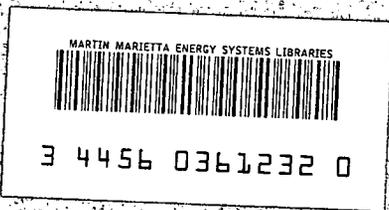
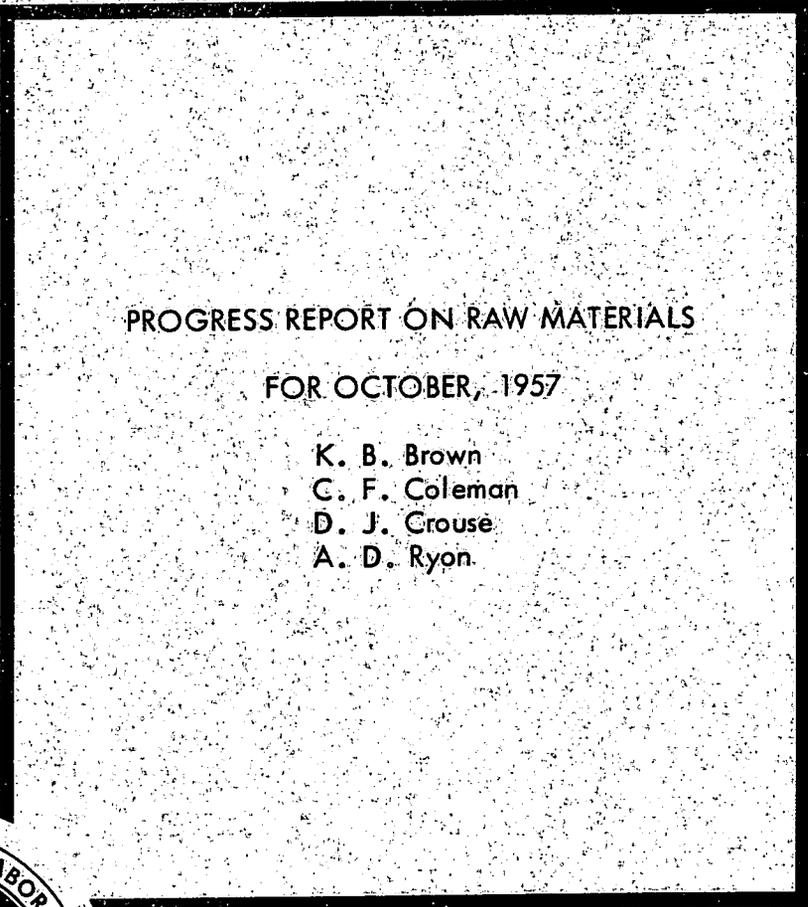


UNCLASSIFIED



CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

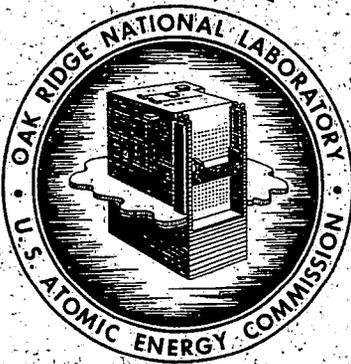
ORNL-2451 *cy H*
Technology-Raw Materials



PROGRESS REPORT ON RAW MATERIALS

FOR OCTOBER, 1957

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



CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY

OPERATED BY

UNION CARBIDE NUCLEAR COMPANY

Division of Union Carbide Corporation



POST OFFICE BOX X • OAK RIDGE, TENNESSEE

UNCLASSIFIED

Printed in USA. Price 75 cents. Available from the

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

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

UNCLASSIFIED

Report Number: ORNL-2451

Contract No. W-7405, eng 26

CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT ON RAW MATERIALS

FOR OCTOBER, 1957

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

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

DATE ISSUED

JAN 29 1958

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



3 4456 0361232 0

UNCLASSIFIED

INTERNAL DISTRIBUTION

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

EXTERNAL DISTRIBUTION

96. R. F. Bacher, California Institute of Technology
97. John Breitenstein, National Lead Company (Winchester)
- 98-106. E. C. Van Blarcom, Division of Raw Materials, Washington
107. Division of Research and Development, AEC, ORO
- 108-575. Given distribution as shown in TID-4500 (13th ed. Rev.) under Technology-Raw Materials category (75 copies - OTS)

CONTENTS

	Page
1.0 Systematic Studies	4
2.0 Process Development Studies	11
3.0 Engineering Studies	19
4.0 Fundamental Studies	22

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¢)	June, ORNL-2380 (\$1.00)
February, ORNL-2269 (25¢)	July, ORNL-2388 (75¢)
March, ORNL-2306 (25¢)	August, ORNL-2399 (\$1.00)
April, ORNL-2346 (25¢)	September, ORNL-2443 (\$1.25)
May, ORNL-2366 (25¢)	

ABSTRACT

Systematic Studies. A series of experimental dilaurylpolypropoxy amines showed only fair uranium extraction power from dilute sulfate solution. There was little change in behavior with change in propoxy chain length from 1 to 40 units, except that only with the longest-chain sample were phase separations good.

Loss of di(2-ethylhexyl)phosphoric acid (D2EHPA) from 0.1 M solution in kerosene to dilute acidic sulfate solutions, measured by distribution of P-32-labeled reagent, was <1 mg/liter of aqueous solution at 25°C and <5 mg/liter at 50°C. The corresponding losses to 10 M HCl solution were 1.5 and 5 mg/liter. On prolonged contact (100 hr) a small but measurably higher concentration of P-32 was found in the aqueous phase, which is attributed to slight (~0.01%) hydrolysis of the D2EHPA.

In preliminary tests of cation exchange between sodium di(2-ethylhexyl)phosphate solutions in modified Amsco 123-15 and aqueous neutral-to-basic nitrate solutions, strontium was preferentially distributed to the organic phase, with Sr/Na separation factors of about 30. Cesium was extracted less than sodium.

Process Development Studies. The inorganic phosphate content of a Dapex process vanadium(IV) strip solution was decreased sufficiently by passage through a zirconium oxide column to permit direct ammonia precipitation of a vanadium product meeting phosphorus specifications. Losses of zirconium to the strip solution were low. The phosphate was partially eluted from the column with dilute sodium hydroxide.

Stripping rates of vanadium and contaminants from 0.25 M D2EHPA/kerosene with 1 M H₂SO₄ were compared at 25° and 50°C, in a study of the possibility of avoiding contaminant buildup by

acid stripping alone. The stripping rates of vanadium(IV), aluminum, and especially iron(III) were markedly increased at the higher temperature. The rates were essentially the same with or without TBP (0.2 M) in the organic phase.

Engineering Studies. Comparison of the rate of uranium extraction by Dapex solvent at aqueous to solvent ratios of 4/1 and 1/1 shows that the rate constants agree when adjusted for the fraction of aqueous phase present in the mixer. The stage efficiency of the mixer with continuous flow remained virtually unchanged when the aqueous flow rate was constant and the aqueous to solvent ratio in the mixer was changed from 4/1 to 1/1.

Fundamental Studies. In continued study by infrared spectrophotometry of the molecular association between di(2-ethylhexyl)phosphoric acid (D2EHPA) and tri-n-octylphosphine oxide (TOPO) in n-octane, measurements of the dependence on TOPO concentration at constant D2EHPA concentrations indicated the existence of a 2(D2EHPA):(TOPO) complex, in addition to the (D2EHPA):(TOPO) complex previously reported. The data are well fitted by values for the formation constants of

$$K_1 = (D2EHPA \cdot TOPO) / (D2EHPA_2)^{1/2} (TOPO) = 30 \pm 5$$
$$K_2 = (D2EHPA_2 \cdot TOPO) / (D2EHPA_2) (TOPO) = 100 \pm 50$$

The concentration of $D2EHPA_2 \cdot TOPO$ was much lower than that of $D2EHPA \cdot TOPO$ over most of the range of solutions examined.

1.0 SYSTEMATIC STUDIES

In addition to the studies described below, systematic studies during the month included (1) preliminary study of the applicability of amine and organophosphorus extractants to separations in fuel reprocessing and waste disposal, (2) tracer phosphorus determination of monoalkylphosphoric acid extractant losses, (3) purification methods for certain alkylamines, and (4) uranium extractions with high and low concentrations of N-benzylheptadecylamine.

1.1 Screening of Organonitrogen Compounds (J. G. Moore)

The uranium extraction power of a series of propoxy amines* (Table 1.1) was examined as described in previous monthly reports. These were dilauryl(2-hydroxypropyl)amine and the corresponding dilauryl(polypropoxy)amines with 2, 3, 4, 10, and 40 propoxy units in the polyether chain. They showed only fair uranium extraction power from the sulfate test solution, lower when in kerosene than when in benzene. The highest weight amine, 212/50, showed less difference than the others between kerosene and benzene. It also gave good phase separation in both benzene and kerosene, while with the others separation was

*Experimental amines submitted for evaluation by Armour Chemical Division, Chicago.

Table 1.1 Preliminary Tests of Uranium Extractions
from Sulfate Solutions

Compound	No. of Propoxy Groups ^a	Batch No.	Concn, M	U Extracted and Extraction Coeff. (o/a)				Phase Sep'n
				Kerosene		Benzene		
				%	E _g ^o	%	E _g ^o	
Propomeen ^a								
212/11	1	313A	0.1	66	2	94	15	Poor
212/12	2	319A	0.01	13		38		Poor
			0.1	67	2	95	20	
212/13	3	320A	0.01	13		39		Poor
			0.1	65	2	94	15	
212/14	4	322A	0.1	78	4	96	25	Poor
212/20	10	323A	0.1	77	4	95	20	Poor
212/50	40	324A	0.1	93	15	96	25	Good

^aDilaurylpropoxyamines, $(C_{12}H_{25})_2N(CH_2-\underset{\text{CH}_3}{\text{CHO}})_nH$.

poor, especially in kerosene. The equivalent weights determined by direct titration (Table 1.2) are reasonably consistent with the theoretical values but suggest some mixture of chain lengths and/or the presence of inert impurities. The good phase separation of the compound with the highest proportion of ether groups suggests that the emulsions formed by the others might be due to a characteristic impurity rather than to the ether chains.

Table 1.2. New Organonitrogen Compounds, Assay by
Direct and Differential Titration

Compound	No. of Propoxy Groups ^a	Batch No.	% by Differential Titration			Equivalent Weight	
			Prim.	Secn.	Tert.	Theo.	Found
Propomeen ^a							
212/11	1	313A	3	9	87	412	408
212/12	2	319A	3	2	95	470	503
212/13	3	320A	3	2.5	94.5	528	508
212/14	4	322A	-	-	-	586	637
212/20	10	323A	-	-	-	934	950
212/50	40	324A	-	-	-	2677	2555

^aDilaurylpropoxyamine, $(C_{12}H_{25})N(CH_2-\underset{\text{CH}_3}{\text{CHO}})_nH$

1.2 Solvent Extraction Reagent Losses through Distribution to the Aqueous Liquor (J. M. Schmitt, C. A. Blake, W. T. Rainey)

The loss of purified di(2-ethylhexyl)phosphoric acid (D2EHPA) was measured by distribution from kerosene to acidic solutions of process interest using radioactive tracer analysis. Previous losses in batch equilibrations were measured by titrations of the organic phase before and after aqueous contact (ORNL-1903, p. 57) and by use of tracer D2EHPA with a low specific activity (ORNL-2172, p. 108). Although all those losses were low from the standpoint of process economy, <10 mg/liter, they were not in complete internal agreement. The present measurements with D2EHPA containing a higher specific activity of P-32 confirmed the lower of the previous measurements, <1 mg/liter, to dilute sulfuric acid and acidic sulfate solutions from 0.1 M D2EHPA at 25°C. Further measurements at higher D2EHPA concentration and at higher temperature showed losses still less than 20 mg/liter from 0.4 M D2EHPA in 4 hr contact at 50°C.

D2EHPA Loss from Kerosene at 25°C. The losses at 25°C with 0.1 M reagent were less than 0.7 mg/liter to several sulfate solutions and 1.5 mg/liter to 10 M HCl (Table 1.3). Increasing the reagent concentration to 0.4 M increased the losses in nearly the same proportion. Adding tributylphosphate (TBP) to the organic phase decreased the loss at the 0.4 M level, while the losses at the 0.1 M level (already very low) were not visibly affected.

Although the losses at 1 and 16 hr (Table 1.3) were essentially the same as at 10 min, indicating no measurable degradation of D2EHPA to more water-soluble materials in that time, some evidence was noted of degradation in ~100 hr. After three of the 10-min tests were completed (0.1 M D2EHPA contacted with 0.5 M SO_4^- , 1.0 M H_2SO_4 , and 10 M HCl), the phases were permitted to remain in contact without agitation for 4 days. After this time the phosphorus activity (equivalent to ~3 mg D2EHPA/liter) was higher in each aqueous phase. A fresh aqueous solution, after 10-min equilibration with the same organic solution, showed an intermediate tracer phosphorus activity, and subsequent fresh aqueous solutions (10-min equilibrations) showed the low level of phosphorus activity originally observed. This is attributed to slow degradation of a small amount of the D2EHPA (~0.01%), presumably to mono(2-ethylhexyl)phosphoric acid, which was not completely lost to 1 vol of aqueous solution but was to 2 vol.

D2EHPA Loss from Kerosene at 50°C. Loss of reagent from the organic phase was somewhat higher at 50 than at 25°C (Table 1.3). Since the 50°C values were from single instead of multiple determinations, so that there is no direct indication of the reproducibility of the distributions at the higher temperature, close intercomparison may not be justified. However, the increased loss to both H_2SO_4 and HCl on increasing the contact time from 1 to 4 hr suggests that a part of the losses at 50°C may be due to slight hydrolysis of the D2EHPA. The much lower loss in the single test with Liquor A than that with the 0.5 M sulfate solution is surprising, since the solutions are similar in major ionic composition. If this low loss value is real, it must be attributed to the effects of the extracted metal ions in the organic phase.

Table 1.3 D2EHPA Loss from Kerosene Solutions to Aqueous Acidic Liquors

10 min agitation at aqueous/organic phase ratio of 1/1

Aqueous Phase	Amount D2EHPA Lost to Aqueous Phase, mg/liter						
	25°C ^a				50°C ^b		
	0.1 M D2EHPA		0.4 M D2EHPA		0.1 M D2EHPA, 4 hr	0.4 M D2EHPA	
	No Additive	0.1 M TBP ⁻ Added	No Additive	0.14 M TBP ⁻ Added		1 hr	4 hr
0.5 M SO ₄ ⁼ , pH 1	0.5 ^c	0.5	2	---	4	9	9
1.0 M H ₂ SO ₄	0.4 ^d	0.4	2	0.3	4	5	10
10 M HCl	1.5 ^e	---	5	2	5	9	17
Liquor A ^f	0.6	0.5	4	---	0.6	---	---
Liquor B ^g	0.7	---	---	---	---	---	---

^aAverage of 3-6 determinations.

^bSingle determinations.

^cLoss after 1 hr = 0.4 mg/liter, after 16 hr = 1 mg/liter.

^dLoss after 1 hr = 0.3 mg/liter, after 16 hr = 0.6 mg/liter.

^eLoss after 1 hr = 1.1 mg/liter, after 16 hr = 1.5 mg/liter.

^f0.5 M SO₄⁼, pH 1, 0.05 g U/l, 2 g Fe²⁺/liter, 0.5 g Fe³⁺/liter, 2 g Al/liter.

^g0.5 M SO₄⁼, pH 1, 4.0 g U/l, 2 g Fe²⁺/liter, 0.5 g Fe³⁺/liter, 2 g Al/liter.

Test Solutions and Tracer Reagent. The aqueous test solutions were chosen on the following bases: 0.5 M SO_4^- , pH 1, corresponds to the anionic concentration and pH level of many raw materials leach liquors; 1 M H_2SO_4 is a probable stripping solution for vanadium; 10 M HCl is a potential stripping solution for uranium; and the last two solutions approximate certain typical process liquors, B corresponding to the feed composition and A to the composition near the raffinate end of the extraction system.

The tracer D2EHPA was prepared by reaction of 2-ethylhexanol with POCl_3 containing trace amounts of P-32. The sodium salt of the acid was separated from by-product phosphorus acids by extraction into ethyl ether after neutralization with NaOH. The ether phase was then acidified with HCl, converting the sodium salt to free D2EHPA, which was scrubbed several times with additional HCl and water. The ether was evaporated and the D2EHPA was dissolved in kerosene.

Titration of the kerosene solution, showing less than 0.01 equivalent of weak hydrogen for each equivalent of strong hydrogen present, indicated low acidic impurity. Dr. W. H. Baldwin of the ORNL Chemistry Division, who assisted in the synthesis of the reagent, has prepared a solid cyclohexylamine salt of D2EHPA (1 amine/1 D2EHPA) which melts sharply at 170°C . Mixed melting points of the derivatives of the tracer reagent and of D2EHPA prepared from Tergitol P-28 (sodium di(2-ethylhexyl)phosphate) indicated identity.

1.3 Strontium-Sodium and Cesium-Sodium Exchange in Di(2-ethylhexyl)phosphate (C. A. Blake, D. E. Horner)

Cation exchange with sodium di(2-ethylhexyl)phosphate (D2EHP) in modified Amsco 123-15 solution was examined as a possible means of extracting radioactive strontium and cesium from waste solutions. Preliminary tests showed preferential extraction of strontium, but not of cesium, over sodium from neutral-to-basic nitrate solutions.

The separation factors for strontium over sodium (Table 1.4) scattered around a level of about 30. No change in separation was apparent with change of D2EHP concentration (0.1-0.4 M) or pH (~8 to >11 for 0.1 M D2EHP). Equilibration appeared to be complete in 10 min; shorter times were not tested. Provided the separation factor is similar down to low strontium concentrations, multistage extraction should give effective strontium removal from a sodium nitrate solution of this type.

The separation factors for cesium over sodium (Table 1.5) were less than unity, indicating preferential distribution of sodium to the organic phase. The separation factors scattered around a level of 0.4, showing little if any shift with cesium level, pH, or choice of diluent modifier.

The sodium D2EHP solutions for these tests were prepared by treating D2EHP solutions of the stated molarity with 15% NaOH.

Table 1.4 Strontium-Sodium Exchange in
Di(2-ethylhexyl)phosphate

Initial aq. soln.: 1 M NaNO₃ and 0.1 M Sr(NO₃)₂

Initial org. soln.: 0.1, 0.2, or 0.4 M NaR₂PO₄
in Amsco 123-15 containing 0.15, 0.2, or 0.3

M TBP

Phase ratio, a/o = 1/1, room temperature, agita-
tion in Burrell shaker

D2EHP Concn., M	Contact Time	pH		% of Sr Extracted	Separation Factor, ^a (Sr/Na) _{org}
		Init.	Final		
0.1	10 min	2.2	8.7	41	29
	64 hr	2.2	7.5	38	21
	64 hr	6.9	11.4	37	27
0.2	10 min	2.2	---	62	32
	64 hr	2.2	11.7	71	32
	64 hr	2.2	10.8	74	45
0.4	10 min	2.2	---	82	21
	64 hr	2.2	10.9	88	33

^a Separation factor = $\frac{(Sr)_{org}/(Na)_{org}}{(Sr)_{aq}/(Na)_{aq}} = \frac{D_a^O(Sr)}{D_a^O(Na)}$.

Table 1.5 Cesium-Sodium Exchange in
Di(2-ethylhexyl)phosphate

Initial aq. soln.: ~2 M (CsNO₃ + NaNO₃)
Initial org. soln: 0.1 M NaR₂PO₄ in Amsco 123-15
modified with TBP or Tridecanol
Phase ratio a/o = 1/1, room temperature, 64 hr
contact time in Burrell shaker

Init. Cs, M	Aq. Conc. Na, M	pH		% of Cs Extracted	Separation Factor, ^a (Cs/Na) _{org}
		Init.	Final		
0.2	1.8	8.0	11.8	2.3 ^b	0.34
	1.7	---	9.4	2.3 ^b	0.41
	1.8	8.0	11.6	1.9	0.31
	1.7	---	9.9	2.5	0.42
	1.9	11.9 ^c	>13	1.9	0.37
1.0	1.0	7.9	11.7	3.5	0.42
	0.9	---	8.8	3.8	0.47

$$^a \text{Separation factor} = \frac{(\text{Cs})_{\text{org}} / (\text{Cs})_{\text{aq}}}{(\text{Na})_{\text{org}} / (\text{Na})_{\text{aq}}} = \frac{D_a^{\text{O}}(\text{Cs})}{D_a^{\text{O}}(\text{Na})}$$

^bDiluent modified with 0.1 M tridecanol in the first two tests, with 0.15 M TBP in the others.

^cNaOH at 0.1 M in the initial aqueous solution.

Some excess sodium hydroxide was extracted into the organic solution (ORNL-2172, p. 44), which, on re-equilibration with the aqueous test solutions, caused the rather large pH changes noted.

2.0 PROCESS DEVELOPMENT

In addition to the studies described below, process development projects during the month included (1) evaluation in continuous equipment of the sodium carbonate method for stripping thorium from amines, (2) investigation of extraction characteristics and molybdenum compatibility of some new amines, (3) study of the effect of dissolved silica on phase separation in the Amex system, and (4) dissolution of uranium from ores by a sodium carbonate pugging treatment.

2.1 Removal of Phosphate from Dapex Vanadium Strip Solutions with Zirconium Oxide (F. G. Seeley)

Preliminary studies of methods of controlling the phosphate content of Dapex vanadium products to specification limits, i.e., $P/V_2O_5 = <0.05\%$, were described previously (ORNL-2399). It was shown that, during extraction, important amounts of inorganic phosphate can be transferred from the leach liquor to the solvent (presumably by extraction as a cationic metal complex) and subsequently transferred to the sulfuric acid strip solution. Although separation from phosphate was favorable when the vanadium was precipitated from the strip solution as "red cake," the phosphate was carried almost quantitatively to products derived by precipitating vanadium(IV) with ammonia. Since the latter precipitation method may have certain advantages with respect to process operation, development of a useful method for separating the phosphate from solution prior to vanadium precipitation is desirable.

In the course of their investigation of the ion exchange properties of various inorganic materials, Kraus and Phillips showed hydrous zirconium oxide to have unusual anion exchange properties in acidic solutions.* Their work suggested the possibility of removing the phosphate from the strip solution by adsorption on a bed of zirconium oxide.

Preparation of the Zirconium Oxide. Two samples of zirconium oxide were prepared by dissolving zirconyl chloride in water, precipitating with ammonia to pH 8.5, filtering, and washing. The wet cakes were dried** to constant weight at either 200 or 300°C. The dried precipitates were ground and passed through a 100 mesh screen.

*K. A. Kraus and H. O. Phillips, "Anion Exchange Properties of Hydrous Zirconium Oxide," J. Am. Chem. Soc., 78: 249 (1956).

**According to Kraus and Phillips the temperature at which the precipitate is dried determines its degree of activity as an exchanger. The adsorptive capacity decreases as the drying temperature is increased but this effect does not become excessive below 300°C.

Analyses showed

<u>Drying Temp., °C</u>	<u>ZrO₂, %</u>	<u>Loss on Ignition at 1000°C, %</u>
200	85.9	14.3
300	89.4	10.6

Batch Tests. In a series of batch tests, varying amounts of the two zirconium oxide samples were stirred in a beaker for either 5 or 30 min with synthetic strip solutions of pH 0.4 and 1.5. Both solutions contained 1.1 g of PO₄ per liter and, except for the pH, were similar in composition. After each contact the zirconium oxide was filtered off and the filtrates were analyzed for phosphate.

Phosphate adsorption was somewhat higher with the 200°C than with the 300°C oxide (Fig. 2.1). In general, phosphate removal was more effective at pH 1.5 than pH 0.4 and after 30 min contact than in 5 min. In the tests at pH 0.4 (but not at pH 1.5) zirconium and phosphate slowly precipitated after the solution had been separated from the zirconium oxide.

Column Test. Based on the promising batch test results, a column test was made with another batch of zirconium oxide which had been dried at 300°C and screened. To avoid excessive resistance to solution flow, only the -50+80 mesh fraction was used. This material was loaded into a glass column (~0.9 cm i.d.) to a depth of 28 cm. The total weight of the zirconium oxide was 27 g and the wet settled volume was approximately 19 ml.

A synthetic vanadium strip solution (pH 1.5), similar to that used in the batch tests but containing only 0.55 g of PO₄ per liter, i.e., P/V₂O₅ = 0.31%, was passed through the column at a flow rate of approximately 2.7 ml/min (~60 gal/ft²/hr). Phosphate analyses of effluent samples showed essentially complete removal of phosphate until about 20 column volumes (19 ml each) of solution had passed through the column (Fig. 2.2). At this point the phosphate began to break through slowly, increasing from 0.01 g/liter after 30 column volumes to 0.04 g/liter after 40 column volumes. The latter figure corresponds to a P/V₂O₅ ratio in the solution of 0.023%, or approximately half the allowable phosphorus. The test was discontinued after 44 column volumes of solution had passed the column. The overall removal of phosphate for the test was about 98% and the calculated average loading in the column was about 16 g of PO₄ per 1000 g of adsorbent. The zirconium concentration in the column effluent decreased steadily over most of the run, finally appearing to reach a constant value of approximately 0.01 g/liter:

<u>Column Volumes of Effluent</u>	<u>Zr in Effluent, g/liter</u>
9	0.14
14	0.08
20	0.06
22	0.04
40	0.01
41	0.01
43	0.01

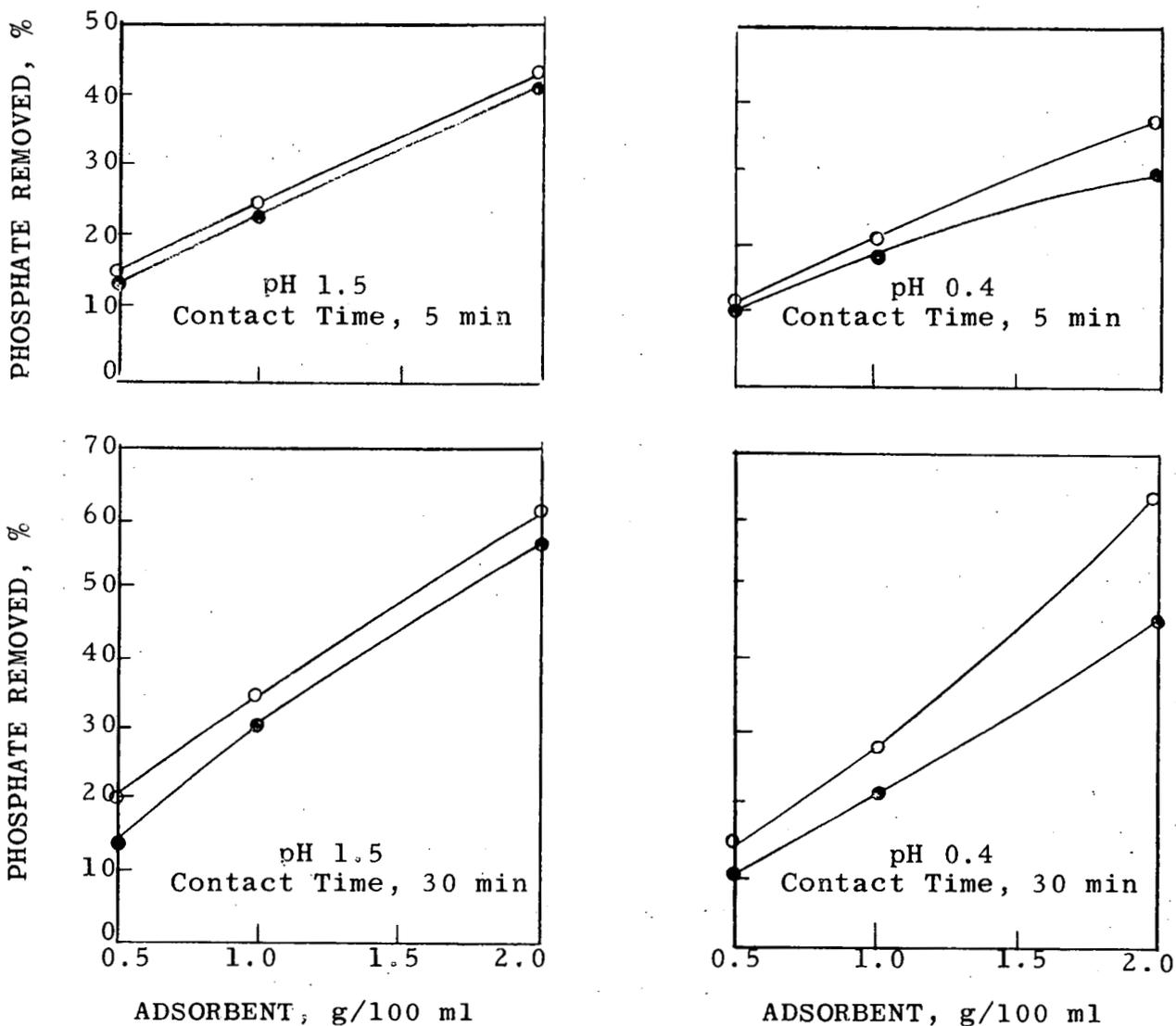


Fig. 2.1 Adsorption of Phosphate on Zirconium Oxide. Synthetic strip solution, in g/liter, 31.4 V(IV), 0.63 Fe(III), 0.44 Al, 1.1 PO₄, 98 SO₄, pH 0.4 or 1.5 (pH adjustment made with NH₃)

- zirconium oxide dried at 200°C
- zirconium oxide dried at 300°C

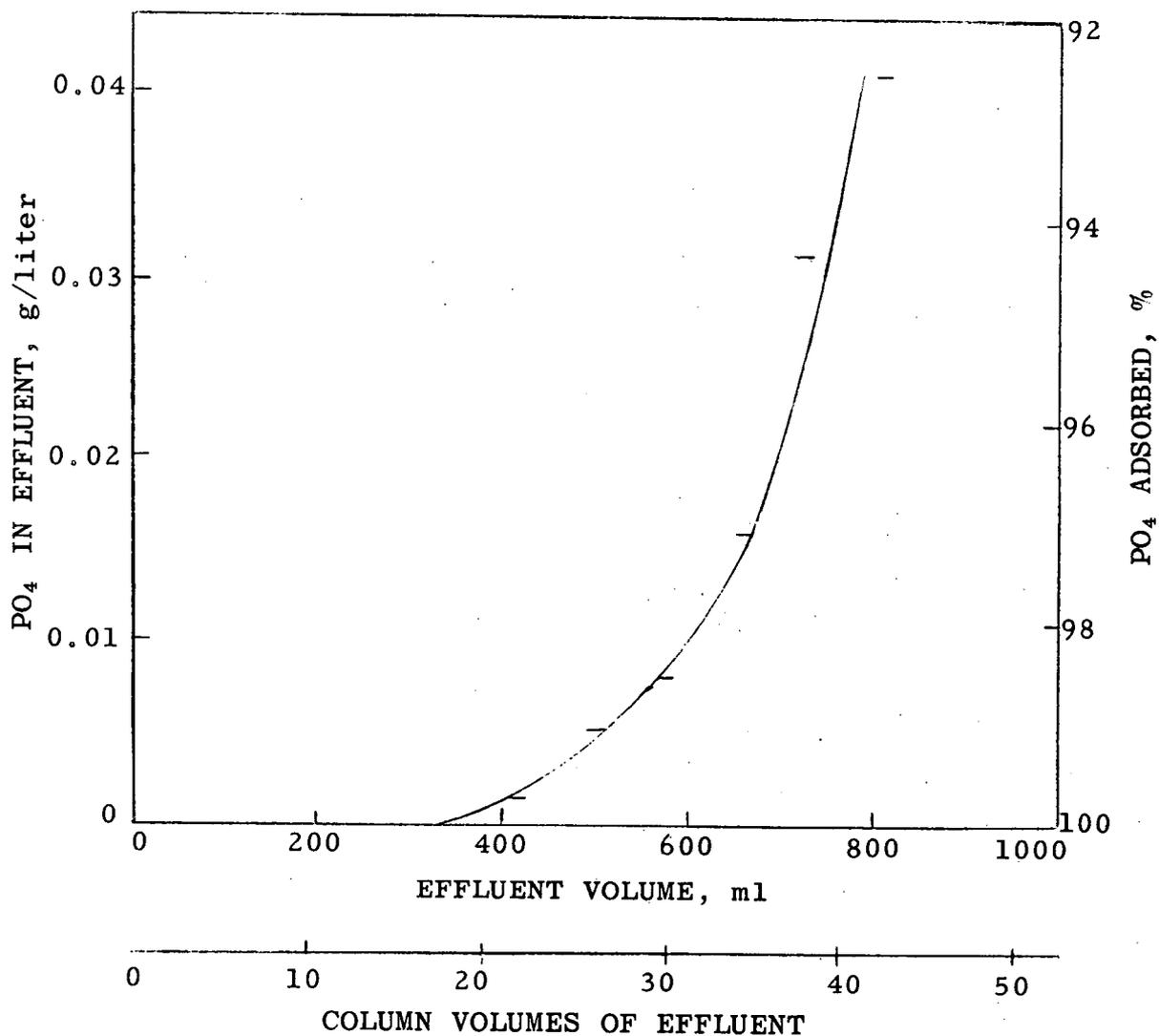


Fig. 2.2 Adsorption of Phosphate on a Column of Zirconium Oxide. Synthetic strip solution, g/liter, 31.8 V(IV), 0.6 Fe(III); 0.4 Al, 0.55 PO₄, 98 SO₄, pH 1.6; zirconium oxide dried at 300°C, -50+80 mesh, weight 27 g, height in column 28 cm, wet settled volume 19 ml; solution flow rate 2.7 ml/min (~60 gal/ft²/hr).

The relatively high zirconium losses in the initial period of the run can probably be attributed to the presence of zirconium oxide fines which gradually were eliminated as the run progressed. Zirconium losses even at the rate of 0.14 g/liter are of minor cost significance, corresponding to a zirconium consumption of only 0.0025 lb per pound of V_2O_5 .

Following the loading cycle, the column was washed with 8 column volumes of water and elution of the phosphate with dilute caustic was attempted. Phosphate removal during the water wash was negligible. Approximately 21 column volumes of 0.1 M NaOH and then 9 volumes of 0.5 M NaOH were passed through the column at a flow rate of approximately 4 ml/min (~90 gal/ft²/hr). Phosphate analyses of small eluate samples taken after passage of the indicated column volumes were

<u>Eluant</u>	<u>Column Volumes</u>	<u>Eluate</u>	
		<u>pH</u>	<u>PO₄, g/liter</u>
0.1 M NaOH	3	2.4	< 0.005
	5	2.6	< 0.005
	10	-	< 0.005
	12	-	0.02
	15	2.6	0.16
	17	4.7	0.53
	19	10.1	0.84
	21	12.1	0.64
	0.5 M NaOH	1	12.2
2		12.5	2.7
3		12.5	1.7
4		12.5	1.2
6		12.5	0.66
8		12.5	0.44
9		12.5	0.37

On the basis of composite eluate analyses, the total phosphate removed from the column in the eluting cycle was approximately 65% of that initially adsorbed. This value is being checked by direct analysis of the zirconium oxide.

Methods of increasing the elution efficiency including the use of more concentrated caustic solutions, lower elution flow rates, and possibly elevated temperatures are being examined. Tests are also being made to determine whether the zirconium oxide will maintain its sorption capacity in cyclic operation.

2.2 Rate of Stripping of Vanadium(IV), Iron(III), and Aluminum from Di(2-ethylhexyl)phosphoric Acid (F. G. Seeley)

In the Dapex process for vanadium recovery as originally proposed, vanadium(IV) is extracted with 0.2-0.4 M di(2-ethylhexyl)-phosphoric acid (D2EHPA) and stripped with 1 M H_2SO_4 at ambient temperature. Under these stripping conditions, some of the extracted impurity metals, such as Fe(III), aluminum, and titanium are not

removed effectively from the organic phase. To prevent their buildup to a point of eventual interference with extraction efficiency, a fraction of the solvent stream is regenerated by contact with sodium carbonate solution before it is recycled to the extraction system.

Recently, the Kerr-McGee Oil Industries, Inc. has reported (private communication) that 1 M H_2SO_4 stripping at higher temperatures removes the impurity metals more effectively. Consequently, further tests have been made at this laboratory to study the effect of temperature on stripping, particularly on the relative stripping rates of vanadium(IV), iron(III), and aluminum. These relative rates are important to operating practice in setting a balance between the extent of contamination of the strip solution and the amount of solvent regeneration required.

Organic solutions consisting of 0.25 M D2EHPA in kerosene or kerosene + 0.2 M TBP* diluent were loaded with vanadium(IV), iron(III), or aluminum immediately prior to the stripping tests. The extracts were then stripped by contact with 1 M H_2SO_4 in a baffled mixer using a stirring speed of ~600 rpm. Samples of the mixed phases were withdrawn at specific time intervals, allowed to separate over a period of approximately 1 min, and analyzed.

Stripping of Vanadium(IV). Organic extracts loaded with 3.5 g V(IV) per liter were stripped at 25 and 50°C, o/a phase ratio 10/1 (Fig. 2.3). The equilibrium distribution, reached within 20 min, was essentially the same at both temperatures. Stripping was quite rapid at 50°C, reaching ~85% of its equilibrium value after 1 min and >95% after 2.5 min. Stripping was much slower at 25°C, reaching 85% of equilibrium only after ~5 min and 95% after ~10 min. In the presence of TBP slightly more vanadium was stripped at equilibrium, but the relative rates were essentially the same as in its absence.

It should be noted that the particular rates indicated in Fig. 2.3 pertain only to the particular mixing conditions used. Much faster vanadium stripping, at room temperature, has been generally observed when mixing has been more vigorous and when the phase ratio was closer to unity.**

Iron(III) and Aluminum Stripping. Organic extracts loaded with either 1.2 g of Fe(III) or 0.8 g Al/liter were stripped at 25 or 30°C and at 50°C, with an a/o phase ratio of 1/1. Iron stripping was extremely slow at 25°C (Fig. 2.4), only about 5% of the iron being stripped after 20 min and 10% after 60 min, presumably still far from equilibrium. Increasing the temperature to 50°C greatly increased the stripping rate, with approximately 25% of the iron stripped in 10 min. Beyond 10 min, the extent of stripping from the solvents

* Use of a diluent modifier is recommended to prevent separation of the sodium salt of D2EHPA as a third liquid phase during alkaline regeneration. Although both TBP and long chain alcohols are effective modifiers, TBP is preferred since it does not significantly affect vanadium extraction, whereas the alcohol severely depresses the vanadium coefficient.

** In studies of the Dapex uranium extraction system by the Engineering Section (ORNL-2380), the rate of mass transfer was dependent on the phase ratio during mixing, being more rapid at a/o phase ratios of 1/1 than at a relatively high ratio, e.g., 4/1.

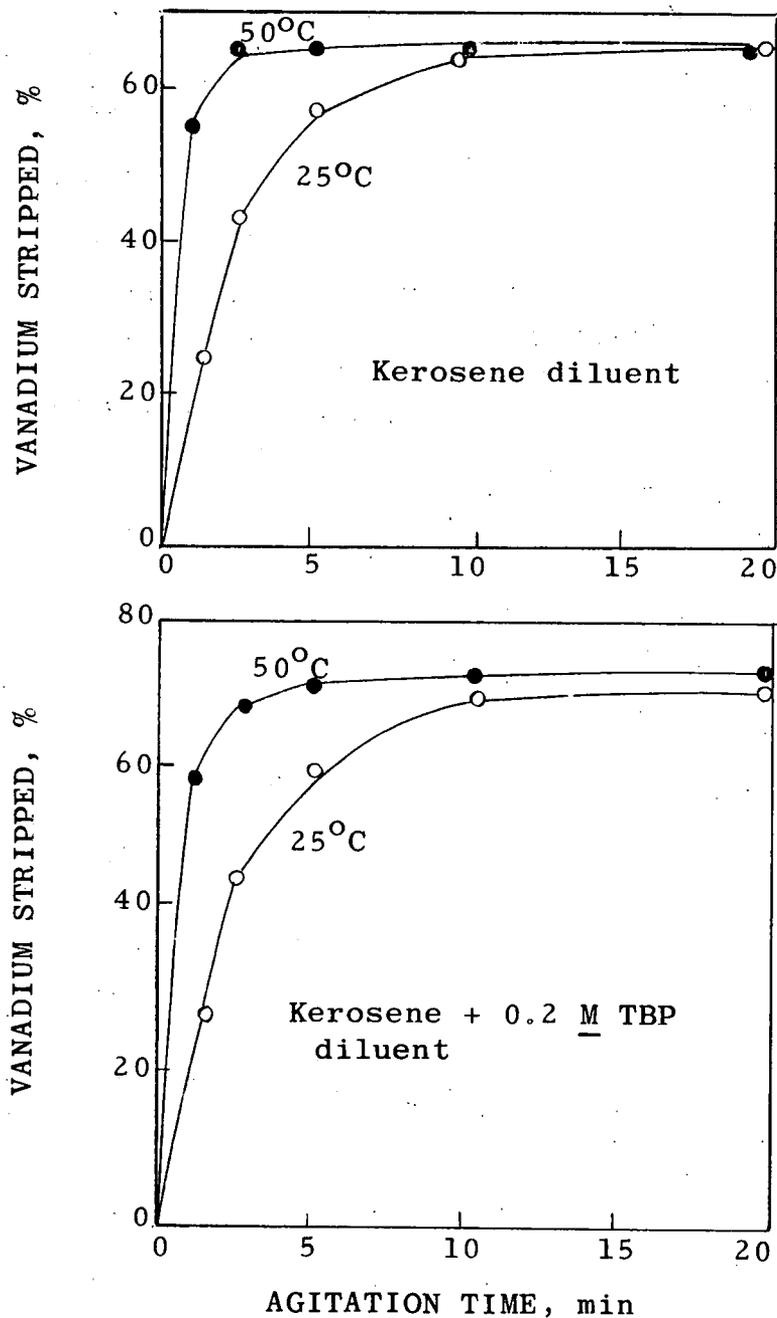


Fig. 2.3 Rate of Vanadium(IV) Stripping from 0.25 M D2EHPA with 1.0 M H₂SO₄. Ten volumes of extract (3.5 g V(IV) per liter) mixed with 1 vol of 1.0 M H₂SO₄ in a baffled beaker at ~600 rpm stirring speed; organic continuous mixing.

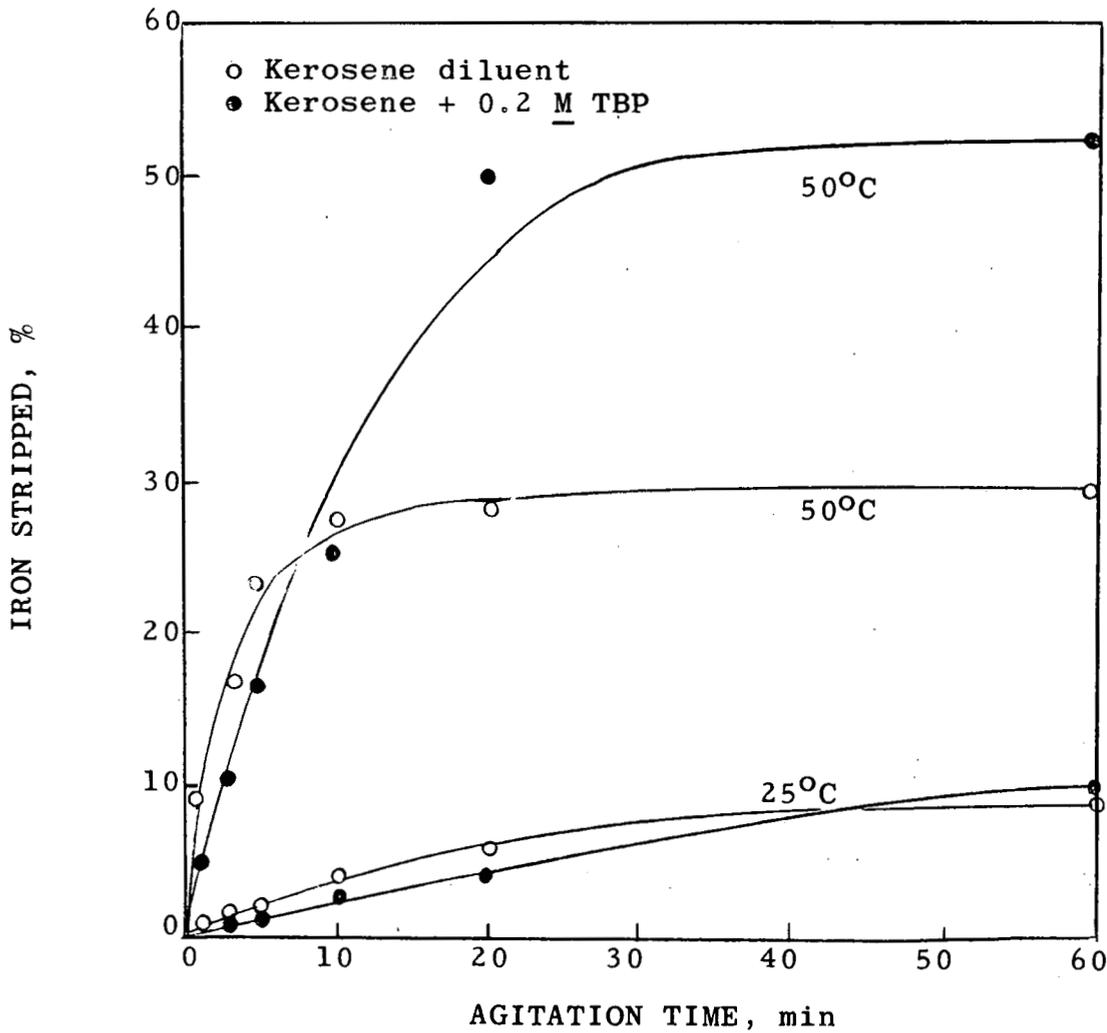


Fig. 2.4 Rate of Iron(III) Stripping from 0.25 M D2EHPA with 1.0 M H₂SO₄. Equal volumes of extract (~1.2 g Fe(III) per liter) and 1.0 M H₂SO₄ mixed in a baffled beaker at ~600 rpm stirring speed; organic continuous mixing.

with and without TBP diverged widely, with ~50% of the iron removed in the presence of TBP and only ~30% in its absence, in 60 min. The curves suggest that the 50°C stripping was near equilibrium at 60 min, and it was not much less in 20 min than in 60 min.

Aluminum was stripped more rapidly and more completely than iron (Fig. 2.5). However, at 30°C the rate was still relatively slow, with ~25% stripped in 10 min, 60-75% in 20 min, and 85-95% in 60 min. At 50°C, >95% stripping was obtained in less than 10 min. At 30°C the rate of stripping was noticeably faster when TBP was present in the solvent.

The foregoing results are all from tests made with the organic phase continuous in the mixer (see ORNL-2172, p. 76 for procedure). In tests with the aqueous phase continuous results were essentially the same.

In process practice, the advantage or disadvantage of the higher iron and aluminum stripping rates occurring at higher temperatures would depend primarily on the choice of method for subsequent recovery of vanadium from the pregnant strip solution. If the vanadium is recovered as "red cake" by addition of sodium chlorate to the solution and heating, relatively high concentrations of metal contaminants in the strip solution can be tolerated since separation from vanadium is good in the precipitation. In this case, hot stripping would appear advantageous both for improved vanadium stripping and for decreased need of solvent regeneration. In contrast, when vanadium is recovered by hydrolytic precipitation with ammonia, most of the iron and aluminum also precipitate, so that increased product contamination would probably outweigh the advantages obtainable from hot stripping when ammonia precipitation is used.

3.0 ENGINEERING STUDIES

In addition to the studies described below, engineering studies during the month have included (1) batch phase separation tests for comparison of different amines, diluents, and modifiers in the Amex process, (2) determination of flow capacity and scale-up factors for gravity settlers for the extraction section of the Amex process, and (3) effect of coalescers for recovery of entrained solvent in aqueous raffinate.

3.1 Effect of Phase Ratio on the Rate of Uranium Extraction by Dapex Type Solvent (F. L. Daley)

Studies of the rate of uranium extraction from typical sulfuric acid leach liquors by a Dapex type solvent in a batch mixer (ORNL-2366) and under continuous flow conditions (ORNL-2380) at an aqueous/solvent ratio of 4/1 were reported previously. Similar studies have been made at an aqueous/solvent ratio of 1/1 to study the effect of phase ratio on the rate of uranium extraction.

The tests were conducted in a 6-in. baffled tank mixer equipped with a 3-in. 6-bladed turbine as described in ORNL-2269. The

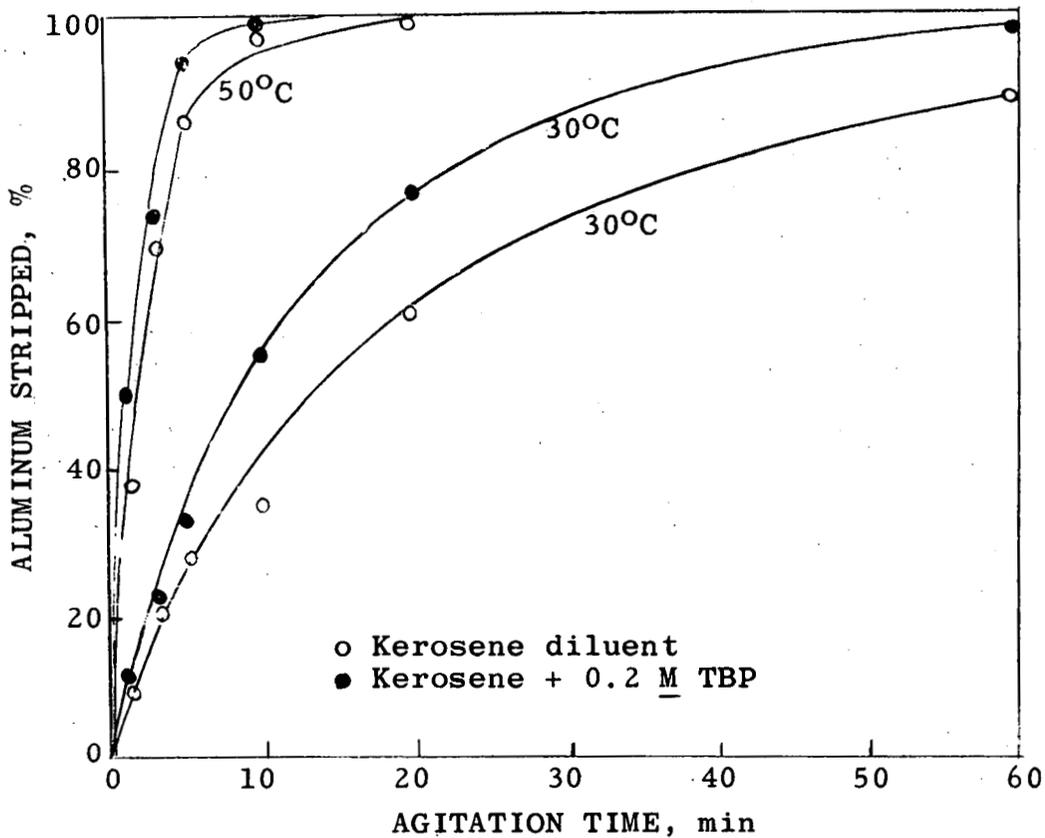


Fig. 2.5 Rate of Aluminum Stripping from 0.25 M D2EHPA with 1.0 M H₂SO₄. Equal volumes of extract (~0.8 g Al per liter) and 1.0 M H₂SO₄ mixed in a baffled beaker at 600 rpm stirring speed; organic continuous mixing.

solvent was 0.1 M D2EHPA in kerosene containing 30 g/liter TBP. The composition of the feed liquor, in g/liter, was 1.2 U, 0.3 Fe(III), 1.0 V(IV), 2.8 Al, 50 SO₄, and 1.9 PO₄ at pH 1. The tests were made to simulate the loaded stage in a countercurrent extraction circuit with solvent recycle to maintain an aqueous/solvent ratio of 1/1 in the mixer. To accomplish this 4 parts of feed liquor (1.21 g of uranium per liter) were contacted with 1 part of barren solvent and 3 parts of loaded solvent (4.0 g of uranium per liter). Complete transfer of uranium would give a solvent loaded to 80% of the maximum equilibrium loading from the aqueous feed. The tests were made at a temperature of 25 ± 1°C.

The rate constant K' was calculated from the data obtained from the batch test in the same way as described in ORNL-2269. The rate constant obtained at an aqueous/solvent ratio of 1/1 and the rate constant obtained under similar conditions at an aqueous/solvent ratio of 4/1 (ORNL-2366) were adjusted for the fraction of aqueous present in the mixer (R/V) where R is the volume of aqueous and V is the total volume of the mixer. The values of K'R/V agreed closely:

Run No.	a/o Phase Ratio	Turbine Speed, rpm	Power Input, hp/1000 gal	K' min ⁻¹	K'R/V
85	4/1	524	20	1.44	1.15
183	1/1	524	20	2.12	1.06

For the continuous-flow tests, at an aqueous/solvent ratio of 1/1, the aqueous flow rate was 0.243 gal/min and the power input was varied from 2.5 to 220 hp/1000 gal. The mixing was controlled to give a solvent continuous dispersion. The Murphree stage efficiency was calculated (for the continuous flow tests, at an aqueous/solvent ratio of 1/1) in the same way as described in ORNL-2380. The results (Table 3.1) show an increase in Murphree efficiency with increasing power input from 57.8% at 2.5 hp/1000 gal to 88.2% at 220 hp/1000 gal.

Table 3.1 Summary of Results of Continuous-flow Tests

Run No.	Aqueous U Conc., g/liter		Impeller Speed, rpm	Power per Mixer Vol., hp/1000 gal	Murphree Extraction Efficiency, %
	In	Out			
672	1.21	0.565	262	2.5	57.8
673	1.21	0.450	350	5.7	68.8
674	1.21	0.335	524	20	80.6
675	1.21	0.285	787	67	86.7
676	1.21	0.265	1170	220	88.2

Comparison of these results with those previously obtained (ORNL-2380) at the same aqueous flow rate and at an aqueous/solvent ratio of 4/1 (Table 3.2) shows that the stage efficiency was not greatly affected by changing the aqueous/solvent ratio from 4/1 to 1/1. Consequently, mixers designed for a specific aqueous flow

rate should operate at fairly constant efficiency independent of the amount of solvent recycle within the limits of phase ratios tested.

Table 3.2 Effect of Phase Ratio on Extraction Efficiency

Aqueous Flow, gal/min	a/o Phase Ratio	Murphree Extraction Efficiency, %				
		Power per Mixer Vol. (hp/1000 gal)				
		2.5	5.7	20	67	220
0.243	1/1	57.8	68.8	80.6	86.7	88.2
0.237	4/1	66.0	75.7	77.4	80.7	86.1

4.0 FUNDAMENTAL STUDIES

In addition to the work described below, fundamental projects studied during the month have included (1) measurements of aggregation of amine salts and uranyl-amine salt complexes by light scattering, (2) measurement of dielectric constants of organic solutions of amine salts, and (3) examination of dialkylphosphoric acid--phosphine oxide association by isopiestic measurements.

4.1 Interaction Between Di(2-ethylhexyl)phosphoric Acid and Tri-n-octylphosphine Oxide in n-Octane (H. T. Baker, C. F. Baes, Jr.)

In the previous report results of an infrared spectrophotometric investigation of the interaction between the components of synergistic extractants were described. In the case of di(2-ethylhexyl)phosphoric acid (A) and tri-n-octylphosphine oxide (B) in n-octane, an interaction product was found by the method of continuous variations in which the mole ratio of B/A₂ (A being dimeric) was 2, i.e., the ratio B/A = 1.

For more detailed examination of this interaction, the concentration dependence on B was measured at constant concentrations of A (Fig. 4.1). As before, the quantity D is the difference between the observed absorbency and that expected if the absorbencies of A and B were additive (i.e., no interaction) in mixed solutions. D was measured as a function of the concentration of B at A = 0.1 M and A = 0.05 M. Both the appearance of the P=O band at 1280 cm⁻¹ associated with the interaction product (Fig. 4.1) and the disappearance of the P=O band at 1233 cm⁻¹ associated with A₂ were measured.

Assuming the following equilibrium



(which was suggested by the continuous variation results) to be the only important interaction taking place, it may readily be shown that D should be proportional to the concentration of AB. Therefore, it is possible to calculate a value for K₁ from each point on the curve upon the choice of a proportionality constant. This procedure gives values of K₁ which vary from 20 to 40. The assumption that the addition compound is A_nB_n, where n is an integer

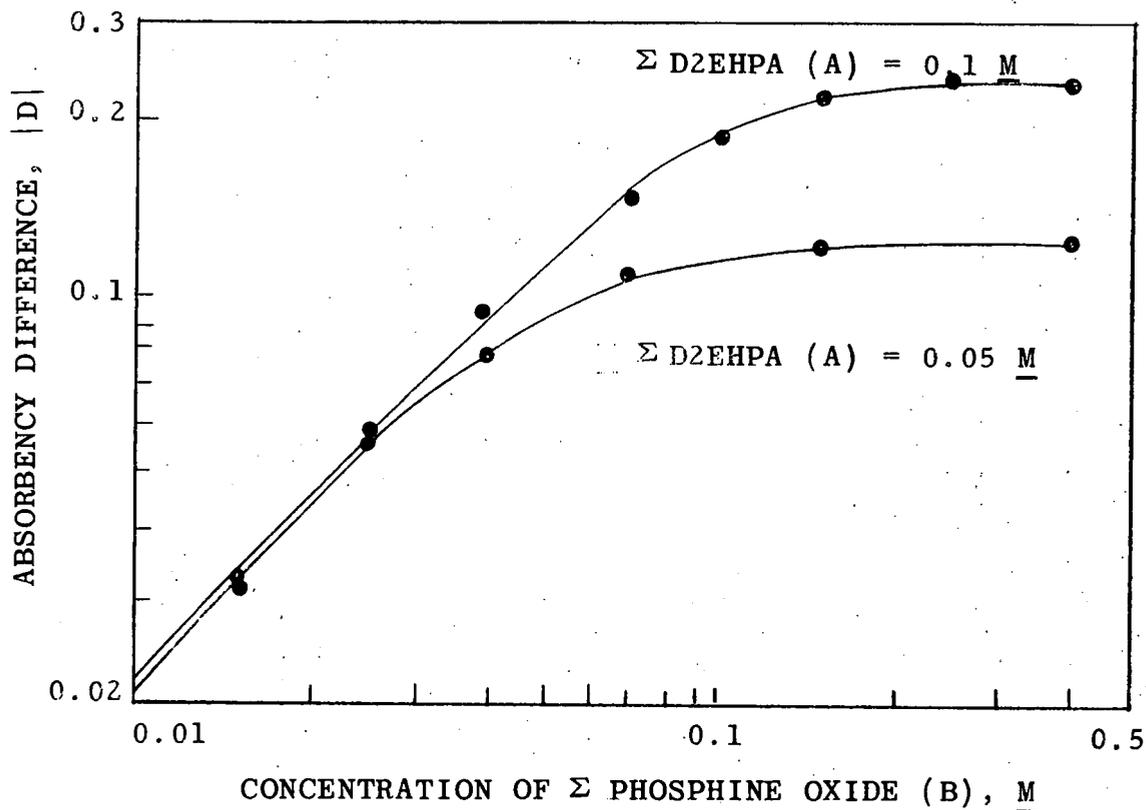
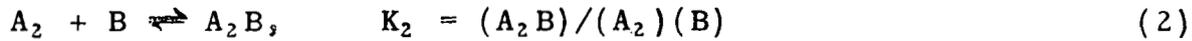


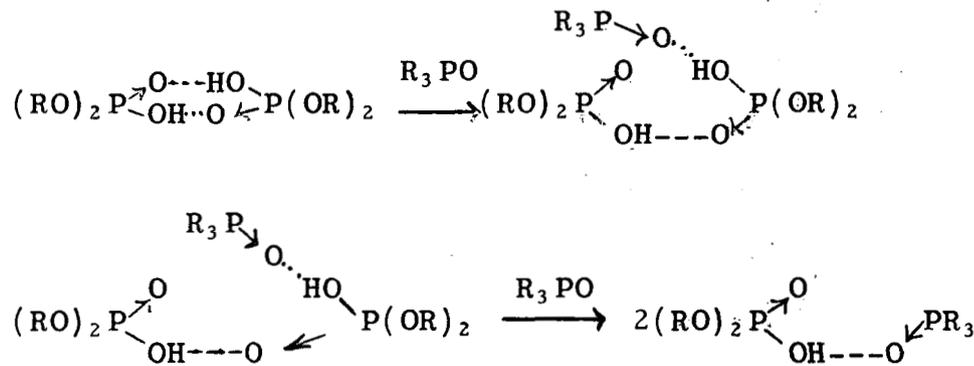
Fig. 4.1 Dependence on the Concentration of Phosphine Oxide (B) of the Difference D between Calculated and Observed Absorbencies at 1280 cm^{-1} in Mixtures with 0.05 and 0.1 M Di(2-ethylhexyl)phosphoric Acid (A).

greater than unity, leads to much larger fluctuations in K_1 (e.g., for A_2B_2 , K_1 varies by more than a factor of 10).

The lack of constancy of K_1 suggests that more than one addition compound is formed. The most reasonable choice for the additional equilibrium is



Thus, one can picture the interaction between A_2 and B as proceeding in two steps:



In terms of these reactions, the present data can be accounted for quite satisfactorily. The assumed relation between D, AB, and A_2B is $D = k(A_2B + AB)$. The resulting K values are $K_1 = 30 + 5$ and $K_2 = 100 + 50$. The relative concentrations of A_2 , A_2B and AB given by these K values are indicated in Fig. 4.2. It is seen that the concentration of A_2B is never more than ~50% of AB and generally it is much less than AB. Consequently, it is not surprising that the formation of A_2B was not apparent from the continuous variation measurements.

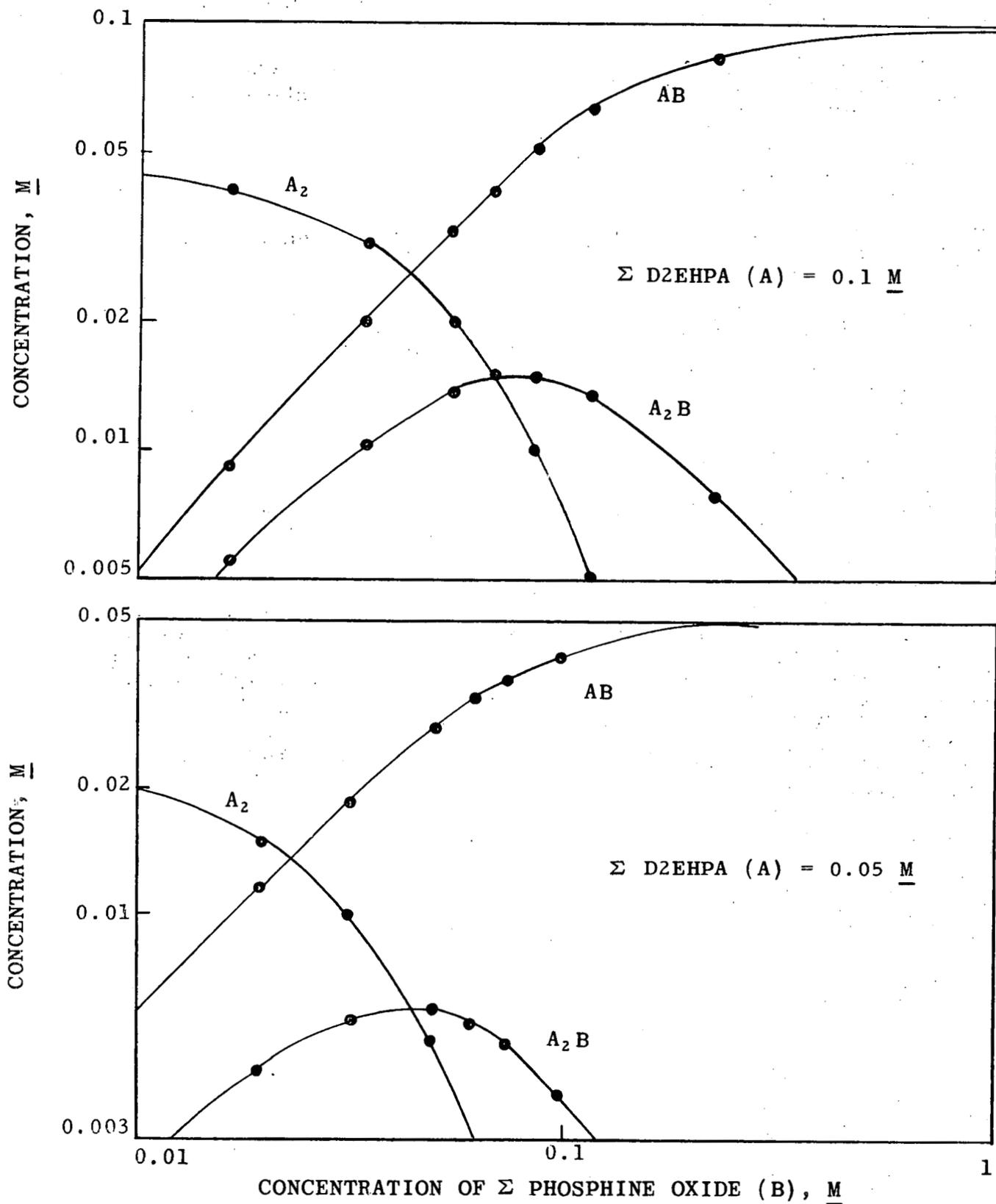


Fig. 4.2 Dependence of Relative Concentrations of Species in Solution on the Total Concentrations of Phosphine Oxide (B) and Di(2-ethylhexyl)phosphoric Acid (A).