uranium precipitated with either sodium or ammonium hydroxide. Base requirements for precipitation at pH 8 were 0.43 lb NaOH or 0.20 lb NH_3 per pound of U_3O_8. Tests were also made in which approximately 20% additional base was added, i.e., 0.51 lb NaOH or 0.24 lb NH_3 per pound of U_3O_8.

The precipitate slurries were digested 3 hr at 60°C and centrifuged. The precipitates were washed by reslurrying with hot 1% NH_3--1% NH_4NO_3 solution and dried at 110°C.

Poor rejection of molybdenum was obtained in both tests with ammonia precipitation (Table 2.1). With sodium hydroxide, rejection of molybdenum was also poor at a terminal pH of 8 but improved considerably when 20% more caustic was added to give a terminal pH of 10.5. In this test, the product contained 1.3% molybdenum or about 17% of that initially present in the strip solution. This product does not meet specifications. However, it seems likely that further improvement could be obtained by a further increase in caustic addition.

In all the acidification-precipitation experiments, a yellowish-green solid formed during the acidification step. This material was not separated from the liquor before adding the ammonium or caustic in the tests shown in Table 2.1. Later, in another test, some of this solid was filtered off and found by chemical analysis to contain 80% of the molybdenum and 7% of the uranium that was originally present in the strip solution. Digestion of the solid with dilute caustic gave a good separation of molybdenum from the uranium.

3.0 ENGINEERING STUDIES

In addition to the studies described below, engineering studies during the month have included: (1) kinetics of vanadium extraction with Dapex-type organic, (2) stage efficiency of the baffled tank mixer for uranium extraction in the Dapex process, and (3) phase separation and entrainment of organic in the Dapex uranium extraction process.

3.1 Batch Kinetic Studies of Dapex Uranium Extraction (F. L. Daley)

The kinetics of uranium extraction from a leach liquor containing relatively high concentrations of uranium and vanadium were reported previously (ORNL-2269). The results of additional kinetic studies are reported here for uranium extraction from a synthetic liquor whose composition is typical for many sulfuric acid leach solutions produced in western mills. Extraction rate constants were evaluated as a function of mixer power in 6- and 12-in.-dia mixers. Impeller size and location were also compared.

The tests were conducted in the same mixer tanks described in ORNL-2269, and the impellers were flat-bladed turbines with six blades. The organic extract was 0.1 M di(2-ethylhexyl)-phosphoric acid in kerosene containing 30 g/liter tributylphosphate. The synthetic leach liquor composition in g/liter was 1.2 U, 0.3 Fe(III), 1 V(IV), 2.8 Al, 50 SO_4, and 1.9 PO_4 at pH 1.0. In all tests the aqueous/organic ratio was 4/1, and the mixing was controlled to give aqueous-continuous dispersions. Samples were dipped from the mixer at timed intervals without interruption of the mixing.

The rate constant, K', was calculated from the uranium concentrations in the aqueous phase in the same way as described in ORNL-2269. Table 3.1 shows the aqueous uranium concentration and resulting values of K' for each test.

Table 3.1. Uranium Concentration in Raffinates vs. Time

Test No.	Uranium concentration, g/liter									K', min^{-1}
	0 sec	10 sec	20 sec	30 sec	45 sec	60 sec	120 sec	240 sec	480 sec	
81	1.16	0.89	0.83	0.75	0.63	0.57	0.38	0.23	0.16	0.74
83		0.78	0.67	0.61	0.49	0.43	0.29	0.19	0.16	1.08
85		0.71	0.62	0.50	0.41	0.34	0.22	0.17	0.16	1.44
87		0.52	0.41	0.32	0.26	0.23	0.17	0.16	0.17	2.46
97		0.52	0.38	0.30	0.24	0.20	0.16	0.18	0.19	2.94
57		0.52	0.41	0.31	0.26	0.23	0.17	0.18	0.18	2.40
63		0.44	0.38	0.28	0.24	0.21	0.17	0.17	0.17	2.82
59		0.52	0.39	0.34	0.28	0.24	0.18	0.17	0.18	2.28
61		0.48	0.33	0.30	--	0.22	0.17	0.17	0.18	2.70
79		0.68	0.58	0.49	0.40	0.34	0.22	0.17	0.17	1.39
73		0.70	0.59	0.51	0.41	0.35	0.23	0.19	0.19	1.39
65		0.59	0.49	0.40	0.33	0.28	0.19	0.19	0.19	1.79
67		0.58	0.47	0.37	0.30	0.26	0.19	0.18	0.18	2.00
77		0.51	0.41	0.32	0.26	0.22	0.18	0.18	0.20	2.46
75		0.51	0.39	0.31	0.25	0.28	0.19	0.19	0.20	2.56
99		0.79	0.70	0.60	0.51	0.42	0.29	0.20	0.17	1.10
101		0.85	0.76	0.66	0.57	0.48	0.34	0.22	0.18	0.99
69		0.69	0.55	0.45	0.37	0.31	0.22	0.17	0.18	1.60
71		0.76	0.63	0.53	0.45	0.39	0.26	0.21	0.20	1.23

The effect of power input on the rate of uranium extraction is shown in Table 3.2 and Fig. 3.1. The value of the rate constant K' increased with approximately the cube root of power input for both the 6- and 12-in. mixers. Slightly higher rates were obtained in the 12-in. mixer at the same power input showing that scale up of mixers on the basis of power input would result in some over design of the power requirements.

Table 3.2 Effect of Power Input on Rate of Uranium Extraction

	6-in Mixer, 3-in. Turbine			12-in. Mixer					
				4-in. Turbine			6-in. Turbine		
		Turbine			Turbine			Turbine	
Power, hp/gal	Run No.	Speed rpm	K' min^{-1}	Run No.	Speed rpm	K' min^{-1}	Run No.	Speed rpm	K' min^{-1}
0.0025	81	262	0.74	99	323	1.10	101	165	0.99
0.0059	83	350	1.08	79	430	1.39	--	--	--
0.020	85	524	1.44	65	647	1.79	69	329	1.60
0.067	87	787	2.46	77	970	2.46	--	--	--
0.22	97	1170	2.94	--	--	--	--	--	--

The effect of the ratio of turbine diameter to tank diameter on rate of uranium extraction was tested in the 12-in. mixer with 2-, 3-, 4-, 6-, and 8-in. turbines (Table 3.3). Each turbine was operated at a speed to give the same power input (0.02 hp/gal). The results show that the value of rate constant increased with decreased turbine diameter for all sizes tested. Consequently the most efficient use of mixer power is obtained by using a small turbine at a high speed.

Table 3.3 Effect of Turbine/Tank Diameter Ratio (12-in. mixer) at Constant Power (0.020 hp/gal) on Rate of Uranium Extraction

Run No.	Turbine		D/T	K', min^{-1}
	Diameter, in.	Speed, rpm		
57	2	2050	0.167	2.40
59	3	1040	0.250	2.28
65	4	647	0.333	1.79
69	6	329	0.500	1.60
71	8	204	0.667	1.23

The effectiveness of the turbine located at the center of the mixer tank was compared with the turbine located one diameter off the bottom. The rate constant was slightly greater when the turbine was located near the bottom. However, the difference was so small that choice of turbine location cannot be considered an important design criterion.

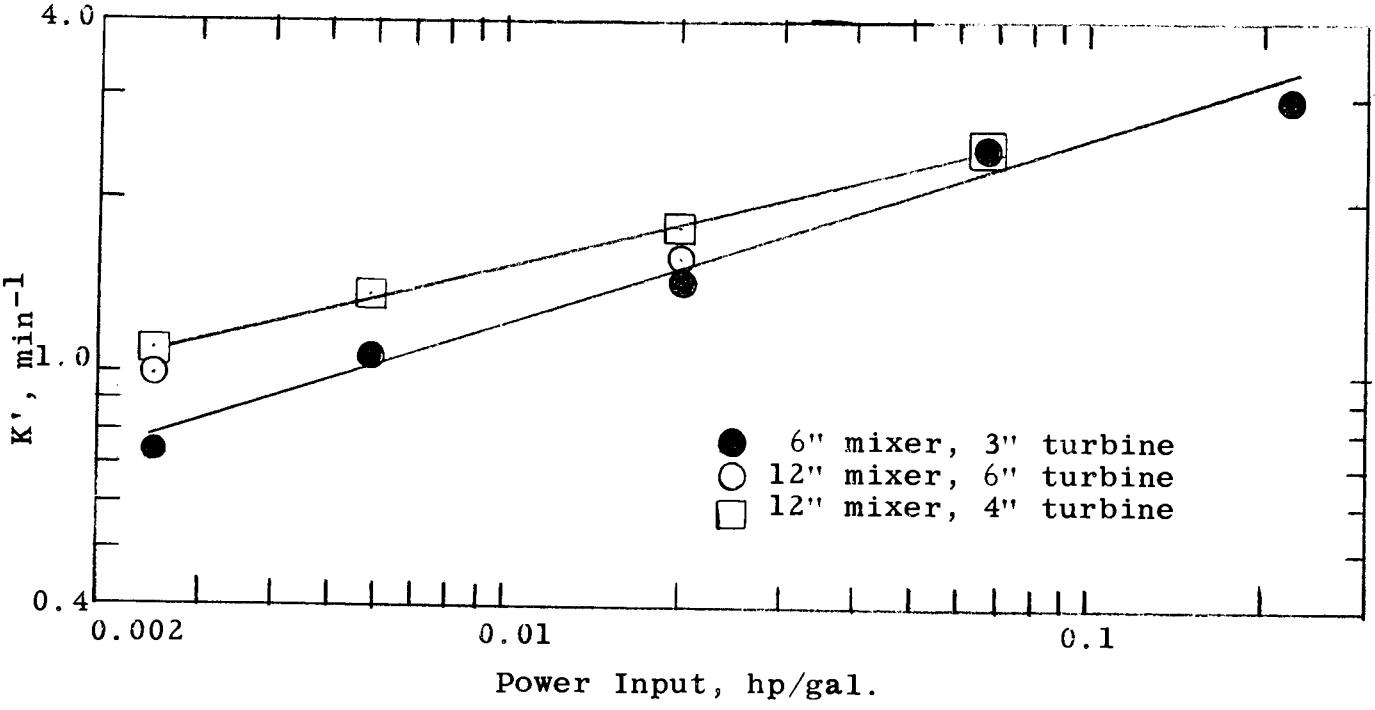


Fig. 3.1 Correlation of Rate Constant and Mixer Power

Table 3.4 Effect of Turbine Position (12-in. mixer) on Rate of Uranium Extraction

Turbine			Turbine centered		Turbine one diameter off bottom	
Diameter, in.	Speed, rpm	Power, hp/gal	Run No.	K', min^{-1}	Run No.	K', min^{-1}
2	2050	0.020	57	2.40	63	2.82
3	1040	0.020	59	2.28	61	2.70
4	430	0.0059	79	1.39	73	1.39
4	647	0.020	65	1.79	67	2.00
4	970	0.067	77	2.46	75	2.56