

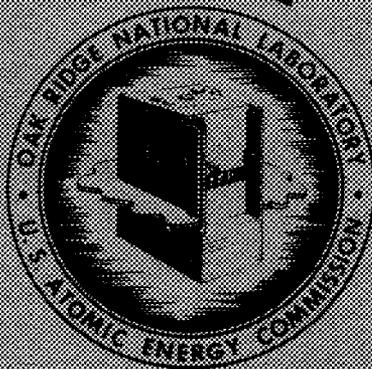
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PROGRESS REPORT: FURTHER STUDIES OF THE  
DIALKYLPHOSPHORIC ACID EXTRACTION  
(DAPEX) PROCESS FOR URANIUM

C. A. Blake  
D. J. Crouse  
C. F. Coleman  
K. B. Brown  
A. D. Kelmers



**OAK RIDGE NATIONAL LABORATORY**

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**UNION CARBIDE NUCLEAR COMPANY**

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CHEMICAL TECHNOLOGY DIVISION  
Chemical Development Section C

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ABSTRACT

Progress is reported on certain aspects of the Dapex process, including further study of miscibility modifiers for the kerosene diluent, synergistic extractant combinations, stripping of extracted uranium, and continuous countercurrent demonstration on actual plant liquors.

Note:

Mention of any proprietary material by trade name is not intended to mean that this product alone will perform the function for which it is specified.



## SUMMARY

Systematic testing and development of uranium extraction by the Dapex process have been continued. The results obtained in study of certain aspects of the process are as follows:

### Reagents for Modification of the Organic Extractant

As previously reported, the sodium salt of di(2-ethylhexyl)phosphoric acid (D2EHPA) separates from unmodified kerosene diluent as a third phase, but modification by means of certain long-chain alcohols will maintain miscibility. Over 50 additional compounds (alcohols, ketones, ethers, esters, neutral organophosphorus compounds, hydrocarbons, and chloro- and nitro-hydrocarbons) were tested for their ability to maintain miscibility of 0.1 M sodium di(2-ethylhexyl)phosphate in kerosene. Of these, some primary alcohols, some secondary alcohols without severe branching, an alkylphenol, 2-ethylhexylchloride, and several of the phosphorus compounds were effective at concentrations of 3 w/v % or less. The minimum effective modifier concentration was determined as a function of D2EHPA concentration from 0.1 to 0.4 M for ten of the better modifiers.

Excepting the phosphorus compounds, all the modifiers tested depressed the uranium extraction power. In contrast, every combination tested of a neutral organophosphorus compound with D2EHPA showed much greater uranium extraction power than could be accounted for as the cumulative extraction power of the individual reagents, i.e., showed a strong synergistic enhancement of extraction. The magnitude of the enhancement varied with reagent structure, e.g., 6-, 20-, and 50-fold increase of extraction coefficient with tributylphosphate (TBP), dibutyl butylphosphonate (DBBP), and tributylphosphine oxide (TBPO), respectively, over that with D2EHPA alone. The higher extraction power allows more complete extraction in fewer stages, or extension of the Dapex process to liquors otherwise difficult to extract. Selectivity for uranium over common contaminants such as iron(III), vanadium(IV), aluminum, molybdenum, and titanium was not impaired by addition of TBP or DBBP, and under some conditions it was improved.

Loss rates of several of the modifiers to various aqueous solutions was measured. The previously-described method for determination of modifier concentration in the organic phase by titration to the critical miscibility point has been developed further, and a detailed procedure is given. Some loss rates of modifiers (and of D2EHPA) were also measured using radioactive tracer phosphorus compounds. The preliminary estimates previously reported of reagent make-up costs were extended to include the newer modifiers. The contribution to total cost estimated for make-up of decyl or tridecyl alcohols is less

than for the octyl alcohols previously reported. That for make-up of the synergistic modifiers is not much greater than for the better alcohols, so that the advantages in uranium extraction would appear more than enough to offset the cost difference.

### Stripping of Uranium

Stripping with ammonium carbonate instead of sodium carbonate offers the advantage of a  $U_3O_8$  product of relatively low cation content, potentially more suitable for some of the processes now being considered for manufacture of pure uranium compounds. Also, the ammonium salt of D2EHPA is miscible in kerosene modified with a smaller amount of diluent modifier than is required for miscibility of the sodium salt. The use of ammonium carbonate has been promising in batch tests and in a single continuous countercurrent run, although further study is required, particularly of the completeness of stripping of extracted materials other than uranium. Uranium stripping was essentially complete in both the batch tests and in the continuous countercurrent test (two stripping stages) when sufficient ammonium carbonate was supplied, which was not much in excess of the stoichiometric requirement calculated on basis of the ammonium content and the assumed reaction equations previously reported. Phase separation was good. Conditions for optimum product purity have not yet been studied; in a single precipitation test a portion of the pregnant strip solution was filtered, then treated with steam to remove ammonium carbonate. The resulting precipitate, washed and dried at  $120^{\circ}C$ , contained 88.8%  $U_3O_8$ , 0.17%  $Fe_2O_3$ , 0.14%  $Al_2O_3$ , and 2.15%  $NH_3$ .

A few stripping tests with other bases were not promising. Sodium hydroxide solutions gave difficult phase separation. Stripping was not complete with slurries of magnesium oxide or calcium hydroxide or carbonate.

When the sodium or ammonium dialkylphosphate is formed in the organic phase during alkaline stripping, some water and some excess base also enter the organic phase. The extent of these extractions was measured under several conditions of varying composition and temperature. The amount of water extracted, and hence the increase of organic volume, was approximately proportional to the D2EHPA concentration, and was about 3% for 0.1 M D2EHPA when treated with 10% sodium carbonate solution. There was a corresponding decrease in aqueous volume, the total volume remaining constant.

Working curves were prepared for convenient estimation of sodium carbonate consumption in stripping as a function of D2EHPA concentration, uranium loading, and excess of sodium carbonate allowed over stoichiometric. They also provide means for estimating any effects of the aqueous volume

decrease mentioned above on the final uranium concentration to be obtained in the loaded strip solution, and on the range of initial sodium carbonate concentrations which will produce loaded strip solutions within the range of stable sodium uranyl tricarbonate solubility.

Stripping tests with solutions of mineral acids confirmed and extended the results previously reported. Stripping coefficients from 0.1 M D2EHPA (unmodified or alcohol-modified) were greater than unity with concentrations of 2 M sulfuric or phosphoric acid or 4 M hydrochloric acid, and generally increased with increasing acid concentration. However, the dependence of stripping coefficient from alcohol-modified D2EHPA on hydrochloric acid concentration was complex, showing a local maximum in the range 6-9 M and a local minimum in the range 9-11 M. (As a result of this behavior, the presence of alcohol aids stripping at some hydrochloric acid concentrations but impairs it at others.) In the presence of TBP (synergistic extractant combination) the stripping coefficients were too low for practicable utility.

Some comparisons were made of acid stripping of uranium from mono- and dialkylphosphoric acids. The dependence of stripping coefficient on hydrochloric acid concentration was somewhat higher with the mono than with the dialkyl reagent tested, while its dependence on organic reagent concentration was somewhat lower.

### Continuous Countercurrent Tests

Continuous countercurrent extraction runs (with sodium carbonate stripping) were made to compare the performance of combinations of D2EHPA with different additives, and to demonstrate the processing of two actual plant liquors from Western mills. Design and operation of the bench-scale extraction equipment is described. Uranium extraction from a synthetic liquor (0.5 M sulfate) was 99.3% complete in four mixer-settler extraction stages with 0.1 M D2EHPA - 1.5 w/v % capryl alcohol, 99.9% and >99.9% complete in three stages with, respectively, 0.1 M D2EHPA - 3 w/v % TBP and 0.1 M D2EHPA - 2.5 w/v % DBBP. Physical performance was good with all three extractants.

Extraction from the actual plant liquors was good, and conformed to the expected behavior. "Plant D" liquor contained (inter alia) 1 g U/l, 5 g Fe/l, and 110 g SO<sub>4</sub>/l at pH 0.5. Before extraction it was adjusted to 74 g SO<sub>4</sub>/l at pH 1.2 with lime, and iron(III) was reduced to iron(II) with powdered iron metal. Five mixer-settler extraction stages with 0.1 M D2EHPA - 3 w/v % TBP gave 99.4% uranium recovery (6 ppm U in raffinate, 5 g U<sub>3</sub>O<sub>8</sub>/l in pregnant organic, 40 g U<sub>3</sub>O<sub>8</sub>/l in pregnant sodium carbonate strip). Some of the

vanadium was extracted, but very little of the iron or aluminum. Most of the titanium and molybdenum was extracted, but the total quantities present were too low to be important.

"Plant C" liquor contained 6 g U/l, 0.6 g Fe(III)/l, and 116 g SO<sub>4</sub>/l at pH 0.15. When extracted as received and also when adjusted to 69 g SO<sub>4</sub>/l, pH 0.45, five mixer-settler extraction stages with 0.16 M D2EHPA - 4.7 w/v % TBP gave >99.9% uranium extraction (~1 ppm U in raffinate, 9 g U<sub>3</sub>O<sub>8</sub>/l in pregnant organic, 50 g U<sub>3</sub>O<sub>8</sub>/l in pregnant carbonate strip). Some vanadium was extracted, and a portion of this was removed by acid scrubbing before stripping. Uranium product was prepared from the pregnant strip solutions by both sodium hydroxide precipitation and acidification-ammonium precipitation. Product grades (washed and dried at 120°C) were about 80% U<sub>3</sub>O<sub>8</sub>.

With both liquors, phase separation was good, and all extracted metals were stripped essentially completely out of the recycle organic.

#### Rate of Phase Separation

One particular circuit of "Plant C" produces a liquor by direct leaching of separated ore sands, which at times has given slow phase separation from the D2EHPA-TBP-kerosene extractant. Laboratory tests on samples of "bad" liquor from this circuit showed slow phase separation, of varying degrees of severity, whenever liquor and extractant were mixed with the extractant dispersed and the aqueous phase continuous. These same samples all showed rapid separation when mixed with the organic phase continuous. Under the conditions that gave slow phase separation, the separation was better when the extractant did not contain a miscibility modifier (TBP or alcohol).

Several anionic surfactants were found to increase the rate of separation after aqueous-continuous mixing, and one, Lomar PW, gave satisfactorily rapid separations under nearly all conditions tested when used at concentrations as low as 20 ppm in the aqueous phase. However, increased entrainment of organic in the raffinate was noted in a continuous countercurrent extraction; further testing of this effect is required. In a single test, Lomar PW did not affect the separation rate (already rapid) after organic-continuous mixing.

Methods of identifying and controlling the phase-continuity are described.

## Comparison of Uranium Extraction Power of Alkylphosphoric Acids

Tests have been continued comparing uranium extraction by purified monoalkyl- and dialkylphosphoric acids. The general relationships conformed with those previously reported. Throughout, extractions by the monoalkyl reagents were higher than by the corresponding dialkyl reagents. Extraction by the dialkyl reagents was much higher when the diluent was kerosene than when it was carbon tetrachloride; less difference between the two diluents was found in extraction by the monoalkyl reagents. Addition of long-chain alcohol depressed uranium extraction power of both monoalkyl and dialkyl reagents.

The previously-noted correlation between increased branching, decreased relative acid strength, and decreased uranium extraction power of dialkylphosphoric acids was confirmed, except that a reversal was encountered in extraction from 1.4 M phosphate solution by bis(diiso-butylmethyl)-phosphoric acid (the most severely branched of the reagents tested) in carbon tetrachloride. This reagent in kerosene also showed higher than expected extraction of uranium(VI) from phosphoric acid solutions (3-5 M). It showed surprisingly high extraction of uranium(IV) from phosphoric acid, in contrast to the other dialkylphosphoric acids tested, which extracted less uranium(IV) than uranium(VI).

The sources and apparent purities of the alkylphosphoric acids used are described. Further study has been made of the estimation of a small quantity of monoalkylphosphoric acid in dialkylphosphoric acid by the distortion it produces in a titration curve.



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## INTRODUCTION

The testing and evaluation of new reagents for the separation of uranium, vanadium, thorium, molybdenum, and other metal values by solvent extraction from raw materials and process solutions has been a major activity of this laboratory\* for several years. As a result of this work several new solvent extraction processes have been developed for the recovery of these materials from acid solutions. Two processes have received most of the attention to date: the Dapex process utilizing dialkylphosphoric acids and the Amex process utilizing long chain amines. The Amex process and some of its applications are described in other reports from this laboratory.

As previously described,<sup>(1)</sup> the extractant used in the Dapex process is a solution of a selected dialkylphosphoric acid in an inert diluent, usually the commercially available di(2-ethylhexyl)phosphoric acid in kerosene. Uranium is stripped from the pregnant extract with either a concentrated mineral acid or (preferably) a base. With alkaline stripping it is advantageous to modify the kerosene diluent so as to prevent separation of the alkali dialkylphosphate salt. Several classes of effective modifiers have been found. Some of these depress the uranium extraction power of the extractant, but certain others produce a large and useful synergistic enhancement of uranium extraction power. The Dapex process accomplishes selective extraction of uranium from process solutions containing relatively large quantities of contaminating metals, and it provides a means for separate recovery of both uranium and vanadium from solutions in which they coexist. It is being used in at least two Western uranium processing plants.

The present report is supplementary to ORNL-1903<sup>(1)</sup> on certain aspects of the Dapex process. These include evaluation of new miscibility modifiers, alkaline stripping with sodium carbonate, ammonium carbonate and other reagents, acid stripping, phase separation, and further correlation of extraction behavior with molecular structure.

The scope of this report includes bench-scale batch and continuous countercurrent process tests with both synthetic and actual plant liquors. It does not include scale-up testing, which is being reported by the Process Test Section, nor fundamental investigations of the extraction system which will be reported separately. Progress reports on the extraction of vanadium by the Dapex process and on the study of synergistic extractants are in preparation.

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\*Chemical Development Section C, Chemical Technology Division; formerly Raw Materials Section of Materials Chemistry Division.

## REAGENTS FOR MODIFICATION OF THE ORGANIC EXTRACTANT

The use of long chain alcohols, added to the organic phase to prevent third phase formation during sodium carbonate stripping of dialkylphosphoric acid extractants in the Dapex process, has been described in ORNL-1903. However, along with this desirable property, the particular alcohols utilized also had the disadvantage of depressing the uranium extraction coefficient. Although the magnitude of the effect was not prohibitive for many applications, the overall process efficiency was nevertheless significantly reduced.

These results suggested a further search for additives which would:

- 1) prevent third phase formation during alkaline stripping,
- 2) leave the uranium extraction power unimpaired,
- 3) leave selectivity for uranium unimpaired, i.e., not increase the extraction of contaminants,
- 4) have low distribution to (solubility in) the aqueous phase contacted,
- 5) contribute little additional cost to the Dapex process.

Over 50 compounds were examined in this regard, including alcohols, ketones, esters, ethers, neutral organophosphorus compounds, hydrocarbons, and chloro- and nitrohydrocarbons.

### Amounts Required to Maintain Miscibility

Table 1 lists the compounds screened and describes the procedure by which their ability to prevent third-phase formation was tested.

The amounts of the primary alcohols (molecular weights 130-200) required to maintain miscibility of 0.1 M sodium di(2-ethylhexyl)phosphate in kerosene were between 0.8 and 1.5 w/v %\* (0.05 and 0.08 M), with only the highly branched 3-neopentyl-5,5-dimethylhexanol requiring more than 1 w/v %. Benzyl alcohol was a little less effective, requiring 2 w/v % (0.19 M).

The amounts required of the secondary alcohols capryl (i.e., n-octanol-2) and 2-methylcyclohexanol were 0.8 and 1.0

---

$$*w/v \% = \frac{\text{weight of modifier (grams)}}{\text{weight of organic phase (ml)}} \times 100$$

Table 1

TESTING OF MODIFIERS FOR PREVENTING THIRD-PHASE FORMATION

Procedure

Equal volumes of 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene and 10 w/v % sodium carbonate solution were contacted to form three phases. The mixture was titrated with modifier until, after mixing and centrifuging, the third phase just disappeared. A 10 w/v % solution of modifier in kerosene was used as titrant when requirements were low, 100% modifier being used elsewhere.

<u>Modifier</u>	<u>Mol. Wt.</u>	<u>Final Conc. Di(2-ethylhexyl)-phosphoric Acid (M)</u>	<u>Requirement for Miscibility</u>	
			<u>M</u>	<u>w/v %</u>
<u>Primary Alcohols</u>				
n-Octanol	130	0.1	0.07	0.9
2-Ethylhexanol	130	0.1	0.06	0.8
4-Ethyloctanol	158	0.1	0.06	0.9
"Mixed Primary Decyl"	158	0.1	0.05	0.8
"Mixed Primary Tridecyl"	200	0.1	0.05	1.0
3-Neopentyl-5,5-dimethylhexanol	200	0.1	0.08	1.5
Benzyl Alcohol	108	0.1	0.19	2.0
<u>Secondary Alcohols</u>				
Capryl	130	0.1	0.06	0.8
5-Ethylnonanol-2	172	0.1	0.15	2.5
Diisobutylcarbinol	144	0.1	0.28	4.0
2,6,8-Trimethylnonanol-4	186	0.1	0.40	7.5
7-Ethyl-2-methylundecanol-4	214	0.1	0.35	7.5
3,9-Diethyltridecanol-6	256			>12

Table 1 (Cont'd.)

TESTING OF MODIFIERS FOR PREVENTING THIRD-PHASE FORMATION

Modifier	Mol. Wt.	Final Conc. Di(2-ethylhexyl)- phosphoric Acid (M)	Requirement for Miscibility	
			<u>M</u>	w/v %
2-Methylcyclohexanol	114	0.1	0.09	1.0
<u>Phenol</u>				
Nonylphenol	221	0.1	0.03	0.7
<u>Neutral Organophosphorus Compounds</u>				
Tri(n-butyl)phosphate	266	0.1	0.08	2.2
Tri(n-amyl)phosphate	308	0.1	0.10	3.1
Tri(2-ethylhexyl)phosphate	434	0.09	0.21	9.2
Triphenylphosphate	326			>5*
Tricresylphosphate	368			>20
Di-n-butyl n-butylphosphonate	250	0.1	0.06	1.4
Di(2-ethylhexyl) 2-ethylhexylphosphonate	418	0.09	0.23	9.5
Di-n-butyl benzenephosphonate	270	0.1	0.13	3.5
Di-n-butyl chloromethylphosphonate	243	0.1	0.06	1.4
Di(2-ethylhexyl) chloromethylphosphonate	355	0.1	0.11	3.7
n-Butyl di-n-butylphosphinate	234	0.1	0.04	0.9
n-Butyl di-n-hexylphosphinate	290	0.1	0.03	0.8
Tri(n-butyl)phosphine oxide	218	0.1	0.05	1.1
Tri(n-octyl)phosphine oxide	386	0.08	0.02	0.7
Tri(n-decyl)phosphine oxide	470	0.08	0.02	0.8

1  
4  
1

Table 1 (Cont'd.)

TESTING OF MODIFIERS FOR PREVENTING THIRD-PHASE FORMATION

Modifier	Mol. Wt.	Final Conc. Di(2-ethylhexyl)- phosphoric Acid (M)	Requirement for Miscibility	
			M	w/v %
Tri-n-butylphosphite (83%)	250	0.09	0.27	7
Tri(2-ethylhexyl)phosphite (92%)	418	0.08	0.45	19
<u>Ketones</u>				
Methylisopropyl	86	0.08	2.1	18
Methylisobutyl	100	0.08	1.6	16
Methyl-n-hexyl	128	0.09	0.4	5
Diisobutyl	142			>20
<u>Ethers</u>				
Di-n-propyl	102			>20
Diisopropyl	102			>20
Di-n-butyl	130	0.08	1.2	15
Benzylmethyl	122			>20
p-Cresylmethyl	122			>20
$\beta, \beta'$ -Dichloroethyl	143			>20
Di-n-butyl "carbitol"	218	0.09	.43	9
Dibutoxy tetraglycol	306	0.09	.36	11
<u>Esters</u>				
n-Butyl acetate	116	0.09	0.6	7
Isoamyl acetate	130	0.1	0.3	4
n-Butyl n-butyrate	144			>17
Isobutyl isobutyrate	144	0.08	1.2	18

Table 1 (Cont'd.)

TESTING OF MODIFIERS FOR PREVENTING THIRD-PHASE FORMATION

Modifier	Mol. Wt.	Final Conc. Di(2-ethylhexyl)- phosphoric Acid (M)	Requirement for Miscibility	
			M	w/v %
Ethyl benzoate	150	0.09	0.8	12
Benzyl acetate	150	0.08	1.3	19
Diethyl succinate	174	0.08	1.1	19
Di-n-butyl succinate	230			>20
Di-n-butyl phthalate	278			>20
Dioctyl phthalate	390			>20
<u>Chloro- and Nitrohydrocarbons</u>				
2-Ethylhexyl chloride	148	0.1	0.09	1.3
Trichloroethylene	131			>20
Carbon tetrachloride	154			>20
Benzotrichloride	195			>20
1-Nitropropane	89			>20
2-Nitropropane	89			>20
Nitrobenzene	123			>20
<u>Hydrocarbons</u>				
Toluene	92			>20
Isopropyl benzene	120	0.08	1.2	14

\*Solubility limit of triphenylphosphate in kerosene is about 5 w/v %.

w/v % (0.06 and 0.09 M), similar to the primary alcohols. About three times as much 5-ethylnonanol-2 was required, although it is structurally similar to capryl alcohol in the region of the hydroxy group. Still more was required of the heavier and more highly branched alcohols, 4 to 8 w/v % (0.3 to 0.4 M) of the 2-methyl-4-hydroxy compounds (diisobutyl carbinoI, trimethylnonanol, ethylmethylnundecanol) and more than 12 w/v % of the diethyltridecanol-6.

The only phenolic compound tested, nonylphenol,\* was even more effective than the primary alcohols, with 0.7 w/v % (0.03 M) required.

Of the neutral organophosphorus compounds tested, those with at least one straight chain alkyl group bonded directly to the phosphorus were similar to the primary alcohols in effectiveness, 0.7 to 1.4 w/v % (0.02 to 0.06 M) being required. The tri(n-alkyl)phosphates were a little less effective, requiring 2.2 w/v % (0.08 M) with butyl and 3.1 w/v % (0.10 M) with amyl. The phosphates and the phosphonate with three 2-ethylhexyl groups were poorer, about 10 w/v % (>0.2 M) required, presumably showing an effect of too much branching crowded around the central atom. Dibutyl chloromethylphosphonate was similar to dibutyl butylphosphonate, while di(2-ethylhexyl) chloromethylphosphonate was a little less effective. The two tri-aryl phosphates tested were not useful, but dibutyl benzenephosphonate was effective to about the same degree as triamylphosphate and di(2-ethylhexyl) chloromethylphosphonate.

Of the foregoing alkyl phosphorus compounds, the tri-butylphosphate, tri(2-ethylhexyl)phosphate, dibutyl butylphosphonate, and the two chloromethylphosphonates are commercially available, the first two in production quantities and the others in experimental quantities.

2-Ethylhexyl chloride was also effective, with 1.3 w/v % (0.09 M). Of the other compounds tested, only isoamyl acetate, methylhexyl ketone, butyl acetate, and dibutyl "carbitol" were able to prevent third phase formation on addition of amounts less than 10 w/v %.

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\*Koppers G-5102030; structure not stated.

Measurements of modifier requirements\* as a function of reagent (di(2-ethylhexyl)phosphoric acid) concentration have been made for certain of the above compounds and the results are summarized in Table 2 by means of constants for use in a simple empirical equation. The following procedure was used for measuring these requirements:

- 1) Prepare kerosene solutions having desired range of concentrations of di(2-ethylhexyl)phosphoric acid (e.g., 0.05 to 0.5 M).
- 2) Contact a sample (e.g., 5 ml) of each reagent solution with an equal volume of 10% sodium carbonate.
- 3) Centrifuge the mixture and observe for the presence of a third phase.
- 4) When a third phase is present, add from a calibrated dropper a 10% kerosene solution of the modifier being tested, shaking and centrifuging after each addition until the third phase just disappears.
- 5) From the volumes added and the known original reagent (di(2-ethylhexyl)phosphoric acid) concentration calculate the final reagent and modifier concentrations.
- 6) Plot modifier concentration vs. final reagent concentration.

Since modifier requirements increase slightly with increasing temperature, the curve should be established for the temperature at which the extractant is to be used.

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\*It should be noted that the modifier requirement as discussed in this section and listed in Table 2 is the measured critical concentration for miscibility of  $\text{NaR}_2\text{PO}_4$  at the temperature specified and in the absence of any other solute. The minimum operating requirement in a process will, of course, be this critical concentration plus a reasonable margin to cover variations. Besides the variations to be expected in concentrations, temperature, etc., miscibility will also be affected by the amount of uranium still in the organic phase when stripping is partially completed. For example, in stripping 0.1 M di(2-ethylhexyl)phosphoric acid/kerosene, loaded to 6 g U/T, with 10% sodium carbonate, the critical concentration of TBP required was found to increase with residual uranium as follows:

g U/l organic:	0	0.03	0.09	0.17	0.19	0.28
w/v % TBP required:	2.2	2.2	2.3	2.4	2.5	2.7

Table 2  
CONCENTRATIONS OF MODIFIERS REQUIRED  
FOR PREVENTING THIRD-PHASE FORMATION

Minimum\* Modifier Concentration =  $A + B \underline{M}$

where  $\underline{M}$  = molarity of di(2-ethylhexyl)-  
 phosphoric acid, between 0.1  
 and 0.4, in kerosene

Modifier	Temp. °C	Minimum Modifier Concentration**			
		w/v %		$\underline{M}$	
		A	B	A'	B'
Capryl alcohol	26	0.5	4.0	0.040	0.31
2-Ethylhexanol	30	0.6	4.0	0.046	0.31
4-Ethyl octanol	27	0.5	4.0	0.032	0.25
"Mixed primary decyl alcohols"	30	0.4	4.6	0.024	0.29
"Mixed primary tridecyl alcohols"	30	0.6	4.6	0.029	0.23
Tributylphosphate	28	1.7	5.3	0.063	0.20
Dibutyl butylphosphonate	28	0.8	5.2	0.034	0.21
Butyl dibutylphosphinate	28	0.3	6.2	0.011	0.26
Butyl dihexylphosphinate	27	0.5	3.1	0.016	0.11
Tributylphosphine oxide	31	0.2	9.0	0.007	0.41

\*See note, p. 8.

\*\*Minimum Modifier Concentration given in

w/v % with parameters A and B  
 molar concentration with parameters A' and B'.

The requirements of each of the modifiers tested followed a straight line within the concentration range studied, and on a molar basis the equations are remarkably similar. Apart from the obvious use of these data in calculating the compositions needed for mixed extractants, they also serve as calibration curves in the determination of modifier concentrations in unknown samples of extractants (see below).

Tributylphosphate was also tested for maintaining miscibility in Napoleum 470, a high boiling petroleum fraction marketed by the Deep Rock Oil Company. The amount of tributylphosphate required was approximately the same as was required in kerosene.

### Effects of Modifiers on Uranium Extraction

The effects of several of the foregoing modifiers on uranium extraction from acidic sulfate solution by 0.1 M di(2-ethylhexyl)phosphoric acid was examined in single stage tests. The resulting extraction coefficients are shown in Table 3. Two widely diverging effects were found: All the additives tested except the organophosphorus compounds depressed the uranium extraction coefficient; in contrast, every combination tested of a neutral organophosphorus compound with di(2-ethylhexyl)phosphoric acid showed much greater uranium extraction power than did the acid reagent alone. Since these neutral compounds when used alone extract little uranium from this type of solution (ORNL-2002), the extraction power shown by the combination is also much greater than can be accounted for as cumulative extraction power of the components acting separately. In other words, a strong synergistic enhancement is shown. It may be noted that the increase in the extraction coefficient observed in varying the synergistic additive from tri-n-butylphosphate to tri-n-butylphosphine oxide is reminiscent of the variation in coefficient when these reagents alone are used to extract uranium from appropriate solutions.<sup>(2)</sup> Extraction coefficients obtained with other n-alkyl phosphorus compounds were similar to those with the corresponding n-butyl compounds. Results parallel to those shown in Table 3 from weakly acidic sulfate solution have been obtained in extractions from 1.5 M sulfuric acid solution. Combinations with dibutyl and di(2-ethylhexyl) chloromethylphosphonates showed about the same enhancement of extraction power as those with dibutyl butylphosphonate and tributylphosphate, respectively. Compounds with three 2-ethylhexyl radicals gave extraction coefficients which were much lower than with the corresponding n-alkyl compounds, but still considerably higher than with the acid reagent alone.

Table 3

EFFECT OF MODIFIER UPON URANIUM EXTRACTION

Aqueous Phase: 0.5 M SO<sub>4</sub>, pH 1, 0.004 M U(VI)  
 Organic Phase: Di(2-ethylhexyl)phosphoric acid and  
 modifier in kerosene  
 Phase Ratio: 1<sup>a</sup>/1<sup>o</sup>  
 Agitation: 10 minutes, wrist-action shaker  
 Room Temperature

Modifier	Modifier Conc.		Di(2-ethylhexyl)- phosphoric Acid Conc. (M)	E <sub>a</sub> <sup>o</sup>
	(M)	w/v %		
None			0.1	135
<u>Alcohols</u>				
2-Ethylhexanol	0.06	0.8	0.1	78
Capryl	0.06	0.8	0.1	70
"Mixed primary decyl"	0.05	0.8	0.1	77
"Mixed primary tridecyl"	0.05	1.0	0.1	77
Benzyl alcohol	0.19	2.0	0.1	86
2-Methylcyclohexanol	0.09	1.0	0.1	78
Nonylphenol	0.03	0.7	0.1	97
<u>Neutral Organophosphorus Compounds</u>				
Tributylphosphite	0.07	7	0.1	700
Tributylphosphate	0.08	2.2	0.1	800
Dibutyl butylphosphonate	0.08	1.4	0.1	3000
Butyl dibutylphosphinate	0.10	0.9	0.1	2500
Tributylphosphine oxide	0.05	1.1	0.1	7000
<u>Others</u>				
Methyl-n-hexyl ketone	0.42	5	0.09	92
Isopropyl ether	2.1	21	0.07	68
Dibutyl "carbitol"	0.43	9	0.09	92
n-Butyl acetate	0.63	7	0.09	105
Isoamyl acetate	0.30	4	0.1	110
Isopropyl benzene	1.2	14	0.08	88
2-Ethylhexyl chloride	0.09	1.3	0.1	70

The extractions compared in Table 3 were all made at pH 1. The relative effects of capryl alcohol and tributylphosphate on uranium extraction are similar at other pH levels, as shown in Figure 1 by the approximately parallel curves from pH 0.5 to >2.

Isotherms for extraction of uranium from acidic sulfate solution have been obtained for the di(2-ethylhexyl)phosphoric acid - tributylphosphate and the di(2-ethylhexyl)phosphoric acid - dibutyl butylphosphonate synergistic extractant combinations. In Figure 2 these isotherms are compared to those obtained with di(2-ethylhexyl)phosphoric acid alone and modified with capryl alcohol. (The aqueous solutions extracted were not identical, but were sufficiently similar for comparison.) The extreme left-hand portions of these curves illustrate the effects listed in Table 3. The initial slopes, which are proportional to the extraction coefficients obtained before any loading limitation is encountered, show the lowered extraction with capryl alcohol and the enhanced extraction with tributylphosphate and dibutyl butylphosphonate. This higher extraction power at low uranium levels can be very advantageous in continuous countercurrent extraction since it provides more efficient reduction of raffinate uranium level per stage, i.e., lower raffinates can be obtained in a set number of stages, or fewer stages are required to obtain a specified low raffinate. It also provides obvious advantages in extraction to obtain high uranium loading from a very low grade aqueous liquor, or in application to liquors unusually difficult to extract.

At the higher uranium levels shown in Figure 2 the extraction isotherms tend to converge, as the effects of loading begin to overshadow the extraction power. It may be noted that the curves for the synergistic combinations leveled off even more than the others in the region above 0.2 g uranium per liter aqueous, so that the unmodified extractant crossed over to appreciably higher organic uranium loading above about 0.5 g U/l aqueous. Actually, all the curves continue to rise gradually as the aqueous uranium level is increased beyond the range shown here, and at very high aqueous uranium levels (e.g., 50 g U/l) they approach an asymptote of 12 g U/l organic, which is the stoichiometric loading limit expected with 0.1 M reagent if two moles of di(2-ethylhexyl)phosphoric acid are associated with each mole of uranium.

In the foregoing paragraphs it has been possible only to give a very brief description of the synergistic enhancement of uranium extraction, presented as one aspect of the use of miscibility-modifiers. Extensive systematic and developmental testing has been carried out with certain synergistic combinations, considered as new and significantly different

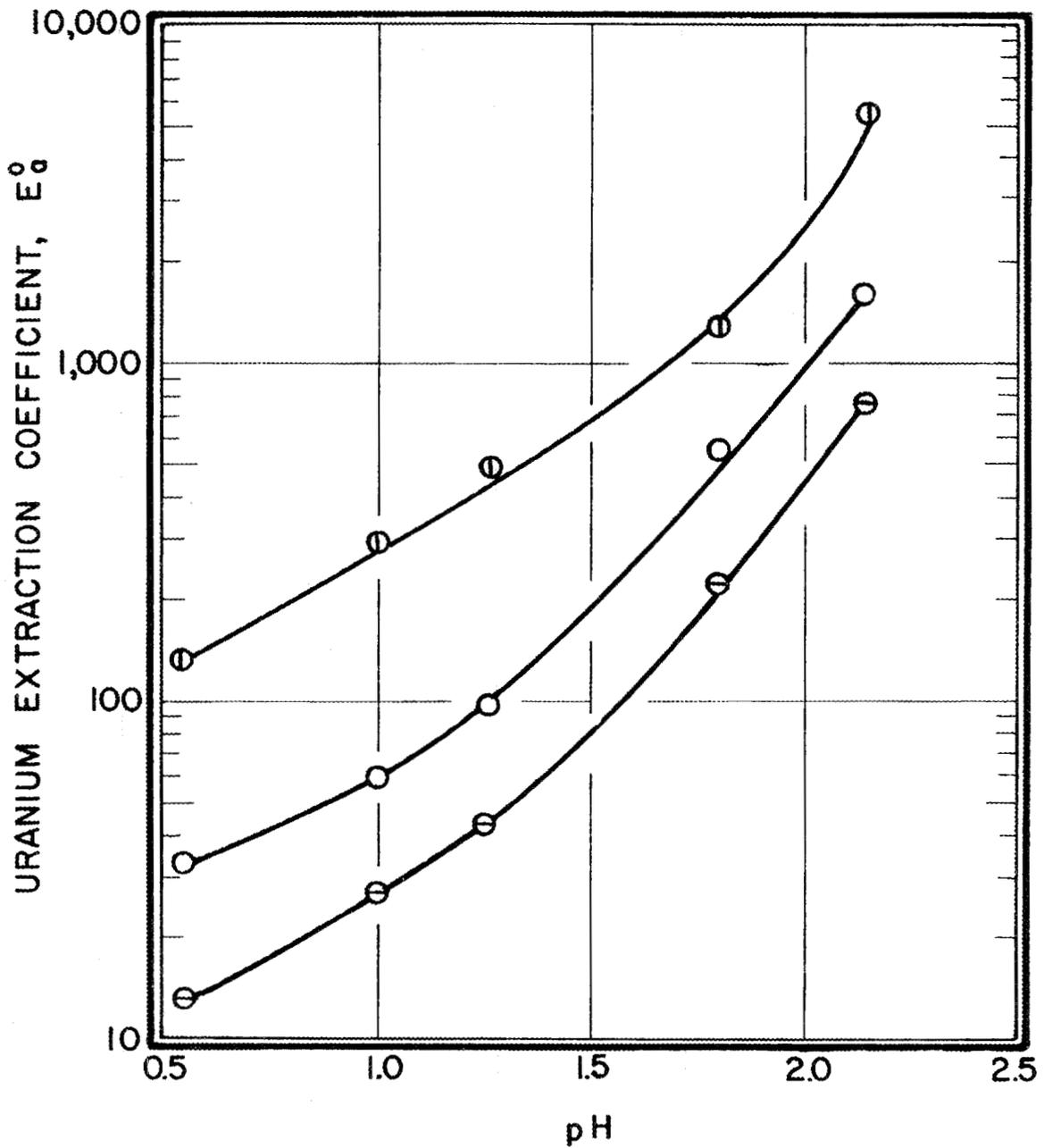


Figure 1

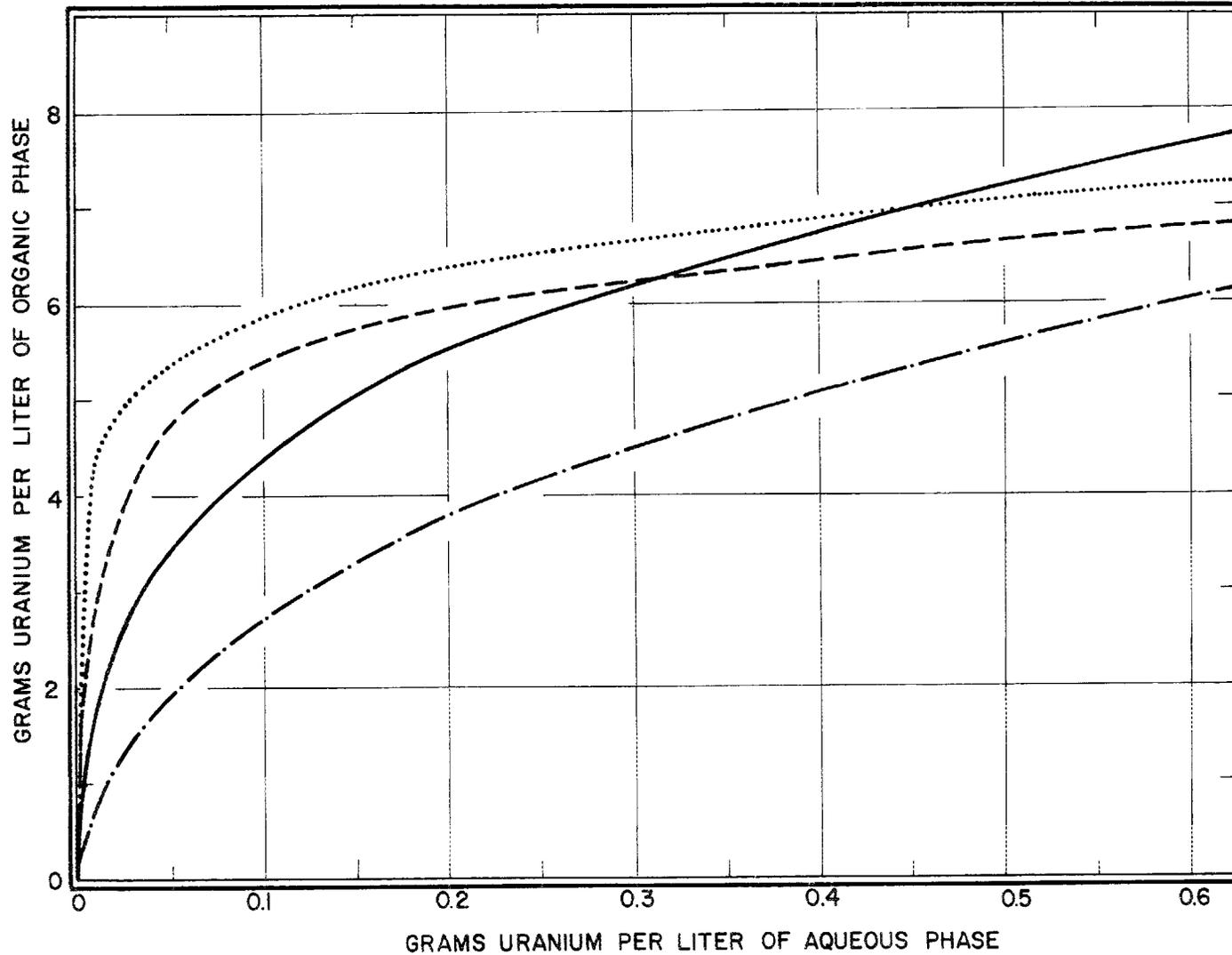
EFFECT OF MODIFIERS ON pH DEPENDENCE OF URANIUM EXTRACTION

Aqueous Phase: 0.005 M U, 0.5 M SO<sub>4</sub>

Organic Phase: 0.1 M Di(2-ethylhexyl)phosphoric acid in kerosene,

- unmodified
- ⊖ plus 0.11 M (3.0 w/v %) Tri-n-butylphosphate
- ⊙ plus 0.12 M (1.5 w/v %) Capryl Alcohol

Phase Ratio: Aqueous:Organic = 1



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Figure 2

## URANIUM EXTRACTION ISOTHERMS FROM ACIDIC SULFATE SOLUTIONS

(0.005 M U, 0.5 M SO<sub>4</sub>, pH 1)

——— 0.1 M D2EHPA  
 ..... " " + 0.1 M Dibutyl butylphosphonate  
 ——— 0.1 M D2EHPA + 0.11 M Tri-n-butylphosphate  
 -.-.- " " + 0.12 M Capryl Alcohol  
 (Kerosene Diluent)

extractants, and this work will be reported separately. Since tributylphosphate is commercially available at a reasonable price, most attention has thus far been directed at the tributylphosphate - di(2-ethylhexyl)phosphoric acid system. Dibutyl butylphosphonate, available in experimental quantities (potentially available in production quantities at a higher price than TBP), has also been subjected to process testing, and laboratory tests have been recently started with the chloromethylphosphonates.

In contrast to these synergistic combinations with di(2-ethylhexyl)phosphoric acid (and other dialkylphosphoric acids), the corresponding combinations tested of neutral organophosphorus reagents with monoalkylphosphoric acids have not shown any enhancement of extraction power, but rather the same kind of impairment of extraction as shown by addition of, e.g., alcohols (cf. p. 83).

#### Effect of Modifiers on Selectivity for Uranium

The effect of two of the additives described above, tributylphosphate and dibutyl butylphosphonate, on the selectivity of di(2-ethylhexyl)phosphoric acid was investigated by contacting the organic solutions with sulfate solutions of various cations commonly found in leach liquors. Results are presented in Table 4. The ratios of extraction coefficients show the relative changes caused by addition of the modifiers. The coefficients for aluminum, vanadium(IV), and possibly molybdenum were essentially unaffected by addition of these modifiers. Extraction of iron(III) and titanium was repressed, although further experimental results have suggested that this may be a rate rather than an equilibrium difference. As previously shown (Table 3 and Figure 2), the corresponding uranium extraction coefficients are increased greatly at low uranium loading levels. Thus, the selectivity of di(2-ethylhexyl)phosphoric acid for uranium over these other metals is not impaired by the addition of tributylphosphate or dibutyl butylphosphonate. Under some conditions it will be improved, the uranium extraction being increased while extraction of the major interfering contaminants either remains approximately the same or (within probable contact times) is decreased.

#### Loss of Modifiers by Distribution to Acid and Alkaline

##### Aqueous Phases

Because of the importance of reagent losses in the economic evaluation of extraction processes, considerable effort has been placed on the establishment of procedures for the determination of loss of diluent modifiers from the

Table 4

EFFECT OF MODIFIER UPON SELECTIVITY

Organic: 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene, alone or modified with 3.0 w/v % tributylphosphate or 2.5 w/v % dibutyl butylphosphonate.

Aqueous: 0.02 M metal ion (only one metal ion present in each test), 0.3 - 0.5 M SO<sub>4</sub>, pH 1.2 - 1.4.

Contact: Agitated by wrist-action shaker for indicated time, phase ratio 1<sup>a</sup>:1<sup>o</sup>.

	Contact Time, min.	<u>V(IV)</u>	<u>Fe(III)</u>	<u>Al</u>	<u>Mo</u>	<u>Ti</u>
E <sub>a</sub> <sup>o</sup> (Unmod)	2	0.8	0.4	0.01	3.7	2.0
	30	0.7	3.1	0.01	3.4	5.9
E <sub>a</sub> <sup>o</sup> (TBP)	2	---	0.4	0.01	2.7	---
	30	---	2.3	--	2.5	---
E <sub>a</sub> <sup>o</sup> (DBBP)	2	0.6	0.1	0.01	5.4	0.7
	30	0.8	1.7	0.01	4.9	2.5
<u>E<sub>a</sub><sup>o</sup> (TBP)</u> <u>E<sub>a</sub><sup>o</sup> (Unmod)</u>	2	---	1.0	1.0	0.7	---
	30	---	0.7	---	0.7	---
<u>E<sub>a</sub><sup>o</sup> (DBBP)</u> <u>E<sub>a</sub><sup>o</sup> (Unmod)</u>	2	0.8	0.3	1.0	1.5	0.4
	30	1.1	0.5	1.0	1.4	0.4

organic phase. The most useful method continues to be an indirect measure of the loss by titration of the final extractant to the critical miscibility point. While there are some obvious disadvantages to this method, it also has the advantages that it is applicable to any effective miscibility modifier, regardless of its chemical class, and that the property measured in the analysis is the property of interest. Direct measurements of tributylphosphate distribution to aqueous solutions have also been made using radioactive tracer phosphorus. Several other methods have been examined for direct or indirect measurement of alcohol loss, based on various physical or chemical properties, but none of these have yet proved useful.

Indirect Method. The indirect method for the determination of alcohol loss presented in ORNL-1903 can be applied to modifiers in general. The analytical procedure is as follows:

Determination of Modifier Concentration in Organic Phase by Titration to Critical Miscibility Point

- 1) Contact the reagent-modifier-diluent sample (e.g., 5 ml) with an equal volume of 10% sodium carbonate.
- 2) Centrifuge the mixture and observe for the presence of a third phase.
- 3a) When third phase is present, add from a calibrated dropper a standard solution (e.g., 10 w/v %) of the modifier in the same diluent, shaking and centrifuging after each addition until the third phase just disappears.
- 3b) If no third phase is present, add a measured amount of modifier-free diluent solution containing the reagent at a known concentration higher than that in the original solution. Mix, centrifuge and observe for third phase. Repeat until a third phase is observed, then backtitrate as described in 3a.
- 4) From volumes added and the known original reagent (dialkylphosphoric acid) concentration\* calculate the final reagent concentration.
- 5) Determine from the miscibility curve\*\* the

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

\*\*Established as described on page 8. Since the miscibility limit varies slightly with temperature, the curve must be established at the same temperature as is to be used for the analysis.

critical quantity of modifier required to maintain miscibility in the final organic volume, and from this subtract the amount of modifier added in step 3a or 3b. The difference is the amount of modifier in the original sample.

The droppers used each delivered close to 0.025 ml per drop. Duplicate analyses by this procedure have been in reasonable agreement, ordinarily varying no more than plus or minus the equivalent of about one drop of the 10% modifier titrant (corresponding to about  $\pm 0.05$  w/v % in a 5-ml organic sample) in tests arranged so that only a small volume of titrant was required. This has been sufficient for the loss rates measured; use of a microburet is an obvious refinement to obtain higher precision when needed.

Losses of several of the preferred miscibility modifiers to acidic sulfate solutions and to carbonate solutions were measured by single-stage batch equilibrations at high aqueous:organic ratios. The results, Tables 5 and 6, show effects of both the modifier concentration in the organic phase and the composition of the aqueous phase. The results suggest that 2-ethylhexanol was lost to acidic sulfate solutions according to a regular distribution law at low alcohol concentrations (Figure 3), but leveled off at higher concentrations (about 115 ppm in 0.5 M  $\text{SO}_4$ ). Loss of capryl alcohol was similar, while the higher-weight alcohols as expected showed much lower losses. Dibutyl butylphosphonate loss, being about 25 ppm from two different organic concentrations, also appeared to be saturation-limited. Tributylphosphate loss was at about the same level.

Loss of alcohols to 10% sodium carbonate solution (i.e.,  $\sim 1$  M) was a little less than to 0.5 M sulfate solution, while loss of the phosphorus compound was similar or a little higher than to the sulfate solution. Since the volume of carbonate strip solution encountered will normally be much smaller than the volume of raffinate, the losses of modifier to the strip will be correspondingly less important.

Contributions of modifier loss to the costs of the Dapex process are discussed below.

Losses in Continuous Operation. While in principle the precision and sensitivity of loss measurements by single-stage batch equilibration could be improved indefinitely by going to more and more extreme aqueous:organic ratios, in actual practice various experimental difficulties begin to intervene. A better (and more realistic) way to refine the loss measurements is to follow the reagent balance through a sufficiently large number of cycles of continuous operation.

Table 5

MODIFIER LOSS TO ACIDIC SOLUTIONS

(By decrease in organic phase concentration)

Organic: 0.1 M di(2-ethylhexyl)phosphoric acid and indicated modifier in kerosene

Modifier	Aqueous Composition	Phase Ratio a/o	Eq. Concentrations	
			w/v % in org	ppm in aq**
Tributylphosphate	0.5 <u>M</u> SO <sub>4</sub> , pH 1	400	3.5*	<35
Dibutyl butylphosphonate	"	100	0.5	25 ± 10
	"	100	1.1	25 ± 5
Capryl Alc.	"	800	0.5	20 ± 5
	"	100	1.9*	115 ± 15
4-Ethyl octanol	"	800	1.8*	<5
	"	400	1.8*	<10
"Mixed Primary Decyl Alc."	"	400	1.7*	<10
2-Ethylhexanol	"	300	0.8	40 ± 5
	"	400	1.4	110 ± 20
	"	100	1.7*	110 ± 70
	"	200	3.5	115 ± 25
	"	100	4.7	115 ± 35
	0.2 <u>M</u> SO <sub>4</sub> , pH 1	100	1.3	85 ± 45
	"	100	1.7*	125 ± 40
	"	100	3.8	200 ± 40
	"	100	9.5	240 ± 25
	"	400	14.2	260 ± 25

Table 5 (Cont'd.)

MODIFIER LOSS TO ACIDIC SOLUTIONS

\*Modifier concentrations marked are those at about the probable level for use with 0.1 M di(2-ethylhexyl)phosphoric acid, i.e., minimum requirement plus reasonable margin.

\*\*Uncertainty estimated on basis of phase ratio, organic sample volume, and modifier titrant concentration and volume, together with uncertainty of one drop of the titrant at the end point (cf. p. 18).

Table 6

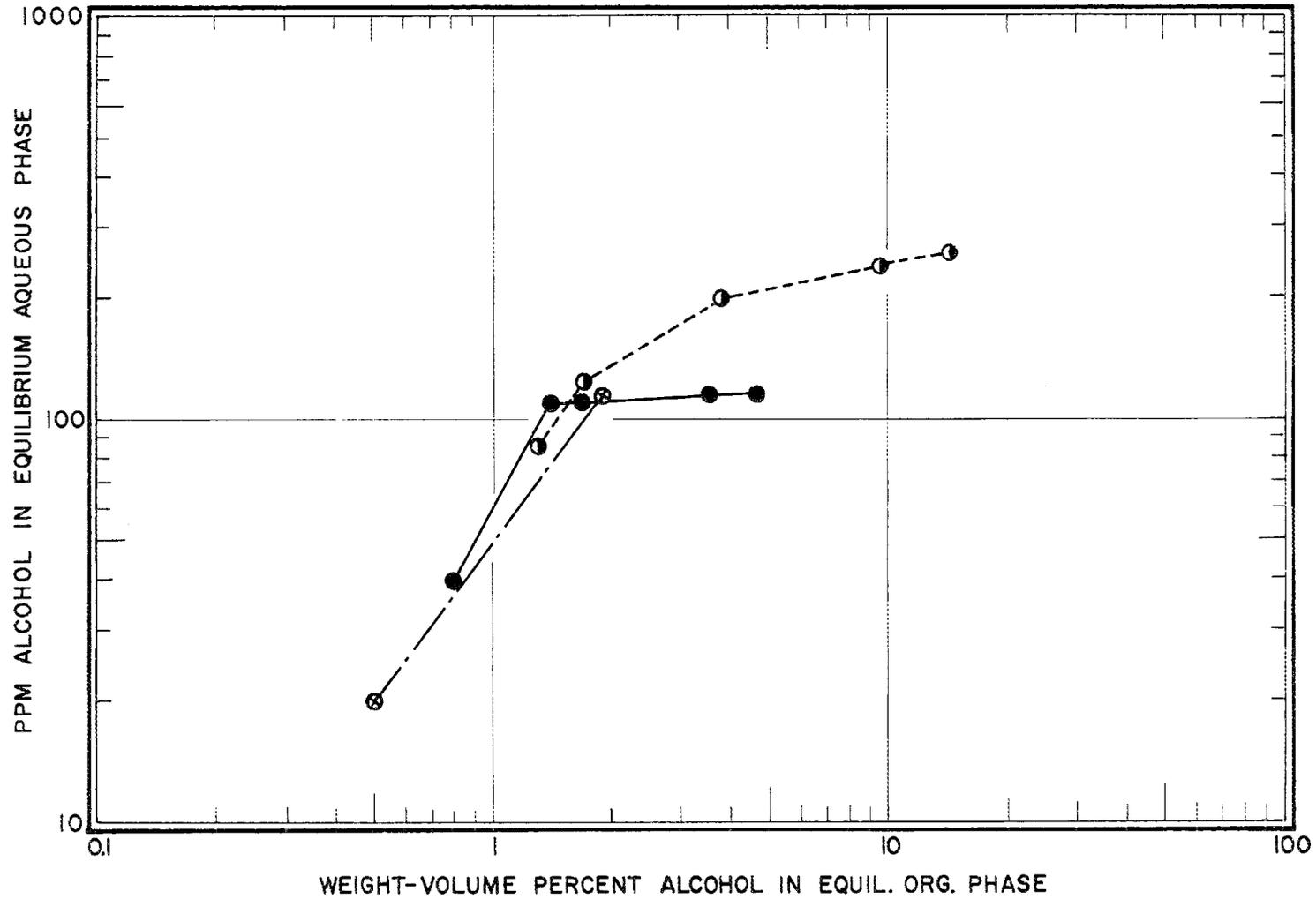
MODIFIER LOSS TO ALKALINE SOLUTIONS

(By decrease in organic phase concentration)

Organic: 0.1 M di(2-ethylhexyl)phosphoric acid and indicated modifier in kerosene

Modifier	Aqueous Composition	Phase Ratio a/o	Eq. Concentrations	
			w/v % in org	ppm in aq*
Tributylphosphate	10% Na <sub>2</sub> CO <sub>3</sub>	400	2.7	35 ± 25
Dibutyl butylphosphonate	"	100	1.1	25 ± 20
	5% (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	50	0.5	30 ± 20
2-Ethylhexanol	10% Na <sub>2</sub> CO <sub>3</sub>	400	1.1	20 ± 10
Capryl Alc.	"	200	1.2	40 ± 10
4-Ethyloctanol	"	200	2.0	<10

\*See note, Table 5.



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Figure 3  
DISTRIBUTION OF MODIFYING ALCOHOLS TO AQUEOUS SULFATE SOLUTIONS

0.1 M Di(2-ethylhexyl)phosphoric Acid in Kerosene Diluent,  
Modified as indicated

- 2-Ethylhexanol to 0.5 M SO<sub>4</sub>, pH 1
- 2-Ethylhexanol to 0.2 M SO<sub>4</sub>, pH 1
- ⊗ Capryl Alcohol to 0.5 M SO<sub>4</sub>, pH 1

This has been done through 95 cycles with 0.1 M di(2-ethylhexyl)phosphoric acid - 1.5 w/v % capryl alcohol in kerosene, as shown in Table 7. This was a normal extraction test from a synthetic leach liquor (composition shown in the table); physical operation of the system was satisfactory, and efficient uranium recovery was obtained throughout the run.

The material balances given in Table 7 show distribution (solubility) losses amounting to 120 ppm capryl alcohol and 10 ppm reagent in the raffinate. Two assumptions were involved in these results, (1) that the distribution loss to the carbonate strip solution was in accordance with previous measurements, and (2) that evaporation of kerosene was negligible. The first assumption had almost no effect on the results, since the volume of strip solution was so small. The second assumption had only a little effect on the alcohol loss results; for instance, the extreme alternative assumption that all the unaccounted volume loss was due to evaporation, with vanishingly small entrainment, would lead to a result of 127 ppm capryl alcohol in the raffinate. (The reagent loss result is a little more sensitive to the assumed evaporation loss, becoming 25 instead of 10 ppm for the extreme assumption of all kerosene loss by evaporation. The value of 10 ppm is somewhat higher than the value indicated — <5 — by the single-stage batch equilibration tests reported in ORNL-1903 and also given by radioactive tracer  $P^{32}$  analysis, Appendix C.)

The value of 120 ppm capryl alcohol in 0.3 M sulfate raffinate is in fairly good agreement with the losses to 0.5 M sulfate measured by single-stage equilibration (Table 5 and Figure 3), and not in serious disagreement with the preliminary estimate of 80 ppm in 0.5 M sulfate reported in ORNL-1903.

These data give no support to the much higher losses of capryl alcohol to acidic solutions which were reported recently from another laboratory, (3,10) apparently as a result of an analytical method based on acetylation related to those mentioned below. Actually, losses of these shorter chain alcohols are more of academic than practical interest since the neutral phosphate compounds or the longer chain alcohols would ordinarily be chosen for process use. However, since a reported disagreement exists, some further attention will, as a matter of record, be given to measurements of low molecular weight alcohol losses by different analytical methods.

Analysis by Radioactive Tracer. A direct measurement of the tributylphosphate lost from di(2-ethylhexyl)phosphoric acid - tributylphosphate - kerosene solution to various aqueous solutions was made by Dr. W. H. Baldwin of the ORNL Chemistry

Table 7  
LOSS OF REAGENT AND MODIFIER IN  
CONTINUOUS COUNTERCURRENT EXTRACTION

<u>Cycle No.</u>	<u>Kerosene Added, ml</u>	<u>Reagent</u>		<u>Capryl w/v %<sup>a</sup></u>	<u>Alcohol g Added</u>	<u>Retd from Settling Tank, ml</u>
		<u>M</u>	<u>g Added</u>			
Initial	1940	0.106	66.1	1.7	33.0	
11					4.7	
20				1.1	7.9	
21						61
30					6.1	
31		0.101		1.4		27
38						36
40					6.1	
50				1.0	8.6	
56						23
60					8.6	
63		0.096		1.3		
67						20
71					8.6	
77	200 <sup>b</sup>	0.095	11.2 <sup>b</sup>		3.0 <sup>b</sup>	
81					8.6	
82		0.103				39
83				1.6		
90					7.0	26
95		0.100		1.4		
<u>Totals in:</u>	2140		77.3		102.2	
<u>Found:</u>						
Samples	435		14.0		6 ± 1	
Final Org	1360	0.104 <sup>c</sup>	45.6	1.4	19 ± 2	
Total	1795		59.6		25 ± 3	
<u>Losses:</u>						
Total	345		17.7		77 ± 3	
Entr.	345 <sup>d</sup>		11.1 <sup>d</sup>		4 <sup>d</sup>	
Dist. to Strip			0.8 <sup>e</sup>		1 <sup>e</sup>	
Dist. to Raff.			5.8		72	
Conc. in Raff.			10 ppm		120 ppm	

Table 7 (Cont'd.)

LOSS OF REAGENT AND MODIFIER IN  
CONTINUOUS COUNTERCURRENT EXTRACTION

Extraction Conditions:

Nominal Flow Rates: - 20 Liquor : 5 Organic : 1 Strip.

Liquor, g/l: 1.2 U, 0.3 Fe(III), 2.7 Fe(II), 3.0 Al, 0.75 V(IV),  
0.1 Mo, 30 SO<sub>4</sub>, pH 1.3; 75-100 ml/min; 604 liters  
total.

Organic: Di(2-ethylhexyl)phosphoric acid and capryl alcohol in  
kerosene; 22-29 ml/min.

Strip: 10% Na<sub>2</sub>CO<sub>3</sub>; 4-5 ml/min.; 28.5 liters total.

Extraction: 2-2.5 min/mixer; aq 1.5-2.5, org 3-5 min/settler.  
3 stages.

Strip: 5-6 min/mixer; aq 17-22, org 3-4 min/settler. 2 stages.

Raffinate Holdup: One hour in settling tank.

Notes:

- a) Uncertainty in capryl alcohol determinations estimated from organic sample volume and modifier titrant concentration and volume to be less than  $\pm 0.2$  w/v % (cf. p. 18).
- b) Added as 0.174 M di(2-ethylhexyl)phosphoric acid, 1.5 w/v % capryl alcohol, in kerosene.
- c) Higher M reagent found in final drained organic than in last flow sample because of partial holdup of the concentrated makeup solution (cycle 77) in a flow meter. The corresponding effect on capryl alcohol concentration was negligible.
- d) Entrainment loss (including 75-100 ml spills), assuming negligible evaporation loss of kerosene. All vessels were closed with plastic sheeting.
- e) Estimated from 27 ppm di(2-ethylhexyl)phosphoric acid (ORNL-1903) and 40 ppm capryl alcohol (Table 6) in 10% Na<sub>2</sub>CO<sub>3</sub> solution.

Division, using labeled  $P^{32}$  tributylphosphate.<sup>(19)</sup> The results are shown in Table 8.

The loss found from 2.5 % solution (0.1 M di(2-ethylhexyl)phosphoric acid) to 0.5 M sulfate, pH 1, is in fair agreement with the limit indicated by indirect measurement (Table 5), while the loss found to 10% sodium carbonate solution is considerably lower than found by indirect measurement (Table 6). The loss to 0.5 M sulfate was considerably less than to 0.2 M sulfate, and losses were somewhat less to the actual leach liquors, which were at somewhat higher sulfate concentration, 0.7 to 0.9 M. This is in accord with the relationship generally found, that distribution of the organic compounds to aqueous solution decreases as the ionic concentration increases. The results also suggest little dependence on pH in the range covered.

The loss from 5% solution (0.3 M di(2-ethylhexyl)phosphoric acid) to 1 M  $H_2SO_4$  was close to twice that from 2.5% solution. The loss to sodium carbonate solution and to sulfate liquor was greater from the 5% solution than from the 2.5% solution, but considerably less than doubled.

Direct Alcohol Analysis. The ORNL Analytical Chemistry Division has given some attention to the possibility of direct determination of capryl alcohol by esterification or by means of some physical property. They reported the following conclusions:<sup>(4)</sup>

"None of the methods for determining micro amounts of alcohol which were investigated are entirely satisfactory. Only the Smith-Bryant method, with and without modification [i.e., methods (2) and (3) below], yields results which may be considered satisfactory. The results which have been obtained by this method are 20 to 25% low although relatively reproducible."

The methods examined were as follows:

1) Acetylation with acetic anhydride by the method of Ogg, Porter, and Willits.<sup>(5,6)</sup> Complete acetylation was not attained. End points of the alkalimetric titrations were indistinct, causing large uncertainty in the results (difference of two large numbers).

Sample	Back Titration, meq of NaOH	mmole of Capryl Alcohol	
		Added	Found
Kerosene	52.2		
0.1 M D2EHPA in Ker.	52.3		
2% C.A. in Ker.	51.4	0.8	0.8
	50.6	3.9	1.6
2% C.A. and 0.1 M D2EHPA in Ker.	51.2	0.8	1.0
	51.9	3.9	0.3

Table 8

LOSS OF TRIBUTYLPHOSPHATE TO AQUEOUS SOLUTIONS

RADIOACTIVE TRACER ANALYSIS<sup>a</sup>

<u>Aqueous Phase</u>	<u>ppm TBP in Aq. Phase</u>
0.1 M di(2-ethylhexyl)phosphoric acid + 2.5 w/v % TBP*/kerosene	
0.2 M SO <sub>4</sub> , pH 1	48, 44, 39
0.5 M SO <sub>4</sub> , pH 1	21, 18, 25
1 M H <sub>2</sub> SO <sub>4</sub>	25, 26
Liquor I: 0.7 M SO <sub>4</sub> , pH 0.6	17, 15
Liquor II: 0.9 M SO <sub>4</sub> , pH 0.4	12, 12
Liquor III: 0.9 M SO <sub>4</sub> , pH 1	10, 12
Liquor IV: 1.2 M SO <sub>4</sub> , pH 0.7	21, 17
Liquor V: 0.7 M SO <sub>4</sub> , pH 1.8	17, 18
10% Na <sub>2</sub> CO <sub>3</sub>	5-12 <sup>b</sup>
0.3 M di(2-ethylhexyl)phosphoric acid + 5 w/v % TBP*/kerosene	
1 M H <sub>2</sub> SO <sub>4</sub>	42-58 <sup>c</sup>
Liquor IV: 1.2 M SO <sub>4</sub> , pH 0.7	27, 26
10% Na <sub>2</sub> CO <sub>3</sub>	8-14 <sup>d</sup>

- a) Tests made by Dr. W. H. Baldwin, ORNL Chemistry Division. (19)
- b) Sixteen measurements in sodium carbonate solution, including strip solutions used after each of the tests with sulfate liquors. Average 8.5 ppm.
- c) Five measurements, average 50 ppm.
- d) Five measurements, average 11.0 ppm.

Liquor (major constituents):

	<u>g/l: U</u>	<u>V</u>	<u>Fe</u>	<u>Al</u>	<u>SO<sub>4</sub></u>	<u>pH</u>
I (Plant B)	1.6	2.7	0.7		70	0.6
II (Plant C)	6	4	0.4	2.8	80-90	0.4
III (= II treated with Na <sub>2</sub> CO <sub>3</sub> )					"	1.0
IV (Plant D)	1.1	3.6	5.5	6.2	120	0.7
V (= IV treated with Ca(OH) <sub>2</sub> )					70	1.8

2) Acetylation with acetyl chloride by the method of Smith and Bryant.<sup>(7)</sup> Acetylation of about 80% of the alcohol was attained fairly consistently. The precision level of the alkalimetric titrations still contributed considerable uncertainty to the results (difference of two large numbers).

Sample	Back Titration, meq of NaOH	mmole of Capryl Alcohol	
		Added	Found
None	3.30 to 3.36, Ave. 3.32		
CCl <sub>4</sub>	3.23, 3.27		
C.A.	3.21	0.122	0.100
	3.19	.141	.117
	3.22	.144	.094
	3.18	.142	.129
	3.17	.142	.141
	3.21	.132	.099
	3.20	.144	.115
	3.20	.138	.110
C.A. + CCl <sub>4</sub>	3.20	0.144	0.110

3) A modification of the method of Smith and Bryant. Instead of hydrolyzing and titrating the unreacted acetyl chloride, it was removed by distillation. The ester was then hydrolyzed, and the resulting acetic acid (equivalent to the alcohol acetylated) was steam distilled and titrated. The overall results appeared about the same as in (2).

Sample	mmoles of Capryl Alcohol	
	Added	Found
C.A. in CCl <sub>4</sub>	0.143	0.102
	.144	.101
CCl <sub>4</sub> extract of C.A. from 0.5 M Na <sub>2</sub> SO <sub>4</sub> soln.	.142	.110
CCl <sub>4</sub> extract of C.A. from a raffinate, 0.5 M SO <sub>4</sub> , pH 1	--	
	--	0.12 mmole/100 ml aq .06 " "

The capryl alcohol content of the raffinate samples had been estimated as 120 ppm (0.09 mmole/100 ml) by difference in the organic phase capryl alcohol concentration before and after equilibration (critical miscibility point method).

4) Direct gravimetric determination after extraction with a volatile solvent (chloroform). Extraction of the alcohol from an aqueous solution appeared to be effective, but

a large amount (e.g., 30%) of the alcohol was lost with the chloroform during evaporation.

5) Effects on electrical properties of kerosene. Measurements were tried with a Fisher high frequency oscilloscope. Capacitance measurements showed no consistent dependence on alcohol content. Conductance measurements did appear to show a consistent dependence, but too low in magnitude to be useful.

<u>Sample</u>	<u>(Arbitrary scale readings)</u>	
	<u>Capacitance</u>	<u>Conductance</u>
Kerosene	32.4	270
2% C.A. in Ker.	32.7	278
0.1 M D2EHPA in Ker.	33.9	288
2% C.A. and 0.1 M D2EHPA in Ker.	32.3	297

6) Effect on surface tension of the aqueous solution (raffinate). The results were too dependent on the manner of testing to be analytically useful.

#### Reagent Costs

Preliminary estimates were reported in ORNL-1903 (pp. 77-80) of costs which included 2.5¢/lb  $U_3O_8$  for 2-ethylhexanol, 1.6¢/lb  $U_3O_8$  for capryl alcohol, or 0.6¢/lb  $U_3O_8$  for 4-ethyl-octanol (together with 10¢/lb  $U_3O_8$  for all other chemical costs). \* These costs per pound of  $U_3O_8$  correspond to 25¢, 16¢, and 6¢ per 1000 gallons of liquor treated, of which approximately 2¢, 2¢, and 3¢ resulted from the assumed entrainment loss and the remainders from the losses by distribution to raffinate and strip.

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\*The conditions specified and assumptions made for the estimates in ORNL-1903 may be briefly summarized as follows:

Liquor: 1 g U/l (1.18 g  $U_3O_8$ /l), 20-50 g  $SO_4$ /l, pH 1-1.7, Fe and V reduced.

Extractant: 0.1 M di(2-ethylhexyl)phosphoric acid and 2 w/v % alcohol in kerosene. Loaded to 4 g U/l (4.72 g  $U_3O_8$ /l).

Strip: 10%  $Na_2CO_3$ . Loaded to 50 g  $U_3O_8$ . Carbonate destroyed with sulfuric acid, uranium precipitated with ammonia.

Entrainment Loss: 0.05 volume percent in the raffinate.

Table 9 presents the additional estimates of costs for miscibility (and synergistic) modifiers which can now be made on basis of the losses reported in Tables 5, 7 and 8, and on the basis of the same assumptions with regard to entrainment. As before, the cost/lb  $U_3O_8$  is based on the arbitrary value of 1.18 g  $U_3O_8$ /liter of liquor.

The contribution of the synergistic type additives to the total reagent cost is not much greater than for the alcohol modifier. It is believed that the advantages in increased extraction efficiency would more than offset the cost differential.

Table 9

ESTIMATED MAKE-UP COSTS FOR MISCIBILITY MODIFIERS

Operating Conditions and Assumptions: See footnote, p. 29.

Modifier	Conc. in Org. w/v %	Liquor		Loss (ppm) in Raff.		Cost, \$ <sup>c</sup>	
		<u>M</u> SO <sub>4</sub>	pH	Entr. <sup>a</sup>	Distr. <sup>b</sup>	per 1000 gal	per lb U <sub>3</sub> O <sub>8</sub> <sup>d</sup>
2-Ethylhexanol	1.7	0.2	1	9	125	28	2.8
"	"	0.5	1	9	110	25	2.5
Capryl Alcohol	1.9	0.5	1	10	115	20	2.0
"	1.3	0.3	1.3	7	120	20	2.1
"Mixed Primary Decyl Alc."	1.8	0.5	1	9	5	3	0.3
"Mixed Primary Tridecyl Alc."	1.7	0.5	1	9	<5	<3	<0.3
Tributylphosphate	2.5	0.2	1	13	45	25	2.5
"	"	0.5	1	13	25	16	1.6
"	"	0.7	0.6	13	20	14	1.4
"	"	0.7	1.8	13	20	14	1.4
"	"	0.9	0.4	13	12	10	1.0
"	"	0.9	1	13	12	10	1.0
"	"	1.2	0.7	13	20	14	1.4
Dibutyl butylphos- phonate	1.1	0.5	1	6	25	40	4.1

a) Entrainment losses on arbitrary assumption of 0.5 ml organic/liter raffinate.

b) Distribution losses from Tables 5, 7, and 8.

c) Based on estimated prices, ORNL-1903, p. 29.

d) Based on arbitrary assumption of 1.18 g U<sub>3</sub>O<sub>8</sub>/liter pregnant liquor.

## STRIPPING OF URANIUM

Uranium stripping from the loaded di(2-ethylhexyl)phosphoric acid extractant with both alkaline and acidic reagents was described in ORNL-1903, with particular attention to the use of sodium carbonate. Continuous countercurrent tests using sodium carbonate stripping are presented in another section of this report. Working curves for the estimation of sodium carbonate consumption and initial concentration limitations, as functions of the process variables, are given in Appendix B.

### Stripping with Ammonium Carbonate

Further studies have been made of ammonium carbonate solutions\* as stripping agents in the Dapex process. As reported previously<sup>(8)</sup> the ammonium salt of di(2-ethylhexyl)phosphoric acid, unlike the sodium salt, is miscible with kerosene at least under many conditions,\*\* and, thus, if ammonium carbonate is utilized for stripping, a diluent modifier may not be necessary. The di(2-ethylhexyl)phosphoric acid alone would give uranium extraction coefficients considerably lower than for the synergistic reagent system but still considerably higher than with the alcohol-modified diluent. Also the possibility is offered for adding synergistic reagents in quantities below those that would ordinarily be used for third phase prevention in sodium carbonate stripping, but sufficient to give some increased extraction power along with insurance

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\*All the solutions reported here were prepared by dissolving reagent grade "ammonium carbonate" in water at room temperature. As expected, they were found to contain excess CO<sub>2</sub>, i.e., some bicarbonate. However, the concentrations are reported here as apparent molarities of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> on basis of the total NH<sub>3</sub> content (including carbamate nitrogen) as determined by Kjeldahl analysis, i.e.,  $M \text{ "(NH}_4\text{)}_2\text{CO}_3\text{"} = (\underline{N} \sum \text{NH}_3)/2$ . Since the stoichiometric reagent requirements are also in effect calculated on basis of the NH<sub>3</sub> content (cf. Equations 5 and 6, ORNL-1903, p. 38), this convention provides a consistent basis for reporting the amounts of excess reagent used.

\*\*Of a large number of preliminary ammonium carbonate stripping tests, most have shown no evidence of third phase formation. However, in a few tests at high temperatures and/or high reagent levels a third phase has been noted to occur. A thorough study of the factors influencing this formation is now underway.

toward miscibility of the ammonium dialkylphosphate salt.\* At the same time, use of ammonia instead of sodium will permit production of a  $U_3O_8$  product of higher assay and relatively low cation content. A product of this nature would be more suitable for some of the processes now being considered for manufacturing pure  $UF_4$  and  $UF_6$ .

In two series of batch tests, 0.1 M D2EHPA in kerosene, loaded to 8.7 and to 6.1 g U/l, was contacted by 0.5 M ammonium carbonate solution at various phase ratios, with the results shown in Table 10. The uranium was efficiently stripped when a sufficient excess of ammonium carbonate was supplied. Precipitates formed slowly (overnight) in some of the strip solutions contacted with the 8.7 g U/l organic. The precipitate was probably ammonium uranyl tricarbonate. No precipitation occurred in the strip solutions from the 6.1 g U/l organic within 20 hours after contacting. In three of the tests, indicated in Table 10, slow phase separations were observed whereas in all the other tests shown in this (and the following) table, phase separation was rapid and clean. Reasons for the poor separation rates are not readily explainable particularly in view of the fact that the conditions of these tests were not appreciably different than several others in which good separation rates were obtained.

In another series of batch tests, 0.1 M D2EHPA in kerosene, containing 2.5 w/v % DBBP\*\* was contacted by 0.55 M and 1.1 M ammonium carbonate solutions over a similar range of phase ratios. As shown in Table 11, efficient uranium stripping was again achieved with both solutions when sufficient excess ammonium carbonate was added to the system. Lower reagent requirements would, of course, be possible in a multistage operation. With the 1.1 M ammonium carbonate solution, uranium precipitation occurred during the stripping except at the lowest organic-to-aqueous phase ratio tested, presumably because the high reagent concentration depressed the solubility of ammonium uranyl tricarbonate. Loss of di(2-ethylhexyl)phosphoric acid into the 0.5 M ammonium carbonate solution of these tests was measured to be  $\sim 0.22$  g/l. Such a loss would be unimportant costwise since the aqueous uranium concentration at this point is relatively high and the volume

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\*In any cases where third phase formation may tend to occur, it is assumed that much lower quantities of diluent modifier could be used for maintaining miscibility of the ammonium salt of the reagent than those found necessary for the sodium salt.

\*\*This is approximately twice the minimum concentration of DBBP required to maintain miscibility when sodium carbonate is used in stripping.

Table 10

URANIUM STRIPPING BY AMMONIUM CARBONATE

0.1 M Di(2-ethylhexyl)phosphoric acid in kerosene (no additive).

Strip Solution:  $\sim 0.5 \text{ M}^a$  ammonium carbonate.

Fifteen minutes agitation in shaker at room temperature.

Phase Ratio o/a	Initial		Final			% Stripped	Excess <sup>b</sup> (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>
	U g/l Organic	pH Aqueous	pH Aqueous	U g/l Aqueous	U g/l Organic		
1	8.7	8.6	8.5	8.5	0.031	99.6	322%
2	"	"	8.1	14.0 <sup>c</sup>	0.075	99.1	111
3	"	"	7.6	26.7 <sup>c</sup>	0.16	98.2	41
4	"	"	7.4	28.7 <sup>c</sup>	1.63	81.3	6
5	"	"	7.5	28.7 <sup>c</sup>	2.9	67	-14
6	"	"	7.6	26.5	3.6	58	-30
1	6.1	8.5	8.4	7.1	0.0069	99.9 <sup>d</sup>	360
2	"	"	8.1	13.4	0.027	99.6 <sup>d</sup>	130
3	"	"	7.7	20.4	0.030	99.5 <sup>d</sup>	53
4	"	"	7.6	24.9	0.74	87.9	15
5	"	"	7.5	22.0	2.4	60	-8
6	"	"	7.6	20.2	2.7	56	-24

a) " $\underline{M} (\text{NH}_4)_2\text{CO}_3$ " = ( $\underline{N}$  total nitrogen as NH<sub>3</sub>)/2; see note p. 32. Concentrations = 0.47  $\underline{M}$  for first six tests and 0.52  $\underline{M}$  for last six.

b) Excess calculated on basis of utilizing the total base strength; cf. equations 5 and 6, ORNL-1903. "-14% Excess" = 14% deficiency, etc.

c) Precipitates formed on standing overnight, probably ammonium uranyl tricarbonate. Precipitates were redissolved for analysis.

d) Slow separation, 5-8 minutes. All other separations in 30-60 seconds.

Table 11

URANIUM STRIPPING BY AMMONIUM CARBONATE

0.1 M Di(2-ethylhexyl)phosphoric acid in kerosene plus 2.5 w/v %  
DBBP<sup>a</sup> loaded to 6.2 g/l U.

Contact Time: 15 minutes.

$\frac{M^b}{(NH_4)_2CO_3}$	Phase Ratio o/a	Initial pH	Final pH	U g/l Aqueous	U g/l Organic	% Stripped	Excess <sup>c</sup> (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>
1.09	1	8.35	8.4	5.04	0.0056	99.9	970%
"	2	"	8.3	(d)	0.0085	99.9	440
"	3	"	8.1	(d)	0.0094	99.8	260
"	5	"	8.0	(d)	0.013	99.8	110
"	10	"	7.5	(d)	2.6	58	7
0.55	1	8.25	8.2	5.3	0.0063	99.9	440
"	2	"	8.0	12.5	0.010	99.8	170
"	3	"	7.7	17.8	0.017	99.7	80
"	5	"	7.3	24.6	1.7	73	8

a) Dibutyl butylphosphonate.

b) " $\frac{M}{(NH_4)_2CO_3}$ " = ( $\frac{N}{N}$  total nitrogen as NH<sub>3</sub>)/2. See note p. 32.

c) Excess calculated on basis of utilizing total base strength. Cf. equations 5 and 6, ORNL-1903.

d) Precipitation of a water-soluble solid occurred. Appeared to be salting out of ammonium uranyl tricarbonate.

small. It has not yet been determined whether any appreciable amount of this di(2-ethylhexyl)phosphate is carried into the uranium product. It may be noted, however, that the amount of phosphorus involved is not high enough to cause serious contamination. If all the 0.22 g/l dialkylphosphate entered the product, from a strip solution loaded to 20 g  $U_3O_8$ /l, it would amount to only about 0.2%  $P_2O_5$  in the product.

A single continuous countercurrent run has been made thus far wherein uranium was extracted from a synthetic leach liquor with 0.1 M D2EHPA - 0.7 w/v % DBBP\* in kerosene, and the loaded organic was stripped with 0.55 M ammonium carbonate. (Continuous countercurrent tests using sodium carbonate stripping are described in a subsequent section.) Operating conditions for the continuous countercurrent run are listed in Table 12 and the distribution of uranium and contaminants in the extraction and stripping systems after four organic cycles is shown in Tables 13 and 14. Nearly complete (99.8%) recovery of uranium was achieved in three extraction stages while operating at a feed ratio of  $4^a/l^o$  (Table 13). Examination of the stripping data in Table 14 shows that essentially complete stripping of uranium was accomplished in two stages at a feed ratio of  $4^o/l^a$ . The quantity of ammonium carbonate employed was 35-40% in excess of the calculated stoichiometric requirements (cf. Equations 5 and 6 in ORNL-1903). Utilization of lesser quantities at the same conditions of operation may have been possible, and almost certainly could be achieved with more stripping stages.

Unfortunately, dependable information was not obtained in this run with respect to the stripping of the small amounts of aluminum and iron that had been extracted into the organic phase. Little, if any, stripping of aluminum is shown, although the concentration level of aluminum was so low as to introduce considerable analytical uncertainty. Only a minor amount of iron was stripped from the organic phase in the first stripping stage. Data on the iron content of the organic phase from the second stripping stage has been discarded since it was discovered that some iron precipitated from the samples on standing and that the precipitated iron was not included in the analyses. However, samples of the pregnant extract taken several times throughout the run all had approximately the same iron content showing that the iron concentration in the organic phase did not build up as the run progressed. Phase separation in the extraction and stripping circuits was good throughout the run.

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\*This is approximately one-half the minimum concentration of DBBP required to maintain miscibility when sodium carbonate is used in stripping, and somewhat less than the concentration which produces the maximum synergistic enhancement of uranium extraction.

Table 12  
OPERATING CONDITIONS FOR  
COUNTERCURRENT AMMONIUM CARBONATE STRIP TEST

Extractors:

Mixers:	Liquor Feed Rate <sup>a</sup>	100 ml/min
	Organic Feed Rate <sup>b</sup>	25 ml/min
	Residence Time	3 min
	Turbine Speed	800-1000 RPM
	Working Volume	~375 ml
Settlers:	Aqueous Residence Time	1 min
	Organic Residence Time	3 min
	Working Volume	~175 ml

Strippers:

Mixers:	0.54 M (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> Feed Rate <sup>c</sup>	6.3 ml/min
	Organic Feed Rate	25 ml/min
	Turbine Speed	350 RPM
	Residence Time	12 min
	Working Volume	~375 ml
Settlers:	Aqueous Residence Time	14 min
	Organic Residence Time	4 min
	Working Volume	~175 ml

a) Liquor Analysis:	U	1.15 g/l
	ΣFe	2.8
	Fe(III)	0.3
	Al	3.0
	SO <sub>4</sub>	44
	pH	1.3

b) Organic 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene + 0.7 w/v % dibutyl butylphosphonate.

c) "M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>" = (N total nitrogen as NH<sub>3</sub>)/2. See note p. 32.

Table 13

EXTRACTION CYCLE DATA -

COUNTERCURRENT AMMONIUM CARBONATE STRIP TEST

	<u>Stage No. 1</u>			<u>Stage No. 2</u>			<u>Stage No. 3</u>			<u>% Extracted</u>
	<u>g/l Org.</u>	<u>g/l Aq.</u>	<u>E<sub>a</sub></u>	<u>g/l Org.</u>	<u>g/l Aq.</u>	<u>E<sub>a</sub></u>	<u>g/l Org.</u>	<u>g/l Aq.</u>	<u>E<sub>a</sub></u>	
U	5.0	0.49	10	1.96	0.036	54	0.14	0.0020	70	99.8 (1)
Fe	0.31	2.8	0.11	0.35	2.8	0.12	0.29	2.8	0.10	3 (2)
Al	0.012	2.9	0.004	0.020	2.9	0.007	0.020	2.9	0.007	0.1 (2)

(1) Based on head liquor and raffinate analysis.

(2) Based on liquor and loaded organic analysis.

All at R.T. - 27°C.

Table 14  
STRIPPING CYCLE DATA -  
COUNTERCURRENT AMMONIUM CARBONATE STRIP TEST

	<u>Stage No. 1</u>		<u>Stage No. 2</u>		<u>% Stripped (1)</u>
	<u>g/l Aqueous</u>	<u>g/l Organic</u>	<u>g/l Aqueous</u>	<u>g/l Organic</u>	
U	19.8	0.090	0.49	0.0012	99.98
Fe	----	0.28	----		
Al	----	0.015	----	0.012	---
NH <sub>3</sub>	12.5		16.9		
pH	7.9		8.6		

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(1) Based on loaded and barren organic analyses.

All at R.T. - 27°C.

Recovery of uranium from the pregnant strip solution has not been studied in any detail. Uranium precipitation and recovery of the stripping reagent for recycle would probably be accomplished by the steam distillation process described by Battelle Memorial Institute for the treatment of ammonium carbonate leach liquors.<sup>(9)</sup> In initial laboratory tests the strip solution from the countercurrent runs was first filtered to remove precipitated contaminants and then treated with steam for one hour. The resulting uranium precipitate was filtered, washed and dried at 120°C. Analyses of the pregnant strip solution, filtrate, and dried product are shown below:

	<u>g/l U</u>	<u>g/l NH<sub>3</sub></u>	<u>% U Precipitated</u>	<u>% NH<sub>3</sub> Volatilized</u>
Pregnant Strip	18.0	11.5	---	---
Filtrate	0.053	0.46	99.7%	91%
Product:	88.8% U <sub>3</sub> O <sub>8</sub> , 0.17% Fe <sub>2</sub> O <sub>3</sub> , 0.14% Al <sub>2</sub> O <sub>3</sub> , 2.15% NH <sub>3</sub>			

As may be observed the bulk of the uranium and ammonia were removed from the solution, and a high grade product was obtained.

In view of the promising results that have been obtained with ammonium carbonate stripping, continued studies are being made, particularly with regard to optimization of ammonium carbonate requirements, stripping of contaminating metals, factors affecting miscibility of the ammonium dialkylphosphate salt in kerosene, etc.

Sodium Hydroxide. As previously reported (ORNL-1903), 5% NaOH solution effectively strips uranium from the organic phase, offering a possibility of stripping and forming a product precipitate in one operation. This possibility was tested in a mixer-settler unit employing 0.1 M D2EHPA in capryl alcohol-modified kerosene loaded to 4.5 g uranium per liter, operated under conditions that have proven quite satisfactory for Na<sub>2</sub>CO<sub>3</sub> strip solutions. However, an emulsion formed in the settler which increased until the settler was completely filled. The phases appeared to be completely emulsified. Thus, while the chemistry of the NaOH strip method is satisfactory, the physical aspects present a severe operational problem.

Basic Slurries. The stripping of di(2-ethylhexyl)phosphoric acid solutions with some of the relatively insoluble bases was investigated, in view of three possible advantages over sodium carbonate stripping: 1) the cost of these insoluble bases per equivalent of base is substantially lower, 2) the final product is formed as a precipitate directly in a one-step

stripping operation, and 3) the calcium and magnesium salts of the alkylphosphoric acid are soluble in kerosene without need of modifiers.

Of the three bases tested,  $\text{Ca}(\text{OH})_2$ ,  $\text{MgO}$ , and  $\text{CaCO}_3$ , only  $\text{Ca}(\text{OH})_2$  showed any appreciable ability to strip uranium, precipitating 20-60% from the extract in one contact. No definite correlation could be found between the amount of uranium stripped and such variables as concentration, excess, temperature, and time. It is suggested that calcium diuranate coated the  $\text{Ca}(\text{OH})_2$  particles and inactivated them.

#### Extraction of Water and Free Base

Volume Changes on Neutralization of Dialkylphosphoric Acid. It was observed during development of the critical miscibility point titration method for determination of miscibility modifier content (ORNL-1903, p. 59; cf. p. 17 above) that the volume of the organic phase changed when equilibrated with different aqueous solutions. The volume of a kerosene solution of dialkylphosphoric acid increased on contact with a basic solution, with an equal decrease in the aqueous volume, and returned to its original volume when re-acidified.\* Processwise, the increase in organic volume during basic stripping may be trivial, but the corresponding decrease in aqueous volume can be significant. When high uranium loadings and high organic:strip ratios are used, some limitation is imposed on the initial sodium carbonate concentration to be used by the possibility of exceeding the uranyl tricarbonate solubility limit (cf. Appendix B). The transfer of some water to the organic phase can set the limiting initial sodium carbonate concentration somewhat lower than it otherwise would be.

Quantitative measurement was made of the volume changes in several equilibrations, as shown in Table 15.\*\* The volume

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\*To avoid any error arising from changing volume, the procedure developed for the titration specifies calculation of the final dialkylphosphate concentration from the known original dialkylphosphoric acid concentration and the volumes added. That is, the molarity of dialkylphosphoric acid which would be obtained on reacidification is used in the critical miscibility calibration curves, rather than the actual molarity of sodium dialkylphosphate which exists when the critical miscibility point is reached.

\*\*Workers at Dow Chemical Company (10) reported a volume increase of 30 ml per liter of 0.12 M di(2-ethylhexyl)phosphoric acid/kerosene - 2 v % capryl alcohol, which is in close agreement with the fourth test in Table 15, equivalent to 32 ml per liter of 0.112 M di(2-ethylhexyl)phosphoric acid/kerosene - 1.0 w/v % 2-ethylhexanol.

Table 15

## VOLUME CHANGES ON CONTACT WITH BASIC SOLUTIONS

Di(2-ethylhexyl)phosphoric acid/kerosene, 1<sup>aq</sup>:1<sup>org</sup> initial

Init. <u>M</u> D2EHPA	Additive	Init. Aq. Phase	Equiln. Temp., °C	Org. Vol. Increase <sup>b</sup> ml/ml
0.224	1.5 w/v % Alc <sup>c</sup>	5 w/v % Na <sub>2</sub> CO <sub>3</sub>	RT	0.068
0.447	None	10 " "	RT	0.120, .124, .122 <sup>e</sup>
0.056	1.0 w/v % Alc	" " "	RT	0.024
.112	1.0 " "	" " "	RT	.032
.224	1.5 " "	" " "	RT	.058
.447	2.0 " "	" " "	RT	.118
0.447	5.0 " TBP	" " "	RT	0.108, .114, .108
.446	" " "	" " "	26°	.111
.446	" " "	" " "	50°	.094
.456	5.2 " "	10.3 " "	50°	.097 <sup>f</sup>
0.447	None	5 w/v % Amm. Carb. <sup>d</sup>	RT	0.140, .144
.447	"	" " "	50°	.117
0.447	2.0 w/v % Alc	" " "	RT	0.100, .108
0.447	2.0 w/v % Alc	1.0 <u>M</u> NaOH	RT	0.138 <sup>e</sup>
0.447	2.0 w/v % Alc	1.5 " "	RT	0.102 <sup>e</sup>
.446	5.0 " TBP	" " "	26°	.095
.446	" " "	" " "	50°	.082
.456	5.2 " "	1.54" "	50°	.090 <sup>f</sup>
0.447	2.0 " Alc	2.0 " "	RT	0.082, .088

Table 15 (Cont'd.)

VOLUME CHANGES ON CONTACT WITH BASIC SOLUTIONS

Notes for Table 15:

- a) Temperature:  $26^{\circ} \pm 1^{\circ}$ ,  $50^{\circ} \pm 0.5^{\circ}$ , R.T. = 26-31°C. Concentrations and volume changes based on volumes at 26° are shown for the 50° equilibrations.
- b) Phase volumes measured with estimated accuracy within  $\pm 0.05$  ml; total volumes (either 10 or 20 ml) remained constant within  $\pm 0.05$  ml.
- c) Alc = 2-ethylhexanol, critical miscibility concentration 1.98 w/v % in 0.447 M reagent/kerosene for contact with 10 w/v %  $\text{Na}_2\text{CO}_3$  at 26°C.
- d) Amm. Carb. = Reagent grade "ammonium carbonate," approximately half  $\text{NH}_4\text{HCO}_3$  and half  $\text{NH}_4\text{CO}_2\text{NH}_2$ .
- e) Third phase formed. "Organic volume" = sum of "normal organic phase" and "third phase."
- f) Small amount ( $\leq 0.1$  ml) of third phase present at 50°, disappeared on cooling to 26°.

changes are seen to be approximately proportional to the concentration of dialkylphosphate. The variations between tests at the same dialkylphosphate concentration could be accidental variations, within a conservative estimate of the expected accuracy, but (especially in view of the reasonable agreement among replicates) they do suggest that transfer of water with the sodium ion was decreased (1) by increased concentration in the aqueous phase, (2) by the presence of TBP, or to a lesser extent by the presence of alcohol, and (3) by increase of the temperature. Transfer of water with the ammonium ion appeared more sensitive to the presence of alcohol.

Transfer of Excess Base to the Organic Phase. In addition to the water extracted by the sodium dialkylphosphate, significant concentrations of sodium hydroxide or sodium carbonate are also transferred from the stripping solution to the kerosene phase. The quantities so transferred were measured by direct analysis in the tests shown in Table 16. These were separate tests, with a single analysis made on each equilibrium organic phase, i.e., Karl Fischer titration for water, acid titration for hydroxide or carbonate, or total carbon dioxide by displacement and absorption. Phase volume changes were measured as shown in most of these tests (the ones also shown in Table 15), in which the phases were separated by standing overnight in stoppered graduated cylinders. The other equilibrations were made in separatory funnels which were centrifuged to separate the phases.

The quantities of excess base found were much too large to be ascribed to entrainment of the equilibrium aqueous phase. It may be suggested that the sodium dialkylphosphate exists in the kerosene phase as dispersed aggregates, perhaps micelles, of sufficiently ionic nature to accept an appreciable distribution of the inorganic ions from the aqueous phase. If this is correct, the amount of excess base extracted may be expected to vary directly with the dialkylphosphoric acid concentration and with some function of the aqueous composition, and also to be sensitive to physical conditions. The preliminary tests of temperature effect included in Table 16 show a small decrease in extraction of sodium carbonate or hydroxide on raising the temperature to 50°C. Essentially the same sodium carbonate extraction was found (at room temperature) whether 2-ethylhexanol or tributylphosphate was used as the miscibility modifier.

The sodium found as carbonate plus bicarbonate,  $\sim 0.05$  M  $\text{Na}^+$  in the final organic volume, corresponding to 0.055 M on basis of the original volume, amounted to 12% excess over that consumed in formation of the sodium dialkylphosphate. The relative magnitude of this in a stripping operation can be illustrated by the following typical example. Assume 0.1 M dialkylphosphoric acid loaded to 4.5 g  $\text{U}_3\text{O}_8$ /liter, stripped

Table 16

## DIRECT ANALYSES OF ALKALI-STRIPPED ORGANIC PHASES

Init. Aq. Phase	Init. Org. Phase	Equiln. Temp. <sup>a</sup> °C	Method of Analysis	Found in Org. Phase <sup>b</sup>	Org. Vol. Increase, %
10 w/v % Na <sub>2</sub> CO <sub>3</sub>	II	RT	K. Fischer Titrn.	92 mg H <sub>2</sub> O/ml	-- <sup>c</sup>
" " "	II	RT	Acid Titrn.	{ 0.014 <u>M</u> Na <sub>2</sub> CO <sub>3</sub> .022 <u>M</u> NaHCO <sub>3</sub>	-- <sup>c</sup>
" " "	IIIa	26°	" "		{ 0.014 <u>M</u> Na <sub>2</sub> CO <sub>3</sub> .020 <u>M</u> NaHCO <sub>3</sub>
" " "	IIIa	50°	" "	{ 0.012 <u>M</u> Na <sub>2</sub> CO <sub>3</sub> .013 <u>M</u> NaHCO <sub>3</sub>	
10.3 " "	IIIb	50°	" "		{ 0.012 <u>M</u> Na <sub>2</sub> CO <sub>3</sub> .016 <u>M</u> NaHCO <sub>3</sub>
" " "	IIIb	50°	" "	{ 0.012 <u>M</u> Na <sub>2</sub> CO <sub>3</sub> .017 <u>M</u> NaHCO <sub>3</sub>	
10 " "	IIIa	RT	Total CO <sub>2</sub>	0.041 <u>M</u> ΣCO <sub>2</sub>	-- <sup>c</sup>
5 " Amm. Carb.	I	50°	Acid Titrn.	Σ0.008 <u>N</u> base <sup>e</sup>	12
1.0 " NaOH	II	RT	" "	Σ0.018 <u>M</u> NaOH <sup>f</sup>	14
1.5 " "	II	RT	" "	Σ0.029 <u>M</u> NaOH <sup>g</sup>	10
" " "	IIIa	26°	" "	.023 " "	10
" " "	IIIa	50°	" "	.020 " "	8
1.54 " "	IIIb	50°	" "	.023 " "	9 <sup>d</sup>
~2 " "	II	RT	" "	0.036 " "	-- <sup>c</sup>
2.0 " "	II	RT	" "	.030 " "	9

Initial Organic Phases:

I.	0.447 <u>M</u>	D2EHPA/kerosene.
II.	0.447 <u>M</u>	" /kerosene + 2.0 w/v % 2-ethylhexanol.
IIIa.	0.446 <u>M</u>	" /kerosene + 5.0 w/v % TBP.
IIIb.	0.456 <u>M</u>	" /kerosene + 5.2 w/v % TBP.

Table 16 (Cont'd.)

DIRECT ANALYSES OF ALKALI-STRIPPED ORGANIC PHASES

Notes for Table 16:

Initial phase ratio, 1:1. Phases separated by standing overnight in cylinders, except as noted.

- a) Temperature:  $26^{\circ} \pm 1^{\circ}$ ,  $50^{\circ} \pm 0.5^{\circ}$ , R.T. = 26-31°C. Concentrations based on volumes at  $26^{\circ}$  are shown for the  $50^{\circ}$  equilibrations.
- b) Concentrations Found are based on the final organic volumes.
- c) Phases separated by centrifuging; volume changes not measured.
- d) Small amounts ( $\leq 0.1$  ml) of 3rd phase present at  $50^{\circ}$ , disappeared on cooling to  $26^{\circ}$ .
- e)  $40.001$  N base in 4.84 ml top phase;  $0.014$  N base in 6.36 ml middle ("3rd") phase. Titration curves did not permit separate estimation of  $\text{CO}_3^{=}$  and  $\text{HCO}_3^{-}$ .
- f)  $40.001$  M NaOH in 2.01 ml top phase;  $0.028$  M NaOH in 3.68 ml middle ("3rd") phase.
- g)  $40.003$  M NaOH in 1.79 ml top phase;  $0.041$  M NaOH in 3.72 ml middle ("3rd") phase.

with 10 w/v % sodium carbonate solution at 20% excess over the stoichiometric requirement calculated from Equations 5 and 6, ORNL-1903. (These conditions require a phase ratio of 9.6<sup>o</sup>:1<sup>a</sup>, and produce a pregnant strip solution at 43 g U<sub>3</sub>O<sub>8</sub>/liter.) Then the sodium carbonate lost to the stripped organic stream, if proportional to that in Table 16, will be about 6% of the total supplied, 0.15 lb Na<sub>2</sub>CO<sub>3</sub>/lb U<sub>3</sub>O<sub>8</sub>, or 1/3¢ per lb U<sub>3</sub>O<sub>8</sub>. The effective excess of sodium carbonate in the aqueous solution will be about 13% instead of 20% over stoichiometric. On the same basis, the volume of carbon dioxide gas released on recycle to the acidic extraction system will be about 0.2 liter per liter of the organic stream. Although not necessarily important in mixer-settler operation,\* such gassing might be important in a column operation. Further examinations are being made of the factors which control the transfer of carbonate into the organic phase.

#### Stripping D2EHPA (with and without Modifier) with Mineral Acids

Data describing the ability of mineral acids and their salts to strip uranium from di(2-ethylhexyl)phosphoric acid were reported in ORNL-1903. Additional stripping tests with solutions of this type have now been made and the results are summarized together with some of the pertinent previous data in Table 17 and Figure 4. Several observations which may be made from the data are as follows:

1) In the previous tests, the uranium stripping coefficients by hydrochloric acid solutions from di(2-ethylhexyl)-phosphoric acid in kerosene modified with 2-ethylhexanol were found to be lower when the hydrochloric acid concentration was 10 M than when it was 6 M, although still considerably higher than when it was only 3 M. The subsequent tests at additional hydrochloric acid concentrations have confirmed the previous results. They show that the stripping coefficients go through maxima in the range between 6 and 9 M, followed by minima between 9 and 11 M, and then rise again with increasing hydrochloric acid concentrations up to the highest tested, i.e., 12 M, the maximum concentration available without special handling. Similar results were obtained when the extractant was modified with tributylphosphate instead of alcohol, maxima and minima occurring at close to the same hydrochloric acid

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\*This amount of gassing is not noticed in the bench-scale mixer-settlers. With organic flow rates in the order of 25 ml/minute, the estimated carbon dioxide evolution is about 5 ml/minute, whereas air is frequently drawn into the mixers in larger volumes.

Table 17

URANIUM STRIPPING WITH ACIDS

Di(2-ethylhexyl)phosphoric acid in kerosene  
 2 g U/liter  
 Phase Ratio = 1  
 10 Min. agitation by wrist-action shaker,  
 25-29°C

Stripping Agent	S <sub>0</sub> <sup>a</sup> from 0.1 M D2EHPA			S <sub>0</sub> <sup>a</sup> from 0.2 M D2EHPA		
	No Additive	2.0 w/v % 2-Ethylhexanol	2.5 w/v % TBP	No Additive	2.8 w/v % 2-Ethylhexanol	3.0 w/v % TBP
3 M HCl	0.6*	1.3*	0.1	0.1*	0.4*	0.03
6 " "	6 *	8 *	0.5	1.6*	2.5*	0.2
7.5 " "	-	9	0.8	4	2.7	0.3
9 " "	35	6	0.4	11	3.0	0.3
10.0 " "	35 *	6 *	---	11 *	2.7*	---
" " "	45	6	0.5	10	2.7	0.3
11.0 " "	30	6	0.9	11	3.1	0.5
12.0 " "	25	8	1.0	11	5.2	0.9
1.5 M H <sub>2</sub> SO <sub>4</sub>	1.0*	1.8*	0.1	0.1*	0.4*	0.03
3 " "	2.5*	6 *	0.4	0.6*	1.7*	0.1
6 " "	14	45 *	2.3	4 *	9 *	0.6
1.5 M H <sub>3</sub> PO <sub>4</sub>	2.1*	5 *	---	0.5*	1.1*	---
3.3 " "	15 *	--	4	---	---	1.2
5.3 " "	100 *	330 *	18	20 *	90 *	6
7.3 " "	--	--	---	---	280	---
11.5 " "	--	--	---	---	850	---
14.7 " "	--	--	---	---	500	---

\*Tests with Reagent Batch No. 276, previously reported in ORNL-1903. All other tests with Reagent Batch No. 303.

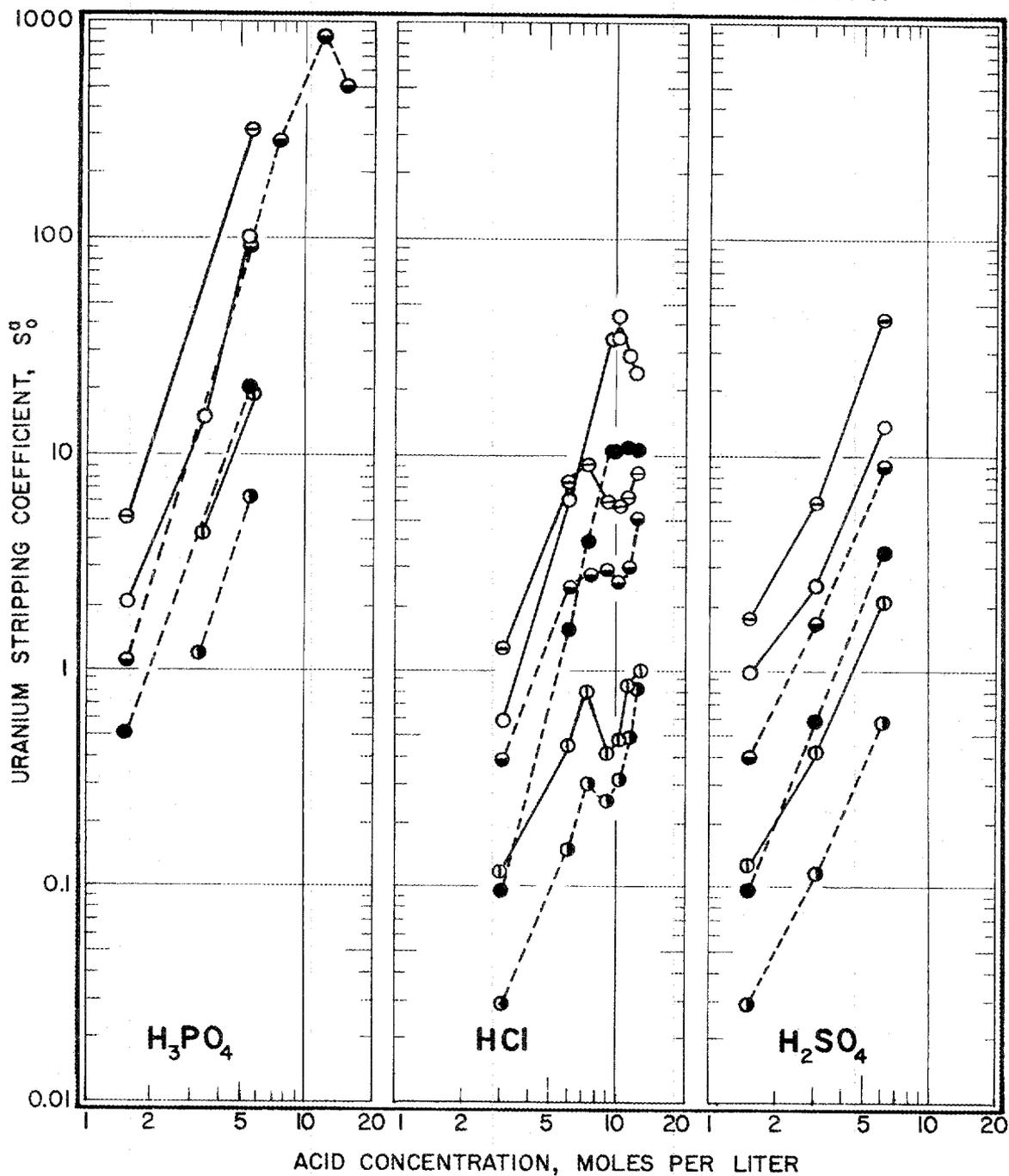


Figure 4

URANIUM STRIPPING WITH ACIDS

- 0.1 M D2EHPA, unmodified
- 0.2 M D2EHPA, unmodified
- " " + 2 w/v % 2-Ethylhexanol
- " " + 2.8 w/v % 2-Ethylhexanol
- " " + 2.5 w/v % Tributylphosphate
- " " + 3.0 w/v % Tributylphosphate

2 g U/l organic phase, kerosene diluent  
 Aqueous:Organic Phase Ratio = 1  
 10 minutes agitation by wrist-action shaker, 25-29°C

concentrations. A different but probably related behavior was shown by the unmodified extractant: the stripping coefficients increased uniformly up to 9-10 M hydrochloric before reaching maxima, and did not show minima in the range tested.\*

2) With either modified or unmodified extractant, the stripping coefficients for the two different levels of D2EHPA (0.1 and 0.2 M) were not nearly as different in magnitude at the higher as at the lower hydrochloric acid concentrations.

3) As reported previously, the uranium extraction coefficients with D2EHPA from moderately acidic solutions are lower when alcohols are present in the diluent. Conformably, in the range of 3-6 M HCl, the stripping coefficients are higher for the alcohol modified solvent than for the unmodified. On the other hand, above about 6 M HCl, due to the effects described above, the D2EHPA was more easily stripped when alone than when alcohol was present.

The presence of TBP, as described earlier, causes a considerable increase in uranium extraction coefficient so that in all cases the stripping of TBP modified solvent was much lower than for the alcohol modified solvent or for D2EHPA alone. The highest stripping coefficients obtained in the presence of TBP were too low for effective practicable utility.

4) Stripping coefficients with sulfuric and phosphoric acids increased uniformly from all solvents with increasing acid concentration in the range of 1.5 - 6 M. Concentrations above this range have not been studied with sulfuric acid.

In a single series with phosphoric acid solutions on 0.2 M D2EHPA modified with alcohol, no unusual effect was noted up to about 12 M. The one test at higher concentration, ~15 M, indicates a decrease in stripping coefficient which may correspond to that found with hydrochloric acid. However, it should be remembered that such high coefficients (>500) are inherently subject to large experimental errors, and this apparent decrease may not be real.

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\*The suggestion previously noted still appears probable, that the drop in stripping power between ~7 and 10 M hydrochloric acid might be related to the increase in extraction power found at high nitrate concentrations (ORNL-1903, p. 53). The further suggestion may be offered, that the rise in stripping power above 10 M hydrochloric acid might result from formation of an aqueous uranyl chloride complex that is unfavorable for extraction by dialkylphosphoric acid. The possible correlation of these stripping data with the uranyl chloride complex constants has not yet been examined.

Stripping Mono(dodecyl)phosphoric Acid (DDPA). Comparative stripping tests with sulfuric and hydrochloric acid were made on the long chain mono(2,6,8-trimethylnonyl-4)phosphoric acid, DPPA, which has been extensively studied and developed for process use by the Dow Chemical Company.\* The test conditions were similar to those of the preceding stripping tests (no diluent modifier present), and the results are compared in Figure 5.

Stripping coefficients at the 0.1 M alkyl reagent level were higher for the di(2-ethylhexyl)phosphoric acid than for DDPA in the concentration range of sulfuric acid tested, 1.5 to 6 M, and also with hydrochloric acid up to 6 M. However, the curves for the monoalkyl reagent are steeper than for the dialkyl reagent, and the coefficients were equal at about 10 M acid. A decrease in the DDPA stripping coefficients in the most concentrated hydrochloric acid corresponded with the decrease already noted for the di(2-ethylhexyl)phosphoric acid. Quadrupling the concentration of DDPA appeared to have close to the same effect on lowering the stripping coefficients as doubling the concentration of di(2-ethylhexyl)phosphoric acid.\*\*

\*Dow Chemical Company has previously reported considerable information with regard to stripping DDPA with hydrochloric acid. Because of differences in method of preparation of the alkyl reagent and differences in the uranium contents of the systems examined, it is difficult to compare results. However, extrapolation of the two-hour experiments presented here appears to be consistent with a stripping isotherm for 0.1 M DDPA and 10 M HCl (three-hour contact) presented in DOW-101,<sup>(11)</sup> page 24, after allowance for the difference in uranium levels.

\*\*Since  $E_a^O(U)$  is known to be proportional to  $(D2EHPA)^2$  in extraction from acidic perchlorate solutions (ORNL-2002), this observation might suggest a corresponding proportionality of  $E_a^O(U)$  to the first power of (DDPA). Stewart and Hicks<sup>(13)</sup> reported preliminary studies showing  $E \propto$  (monobutylphosphoric acid) in extraction from both low and high acid solutions, and proposed the simple reaction



for extraction from at least the high acid solutions. In contrast, the few tests made in this laboratory have indicated E proportional to a power of (monoalkylphosphoric acid) higher than unity: e.g.,  $(DDPA) \sim 1.5$  in extraction from 1 M HClO<sub>4</sub> solution,  $(M2EHPA) \sim 1-2$  in extractions from a variety of solutions at pH 1.<sup>(8)</sup> However, there were more experimental uncertainties in these tests (e.g., reagent purity) than in the tests which defined the concentration dependence on D2EHPA. Workers at Dow Chemical Company<sup>(14,15)</sup> have described extractions with DDPA in terms of formation of a  $[UO_2(HRPO_4)_2]$  complex, without reporting the reasons for

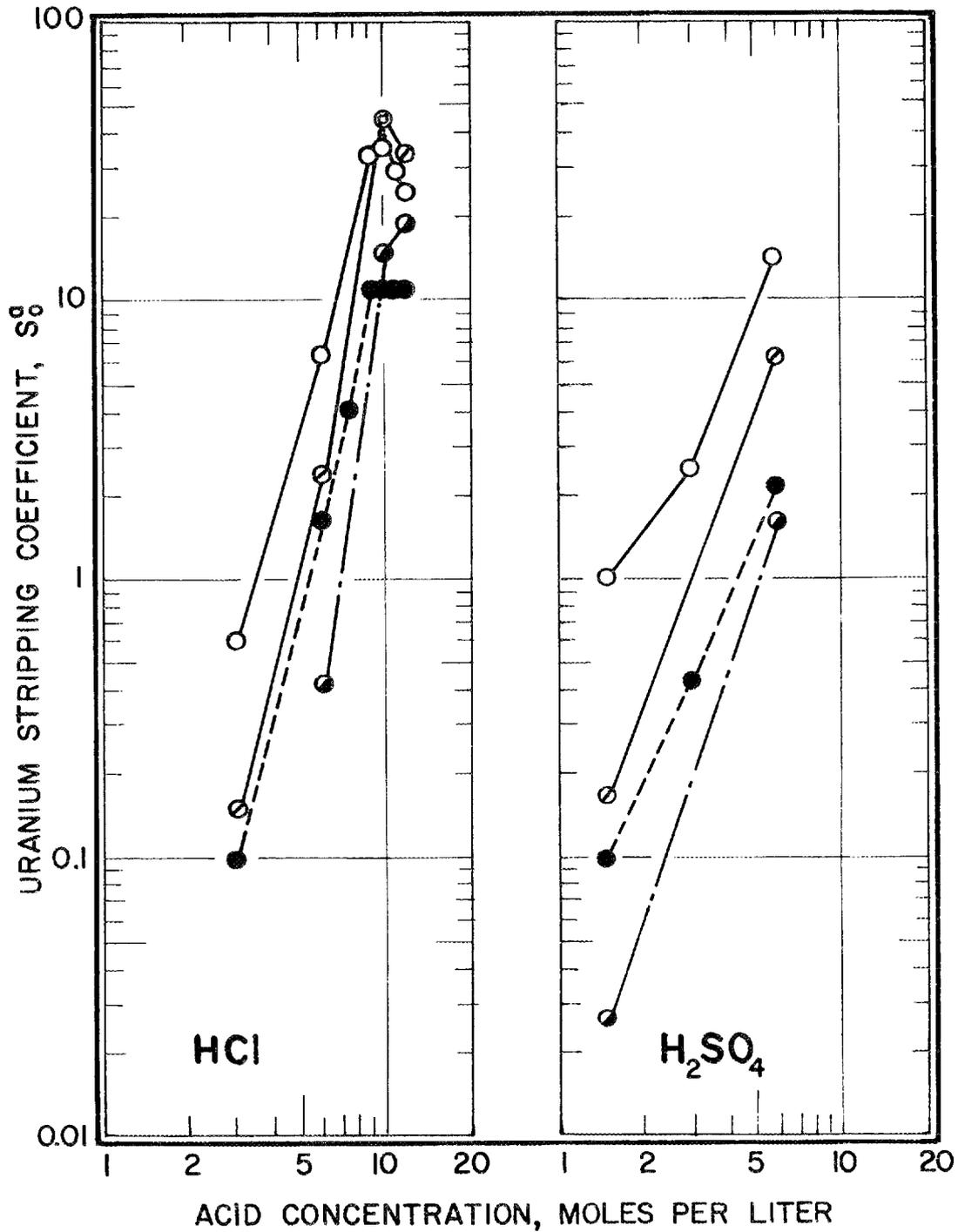


Figure 5

STRIPPING MONODODECYLPHOSPHORIC ACID (DDPA) AND  
DI(2-ETHYLHEXYL)PHOSPHORIC ACID (D2EHPA) WITH ACIDS

- 0.1 M DDPA
- 0.1 M D2EHPA, unmodified
- 0.4 M DDPA
- 0.2 M D2EHPA, unmodified

2 g U/1 organic phase, kerosene diluent  
Agitation in wrist-shaker; D2EHPA 10 min, DDPA 120 min.  
Temperature: 25-29°C

Stripping Rate. Figure 6 demonstrates that equilibrium was reached in less than two minutes when di(2-ethylhexyl)-phosphoric acid in kerosene (modified or unmodified) was stripped with 10 M hydrochloric. Although initial stripping of DDPA is probably rapid, a slow approach to complete equilibrium has been reported for the DDPA with stripping coefficients still increasing after 40 minutes of contact.<sup>(11,12)</sup> In the tests in Figure 5 the D2EHPA and DDPA solvents were contacted for 10 minutes and 120 minutes, respectively, to ensure that essentially equilibrium conditions were obtained.

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choosing this formulation. They reported uranium loadings reaching 1 U:1.75 DDPA,<sup>(15)</sup> which is a little beyond the limit expected for a 1:2 complex. In preparation of a pregnant organic solution for the stripping tests reported here, by extraction from acidic sulfate solution in very high uranium concentration ( $\sim 1.8$  M  $UO_2SO_4$  + 0.5 M  $H_2SO_4$  equilibrium aqueous phase), a uranium loading of only 1 U:1.85 DDPA was reached. These various observations would seem to suggest that a 1:1 complex may be a significant contributor in the extraction, but probably is not the only important extracted species.

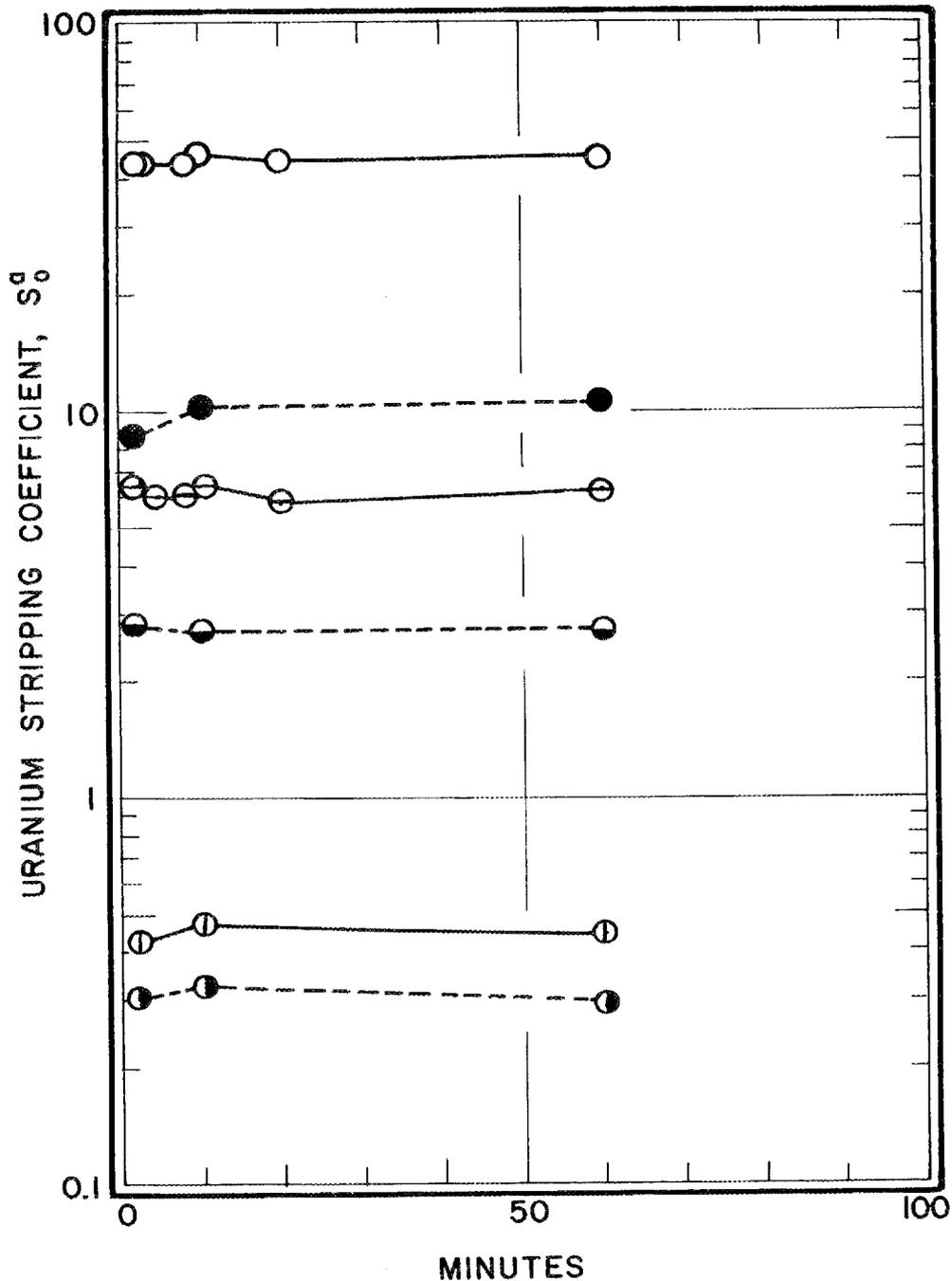


Figure 6

URANIUM STRIPPING RATE WITH 10 M HYDROCHLORIC ACID

- 0.1 M D2EHPA, unmodified
- " " + 2 w/v % 2-Ethylhexanol
- " " + 2.5 w/v % Tributylphosphate
- 0.2 M D2EHPA, unmodified
- " " + 2.8 w/v % 2-Ethylhexanol
- " " + 3.0 w/v % Tributylphosphate

2 g U/l organic phase, kerosene diluent  
Aqueous:Organic Phase Ratio = 1  
Agitation by wrist-action shaker, 25-29°C

## CONTINUOUS COUNTERCURRENT TESTS

Preliminary bench-scale continuous countercurrent tests of the Dapex process (alcohol modification of solvent) were reported in ORNL-1903, the main purpose of these tests being to study the tolerance of the process for iron(III). Since that time further experiments of this type have been made to investigate some of the other process variables and to compare the relative performance of organic solutions of different compositions, e.g., synergistic reagents.

A typical process circuit is shown diagrammatically in Figure 7. Each block in the diagram represents a mixer and settler unit. The mixer is a baffled beaker agitated with a two blade stirrer driven by a variable speed motor. The phases which are combined in the mixer, separate in the settler, one phase advancing to the next stage by gravity and the other phase being transferred in the opposite direction by means of a microbellows pump. The flow rates are regulated with flow meters or by metering pumps. Drawings of the bench-scale equipment along with more detailed descriptions of the operation are given in Appendix A.

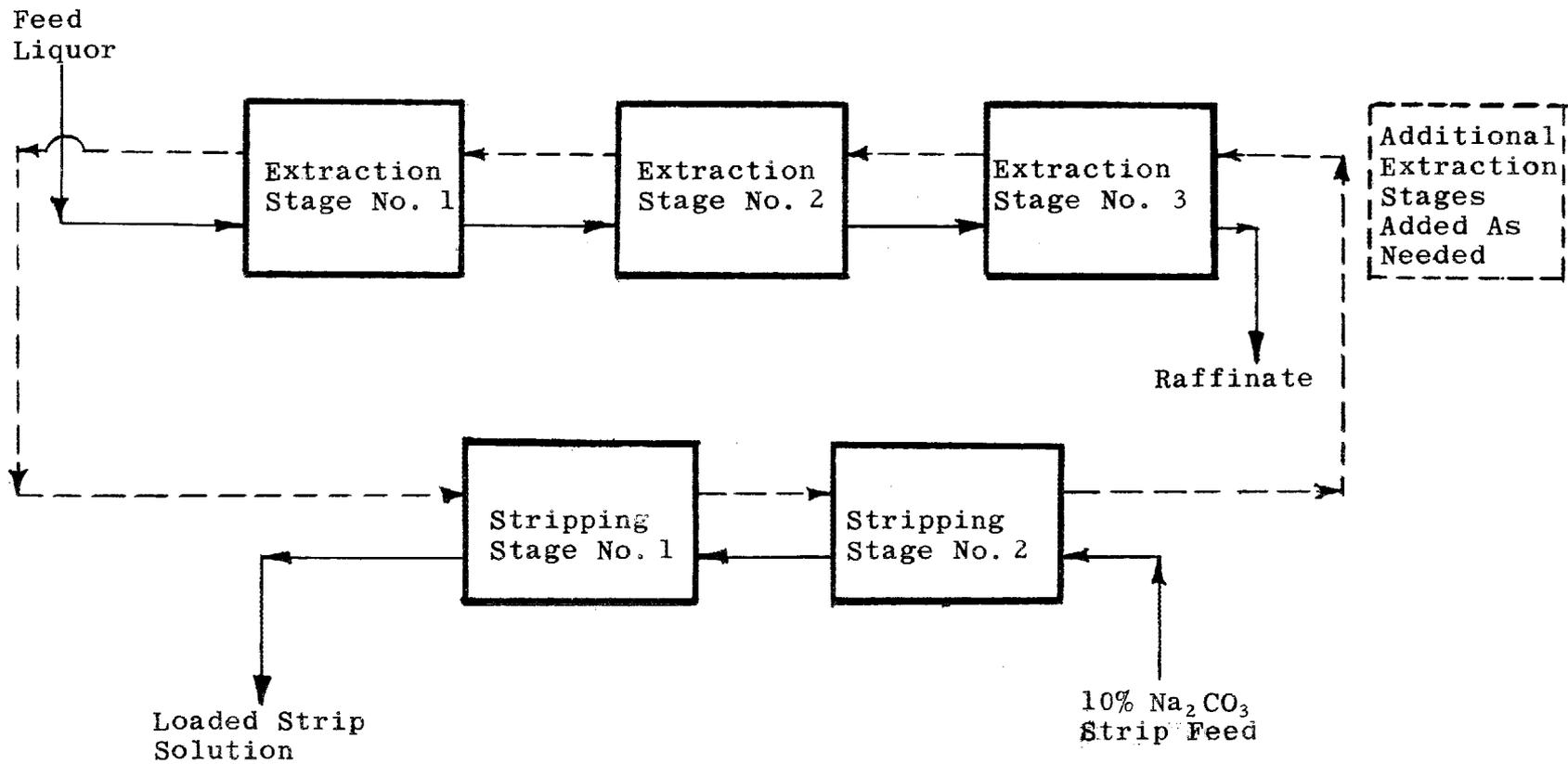
When operating with typical Western ore liquors ( $\sim 1$  g U/l), several volumes of liquor per volume of organic ordinarily are fed to the extraction system. The predominant phase (in this case aqueous) is usually the continuous phase in the mixer. Most clear liquors give a rapid and clean separation when mixed with either the organic or the aqueous phase continuous. A few liquors have been encountered which gave slow breaking emulsions when the aqueous phase was continuous; however, these have separated satisfactorily when the organic phase was maintained continuous.

In order to recover uranium from leach slurries it is necessary to maintain the organic phase continuous by maintaining a high ratio of organic to aqueous in the mixer to avoid emulsion formation. As previously described by workers at Dow Chemical Company, (16) this can be assured in a mixer-settler system by intrastage recycle of the organic from the settler to the mixer. In some of the tests subsequently described intrastage recycle of the organic was provided to simulate the conditions of a slurry extraction process with respect to phase ratio, residence time, etc. The engineering group (Process Test Section) of this division is investigating the mechanical problems associated with slurry extraction.

Steady state data on each process system were obtained after 2 to 4 organic cycles had occurred. This was usually within 5 to 7 hours after start-up depending upon the particular equipment and operational procedures used (see Appendix A).

Figure 7

COUNTERCURRENT EXTRACTION AND STRIPPING CIRCUIT



### Comparison of Different Diluent Modifiers

Using equipment described above, the comparative extraction performance in continuous countercurrent operation of 0.1 M di(2-ethylhexyl)phosphoric acid (D2EHPA) in kerosene when modified with capryl alcohol, tributylphosphate, or dibutyl butylphosphonate was studied on synthetic liquors containing 0.5 M sulfate. Compositions of these liquors and the extraction data obtained are presented in Table 18.

It may be observed that essentially complete extraction of uranium was achieved in three mixer-settler stages with the tributylphosphate (TBP) and dibutyl butylphosphonate (DBBP) modified organics. With capryl alcohol, a lower recovery (99.3%) was obtained in four stages. Although the overall percent uranium recovery for the tributylphosphate and dibutyl butylphosphonate runs was essentially the same, examination of the interstage data shows uranium distribution throughout the system to be more favorable in the latter case. The superior extraction performance of the solvent containing TBP as compared to alcohol and the even better performance with DBBP is in agreement with data from batch tests described in previous sections.

The operating conditions for these tests are given in Table 19. Organic recycle was provided in Tests 1 and 2 in order to approximate the conditions (e.g., with respect to hold-up time and phase continuity) which would be encountered in a slurry extraction system. No organic recycle was provided in Test No. 3. Rapid and clean phase separation was observed in all three tests.

Since the main purpose of the tests (Table 18) was to compare the extraction performance of the different solvents, no particular study was made of the stripping step other than noting that physical performance was satisfactory. The quantities of sodium carbonate utilized in Tests 1 and 2 were in appreciable excess of those required, and stripping efficiencies were, of course, very good. Further discussions of sodium carbonate stripping are given elsewhere in this report (pp. 41-47, 103-107).

### Extraction of Uranium from "Plant D" Liquor

Continuous countercurrent demonstration of the Dapex process for recovery of uranium from a sample of leach liquor received from one of the Western mills (designated "Plant D") was made using 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene + 3 w/v % Tributylphosphate. Prior to extraction most of the ferric iron in the liquor was reduced with powdered iron and its acidity and sulfate concentration were adjusted by the addition of commercial lime. Analyses of the

Table 18

CONTINUOUS COUNTERCURRENT EXTRACTION RUNS:  
COMPARISON OF DIFFERENT DILUENT MODIFIERS

		0.1 M Di(2-ethylhexyl)phosphoric Acid in		
		Test No. 1	Test No. 2	Test No. 3
		Kerosene + 1.5 w/v % Capryl Alcohol*	Kerosene + 3 w/v % TBP*	Kerosene + 2.5 w/v % Dibutyl butyl- phosphonate**
<u>Extraction Stage No. 1</u>				
Aqueous	g U/l	0.81	0.46	0.28
Organic	g U/l	5.1	4.9	5.2
"	g Fe/l	0.31	0.29	0.12
	U E <sub>a</sub> <sup>O</sup>	6	11	19
<u>Extraction Stage No. 2</u>				
Aqueous	g U/l	0.28	0.039	0.019
Organic	g U/l	3.3	1.82	1.3
"	g Fe/l	0.24	0.30	0.12
	U E <sub>a</sub> <sup>O</sup>	14	47	68
<u>Extraction Stage No. 3</u>				
Aqueous	g U/l	0.056	0.0016	0.001
Organic	g U/l	1.1	0.16	0.10
"	g Fe/l	0.17	0.23	0.083
	U E <sub>a</sub> <sup>O</sup>	20	100	100
<u>Extraction Stage No. 4</u>				
Aqueous	g U/l	0.008	Only three	Only three
Organic	g U/l	0.18	stages	stages
"	g Fe/l	0.11	used	used
	U E <sub>a</sub> <sup>O</sup>	23		

Table 18 (Cont'd.)

CONTINUOUS COUNTERCURRENT EXTRACTION RUNS:

COMPARISON OF DIFFERENT DILUENT MODIFIERS

<u>0.1 M Di(2-ethylhexyl)phosphoric Acid in</u>			
	<u>Test No. 1</u>	<u>Test No. 2</u>	<u>Test No. 3</u>
	<u>Kerosene +</u>	<u>Kerosene +</u>	<u>Kerosene +</u>
	<u>1.5 w/v %</u>	<u>3 w/v %</u>	<u>2.5 w/v %</u>
	<u>Capryl Alcohol*</u>	<u>TBP*</u>	<u>Dibutyl butyl- phosphonate**</u>
Uranium Recovery (Based on Raffinate)	99.3%	99.9%	>99.9%
Operation of Extraction Mixers	Organic Recycle	Organic Recycle	No Organic Recycle
<u>Liquor Composition:</u>	U	1.2 g/l	
	Fe(II)	2.7	
	Fe(III)	0.3	
	Al	3.0	
	SO <sub>4</sub>	0.5 M	
	pH	1.3	

Stripping: \*10% Na<sub>2</sub>CO<sub>3</sub> at a phase ratio of 5<sup>o</sup>/1<sup>a</sup>: >99.7% of uranium stripped in two stages.

\*\*10% Na<sub>2</sub>CO<sub>3</sub> at a phase ratio of 7<sup>o</sup>/1<sup>a</sup>: 99.2% of uranium stripped in two stages.

Table 19

EXTRACTION CYCLE OPERATING CONDITIONS FOR

TESTS NOS. 1, 2 AND 3

	Test No.		
	<u>1</u>	<u>2</u>	<u>3</u>
<u>Mixers:</u>			
Feed Ratio - Aqueous/Organic/Organic Recycle	4/1/19	4/1/19	4/1/0
Residence Time <sup>(1)</sup>			
Aqueous	40 sec.	40 sec.	3 min.
Organic	13 min. <sup>(2)</sup>	13 min. <sup>(2)</sup>	3 min.
Stirring Speed	800 RPM	800 RPM	800 RPM
<u>Settlers:</u>			
Aqueous Residence Time	1-2 min.	1-2 min.	1 min.
Organic Residence Time	10-20 min. <sup>(3)</sup>	10-20 min. <sup>(3)</sup>	3 min.

(1) Calculated on the basis that the phase ratio in the mixer is the same as the feed ratio to the mixer.

(2) Organic residence time is approximately 40 seconds in each pass through the mixer. Since each organic increment passes through the mixer twenty times before advancing to the next stage, the total residence time is ~13 minutes.

(3) Single pass residence time is 0.5 - 1 minute.

liquor before and after adjustment are shown in Table 20. The high concentrations of vanadium and iron along with only moderate concentrations of uranium pose a somewhat greater problem to the extraction process than would be encountered in other uranium mills.

The filtered, adjusted Plant D liquor was processed in the laboratory countercurrent apparatus using five mixer-settler units for extraction and two for stripping. In this run, no attempt was made to maintain the organic phase continuous in extraction mixers by intrastage solvent recycle. Physical performance without provisions for such recycle was quite satisfactory with this liquor sample. The operating conditions for the test are given in Table 21. Steady stage data for the extraction operation are shown in Table 22 and for stripping in Table 23.

As observed from Table 22, nearly complete extraction of uranium was obtained in the five unit extraction system. By operating to give 4.3 g U/l ( $\sim 5$  g  $U_3O_8$ /l) in the pregnant organic, the aqueous raffinate contained 0.006 g U/l, equivalent to 99.4% uranium recovery. The extraction coefficients for vanadium were low, but the aqueous concentration was high causing appreciable amounts of this element to be taken into the organic phase. Although about half the vanadium initially extracted was rejected from the solvent as its uranium content increased, the amount remaining was of sufficient quantity to tie up a significant portion of the D2EHPA extractant.\*

Very little extraction of iron or aluminum was obtained. Much of the titanium and most of the molybdenum were extracted; however, the concentration level of these metals was too low to cause any important competition (with uranium) for the reagent.

As shown in Table 23, essentially all of the uranium, iron, titanium, vanadium and molybdenum were removed from the solvent by the sodium carbonate strip. The iron, titanium and part of the vanadium were precipitated by the alkaline solution whereas the molybdenum and the rest of the vanadium remained dissolved along with the uranium. Since the level of extracted aluminum was so low, further analyses for this metal were not made. In other tests, it has been shown that aluminum, like iron and titanium, is almost completely precipitated by the alkaline strip. Physical operation of the

---

\*Extraction isotherm data for Plant D liquor has shown that the proportion of extracted vanadium to uranium is lower at a lower liquor pH. Much of the extracted vanadium can be removed from the organic phase by scrubbing with dilute sulfuric acid (see section on Plant C liquor).

Table 20

ANALYSIS OF ORIGINAL AND ADJUSTED "PLANT D" LIQUOR

	g/l	
	<u>As Received</u>	<u>Adjusted</u>
U	1.05	1.05
V	3.5	3.5
ΣFe	4.8	~6
Fe <sup>+++</sup>	3.0	---
Al	7.3	~7
Ti	0.24	0.07
Mo	0.012	0.008
SO <sub>4</sub>	110	74
pH	0.5	1.2
EMF	---	-328 mv*

Liquor Adjustment: Powdered Fe used to reduce Fe(III); Ca(OH)<sub>2</sub> added to decrease acidity and sulfate concentration.

\*Platinum vs. saturated calomel electrodes. The sign is that of the platinum electrode.

Table 21

OPERATING CONDITIONS FOR COUNTERCURRENT

TESTS WITH "PLANT D" LIQUOR

Extraction Stages:

Feed Ratio a/o	3.5*
Residence Time in the Mixer	2 min.
Stirrer Speed	800-900 RPM
Residence Time in the Settler	
Aqueous	2 min.
Organic	3 min.

Stripping Stages:

Feed Ratio o/a	9
Residence Time in the Mixer	13 min.
Stirrer Speed	350 RPM
Residence Time in the Settler	
Aqueous	20 min.
Organic	6 min.

---

\*Since mechanical difficulties were encountered in maintaining the organic feed rate constant, this value may be low.

Table 22

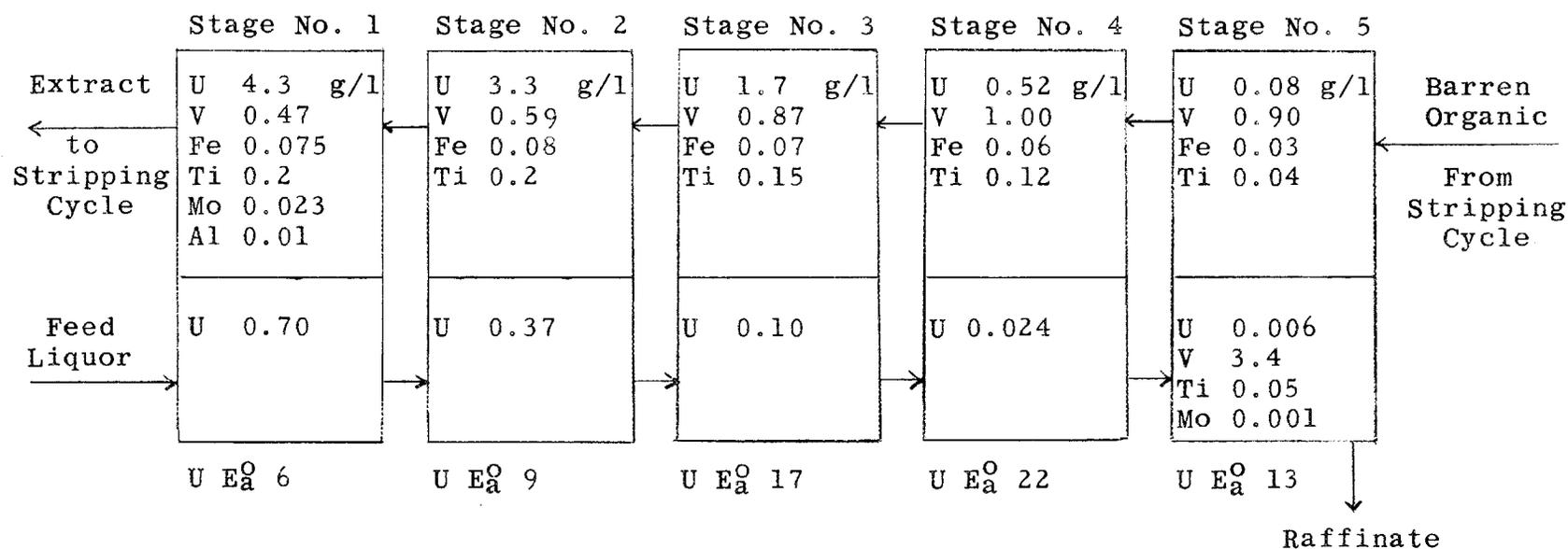
COUNTERCURRENT TEST WITH "PLANT D" LIQUOR

EXTRACTION CYCLE DATA

Organic: 0.1 M Di(2-ethylhexyl)phosphoric acid in kerosene + 3 w/v % tributylphosphate

Aqueous: Adjusted "Plant D" liquor (see Table 20).

Feed Ratio: 4<sup>a</sup>/1<sup>o</sup>



Percent Extracted

U	99.4%	} Closer estimates not possible due to uncertainties in material balances.
V	3 %	
Fe	0.4%	
Al	<0.1%	
Mo	70-85%	
Ti	30-70%	

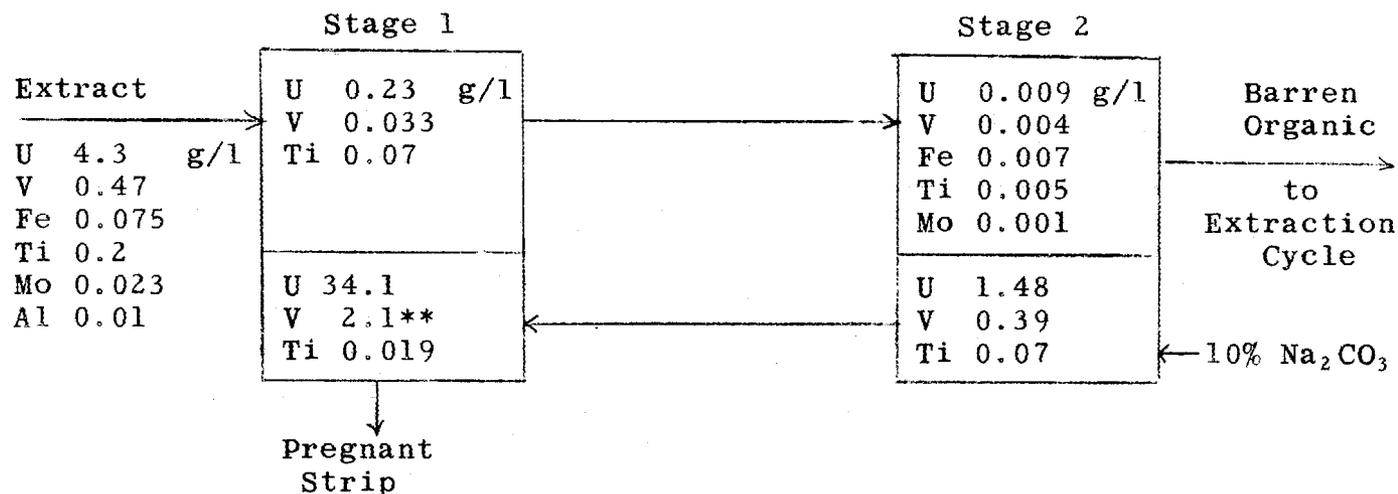
Table 23

COUNTERCURRENT TEST WITH "PLANT D" LIQUOR

STRIPPING CYCLE DATA

Stripping Agent: 10% Na<sub>2</sub>CO<sub>3</sub> solution

Feed Ratio: 9<sup>o</sup>:1<sup>a</sup>



Percent Stripped\*

U	99.8%
V	99 %
Fe	91 %
Ti	93 %
Mo	96 %

Table 23 (Cont'd.)

COUNTERCURRENT TEST WITH "PLANT D" LIQUOR

STRIPPING CYCLE DATA

\*Based on extract and barren organic analysis.

\*\*This represents about 55% of the extracted vanadium. Variable amounts of precipitation have been noted in other tests. The precipitated V(IV) apparently tends to remain in a colloidal form, the degree of coagulation varying with time, temperature and presence of other precipitates. Also, no provisions have been made in the tests to prevent formation of stable V(V). More detailed studies of factors influencing the precipitation of vanadium at this point are being made.

Note: A poor uranium balance was obtained in this test due to flow rate variations and possibly analytical uncertainties.

stripping cycle was smooth with the precipitated contaminants settling rapidly into the aqueous phase. The stripped solvent returning to the extraction cycle contained only a few parts per million of each of the extracted metals.

Uranium product was not prepared from the loaded strip solution. Dissolved vanadium and molybdenum could report in the product, the amounts probably varying with the procedures used. Studies of separations achievable at this point with different operational techniques are being made.

Reagent consumption and the excess of sodium carbonate employed cannot accurately be calculated for this test because of the poor uranium material balance which is probably due to flow rate variations and analytical uncertainties. Such calculations are shown for the countercurrent tests with Plant C liquor in the following section.

#### Extraction of Uranium from "Plant C" Liquor

A sample of sulfuric acid leach liquor from another Western mill (designated "Plant C") was obtained and two continuous countercurrent tests were made with the D2EHPA-TBP solvent. This liquor has a substantially different composition (Table 24) from those previously handled in that the concentrations of uranium, vanadium and free acid ( $\text{pH} = 0.15$ ) are comparatively high. Because of the higher uranium content, somewhat greater than usual concentrations of D2EHPA were used in the solvent (i.e., 0.16 M) along with correspondingly greater concentrations of TBP (4.7 w/v %).

In both tests, since the aqueous concentration of vanadium was high and significant amounts would be extracted (see previous section), provisions were made for scrubbing vanadium from the pregnant solvent. Sulfuric acid at 0.5 M concentration and at a volume of one-twelfth the original liquor was used for this purpose, this concentration and volume ratio having proved effective in batch tests. A small amount of the total uranium was also removed from the solvent in this step; therefore, the scrub solution was recycled to the feed liquor stream. Additional reagent costs (for sulfuric acid) for the scrubbing operation amounted to only about 0.8 cent per pound of total  $\text{U}_3\text{O}_8$  processed.

In the first test (No. 2) the liquor was extracted directly as received ( $\text{pH} = 0.15$ ) using five mixer-settler stages for extraction, one for scrubbing and two for stripping. In the second test (No. 3) the liquor pH was elevated to 0.45 with lime. Since at this higher pH the uranium extraction coefficients will be higher and also more vanadium will be extracted, one less extraction stage (4) and one more

Table 24

ANALYSIS OF "PLANT C" LIQUOR AS RECEIVED

	<u>g/l</u>
U	5.9
$\Sigma V$	4.7
V(V)	4.3
Fe(III)	0.60
Al	2.5
Ca	0.62
Ti	0.077
Mo	0.017
Cu	0.22
PO <sub>4</sub>	3.4
Cl	1.4
SO <sub>4</sub>	116
pH	0.15

scrubbing stage (2) were employed. The operating conditions for these tests are given in Table 25. The phase separation was excellent and no provision for organic recycle was made. Steady state data for each circuit, obtained after approximately four organic cycles had occurred, are given in Tables 26 and 27.

As may be observed, the uranium recovery was very good in both runs, 99.98% and 99.99%, respectively, with a loading level of about 7.5 g U/l being maintained in the pregnant solvents. The scrubbing operation removed 50% of the extracted vanadium in test No. 2 and 80% in test No. 3, leaving only small amounts as a contaminant to the uranium.

As in previous tests, efficient removal of uranium and other metals from the solvent was obtained in the two stripping stages with 10%  $\text{Na}_2\text{CO}_3$ . The loaded strip solution contained 40.5 g U/l in test No. 2 and 42.7 g U/l in test No. 3. Actual quantities of sodium carbonate utilized were about 2.3 and 2.5 lbs per pound  $\text{U}_3\text{O}_8$  or about 30-40% in excess of that required for satisfaction of the chemical reactions involved. Better carbonate utilization could be achieved by increasing the number of stripping stages and loading to a higher level in the strip solution. The Process Test Section of this division is now examining the optimum stripping conditions with respect to reagent utilization efficiency, mixing variables, number of stages, equipment size, etc. In these bench scale tests, the residence time in each mixer of the stripping stage was about 8 minutes. Preliminary tests by the Process Test Section show that with proper mixing, much lower times are possible while still maintaining good stripping efficiencies in two stages with moderate quantities of excess reagent.

Uranium was precipitated from the loaded strip solutions by two different methods described in Table 28. In all cases the product grades were satisfactory, falling in the range of 79-84%  $\text{U}_3\text{O}_8$ . Use of the acid scrub kept the vanadium contamination in the product to a low level (0.55 - 0.71%  $\text{V}_2\text{O}_5$ ). Products obtained by direct precipitation with sodium hydroxide contained only slightly less vanadium than those from the acidification-ammonia precipitation method.

Table 25

OPERATING CONDITIONS FOR TESTS NOS. 2

AND 3 WITH "PLANT C" LIQUOR

Extraction Stages:

Feed Ratio a/o	1.2
Residence Time in the Mixer	4 min.
Stirrer Speed	800-900 RPM
Residence Time in the Settler	
Aqueous	2 min.
Organic	2 min.

Stripping Stages:

Feed Ratio o/a	4.8
Residence Time in the Mixer	8 min.
Stirrer Speed	350 RPM
Residence Time in the Settler	
Aqueous	15 min.
Organic	6 min.

Scrubbing Stages:

Feed Ratio o/a	10
Residence Time in the Mixer	8 min.
Stirrer Speed	800-900 RPM
Residence Time in the Settler	
Aqueous	15 min.
Organic	2 min.

Table 26

COUNTERCURRENT TEST NO. 2 WITH "PLANT C" LIQUOR AS RECEIVED

Organic: 0.16 M Di(2-ethylhexyl)phosphoric acid in kerosene  
+ 4.7 w/v % tributylphosphate.

Aqueous: "Plant C" liquor (see Table 24).

Feed Ratios: Liquor:organic:strip:scrub 12/10/2.1/1.

Strip Solution: 10% sodium carbonate.

Scrub Solution: 0.5 M H<sub>2</sub>SO<sub>4</sub>

Liquor

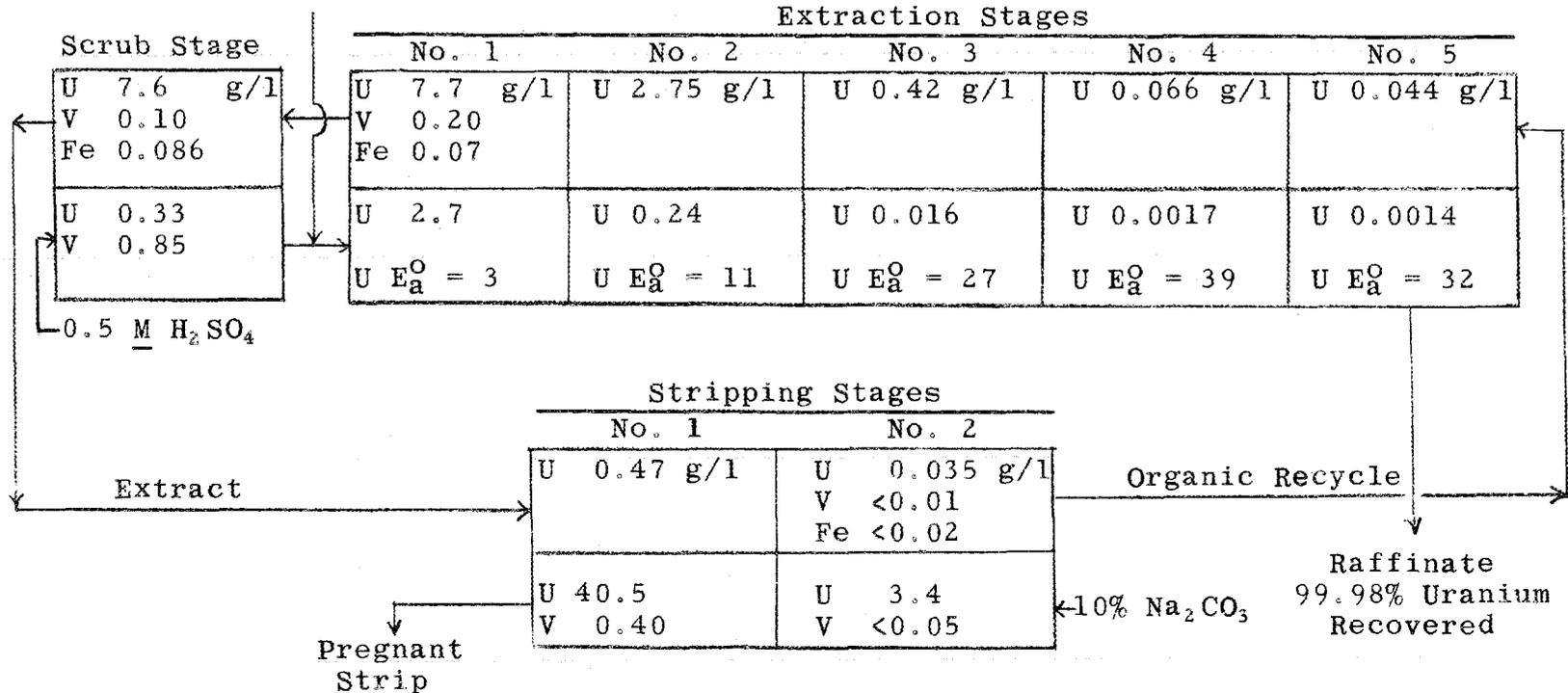


Table 27

COUNTERCURRENT TEST NO. 3 WITH "PLANT C" LIQUOR - ADJUSTED

Organic: 0.16 M Di(2-ethylhexyl)phosphoric acid in kerosene  
+ 4.7 w/v % tributylphosphate.

Aqueous: "Plant C" liquor adjusted with lime to pH 0.45,  
SO<sub>4</sub> lowered to 69 g/l.

Feed Ratios: Liquor:organic:strip:scrub 12/10/2.1/1.

Strip Solution: 10% Na<sub>2</sub>CO<sub>3</sub>.

Scrub Solution: 0.5 M H<sub>2</sub>SO<sub>4</sub>.

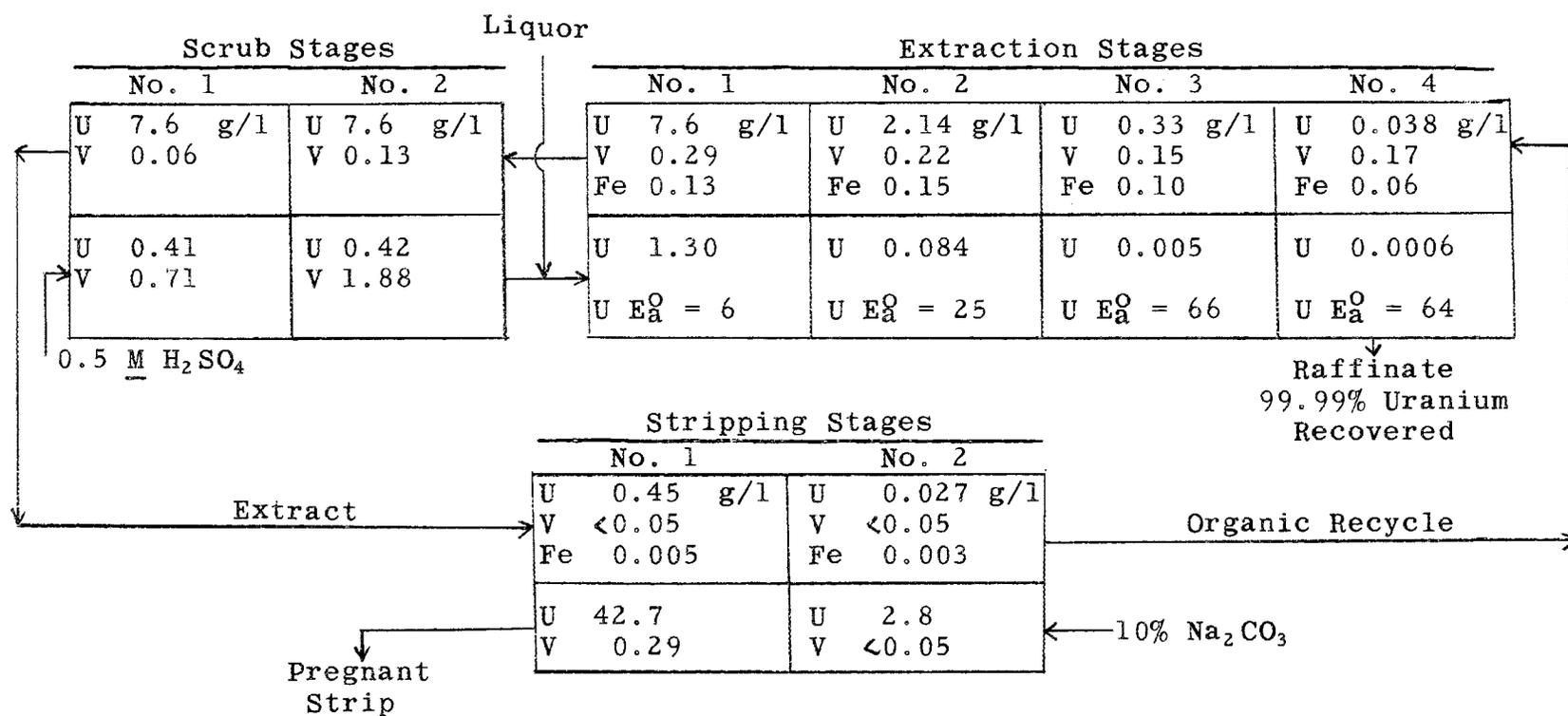


Table 28

PRODUCT GRADE FROM "PLANT C" LIQUOR TESTS

	Test No. 2		Test No. 3	
	NaOH Ppt.	Acidification-Ammonia Precipitation	NaOH Ppt.	Acidification-Ammonia Precipitation
U <sub>3</sub> O <sub>8</sub>	81.3%	84%	79.3%	79.3%
V <sub>2</sub> O <sub>5</sub>	0.68%	0.71%	0.55%	0.71%
Fe <sub>2</sub> O <sub>3</sub>	0.09%	0.09%	0.02%	0.02%
Al <sub>2</sub> O <sub>3</sub>	0.08%	0.09%	0.085%	0.096%
SO <sub>4</sub>	----	3.9%	----	4.8%
Na	8.3%	3.0%	8.3%	2.3%
Loss on Ignition at 500°C	2.6%	3.7%	4.6%	6.2%

Procedure: The pregnant strip solution was filtered to remove basic precipitates. It was then divided into two portions. To one portion a minimum amount of NaOH pellets were added to give essentially complete uranium precipitation. The other portion was made acid to pH 2 with H<sub>2</sub>SO<sub>4</sub>, boiled to drive off CO<sub>2</sub>, and then treated with NH<sub>4</sub>OH to precipitate the uranium product. In each case the product obtained was washed with H<sub>2</sub>O and dried at 120°C.

Quantities of Reagents Expended:

<u>NaOH Precipitation</u>	<u>Test No.2</u>	<u>Test No.3</u>
1b NaOH/1b U <sub>3</sub> O <sub>8</sub>	0.94	1.06
<u>Acidification-Ammonia Precipitation</u>		
1b H <sub>2</sub> SO <sub>4</sub> /1b U <sub>3</sub> O <sub>8</sub>	2.12	2.17
1b NH <sub>3</sub> /1b U <sub>3</sub> O <sub>8</sub>	0.18	0.22

## RATE OF PHASE SEPARATION

In a liquid-liquid solvent extraction system the rate of disengagement of the phases after mixing is of considerable importance in that it dictates the size, and thus the cost, of the settlers required to handle a given liquid throughput. In earlier studies of the Dapex process at this laboratory, rapid phase separations were obtained with all of the clear liquor samples tested. These samples include a variety of synthetic liquors as well as samples of process leach liquors received from two operating Western mills.

Recently, in experimental tests of the Dapex process at one of the Western mills (designated Plant C), emulsion (or slow phase separation) difficulties were occasionally encountered in the extraction cycle while processing leach liquor from one particular circuit of the plant. In this plant the sands and slimes are separated early in the process cycle. The slime fraction undergoes several process operations, including a high temperature calcination, before being leached of its uranium content with sulfuric acid. The resulting "slime liquor" contains most of the uranium and comprises 75-80% of the total volume throughput of liquor in the plant. The sand solids are leached directly with sulfuric acid to produce the "sand liquor" which represents the balance (20-25%) of the total plant uranium liquor throughput. Little difficulty with phase separation has been observed when treating the "slime liquor" irrespective of process conditions (e.g., see section on continuous countercurrent tests). Poor phase separation has, however, been observed periodically in process tests on the "sand liquor."

In view of the inconsistent performance of the "sand liquor," several samples of these solutions which were known to be bad actors were obtained for study at this laboratory (Table 29). A number of tests have been conducted to determine the behavior of various liquor-organic systems and to study the effect of certain mixing variables on the phase separation rate. Although the tests completed thus far do not represent a comprehensive investigation of the problem, they do suggest methods for avoiding the poor phase separations observed with the liquors mentioned above. Additional studies are being made to obtain a more thorough understanding of the variables involved and to determine, if possible, why some liquors give difficulty whereas many others do not.

### Effect of Type of Dispersion (Batch Tests)

A series of batch mixer tests were carried out in which 140 ml of organic and 160 ml of liquor were contacted in a

Table 29  
ANALYSIS OF LIQUORS

		Plant C Sand Leach Liquors					Synthetic Liquor No. 1576
		E	17	18	19	20	
U	g/l	2.8	1.86	1.88	1.80	1.87	1.15
ΣV	"	5.3	2.2	2.6	2.2	2.6	---
V(V)	"	0.01					---
Fe	"	5.6					2.0
Al	"	5.1					2.9
Ti	"	0.03					---
Mo	"	0.03					---
Ca	"	0.7					---
Si	"	0.37					2.2
K	"	0.65					---
Mg	"	4.46					---
Na	"	0.58					---
SO <sub>4</sub>	"	103	108	105	109	95	40.7
PO <sub>4</sub>	"	1.3					1.9
pH		0.6	0.4	0.3	0.4	0.4	1.1

500 ml baffled beaker agitated by a two blade stirrer at 800-900 RPM for two minutes. The stirrer was then shut off and the time required for complete disengagement of the two phases was observed.

The dispersion during mixing can be of two general types - aqueous droplets in a continuous organic phase or organic droplets in a continuous aqueous phase. (It has been shown previously(16,17) that the type of dispersion may greatly affect the rate of phase separation particularly if certain solids are present in the system.) In the batch mixing tests described here, the desired conditions of phase continuity were controlled by the start-up procedure. Aqueous continuous dispersions were obtained by placing the aqueous solution in the mixing vessel, starting the stirrer, and adding the organic phase slowly. Conversely, organic continuous conditions were established by adding the organic solution to the mixing vessel, starting the stirrer, and slowly adding the aqueous. Conductometric measurements provided a convenient method of checking which phase was continuous in the mixer. Probe electrodes attached to an ohmmeter were inserted into the mixing vessel. The resistance of aqueous continuous dispersions was in the range of 50-300 ohms whereas organic continuous dispersions showed a resistance several orders of magnitude greater.

In Table 30 the effect of type of dispersion on the phase separation rate is shown when several bad acting "sand liquors" were contacted with 0.16 M D2EHPA in kerosene + 4 w/v % TBP as described above. When the aqueous phase was continuous the phase separation was poor in all cases. With some of the liquors, separation was achieved in 8 to 10 minutes, while with others a semi-stable band of emulsions formed which did not break completely even after very prolonged standing periods. When the organic phase was continuous, good phase separation (1 - 1.5 minutes) was observed in every case.

#### Continuous Countercurrent Test (Organic Continuous)

As a further check on the results from batch tests a continuous countercurrent test was made with Plant C liquor (Sample E) using the same solvent composition, i.e., 0.16 M D2EHPA in kerosene + 4 w/v % TBP. The organic phase was maintained continuous in the mixers by recycling organic from the settlers to the mixers as described in Appendix A. Since the volume of liquor available was limited, the test was concluded after four organic cycles. Phase separation was satisfactory throughout the run. Although a small band of emulsion appeared in the settlers, it did not increase in size during the test. These results again suggest that the "sand liquors" could be handled satisfactorily so long as organic continuous

Table 30

EFFECT OF THE TYPE OF DISPERSION ON PHASE SEPARATION RATE

Liquor	Separation Time in Minutes	
	Aqueous Phase Continuous During Mixing	Organic Phase Continuous During Mixing
Plant C (Sample E)	20	1.5
" " " 17	>44	1
" " " 18	8	1
" " " 19	>20	1.3
" " " 20	10	1

Organic: 0.16 M Di(2-ethylhexyl)phosphoric acid in kerosene + 4 w/v % tributylphosphate.

conditions are maintained in the mixers. Of course, tests of longer duration would be required to prove conclusively that this is an adequate solution to the problem.

### Effect of Organic Phase Composition

Other batch tests have been conducted to study the performance of organic solvents variable in composition. The aqueous solutions used in these cases were the Plant C "sand liquor" (Sample E) and a synthetic "high silica" liquor (see Table 29). In one series of tests with the different solvents, the organic phase was held continuous during mixing.

The results listed in Table 31 show that after organic continuous mixing, the phase separations were reasonably rapid (and clean) with all of the solvents tested. Generally parallel trends were given by the synthetic liquor and the actual plant liquor. Somewhat more rapid separations were observed for kerosene alone and kerosene containing only D2EHPA than for solvents containing additional constituents, i.e., alcohol or synergistic additives. However, even in the latter cases the rates observed are adequate for effective process application.

After aqueous continuous mixing, the rate of phase separation was much more strongly affected by variation in composition of the organic phase. Parallel trends were again observed with each of the two liquors tested. When kerosene alone was mixed with the liquors, the phases separated in approximately four minutes. A solution of 0.1 M D2EHPA in kerosene gave a much faster separation rate (~1 minute). The addition of capryl alcohol or the synergistic additives, i.e., TBP or dibutyl butylphosphonate, had a strong adverse effect on the phase separation rate under these particular mixing conditions.

In general, from the results of Table 31 it again appears that the best first choice for avoiding phase separation difficulties with bad acting liquors is to operate with organic continuous conditions in the mixer. When aqueous continuous mixing is used difficulties are apparently alleviated by utilizing kerosene solutions of D2EHPA, without a diluent additive, as the extractant. Use of such an extractant would sacrifice the increased extraction efficiency that could be provided by the synergistic reagents. This need not be prohibitive, however, with liquors which are not particularly difficult to extract. Alkaline stripping of the solvent might be accomplished without third phase formation by using ammonium carbonate rather than sodium carbonate as the stripping reagent (see section on Stripping).

Table 31

EFFECT OF ORGANIC PHASE COMPOSITION ON PHASE SEPARATION RATE

<u>Organic</u>	<u>Phase Separation Time in Minutes</u>	
	<u>Plant C Liquor (Sample E)</u>	<u>Synthetic Liquor No. 1576</u>
<u>Organic Phase Continuous During Mixing</u>		
Kerosene	0.4	0.8
0.1 <u>M</u> D2EHPA in kerosene	0.25	1.1
0.1 <u>M</u> D2EHPA in kerosene + 1.5 w/v % capryl alcohol	1.8	2.0
0.1 <u>M</u> D2EHPA in kerosene + 4 w/v % TBP	1.9	1.9
0.1 <u>M</u> D2EHPA in kerosene + 0.7 w/v % DBBP	1.2	1.3
0.1 <u>M</u> D2EHPA in kerosene + 2.5 w/v % DBBP	1.8	2.6
0.16 <u>M</u> D2EHPA in kerosene + 4 w/v % TBP	1.6	2.0
<u>Aqueous Phase Continuous During Mixing</u>		
Kerosene	4	4
0.1 <u>M</u> D2EHPA in kerosene	1.3	1
0.1 <u>M</u> D2EHPA in kerosene + 1.5 w/v % capryl alcohol	>25	>25
0.1 <u>M</u> D2EHPA in kerosene + 2.5 w/v % TBP	20	3.5
0.1 <u>M</u> D2EHPA in kerosene + 2.5 w/v % DBBP	>30	>10
0.16 <u>M</u> D2EHPA in kerosene + 4 w/v % TBP	20	--

As pointed out previously (Continuous Countercurrent Tests) several synthetic liquors and several plant liquors have given good phase separation with the synergistic reagents even when the aqueous phase was continuous during mixing. The poor separation of synthetic liquor No. 1576, after aqueous continuous mixing, is attributed to the high silica content. Similarity in performance of this liquor and the Plant C liquor (Sample E) should not, however, be construed as evidence that silica is responsible for slow phase separation in the latter case. No correlation has been found between the silica concentration and the phase separation properties of several plant liquors. It is, of course, conceivable that an effect from silica might depend upon its physical state rather than its concentration level. Some further attention may be given to this possibility.

### Effect of Surfactants

Preliminary studies have been made of the use of surface active agents to accelerate the rate of phase separation when the liquor and organic had been mixed under aqueous phase continuous conditions. In initial tests a number of different types of surfactants were examined at a relatively high concentration level (2000 ppm in the liquor). It was found that most but not all of the anionic agents increased the rate of phase separation whereas none of the cationic or nonionic surfactants caused any significant improvement, at least at the concentration level studied.

The more promising anionic agents were next tested at lower concentration levels in the liquor. One of these, Lomar PW,\* appeared outstanding in its ability to prevent or break emulsions at a low concentration level. The effect of this reagent on the phase separation rate when various organic solutions were contacted under aqueous continuous mixing conditions with several Plant C "sand liquors" and with the synthetic "high silica liquor" is shown in Table 32. In every case the addition of Lomar PW greatly increased the rate of phase separation.\*\* In most instances addition of as little as 20 parts of Lomar PW/million parts of liquor was sufficient to give a satisfactorily rapid separation rate. At this low concentration level the cost of surfactant addition would be almost negligible.

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\*Lomar PW is the sodium salt of condensed mono-naphthalene sulfonic acid, available from Jacques Wolf and Co. at approximately 16¢/lb.

\*\*A single test was made on the Plant C (Sample 17) liquor with 25 ppm Lomar PW and with organic continuous mixing. The solvent was 0.16 M D2EHPA + 4 w/v % TBP in kerosene. In this case the phase separation rates, already rapid, remained unaffected.

Table 32

## EFFECT OF ADDITION OF LOMAR PW ON PHASE SEPARATION RATE

## UNDER AQUEOUS CONTINUOUS MIXING CONDITIONS

Liquor	ppm* Lomar PW Added	Phase Separation Time in Minutes				
		Kerosene	0.1 M D2EHPA in Kerosene + 1.5 w/v % Capryl Alc.	0.1 M D2EHPA in Kerosene + 2.5 w/v % TBP	0.1 M D2EHPA in Kerosene + 2.5 w/v % DBBP	0.16 M D2EHPA in Kerosene + 4 w/v % TBP
Plant C (Sample E)	None	4	>25	20	>30	20
"	10	-	--	--	--	2.8
"	20	2	15	2.5	10	1.5
"	100	-	--	--	--	1.5
"	200	-	--	--	--	1.5
Plant C (Sample 17)	None	-	--	--	--	>44
"	10	-	--	--	--	3
"	20	-	--	--	--	0.8
"	50	-	--	--	--	0.5
Plant C (Sample 18)	None	-	--	--	--	8
"	10	-	--	--	--	1.3
"	20	-	--	--	--	1.3
"	50	-	--	--	--	1.3
Plant C (Sample 19)	None	-	--	--	--	>20
"	10	-	--	--	--	5
"	20	-	--	--	--	1
"	50	-	--	--	--	0.5
Plant C (Sample 20)	None	-	--	--	--	10
"	10	-	--	--	--	1.3
"	20	-	--	--	--	1.3
"	50	-	--	--	--	1.3
Synthetic Liquor 1576	None	4	>25	3.5	>10	--
"	20	1	0.5	--	0.5	--

\*Parts of Lomar PW/million parts of liquor.

Mixing Conditions: Aqueous phase continuous (see p. 76).

Results from some preliminary cascade tests indicated that most of the Lomar PW remained in the aqueous phase when it was contacted with the organic and thus should be almost completely expelled from the extraction system with the raffinate. Other tests showed Lomar PW to be relatively stable in Plant C "sand liquor," maintaining its effectiveness even after twenty-four hours standing.

#### Continuous Countercurrent Tests with Lomar PW Surfactant

To study the performance of Lomar PW under continuous countercurrent extraction conditions a single run has been made thus far using 0.16 M D2EHPA in kerosene + 4 w/v % TBP as extraction agent to recover uranium from Plant C "sand liquor" (Sample 17). (As shown in Table 32, this liquor-organic combination formed a semi-stable emulsion, i.e., separation time >44 minutes, in batch tests conducted under aqueous continuous mixing conditions when no Lomar PW was present.) Prior to extraction the liquor was dosed with 30 ppm Lomar PW. A mixer-settler system employing four extraction and three stripping stages (10% Na<sub>2</sub>CO<sub>3</sub>) was utilized.

Although aqueous continuous conditions were maintained in the extraction mixers, emulsion difficulties were not experienced over a period of fifteen hours operation (~5.5 complete organic cycles). It was noted that entrainment of organic in the raffinate was appreciably higher than had previously been observed in several other countercurrent tests of the Dapex process. However, after standing one hour most of the entrained organic had separated and could be recovered.

Analytical data are not yet sufficiently complete to definitely show whether or not the presence of Lomar PW influenced uranium extraction efficiency. Further tests with this reagent, and possibly other surfactants, will be made.

COMPARISON OF URANIUM EXTRACTION ABILITY  
OF SEVERAL ALKYLPHOSPHORIC ACIDS

In ORNL-1903 (Appendix C), comparisons were reported of uranium extraction by several monoalkyl- and several dialkylphosphoric acids. These tests have been continued, with the results summarized in Table 33. The estimates of reagent purity given in ORNL-1903 (p. 100 ff, p. 117) apply also to the tests reported here.

The variation of uranium extraction ability with type of aqueous phase anion, its concentration, and solution pH, followed the same patterns found previously. That is, the extractions increased with increased pH and decreased with increased concentration of sulfate or phosphate, phosphate impairing the extraction much more than sulfate.

As before, comparisons were made with both carbon tetrachloride and kerosene as diluents - carbon tetrachloride because it has been the most generally useful diluent in the comparison of a wide range of reagents, and kerosene because it is the diluent of choice for process application when it can be used. The extraction by the dialkylphosphoric acids was generally much better in kerosene than in carbon tetrachloride, and varied in about the same way with reagent structure in both diluents (cf. Figure 8). Throughout, extractions by the monoalkyl reagents were much higher than by the corresponding dialkyl reagents. The relative extractions by the monoalkyl reagents differed less between the two diluents, and while kerosene was a little better for the diisobutylmethyl compound, carbon tetrachloride was a little better for the 3,5,5-trimethylhexyl and 2-ethylhexyl compounds. However, it cannot be assumed that the differences in extraction shown by the different monoalkyl reagents reflect exactly their relative complexing powers for uranium. Besides some uncertainty in purity discussed previously, it should be noted that much larger concentrations of the mono-octyl and -nonyl reagents than of the corresponding dialkyl reagents distribute to the aqueous phase (e.g., 1 to 5 g per liter of 0.4 M phosphate solution, or  $\sim 0.01 - 0.02$  M, from 0.1 M organic solutions, Table 34; cf. Appendix C). This can decrease significantly the actual concentration of reagent in the organic phase, and it also probably introduces competition of unknown magnitude by complexing some uranium in the aqueous phase.

The effect of alcohol on uranium extraction by the monododecyl- and monotetradecylphosphoric acids was found to be similar in nature and magnitude to the effect on extraction by dialkylphosphoric acids.<sup>(1,2)</sup> Addition of 5 w/v % (0.27 M)

Table 33

## COMPARISON OF URANIUM EXTRACTION ABILITY OF SOME ALKYLPHOSPHORIC ACIDS

Uranium(VI) Extraction Coefficients,  $E_a^0$ 

Alkylphosphoric Acid (0.1 M)		Diluent	0.5 M $SO_4$ pH 1	1.5 M $SO_4$ pH 1	0.4 M $PO_4$ pH 1.2	1.4 M $PO_4$ pH 1	1.4 M $PO_4$ pH 2
n-Octyl							
Batch No.	185	mono-	Ker ---	ppt <sup>a</sup> 580	---	ppt <sup>b</sup> 14	---
"	"	di-	Ker 450 <sup>c</sup>	57	80	3	8
	181		$CCl_4$ 90	13	30	1	2
3,5,5-Trimethylhexyl							
Batch No.	163	mono-	Ker ---	400	250 <sup>d</sup>	6	22 <sup>d</sup>
"	"	di-	$CCl_4$ >1000	590	290	15	30
	165		Ker 260 <sup>c</sup>	41	50	2	5
			$CCl_4$ 40	7	8	0.4	0.6
2-Ethylhexyl							
Batch No.	175	mono-	Ker ---	500	200 <sup>d,e</sup>	3	36 <sup>d</sup>
"	"	di-	$CCl_4$ >1000	560	240	17	30
	303		Ker 135 <sup>c</sup>	20	25	1	2
			$CCl_4$ 17	3	3	0.2	0.3
Diisobutylmethyl							
Batch No.	166	mono-	Ker ---	230	105	7	18
"	"	di-	$CCl_4$ 450	130	75	5	15
	314		Ker 10 <sup>c</sup>	2	3	0.5	0.7
			$CCl_4$ 2	1	1	0.6	0.6
Dodecyl <sup>f</sup>							
Batch No.	320	mono-	Ker 650	120	85	6	20
Tetradecyl <sup>g</sup>							
Batch No.	321	mono-	Ker 600	130	105	6	16

Table 33 (Cont'd.)

COMPARISON OF URANIUM EXTRACTION ABILITY OF SOME ALKYLPHOSPHORIC ACIDS

Notes for Table 33:

10 Minutes agitation by wrist-action shaker (except as noted), room temperature, 1<sup>a</sup>:1<sup>o</sup>.

- a) Precipitation (?), 40% of uranium removed from aqueous phase.
- b) Precipitation, 65% of uranium removed from aqueous phase, 0.3% found in organic phase.
- c) Same coefficient found after 1 hour agitation.
- d) Agitation by 30 minutes gentle rolling.
- e) Same coefficient found by 30 minutes rolling, 10 minutes shaking, 80 hours shaking.
- f) Dodecyl = 2,6,8-trimethylnonyl-4.
- g) Tetradecyl = 2-methyl-7-ethylundecyl-4.

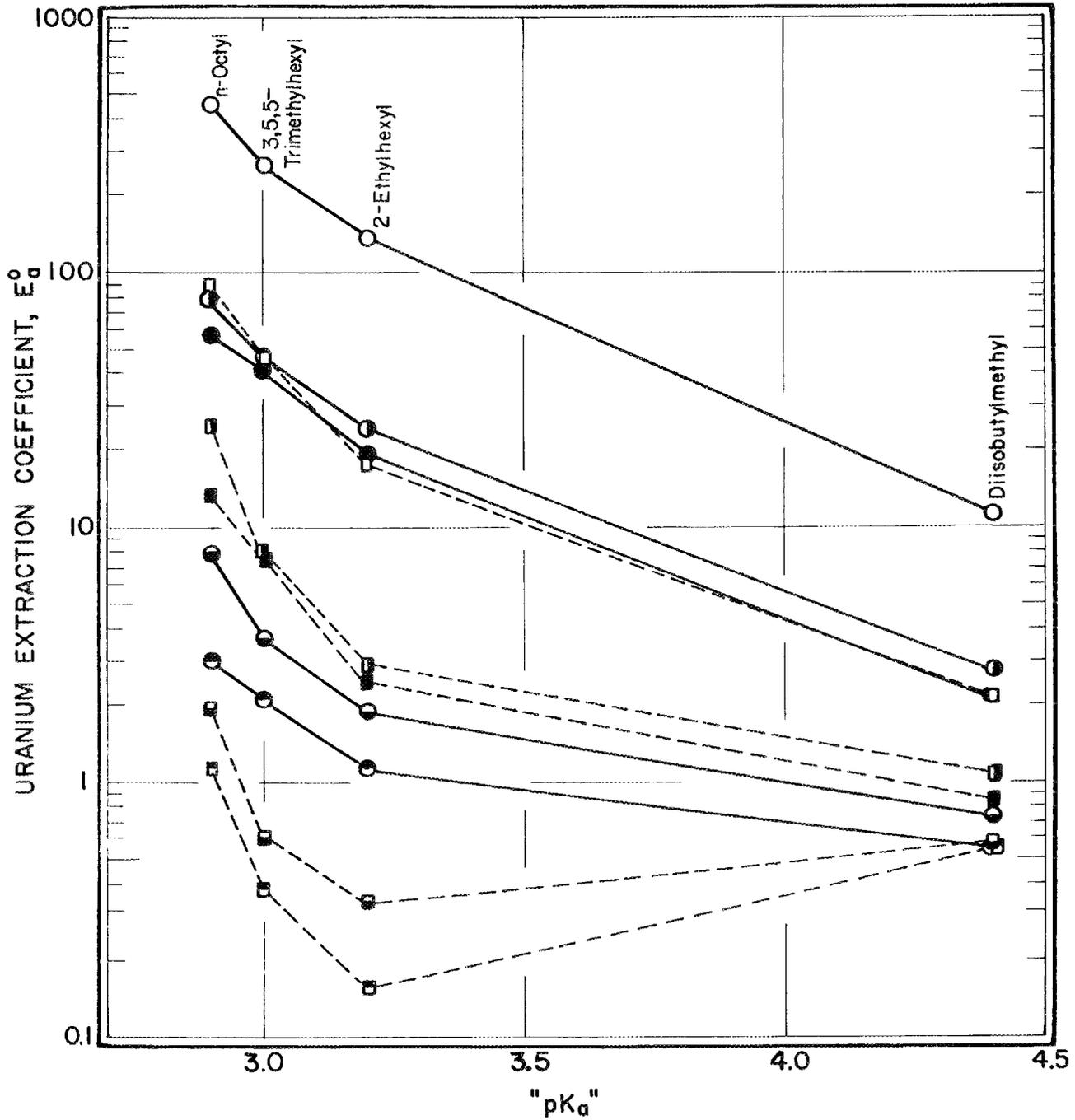


Figure 8

EXTRACTION ABILITY OF DIALKYLPHOSPHORIC ACIDS VS. RELATIVE ACID STRENGTH

Aqueous Phase	0.1 M Dialkylphosphoric Acid	
	In Kerosene	In CCl <sub>4</sub>
0.5 M SO <sub>4</sub> , pH 1	—○—	---□---
1.5 M SO <sub>4</sub> , pH 1	—●—	---■---
0.4 M PO <sub>4</sub> , pH 1.2	—◐—	---◑---
1.4 M PO <sub>4</sub> , pH 1	—◑—	---◐---
1.4 M PO <sub>4</sub> , pH 2	—●—	---■---

Table 34

LOSS OF MONOALKYLPHOSPHORIC ACIDS TO AQUEOUS SOLUTION

Organic: Initially 0.1 M monoalkylphosphoric acid in kerosene or carbon tetrachloride.

Aqueous: 0.4 M  $\text{PO}_4$ , pH 1.

Ten minutes agitation by wrist-action shaker at 25-28°C.

<u>Monoalkyl- phosphoric Acid</u>	<u>Batch No.</u>	<u>Phase Ratio a/o</u>	<u>g Reagent/liter Aqueous Solution</u>	
			<u>from kerosene</u>	<u>from <math>\text{CCl}_4</math></u>
n-Octyl	185	7.5	---	1.4
3,5,5-Tri- methylhexyl	163	7.5	2.3	1.6
2-Ethylhexyl	175	4	4.7	2.8
Diisobutyl- methyl	166	7.5	3.0	2.2

2,6,8-trimethylnonanol-4 to 0.1 M mono-2,6,8-trimethylnonyl-4-phosphoric acid in kerosene depressed the uranium extraction coefficient ( $E_a^O$  out of 0.5 M sulfate solution at pH 1) from 650 (Table 33) to 40, and addition of 5 w/v % (0.23 M) 2-methyl-7-ethylundecanol-4 to 0.1 M mono-2-methyl-7-ethylundecyl-4-phosphoric acid depressed  $E_a^O$  from 600 to 40. The same additions of alcohol depressed  $E_a^O$  out of 1.5 M sulfuric acid solution by both reagents from about 7 to about 0.3. Both reagents, without the deliberate addition of alcohol, are estimated to contain about 0.005 M alcohol in the 0.1 M reagent solutions, originating from residual unreacted alcohol remaining in the reagents.

It was previously noted that the uranium extraction powers of the dialkylphosphoric acids tested decreased with decreasing relative acid strength, which in turn decreased with increasing severity of branching. The data previously presented were for extractions from 0.5 M sulfate solution into carbon tetrachloride solution (ORNL-1903, p. 121). With the exception of extraction from the 1.4 M phosphate solutions by bis(diisobutylmethyl)phosphoric acid in carbon tetrachloride, the same relationship is found to hold for all the extractions listed in Table 33.\* This is illustrated in Figure 8 by the close similarity of all the curves, with the exception just mentioned. (Here as previously, "pK<sub>A</sub>" is the measured apparent pH at half-neutralization in the 75-25 ethanol-water mixture used as the titration medium.)

Relatively higher extraction by bis(diisobutylmethyl)-phosphoric acid from phosphate solution is again shown, and to a greater degree, in extractions from phosphoric acid solutions (Table 35). These extraction coefficients for uranium(VI) by the dialkyl reagents, if plotted on the same axes as Figure 8, will follow curves fairly similar to those shown for the 1.4 M phosphate solutions with carbon tetrachloride. Extractions of uranium(IV) were lower than of uranium(VI) by the 3,5,5-trimethylhexyl and the 2-ethylhexyl reagents, and all of these were too low for other than academic interest. In surprising contrast, the extraction of uranium(IV) by the diisobutylmethyl reagent was found to be orders of magnitude higher. Preliminary results also suggest that synergistic reagent combinations may give additional extraction power for uranium(IV) from these phosphoric acid solutions. The extraction coefficients found approach a level which suggests possible application to commercial wet process phosphoric acid. Further investigation will be made of the extraction behavior of the pure alkylphosphoric acids from such solutions.

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\*Another laboratory has recently reported<sup>(10)</sup> a higher order of magnitude of uranium extraction coefficient from sulfate solution by bis(diisobutylmethyl)phosphoric acid, i.e.,  $E_a^O(U) = 600$  from 0.76 M sulfate solution at pH 1 by 0.1 M reagent in kerosene. No estimate of the reagent purity was given in the report.

Table 35

URANIUM EXTRACTION FROM PHOSPHORIC ACID SOLUTIONS

Organic: 0.25 M Dialkylphosphoric acid in kerosene.

Aqueous: 0.0004 M uranium. Phase Ratio, aqueous/organic = 1.

Ten minutes agitation in wrist-action shaker at room temperature.

<u>Dialkylphosphoric Acid</u>	<u>Batch No.</u>	Uranium			
		<u>Extraction Coefficient, <math>E_a^0</math></u>			
		<u>3.3 <u>M</u> <math>H_3PO_4</math></u>		<u>5.3 <u>M</u> <math>H_3PO_4</math></u>	
		<u>U(IV)</u>	<u>U(VI)</u>	<u>U(IV)</u>	<u>U(VI)</u>
3,5,5-Trimethylhexyl	165	0.2	1.7	0.02	0.1
2-Ethylhexyl	303	0.01	0.4	0.001	<0.01
Diisobutylmethyl	314	25	0.7	4	0.06
" "	plus 0.1 <u>M</u> $Bu_3PO$	60	9	4	0.7

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## APPENDIX A

### DESIGN AND OPERATION OF BENCH SCALE EQUIPMENT

In Figure A-1 an idealized countercurrent extraction-stripping circuit is illustrated. For purposes of discussion, three stages of extraction and two of stripping are shown. In Figure A-2 the same circuit is presented with all the apparatus positioned approximately as it would be mounted on a rack. Mixer-settler units are employed for contacting the phases. The aqueous is allowed to flow from stage to stage by gravity while the organic is advanced by pumps where necessary. Rotameters are used to monitor the flow of aqueous solutions into the system. The flow of organic within the system is regulated by adjusting the pump feeding organic to the extraction system to give the desired flow and setting the other pumps slightly faster to advance all of the organic that comes to them. When it is desired to operate with the organic phase continuous in the mixers, an additional pump is provided for each extraction stage to give intra-stage recycle of organic from the settler to the mixer (see Figure A-8).

In Figures A-3 through A-7 the individual pieces of equipment are sketched. A list of the equipment used and the source of special items is also included (Table A-1). Figure A-8 shows a single stage, connected with tubing and ready for operation. The operation of the gravity leg is indicated. This design\* of a mixer (underfeed-overflow) is felt to be advantageous since short circuiting is minimized and no possibility of back mixing exists. Also, since the settlers are isolated from the mixers, the system may be sampled at leisure after shut-down to determine the distribution throughout the circuit. In the design used in the initial tests (a top feed, bottom outlet mixer) the settlers were not isolated from the mixers and stage samples had to be withdrawn while operating. Unless care is taken in withdrawing the samples the equilibrium of the system can be disturbed, and samples not completely representative of steady-state operation can be obtained. In many of the tests 250 ml instead of 500 ml settlers were used where they provided sufficient settling time. The use of these settlers helped to reduce the organic holdup in the system.

When the equipment has been assembled as shown, the following steps are carried out to set it in operation. Into each mixer-settler compartment the organic and aqueous are placed in the approximate proportions which will be present

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\*Recommended by the Process Test Section of this Division.

Figure A-1  
COUNTERCURRENT CIRCUIT

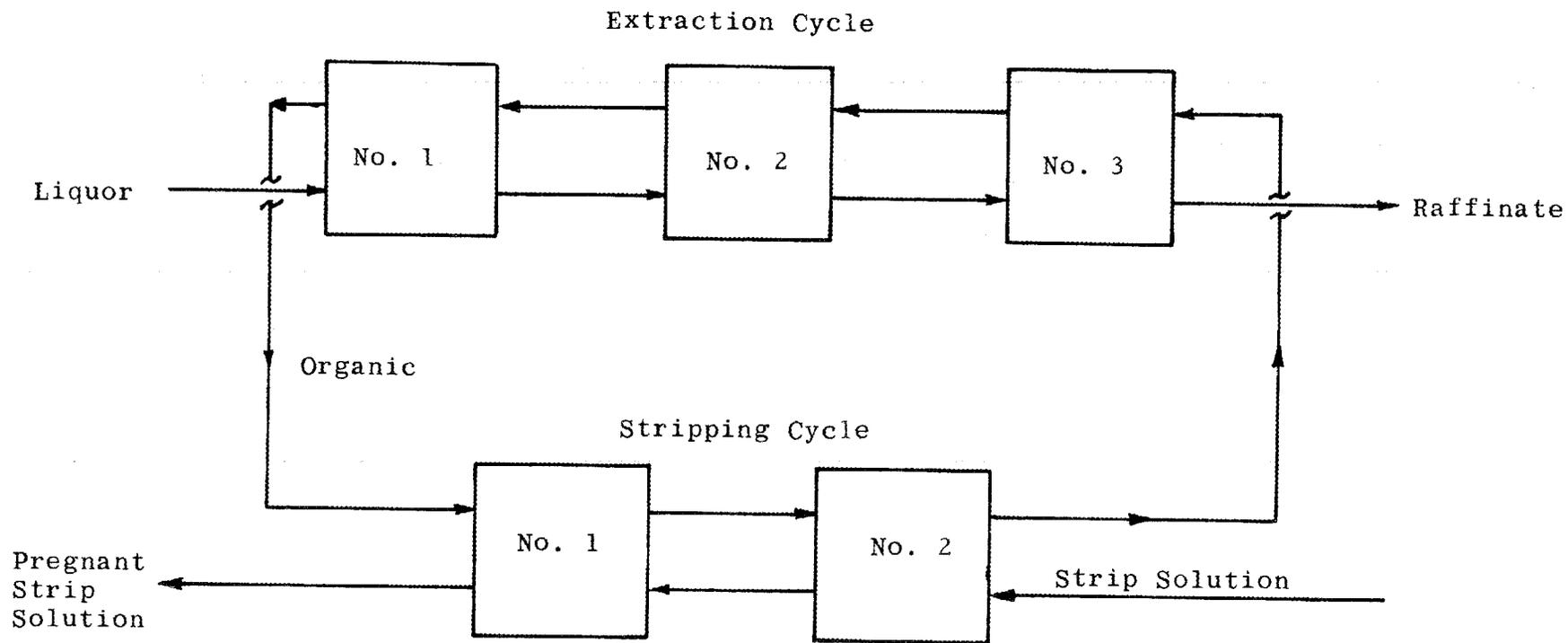


Figure A-2  
EQUIPMENT LAYOUT

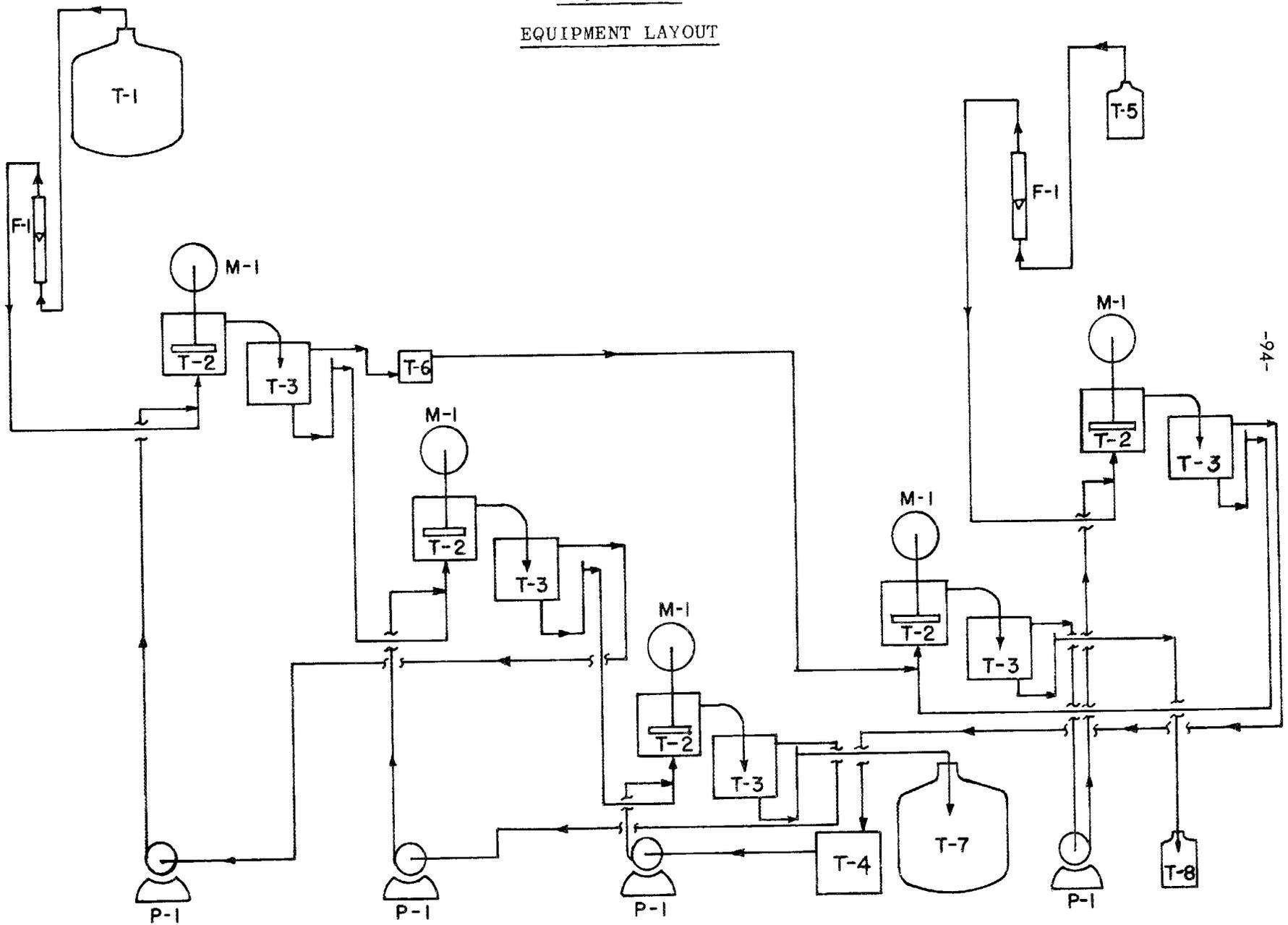
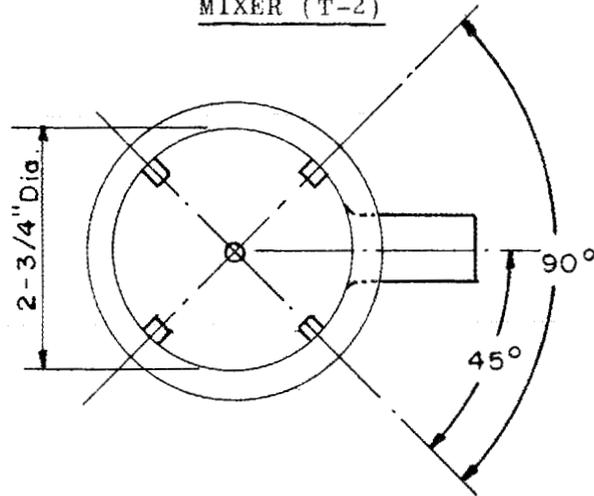


Figure A-3  
MIXER (T-2)

UNCLASSIFIED  
ORNL-LR-DWG. 17386



4 glass baffles  
 $1/4$ " x  $3/16$ " x  $4 - 3/4$ "  
fused to wall of beaker

Item constructed of a  
500 ml tall form Berzelius  
beaker without spout

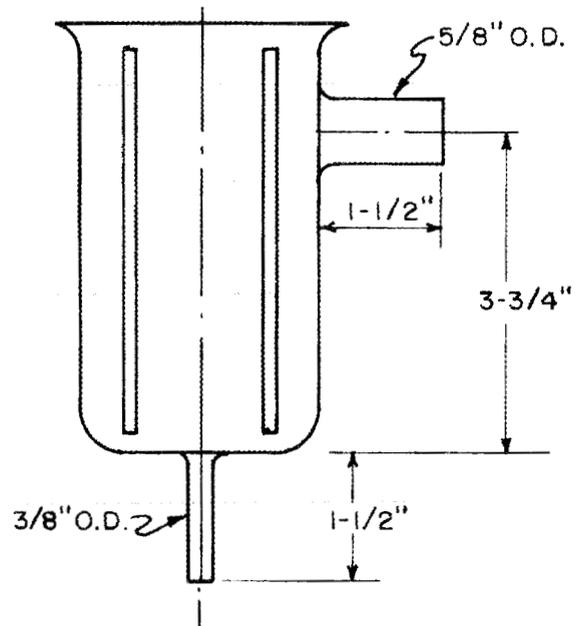


Figure A-4  
SETTLER (T-3)

UNCLASSIFIED  
ORNL-LR-DWG. 17387

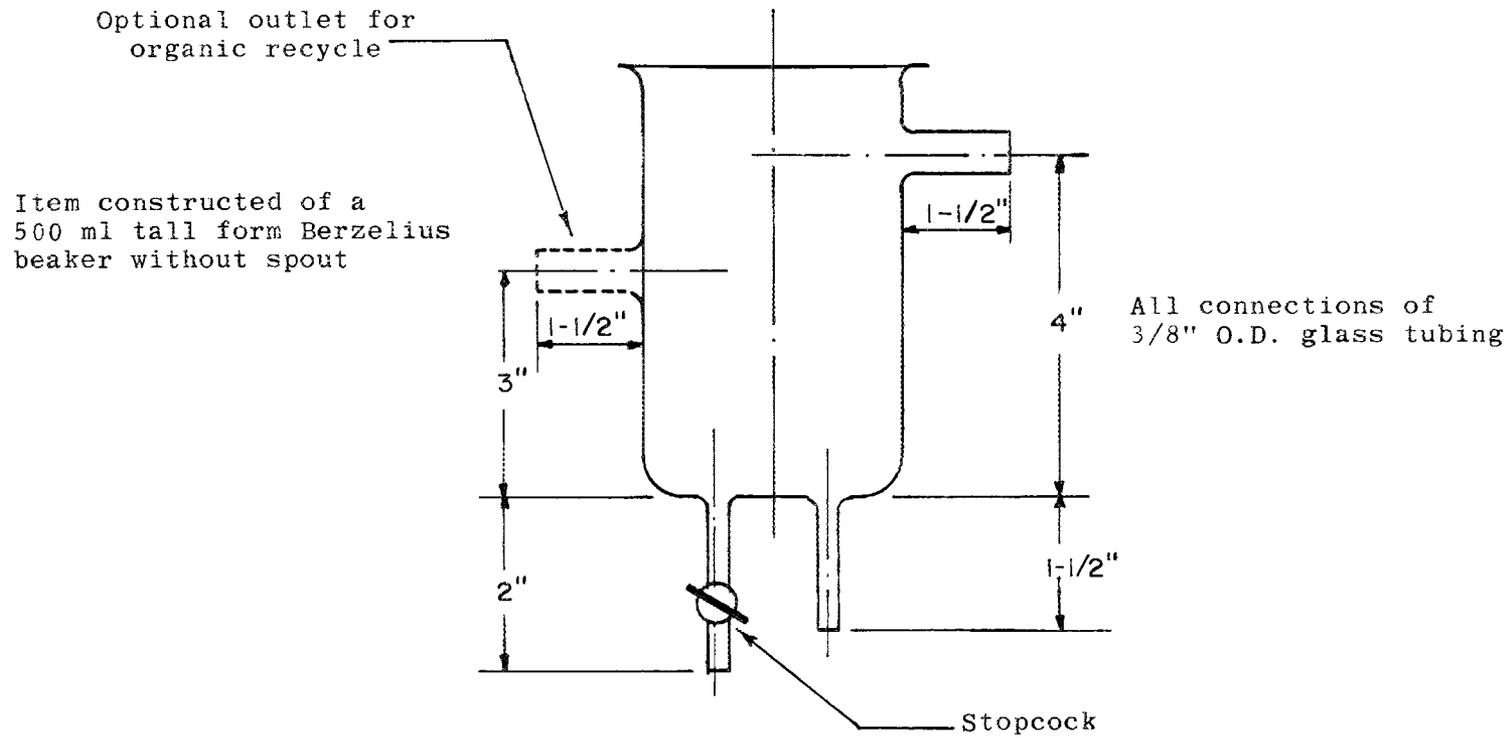
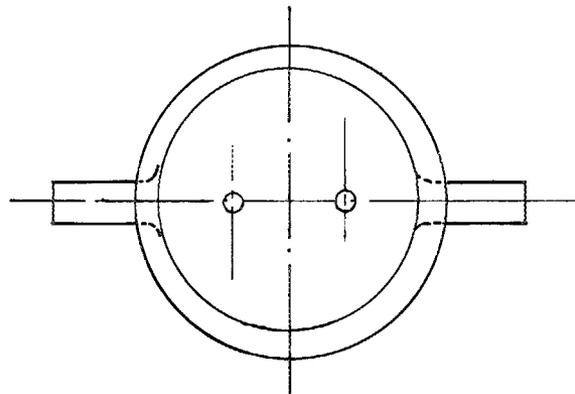
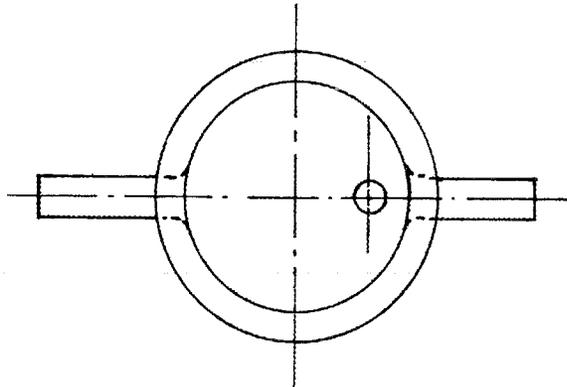
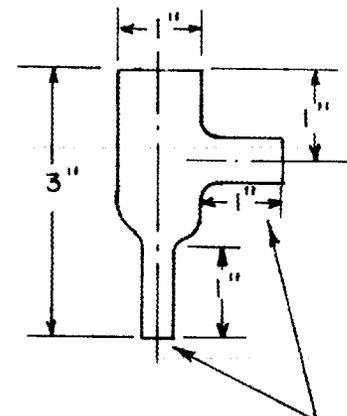


Figure A-5  
RESERVOIR (T-4)

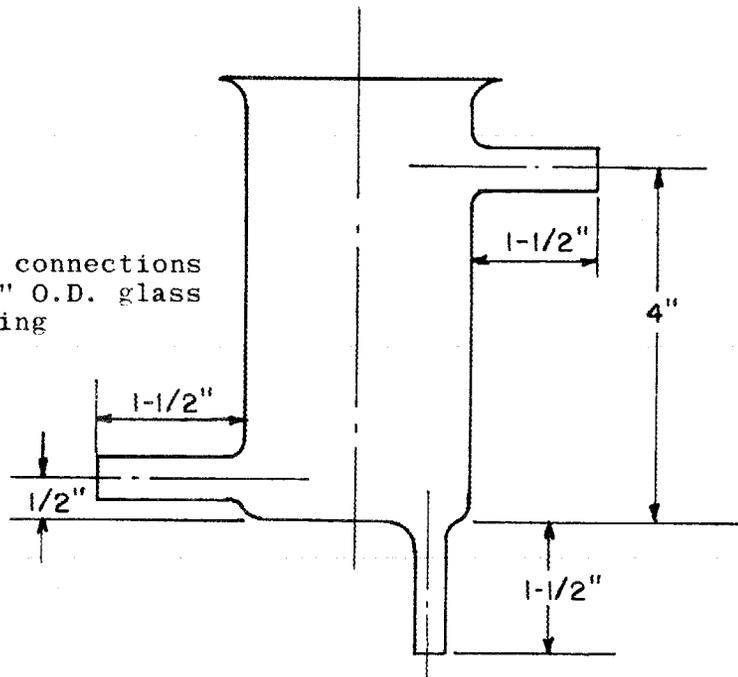
UNCLASSIFIED  
ORNL-LR-DWG. 17388



Gravity leg overflow tube



All connections  
3/8" O.D. glass  
tubing



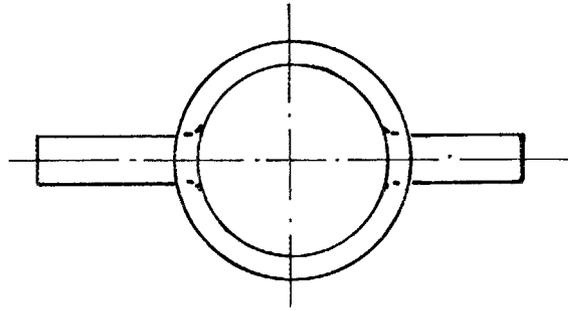
Item constructed of a  
500 ml tall form Berzelius  
beaker without spout

3/8" O.D.  
glass tubing

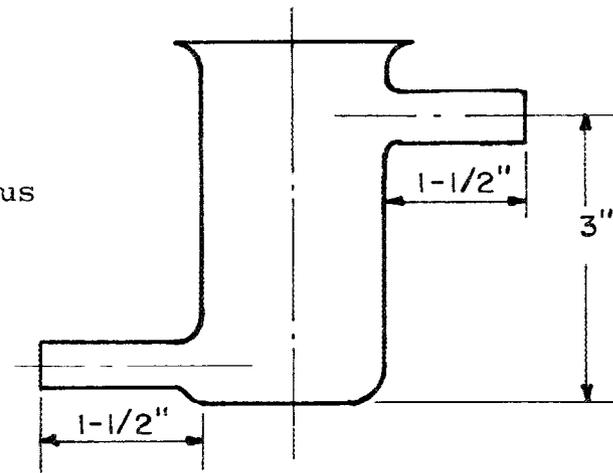
Figure A-6

TRAP (T-6)

UNCLASSIFIED  
ORNL-LR-DWG. 17389



Item constructed of a  
500 ml tall form Berzelius  
beaker without spout

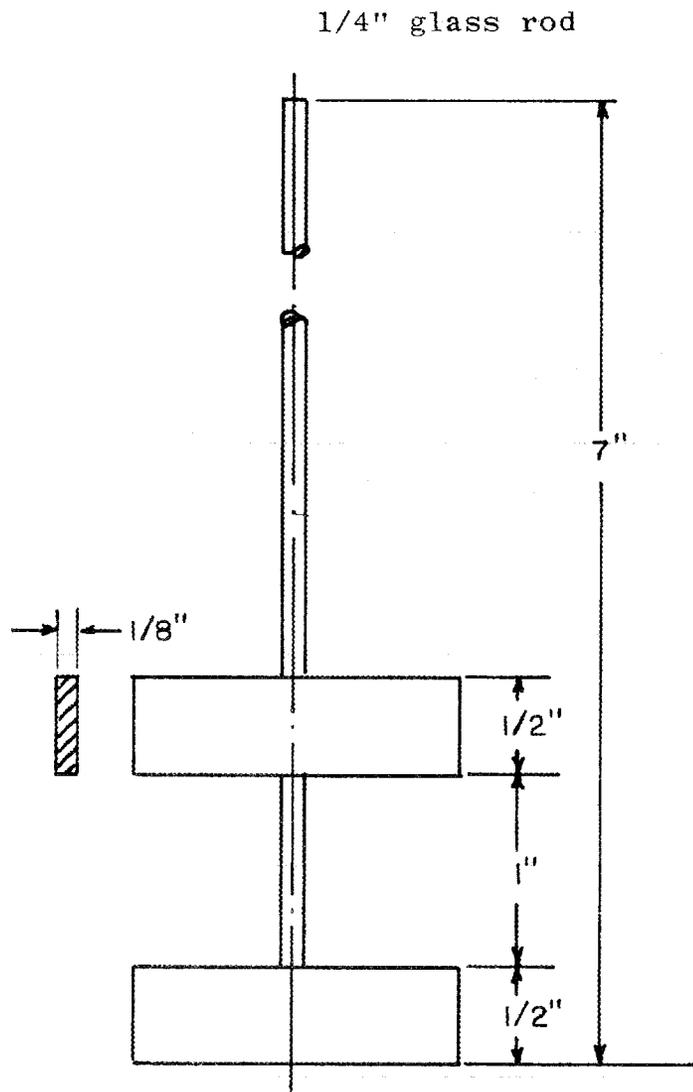


All connections of  
3/8" O.D. glass tubing

Figure A-7

UNCLASSIFIED  
ORNL-LR-DWG. 17390

AGITATOR AND ELBOW



2 glass plates fused to rod

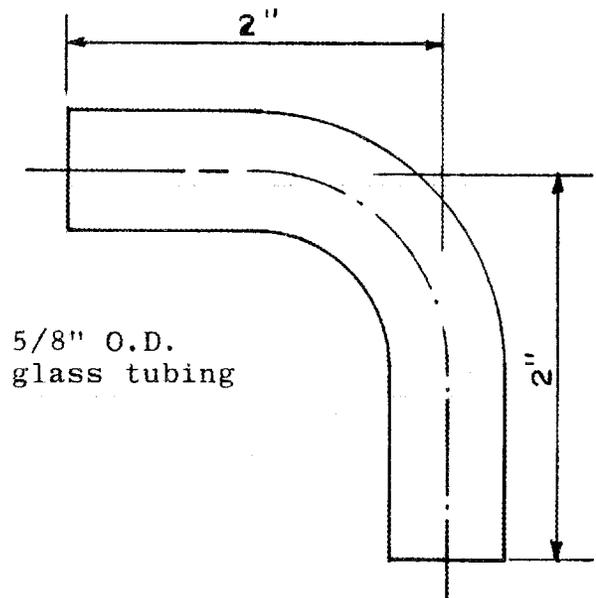
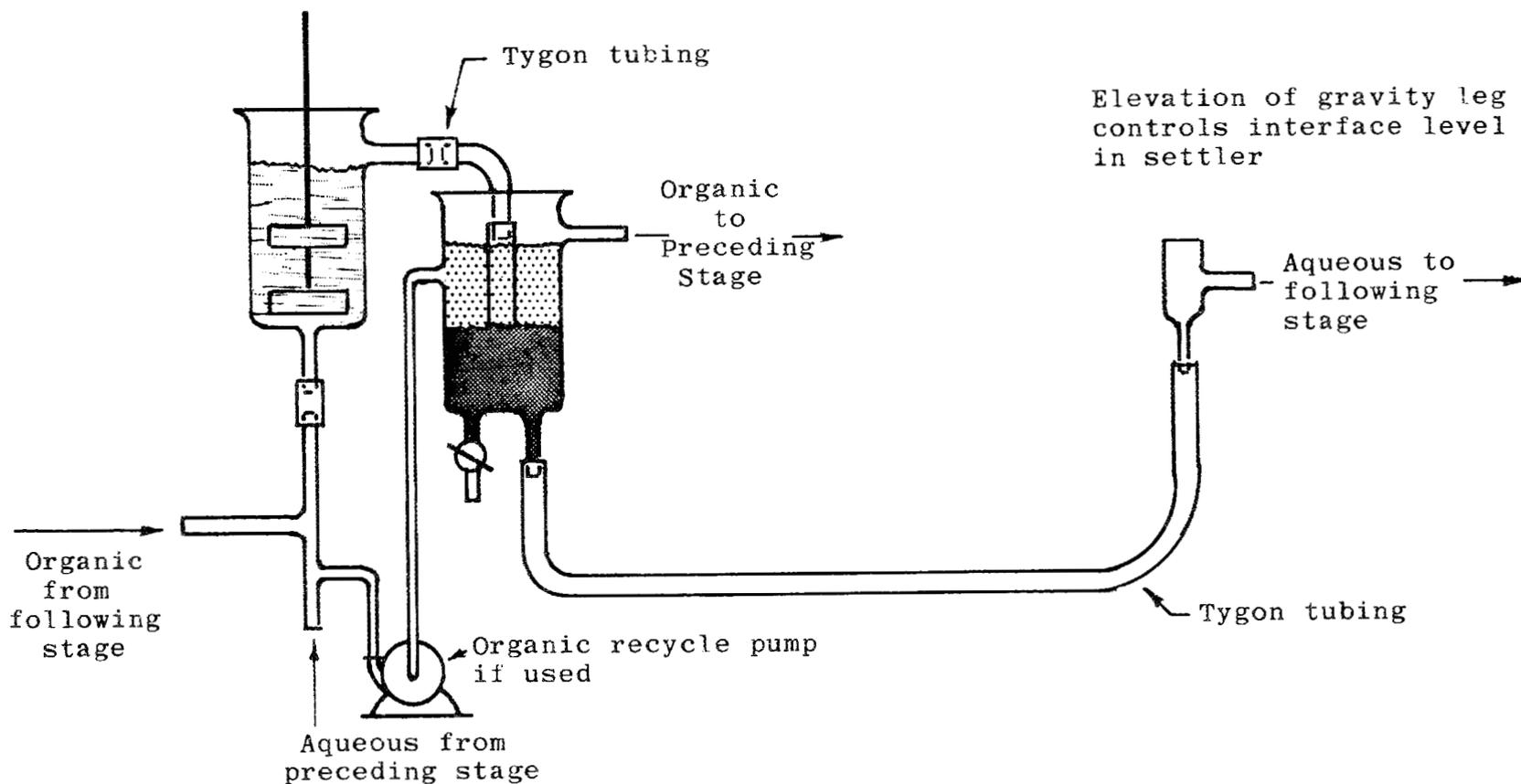


Figure A-8

ONE STAGE CONNECTED FOR OPERATION



Drawing not to scale

Table A-1

EQUIPMENT

<u>Equipment No.</u>	<u>Number Required</u>	<u>Description</u>	<u>Size</u>
T-1	1	Feed liquor container	12 gal carboy
T-2	5	Mixers (see Figure A-3)	
T-3	5	Settlers (see Figure A-4)	
T-4	1	Reservoir (see Figure A-5)	
T-5	1	Feed strip solution container	3.5 gal carboy
T-6	1	Trap (see Figure A-6)	
T-7	2	Raffinate collector	5 gal carboy
T-8	1	Pregnant strip receiver	4 l. bottle
T-2-A	5	Agitators (see Figure A-7)	
T-2-B	5	Elbows (see Figure A-7)	
T-3-A	5	Gravity leg overflow tube (see Figure A-5)	
F-1	2	Rotameter	
P-1	4	Corson-Cervený microbellows pumps (Model 1000, Type C, 3/4" x 3" bellows, Research Appliance Co.)	
M-1	5	Stirring motor (variable speed, Fisher Cat. No. 14-499)	

during operation. Then the stirring motors, pumps, and aqueous feeds are started. The interface in the settlers is maintained at the desired level by adjustment of the gravity legs. If the mixers are to be operated organic continuous, a different start-up procedure is followed. The settlers are filled as before but the mixers are filled with organic only. Then the stirring motors, pumps, and finally aqueous feeds are started. This procedure is essential to insure that organic continuous conditions result.

To shut down the apparatus, first the aqueous and organic feeds into the system, then the inter-stage organic pumps (and the organic recycle pumps if in use), and finally the stirring motors are stopped.

During operation the agitators are run at a speed sufficient to give good stage efficiencies, i.e., greater than 90%. The stage efficiency is determined by withdrawing samples of both phases from the settler and recontacting them (at a phase ratio corresponding to the feed ratio) vigorously in a separatory funnel. The uranium distribution in this sample, which is assumed to be near the point of maximum uranium extraction,\* is then compared with the distribution in the settler to give the approximate stage efficiency. For the equipment described in Figures A-3 to A-8 and the flow rates generally employed ( $\sim$ 100 ml aqueous/min), mixing speeds of 800-1000 R.P.M. have proved adequate.

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\*Equilibrium, of course, is not reached since the extraction of certain contaminants such as ferric iron and aluminum is very slow. Hence prolonged contact times should be avoided to prevent extraction of contaminants in amounts sufficient to impair uranium extraction.

APPENDIX B

REAGENT CONSUMPTION AND CONCENTRATION LIMITS  
IN SODIUM CARBONATE STRIPPING

As described previously, sodium carbonate is consumed during stripping by (1) conversion of the uranyl dialkylphosphate complex to sodium uranyl tricarbonate and sodium dialkylphosphate, and (2) neutralization of any uncomplexed dialkylphosphoric acid to form additional sodium dialkylphosphate. The chemical equations describing these reactions (equations 5 and 6, ORNL-1903) permit calculation of the minimum (stoichiometric) sodium carbonate requirement for stripping uranium from any given pregnant organic extract. Although such calculations are simple and straight-forward, they are somewhat inconvenient for evaluating sodium carbonate consumptions over ranges of process conditions. Accordingly, calculated sodium carbonate consumption data have been summarized graphically in Figure B-1. Here the sodium carbonate consumption (lb  $\text{Na}_2\text{CO}_3$ /lb  $\text{U}_3\text{O}_8$ , left ordinate) is related directly to the uranium concentration obtained in the pregnant organic extract. Variations of dialkylphosphoric acid concentration and of the amount of excess sodium carbonate allowed over the stoichiometric minimum are included as families of curves, whose shape and spacing is sufficiently uniform to permit ready interpolation when required.

Besides estimation of the total amount of sodium carbonate required, choice of the concentration at which it is to be used for stripping can also be important. It is advisable, for example, to avoid exceeding the solubility limit of sodium uranyl tricarbonate in the final solution,\* and that solubility limit is lower in the presence of other sodium salts, including sodium carbonate.<sup>(18)</sup> Thus, for a particular combination of pregnant organic extract, organic: aqueous phase ratio, and percent excess sodium carbonate allowed, there is a concentration of sodium carbonate strip solution which can completely strip the uranium to produce an aqueous solution just saturated with respect to uranium. Use of any higher sodium carbonate concentration might result in precipitation of uranium; if precipitation were then prevented by using a larger volume of the sodium carbonate solution

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\*Metastable sodium uranyl tricarbonate solutions at higher than the stable solubility limit are obtained under some conditions, and hence it might be possible for carbonate strip solutions to be loaded beyond the limits considered in the present calculations.



(still at the higher concentration), the net result would be the less effective utilization of sodium carbonate. Calculated values of this upper limit of initial sodium carbonate concentration are also shown in Figure B-1 (w/v % Na<sub>2</sub>CO<sub>3</sub>, right ordinate) against the same abscissa. Curves are given for several dialkylphosphoric acid concentrations, and interpolation can be readily made to intermediate concentrations. Variation of the percent excess sodium carbonate allowed is not shown here. Actually, the excess allowed does have some effect on the concentration limit, but not so much as to demand consideration. The curves plotted are "safe" values, calculated at the percent excess (~10-20%) which set the lowest limit.

In addition to material balances and sodium uranyl tri-carbonate solubility data, the foregoing calculations required consideration of the change in aqueous volume resulting from transfer of water to the organic phase when the sodium dialkylphosphate is formed (see section on Stripping). As shown in Table 15, this volume change appears to vary somewhat when different modifiers are added. The curves in Figure B-1 were calculated on basis of the volume changes found with di(2-ethylhexyl)phosphoric acid in kerosene modified with 2 w/v % 2-ethylhexanol. Some differences can be expected with other types and concentrations of modifiers, but probably not enough to make a serious shift from the curves as shown.

The final aqueous uranium concentration to be expected in the strip solution entered into the calculations for Figure B-1, but it is not readily obtainable from the resulting curves. (If there were no aqueous volume change, the final aqueous uranium concentration would of course be obtained directly from the organic uranium concentration and the phase ratio, or from the lb Na<sub>2</sub>CO<sub>3</sub>/lb U<sub>3</sub>O<sub>8</sub> and the w/v % Na<sub>2</sub>CO<sub>3</sub> used.) The phase volume ratio, organic:aqueous (initial), required for a particular set of conditions, is readily obtained from the concentration of U<sub>3</sub>O<sub>8</sub> in the pregnant organic, the pounds of sodium carbonate per pound U<sub>3</sub>O<sub>8</sub>, and the initial concentration of sodium carbonate in the strip solution. The volume ratio organic(initial):aqueous(final), which gives the final aqueous uranium concentration directly from the pregnant organic uranium concentration, can then be obtained by means of Figure B-2.\* These curves were calculated

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$$* \frac{V_{org.init.}}{V_{aq.init.}} = \frac{10 (w/v \% Na_2CO_3)}{(g U_3O_8/l org.)(lb Na_2CO_3/lb U_3O_8)}$$

$$\frac{g U_3O_8}{l aq.final} = \left( \frac{g U_3O_8}{l org.} \right) \left( \frac{V_{org.init.}}{V_{aq.init.}} \right) \left( \frac{V_{aq.init.}}{V_{aq.final}} \right)$$

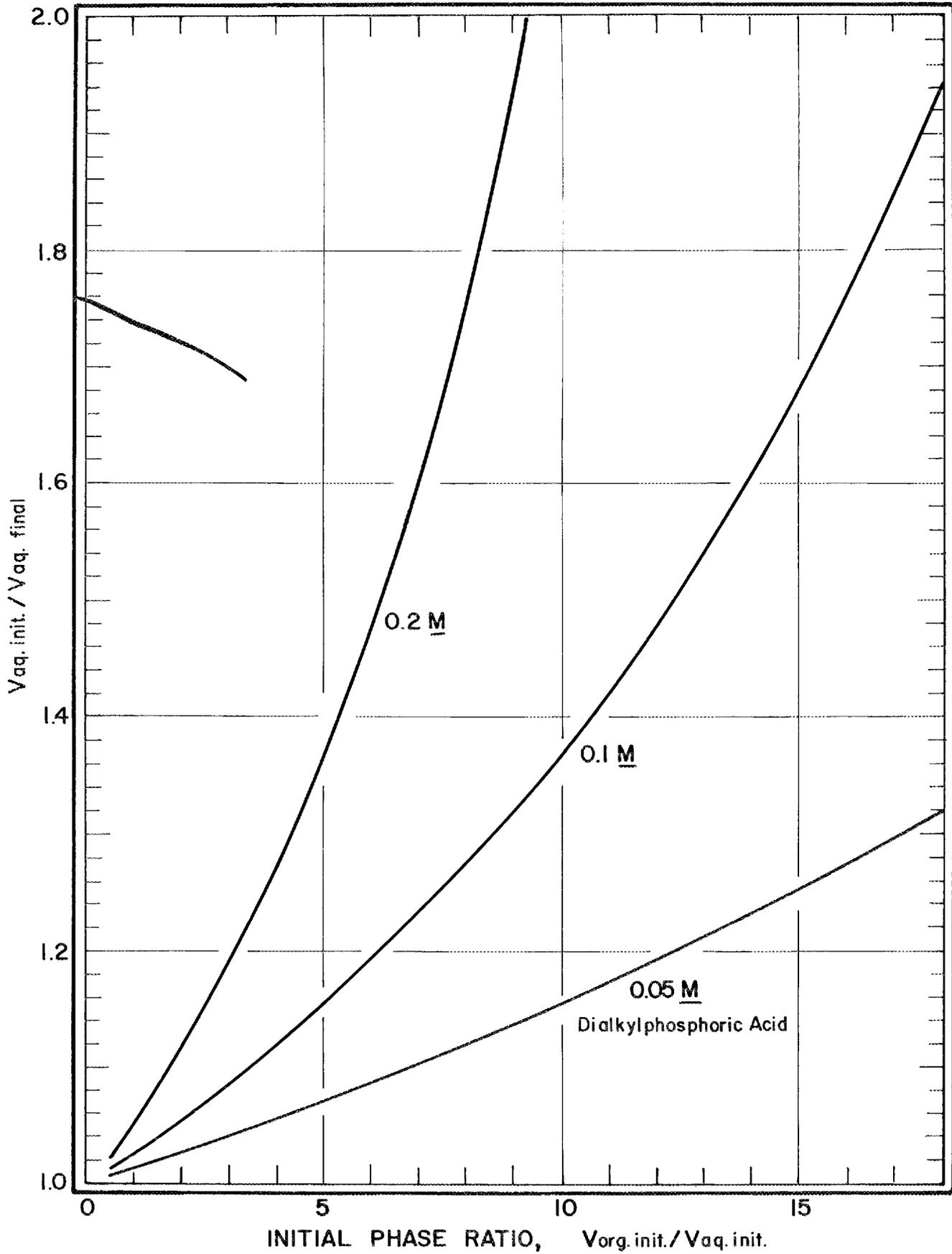


Figure B-2

VOLUME CHANGE DURING ALKALINE STRIP

on the same basis as those of Figure B-1. Here again, some (but probably not serious) difference can be expected with other types and concentrations of modifiers.

In general it may be observed from the data that, under normal process circumstances, the sodium carbonate requirements for stripping are of a very reasonable order. For example, an average level of uranium expected in the pregnant organic phase would be about 5 g  $U_3O_8$ /l for 0.1 M reagent, 10 g  $U_3O_8$ /l for 0.2 M reagent, etc. At these concentrations the stoichiometric requirement of sodium carbonate (from Figure B-1) would be 1.85 lb/lb of  $U_3O_8$ . In actual practice, a multistage operation with excess sodium carbonate would be provided to insure complete stripping and allow for the small amount of sodium carbonate loss to the organic phase (section on Stripping). An excess of 20% over the stoichiometric sodium carbonate should be more than adequate for these purposes, bringing the total consumption to 2.2 lb  $Na_2CO_3$ /lb  $U_3O_8$ .

APPENDIX C

LOSS OF DI(2-ETHYLHEXYL)PHOSPHORIC ACID TO  
AQUEOUS SOLUTIONS

A direct measurement of the di(2-ethylhexyl)phosphoric acid lost from D2EHPA-TBP-kerosene solution to various aqueous solutions was made by Dr. W. H. Baldwin of the ORNL Chemistry Division, using labeled  $P^{32}$  D2EHPA.<sup>(19)</sup> (Cf. measurements of TBP loss, Table 8.) The labeled reagent was prepared by transesterification of labeled orthophosphoric acid to form tri(2-ethylhexyl)phosphate, followed by controlled hydrolysis to the dialkyl acid with ethanolamine, and anion exchange purification. The kerosene solution was equilibrated successively with samples of the aqueous solutions listed (phase ratio 1:1), starting with sodium carbonate, and with sodium carbonate contacted again after each contact with a sulfate liquor. The amounts of reagent lost were determined by counting the activity in each aqueous sample after equilibration.

Repeated loss measurements to each of the acidic solutions except Liquor I showed good internal agreement. With that exception, these results agree with the <5 ppm reported in ORNL-1903.

The loss measurements to 10% sodium carbonate solution were not in close internal agreement, decreasing from ~50 to ~30 ppm in an apparently systematic manner during the course of the tests. If this decrease was actually systematic, it suggests preferential loss of a (labeled) contaminant.\* In comparison, the loss to 10% sodium carbonate previously measured by titration of the acid remaining in the organic phase (at high aqueous:organic phase ratios, with 2 w/v % 2-ethylhexanol used as the diluent modifier, ORNL-1903) was 27 ppm.

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\*Examination of the end-point inflection of a titration curve, as described in Appendix D, indicates not more than around 2% of mono(2-ethylhexyl)phosphoric acid in the di(2-ethylhexyl)phosphoric acid if these two and no other acids were present. Thus it is possible that the actual losses of the dialkyl acid to the aqueous phases may have been even less than the values shown in Table C-1.

Table C-1

LOSS OF DI(2-ETHYLHEXYL) PHOSPHORIC ACID TO AQUEOUS SOLUTIONS

RADIOACTIVE TRACER ANALYSIS<sup>a</sup>

0.1 M D2EHP\*A + 2.5 w/v % TBP/Kerosene, 25°C

<u>Aqueous Phase</u>	<u>ppm D2EHPA in Aq. Phase</u>
0.5 M SO <sub>4</sub> , pH 1	0.4, 0.5, 0.3, 0.6, 0.4
1 M H <sub>2</sub> SO <sub>4</sub>	1.4, 1.2, 1.0
0.4 M H <sub>3</sub> PO <sub>4</sub>	1.2, 0.8, 1.3
10 M HCl	2.9, 2.3, 2.5
Liquor I:	
0.7 M SO <sub>4</sub> , pH 0.6	0.4, 9, 5
Liquor II:	
1.2 M SO <sub>4</sub> , pH 0.15	4, 4
Liquor III:	
1.2 M SO <sub>4</sub> , pH 0.7	3, 3
10% Na <sub>2</sub> CO <sub>3</sub>	50-32 <sup>b</sup>

a) Tests made by Dr. W. H. Baldwin, ORNL Chemistry Division. (19)

b) Nine measurements in sodium carbonate solution, including strip solutions used after each of the tests with sulfate liquors; average, 40 ppm. The results suggested a systematic decrease of loss of P<sup>32</sup> to carbonate solution during the series of tests.

Liquors (major constituents):

g/l:	<u>U</u>	<u>V</u>	<u>Fe</u>	<u>Al</u>	<u>Si</u>	<u>SO<sub>4</sub></u>	<u>pH</u>
I (Plant B)	0.7	2.2	0.6	3.4	2.3	70	0.6
II (Plant C)	5.9	4.7	0.6	2.5		115	0.15
III (Plant D)	1.1	3.6	5.5	6.2		70	1.8

APPENDIX D

DETERMINATION OF SMALL AMOUNTS OF  
MONO(2-ETHYLHEXYL)PHOSPHORIC ACID  
IN DI(2-ETHYLHEXYL)PHOSPHORIC ACID

As was previously described, titration curves for mono- and dialkylphosphoric acids (free of pyro- and polyphosphoric acids) show sharp, well-defined inflections. The inflection for the single hydrogen ion of a dialkylphosphoric acid is similar to that for the stronger of the two hydrogen ions of the corresponding monoalkylphosphoric acid, so that titration to the successive end points for the stronger and weaker hydrogens provides a differential analysis for mono- and dialkylphosphoric acids in mixtures which contain no other acids and no bases. When the amount of monoalkylphosphoric acid in the mixture is very small, the end points merge and cannot be recognized as separate inflections, but appear as a slightly distorted single inflection. Detection of this distortion was previously used as a qualitative test (ORNL-1903), with an estimated sensitivity of about 3 meq mono- in 100 meq dialkylphosphoric acid (e.g., about 1 w % mono(2-ethylhexyl)- in di(2-ethylhexyl)phosphoric acid).

Further study of these titrations has shown that carbon dioxide should be excluded, to avoid downward drifting of the apparent "pH" (glass electrode). Unless the titration is completed very rapidly, the distortion due to carbon dioxide absorption interferes with the distortion due to the weak hydrogen ion from a small amount of monoalkylphosphoric acid. Titrations made under a nitrogen atmosphere (flowing nitrogen in a loosely covered beaker) were free from pH drift.

If the shape of the inflection for pure dialkyl acid is known and is sufficiently reproducible, estimation of the degree of distortion should provide a reasonable quantitative estimate of a small amount of monoalkyl acid present. Some preliminary tests of this possibility have been encouraging. Known mixtures of mono- and di(2-ethylhexyl)phosphoric acids were titrated in 70% ethanol under nitrogen. When the inflections were well separated (with ~25% and with ~100% monoalkyl acid), they were close to "pH" 6.0 and 10.2. When no monoalkyl acid was added, the inflection was close to "pH" 7.5, and the curve was steep although not quite vertical between 6 and 10. For the present calculation, the titer at "pH" 6.0 was arbitrarily taken as equivalent to the total stronger hydrogen ion, and the additional titer to "pH" 10.2 as equivalent to the weaker hydrogen ion, with the following results:

wt % Mono* Added:	0	0.9	2.0	4.3	23.1	100
" " " Found:	0.5	1.5	2.6	5.2	22.8	97

Since this method of calculation is tantamount to the assumption that the titration curve should be vertical between 6 and 10.2 for pure dialkyl acid, whereas an appreciable slope probably should be expected,\*\* the 0.5% is indicated as an upper limit for this batch of dialkyl acid (previously estimated at <1%). Further tests are needed to determine the reproducibility of both the slope of the curve and the end-point "pH" levels.

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\*Mono(2-ethylhexyl)phosphoric acid, Batch 145, previously estimated to contain <5% di-, added to di(2-ethylhexyl)-phosphoric acid, Batch 303, previously estimated to contain <1% mono-.

\*\*As previously described, di(2-ethylhexyl)phosphoric acid shows an apparent  $pK_A$  (half-neutralization "pH") of about 3.2 in the 75% ethanol solution used for these titrations (ORNL-1903). The titration curve calculated for 0.02 M acid with 0.1 M base, using  $pK_A = 3.2$ ,  $C_H \times C_{OH} = 10^{-14}$ , and  $pH = -\log C_H$ , shows a nearly straight portion between pH 6 and 9, with slope of 1 pH unit/0.012 ml titrant. If this be taken as the slope to be expected for pure di(2-ethylhexyl)phosphoric acid in the present titrations, the calculated contents of mono(2-ethylhexyl)phosphoric acid become -

Wt % Mono Found:	0.2	1.2	2.3	4.9	22.6	97
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APPENDIX E

DESCRIPTION OF REAGENTS

Batches of alkylphosphoric acids (used in the tests reported here) which have not been previously described are listed in Table E-1, which may be compared with the corresponding table and the discussion of purity levels in ORNL-1903, Appendix A.

The following reagent batches were described in ORNL-1903 with letter instead of number batch designations.

<u>Reagent</u>	<u>Batch No.</u>	<u>Listed in ORNL-1903 as -</u>
Mono-n-octyl	185	A
Di "	181	A
Mono-3,5,5-trimethylhexyl	163	A
Di "	165	A
Mono-2-ethylhexyl	175	F
Mono-diisobutylmethyl	166	B

Erratum: ORNL-1903, p. 102, for "4-ethyl-1-isobutylmethyl"  
read "~~4-ethyl-1-isobutyloctyl~~."

Table E-1

DESCRIPTION OF REAGENTS

<u>Alkyl Group</u>	<u>Mol. Wt.</u>	<u>Batch No.</u>	<u>Theo. meq/g<sup>b</sup></u>	<u>Acid Assay meq/g<sup>a</sup></u>		<u>Source<sup>c</sup></u>	<u>Remarks</u>
				<u>Strong Acid</u>	<u>Weak Acid</u>		
<u>Dialkylphosphoric Acids</u>							
2-Ethylhexyl	322	303	3.11	3.08	<0.1	C&C	Separated at ORNL from Tergitol P-28
Diisobutylmethyl	350	314	2.86	2.75	<0.1	VC	Separated at ORNL from VC-1-119-B
<u>Monoalkylphosphoric Acids</u>							
2-Ethylhexyl	210	145	4.76	4.50	4.4	V	Separated at ORNL from Victor E-5877
Dodecyl <sup>d</sup>	266	320	3.76	3.59	3.5	ORNL	Separated from hydrolysis product of alcohol-P <sub>2</sub> O <sub>5</sub> -reaction mixture
Tetradecyl <sup>e</sup>	294	321	3.40	3.21	3.2	ORNL	

- a) Based on differential titration in 75-25 ethanol-water mixture with aqueous sodium hydroxide.
- b) For the dibasic (monoalkyl) acids, theoretical meq of either the weaker or the stronger ionizable hydrogen.
- c) C&C = Carbide and Carbon Chemicals Company  
 VC = Virginia-Carolina Chemical Corporation  
 V = Victor Chemical Works  
 ORNL = Oak Ridge National Laboratory
- d) Prepared from 2,6,8-trimethylnonanol-4 by reaction with P<sub>2</sub>O<sub>5</sub> in n-hexane. Hydrolyzed for 2 hours with 6 M HCl. Partitioned between propylene glycol and petroleum ether.
- e) Prepared from 2-methyl-7-ethyl undecanol-4 by reaction with P<sub>2</sub>O<sub>5</sub> in kerosene. Hydrolyzed for 6 hours with 1 N HCl. Partitioned between propyleneglycol and petroleum ether.