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PROGRESS REPORT ON RAW MATERIALS

FOR NOVEMBER, 1957

K. B. Brown
C. F. Coleman
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OAK RIDGE NATIONAL LABORATORY
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CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT ON RAW MATERIALS

FOR NOVEMBER, 1957

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

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

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

OTHER REPORTS IN THIS SERIES

Preliminary,	ORNL-2268 (20¢)	June,	ORNL-2380 ($1.00)
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May,	ORNL-2366 (25¢)	October,	ORNL-2451 (75¢)

ABSTRACT

Systematic Studies. Uranium extraction coefficients with Amberlite LA-2, a new commercial secondary amine of unstated structure, were lower than those with most other commercial secondary amines that have been studied for Amex extraction. Phase separation was rapid when the diluent was benzene but slow (3 min) when it was kerosene. Loss to the aqueous liquor was very low.

Kerosene-tridecanol solutions of an N-alkyl-β-aminocarboxylic acid extracted uranium strongly from dilute nitrate solution, where the simple amines do not extract. Extraction was low from sulfate solution. Phase separation was poor.

Loss of di(2-ethylhexyl)phosphate (D2EHP) from 0.1 M solution in kerosene to neutral and alkaline sodium salt solutions, measured by distribution of P^{32}-labeled reagent, varied greatly with the aqueous salt concentration. Of the variables examined, correlation was best with the sodium ion concentration: log (D2EHP concn) $\propto$ 1/(Na^+ concn). No correlation appeared with pH or choice of anion. At a given Na^+ concentration, the losses varied about ± 30% from the mean. The highest losses were about 250 mg $D2EHP^-$ per liter of aqueous at 1 M Na^+ and 10 mg/liter at 3 M. The losses to the more dilute solutions were higher than was previously assumed in some cost estimates, but the revised contributions to operating costs are still not important, e.g., 0.5 instead of 0.2¢ per pound of U_3O_8.

Revision of previously reported monododecylphosphoric acid (DDPA) losses to acid solutions, to correct for Na^+ extraction, showed losses to 0.5 M sulfate solution, pH 1, of ~60 mg/liter from 0.1 M and ~80 mg/liter from 0.4 M DDPA in kerosene. These were confirmed by P^{32}-labeled reagent distributions. Losses were about twice as great to 10 M HCl as to the sulfate solution in 10-min tests at 25°C, but increased because of hydrolysis with longer times

and especially with higher temperature.

Continued tests of cation exchange between D2EHP and aqueous solutions confirmed the preferential distribution of strontium over that of sodium from nitrate solutions to the organic phase down to trace levels (10 ppm). At constant D2EHP and sodium nitrate concentrations, the strontium distribution coefficient was constant at pH 7.5 to 12 and dropped as expected to low values at pH <3, but at pH ~5 it was an order of magnitude higher than at high pH. Brief tests of cation exchange between DDPA and aqueous solutions showed significant distribution of several alkali and alkaline earth ions to the organic phase even at aqueous pH <2.

Process Development Studies. Uranium extraction isotherms are presented for a new secondary amine, Amberlite LA-2, and for a new sample (from a pilot scale batch) of di(tridecyl)amine, each in kerosene and in kerosene-alcohol diluent. Amberlite LA-2 showed excellent selectivity with respect to ferric iron, but its extraction power was lower and phase separation slower than that of, for example, amine 9D-178. Addition of 3 vol % tridecanol to the diluent appreciably increased the rate of phase separation and increased the uranium extraction coefficients slightly. The extraction characteristics of the di(tridecyl)amine sample were approximately the same as those determined for an earlier sample from the manufacturer.

Studies of the Amex vanadium process showed relatively high extractions of phosphate along with the vanadium. Phosphate extractions were much lower from acid leach liquors that contained Fe(III) and aluminum than from pure vanadium solutions, but were still considerably above the P/V_2O_5 ratio of 5/10,000 allowable in commercial vanadium products. Only a small fraction of the phosphate was removed from the extract by scrubbing with dilute sulfuric acid. However, after the amine had been stripped with a solution of sodium carbonate, separation from phosphate was very favorable during precipitation of vanadium "red cake" from the strip solution. Thus, it is expected that in most cases the Amex process will yield products of acceptable phosphorus content.

Engineering Studies. The entrainment of solvent in the aqueous raffinate in the Dapex extraction process depends chiefly on the type of dispersion and phase ratio in the mixer. In tests of single mixer-settler units with 6- and 48-in.-dia settlers the entrainment was consistently less than 0.2 gal/1000 gal of aqueous for water-in-oil type dispersions. For oil-in-water type dispersions the entrainment decreased with decreasing aqueous/organic ratio, ranging from more than 2 gal/1000 gal at an a/o phase ratio of 4/1 to 0.3 gal/1000 gal at a ratio of 1/1. Entrainment of aqueous in the solvent was less than 1 vol %, which is significant only because this would result in slight contamination of the uranium product.

The flow capacity of a gravity settler for primary break of phases was not affected by changing the pH of the aqueous phase from 0.5 to 1.0.

Fundamental Studies. Molecular weight determinations by light scattering indicated that in benzene solution the normal sulfates of bis(1-isobutyl-3, 5-dimethylhexyl)amine and methyldi-n-octylamine form aggregates averaging ~4 and 8-10 sulfate units, respectively. Determination of water in these and previously studied amine sulfate solutions in benzene showed water contents from <1 to 10 moles per mole of sulfate.

1.0 SYSTEMATIC STUDIES

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

The uranium extraction power of three new samples of commercial amines (Table 1.1) was examined as described in previous reports of this series. One, Amberlite LA-2,* is a new secondary amine of unstated structure. The other two are new batches of amines previously examined, trilaurylamine (cf. ORNL-1734 and -2380) and di(tridecyl)-amine (previous batch designated di(tridecyl P)amine, ORNL-1922).

The extraction coefficient of 10 with the new secondary amine in kerosene, from the usual 1 M sulfate, pH 1, solution, was much lower than that with other secondary amines such as di(tridecyl)amine (Table 1.1), Amine 9D-178 (70-100, ORNL-1922, -2269, -2380), or Amine S-24 (100, ORNL-2269). The coefficient of 35 in benzene was also significantly lower than with di(tridecyl)amine or with Amine 9D-178 (55-75, ORNL-1922, -2269, -2380). Not enough information is available to indicate whether the lower extraction power is inherent in the structure of this reagent, or whether the extraction might be impaired by contaminants (e.g., alcohols) in this sample. The purity of the reagent with respect to amine class (Table 1.2) was good, but in the absence of a theoretical value for the equivalent weight the observed value of 366 gives no information about possible inert contaminants. The loss to a synthetic leach liquor (Fe(III) 5.8, Al 3.3, SO_4 50, PO_4 2, F 1.7 g/liter; pH 0.9) was $\lesssim$1% initially and the aqueous phase contained <5 mg/liter at steady state. The low steady-state loss rate is as expected for an amine of the indicated molecular weight, and shows that the reagent has little if any content of amines of very much lower molecular weight. Phase separation in the extraction tests was good (<1 min) when the diluent was benzene but slow (3 min) when it was kerosene. This, like the low extraction coefficients, might be characteristic of the amine structure or might be due to a contaminant.

The assay and extraction performance of the new sample of di(tridecyl)amine were in general similar to those of the preceding batch (ORNL-1922). The new batch shows less primary amine, 4 instead of 9%, and about 10% excess equivalent weight (due to inert contaminants or larger-than-nominal alkyl groups) instead of ~5%.

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*Submitted for evaluation by Rohm and Haas Company, Resinous Sales Development Dept., with the information that it will be available in commercial quantities sometime after July 1, 1958, and meanwhile in development quantities.

Table 1.1 Preliminary Tests of Uranium Extraction from Sulfate Solutions

Compound	Batch No.	Concn., M	Kerosene %	Kerosene E_a^o	Benzene %	Benzene E_a^o	Phase Separation
Secondary amines							
Di(tridecyl)amine	227B	0.1	98[a]	60[a]	99	200	Good
Amberlite LA-2	325A	0.01	38	-	37	-	Poor in kerosene
		0.1	91	10	97	35	
Tertiary amine							
Trilaurylamine	86D	0.01	43	-	48	-	Good; organic slightly cloudy
		0.1	99	160	99	185	

[a]Di(tridecyl)amine in kerosene + 3 vol % tridecanol: 99% extraction, E_a^o = 75

Table 1.2 Analyses

Compound	Batch No.	Source[a]	% by Differential Titration Prim	Sec	Tert	Equivalent Wt Theo	Found
Di(tridecyl)amine	227B	C	4	94	<2	382	405
Amberlite LA-2	325A	R	1	97	2	-	366
Trilaurylamine	86D	ADM	4	>3	>92	522	560

[a]ADM = Archer-Daniels-Midland Co., Minneapolis, Minn.
C = Union Carbide Chemicals Co., New York
R = Rohm and Haas Co., Philadelphia

Extraction was a little lower (60 vs 85) with kerosene as the diluent, and higher (200 vs 120) with kerosene. The reagent solution in kerosene was slightly cloudy at room temperature. The loss to synthetic leach liquor was ~1% initially, and the concentration in the aqueous phase at steady state was <5 mg/liter. Phase separation was good.

Extraction coefficients with the new sample of trilaurylamine were somewhat higher than with the previous sample from the same source in both benzene, 185 vs 150, and kerosene, 160 vs 80 (ORNL-2380). The assay showed a little less secondary amine content (>3 vs 9%), and the excess equivalent weight amounted to about 10% in both. Loss to synthetic leach liquor was <1% initially and the concentration in the aqueous phase was <5 mg/liter at steady state. Phase separation was good except that a perceptible layer of emulsion remained between the phases after long standing and the organic phase was slightly cloudy.

β-Amino Acid. Solutions of N-coco-β-aminobutyric acid* in kerosene-tridecanol diluent extracted uranium strongly from dilute nitrate solution. Extraction coefficients were 3000 or more with 5 vol % reagent (<0.1 M) in kerosene modified with 5, 10, or 20 vol % tridecanol from 0.1 M aqueous nitrate solution at pH 2.4. These are of the same order as the extraction coefficients with phosphine oxides, i.e., 1000-1500 from 0.1 M nitrate at pH 1 (ORNL-1964), and much higher than with TBP. The dependence of extraction on reagent concentration and pH has not yet been measured. Extraction coefficients with the same reagent solutions were low (~0.3) from 1 M sulfate solution at pH 1. Phase separation with this reagent sample was very slow.

Two other acid reagents also obtained from Armour Chemical Division, α-sulfostearic and α-sulfopalmitic acids, extracted little if any uranium from either sulfate or nitrate solution. Phase separation with these samples was also very slow.

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

In continuation of the distribution measurements of tracer-phosphorus labeled reagents reported last month (ORNL-2451, sec. 1.2), losses were measured of di-(2-ethylhexyl)phosphate (D2EHP) to alkaline solutions such as may be encountered in alkaline stripping, and of monododecylphosphoric acid (DDPA) to acid solutions.

1.2.1 D2EHP Losses to Alkaline Solutions

The concentrations of D2EHP** lost from 0.1 M solution in

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* Obtained from Armour Chemical Division, Chicago; Stated to be 55% aqueous gel, containing a slight contamination of crotonic acid; coco represents n-alkyls, mainly lauryl, from coconut oil.

** The preparation and purification of the P^{32}-labeled reagent was described in the preceding month's report, ORNL-2451, sec. 1.2.

kerosene to aqueous sodium salt solutions showed a close inverse correlation with the aqueous sodium ion concentration. The previously reported losses determined by titration of the organic phase before and after equilibration at high aqueous/organic phase ratios (ORNL-1903, p. 59) show approximately the same correlation with sodium ion concentration (Table 1.3). There was little if any correlation with the choice of aqueous anion [$CO_3^{=}$, OH^-, $SO_4^{=}$, Cl^-, $UO_2(CO_3)^{4-}$] or the pH (~7 to >14). Correlation with ionic strength was not so good as with sodium ion concentration. There was little if any difference in loss from kerosene solutions whether unmodified (two organic phases) or modified with TBP.

A semi-log plot of loss against sodium ion concentration (Fig. 1.1) shows a fairly linear dependence, although with the points falling in a band instead of on a single line. Part of this spread is due to experimental scatter, and a part may also be due to relatively minor effects of the other variables. The magnitude of the loss at a given sodium ion concentration averaged somewhat higher in the radiotracer tests than in the earlier titration tests with carbonate solutions,* ranging from about the same as the earlier results to about twice as great. Since the systematic and the random variations within this plot have not been distinguished, no attempt was made to summarize the results by a fitted line. It may be useful to note, however, that the highest losses found would fall beneath a line corresponding to 250 mg D2EHP/liter aqueous at 1.0 M Na^+ and 10 mg/liter at 3.0 M.

Two organic phases were present in the test without diluent modifier. Since most of the Na-D2EHP was in the relatively small volume of the heavier phase, its concentration was considerably higher than 0.1 M. However, the loss found (46-59, average 53) was not much higher than that found from 0.1 M solution modified with TBP (32-50, average 40). While this might be due only to "saturation" of the aqueous phase, it is also consistent with the suggestion previously made, on the basis of free-base extraction (ORNL-2172, p. 44), that the Na-D2EHP may exist as aggregates or micelles in the modified kerosene solution. The composition of such aggregates might be rather close to that of the third phase separating from unmodified kerosene solution, and thus give about the same distribution to an aqueous phase. If so, the losses (when the diluent is modified to maintain miscibility) should vary little if any with the nominal D2EHP concentration. Only two radiotracer tests were made of loss from solutions of higher D2EHP concentration (0.4 M). While these showed poor agreement, 104 and 58 mg D2EHP per liter of 10% sodium carbonate solution, they both fall close to some of the 0.1 M D2EHP points in Fig. 1.1 (final estimated Na^+ concentration = 1.6 M), suggesting again that the loss rate was nearly independent of the organic Na-D2EHP concentration.

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*This difference might indicate that the loss is decreased by 2-ethylhexanol, used to modify the kerosene diluent in the earlier tests, but not appreciably by TBP, the only modifier used in the radiotracer tests.

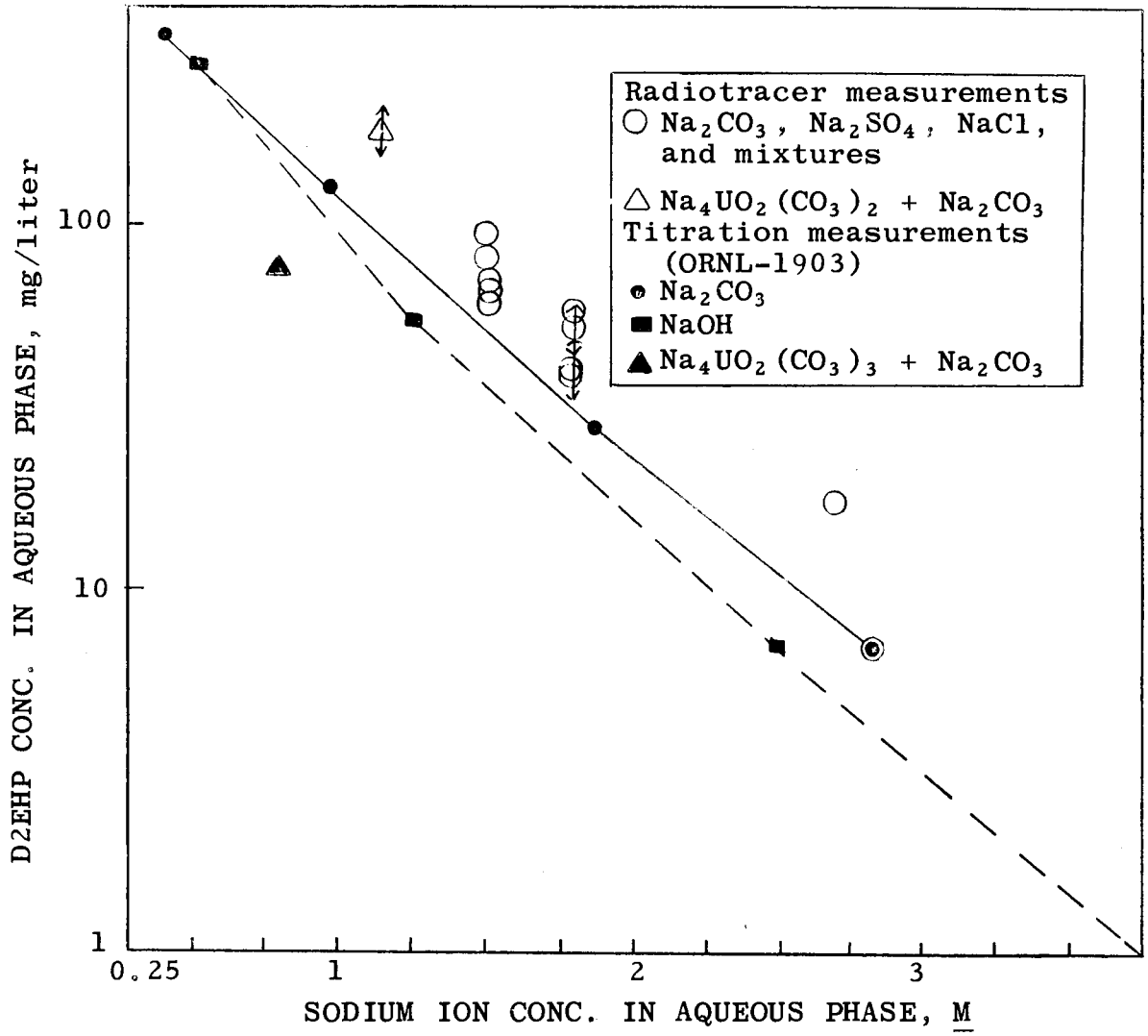


Fig. 1.1 D2EHP losses to Alkaline Solutions. Aqueous concentration of di(2-ethylhexyl)phosphate in equilibrium with 0.1 M solution in kerosene (see Table 1.3).

Table 1.3 Di(2-ethylhexyl)phosphate Losses to Alkaline Solutions

Initial organic phase, 0.1 M D2EHPA in kerosene modified as indicated; 10 min contact; room temperature

Solute	Na^+ Conc., M	D2EHP Conc., mg/liter	Diluent Modifier[a]	Concen., M	Ref.
Na_2CO_3	0.38	325	2EHOH	0.15	ORNL-1903
	0.94	125	2EHOH	0.15	ORNL-1903
	1.5[b]	93[c]	TBP	0.1	
	1.79	40[c,d]	TBP	0.15	ORNL-2172
		39[c]	TBP	0.15	
		51[c]	TBP	0.15	
		53[c,e]	None		
	1.89	27	2EHOH	0.15	ORNL-1903
	2.73	16[c]	TBP	0.21	
	2.83	7	2EHOH	0.15	ORNL-1903
		7[e,f]	TBP	0.21	
NaOH	0.5	270	2EHOH	0.15	ORNL-1903
	1.25	55	2EHOH	0.15	ORNL-1903
	2.50	7	2EHOH	0.15	ORNL-1903
	3.75	1	2EHOH	0.15	ORNL-1903
Na_2SO_4 (pH ~6)	1.5[b]	63[c]	TBP	0.1	
Na_2SO_4/Na_2CO_3 = 2/1	1.5[b]	83[c]	TBP	0.1	
Na_2SO_4/Na_2CO_3 = 1/2	1.5[b]	67[c]	TBP	0.1	
NaCl (pH ~6)	1.5[b]	70[c]	TBP	0.1	
$NaCl/Na_2CO_3$ = 4/1	1.5[b]	71[c]	TBP	0.1	
$NaCl/Na_2CO_3$ = 1/1	1.5[b]	69[c]	TBP	0.1	
$Na_4UO_2(CO_3)_3/Na_2CO_3$ = 1/2.7	0.79	75	2EHOH	0.15	ORNL-1903
$Na_4UO_2(CO_3)_3/Na_2CO_3$ = 1/1.4	1.13	180[c,g]	TBP	0.15	

Table 1.3 (Cont'd)

[a]2EHOH = 2-ethylhexanol; TBP = tributyl phosphate.

[b]Initial organic phase contained 0.1 M Na-D2EHP instead of D2EHPA.

[c]These values determined by counting P^{32} in the aqueous phase after equilibration at phase ratio of 1/1, 23-27°C. All others determined by difference in organic phase titer before and after equilibration at aqueous/organic = 100/1, 29-33°C, except that the sodium uranyl tricarbonate tests were at aqueous/organic = 17/1, 20°C.

[d]Average of nine tests, 32-50 mg D2EHP/liter.

[e]Average of eight tests, 46-59 mg D2EHP/liter.

[f]Average of three tests, 6, 7, 7 mg D2EHP/liter.

[g]Average of five tests, 150-210 mg D2EHP/liter.

Estimates of process operation costs have been based on reagent losses to carbonate stripping solution of 75 (ORNL-1998) to 30 mg/liter (ORNL-1903). The resulting contributions to the estimated reagent costs have been less than 0.2¢ per pound of U_3O_8 recovered (based on a reagent cost of $1.00 per pound and a uranium concentration in the stripping solution of 40 g of U_3O_8 per liter or more). On the same basis, losses up to 200 mg/liter would still contribute less than 0.5¢ per pound of U_3O_8 to the reagent costs. Although this loss varies more with the final sodium ion concentration than was previously appreciated, it is still of minor importance, compared with the major considerations of obtaining maximum carbonate utilization and maximum uranium loading within its solubility limits, in choosing the stripping conditions. Moreover, if the sodium carbonate is increased above its optimum concentration (cf. ORNL-2172, p. 103), in order to decrease the reagent loss on a volume basis, the loss per weight of U_3O_8 recovered may even increase because of the increased volume of strip solution required.

1.2.2 DDPA Losses to Acidic Solutions

Titration Measurements. The solubility distribution losses of monoalkylphosphoric acids reported in ORNL-2380, p. 21, were erroneously high because appreciable amounts of extracted sodium ion caused low titers in the reagent solutions after equilibration. (Cf. extraction of Na^+ and other cations by DDPA at low pH, sec. 1.4.) Only the titer from zero to the first inflection is affected by the extracted Na^+. Accordingly, the losses were recalculated from the same titration curves, using the titer between the first and second inflections. The results (Table 1.4) are significantly lower than the values previously reported, and indicate (by interpolation) good agreement with the 0.1 g/liter loss from 0.34 M DDPA to 0.35 M sulfate solution reported in DOW-97. Qualitatively, the corrected losses show the same correlations as noted before with molecular weight and reagent concentration. In addition, the DDPA loss now shows a decrease with increasing aqueous sulfate concentration, which was previously masked by the corresponding increasing error from sodium extraction.

Table 1.4 Solubility Distribution Losses of Monoalkylphosphoric Acids

Analyzed by titration before and after equilibration
(Replacing part of Table 1.7, ORNL-2380)

Reagent	Final Organic Concn., M	Phase Ratio at Contact (a/o)	Amount, g/liter Organic Phase	Amount, g/liter Aqueous Phase
		0.5 M sulfate, pH 1		
DDPA[a]	0.083	75	20.0	0.061
	0.484	50	120	0.087
TDPA[b]	0.101	100	26.5	<0.005
HDPA[c]	0.10	400	33.6	<0.005
		0.2 M sulfate, pH 1		
DDPA[a]	0.475	50	120	0.133
HDPA[c]	0.10	400	33.6	<0.005

[a]Prepared from 2,6,8-trimethylnonanol-4.

[b]Prepared from 1-isobutyl-4-ethyloctanol.

[c]Prepared from 3,9-diethyltridecanol-6.

Radiotracer Measurements. The concentrations of P^{32}-labeled DDPA found in 0.5 M sulfate solution, pH 1, after equilibration with 0.1 and 0.4 M DDPA solutions in kerosene (Table 1.5) are in fairly close agreement with the titration measurements. Losses to this solution were only slightly higher at 50 than at 25°C, and did not increase with time at either temperature, indicating that hydrolysis to water-soluble $H_3P^{32}O_4$ was not significant in the equilibrations with this solution. Addition of uranium, iron, and aluminum to the aqueous solution (Liquor A) decreased the DDPA loss slightly, and also appeared to cause a further decrease of loss with time. If this is real, it might indicate initial supersaturation of the aqueous phase, but it more likely results from slow extraction of iron and aluminum.*

*The three 10-min loss values for each set of conditions in Table 1.5 were obtained by three consecutive contacts of one organic sample with fresh aqueous samples. Thus the decrease in 10-min results observed with Liquor A, 51-32-27 and 60-46-47, could also result from slow extraction of iron and aluminum.

Table 1.5 DDPA[a] Loss from Kerosene Solutions to Aqueous Acidic Liquors

Aqueous/organic phase ratio = 1/1
Analyzed by counting the P^{32} in the equilibrium aqueous phase

Initial DDPA, M	Temp, °C	Contact Time	Amount of DDPA lost to Aqueous Phase, mg/liter: 0.5 M SO_4, pH 1	Liquor A[b]	1 M H_2SO_4	10 M HCl
0.1	25	10 min	60,65,66	51,32,27	-	129,131,131
		1 hr	65	16	-	145
0.4	25	10 min	85,76,73	60,46,47	86,80,87	164,163,160
		1 hr	72	42	-	193
0.1	50	1 hr	75	45	-	1020
		4 hr	65	25	-	-
		16 hr	70	30	-	13000
0.4	50	1 hr	95	100	-	1500
		4 hr	75	85	-	4800

[a]DDPA = mono(2,6,8-trimethylnonyl-4)phosphoric acid.
[b]0.5 M $SO_4^{=}$; pH 1; U 0.05, Fe(II) 2, Fe(III) 0.5, Al 2 g/liter.

Losses to 10 M HCl in 10-min contacts at 25°C were about twice the losses to the 0.5 M sulfate solution. These did increase slightly with time, suggesting that hydrolysis made a measurable contribution to the loss. The losses to 10 M HCl were much higher at 50°C, and increased drastically with time, indicating that here the hydrolysis was of major importance. The losses from 0.4 M reagent at 50°C agree with values reported by the Dow Chemical Company, 2 g/liter in 1 hr and ~5 g/liter in 4 hr (DOW-117).

The labeled DDPA was prepared by reacting P_2O_5, 2,6,8-trimethylnonanol-4, and anhydrous $H_3P^{32}O_4$ in kerosene. The resulting DDPA (mixed tracer and carrier) was then separated and purified by the procedure described in ORNL-2380, p. 15.

1.3 Strontium-Sodium Exchange in Di(2-ethylhexyl)phosphate
(J. X. Khym, D. E. Horner)

Study was continued of cation exchange in hydrocarbon solutions of di(2-ethylhexyl)phosphate (D2EHP) as a possible means of extracting radioactive strontium from waste solutions, using radiotracer strontium in order to determine a wide range of strontium concentrations. The preliminary tests reported last month in this system showed no apparent change in separation factor, i.e., the ratio of distribution coefficients $D_a^o(Sr)/D_a^o(Na)$, with pH in the range ~8 to ~12 or with D2EHP concentration in the range 0.1-0.4 M. Subsequent tests confirmed the independence from pH in alkaline solutions, but showed a

slight decrease of separation factor with increasing D2EHP concentration when the strontium concentration was low. In addition, the strontium distribution (at least at low strontium concentrations) to the organic phase was much higher from very slightly acid solutions (pH 4-6) than from alkaline solutions.

Alkaline Solutions. The strontium distribution and strontium-sodium separation varied significantly with the concentrations of D2EHP, sodium nitrate, and strontium (Table 1.6). They varied only slightly, and apparently randomly, with pH, contact time, and choice of hydrocarbon diluent.

At 10 ppm strontium (1.14×10^{-4} M), where its distribution had essentially no effect on the sodium concentrations, and also at 1000 ppm strontium where the effect was still slight, the strontium distribution coefficients increased by a factor of about 3 as the D2EHP concentration was increased from 0.1 to 0.4 M, and the corresponding separation factors decreased slightly. In terms of the expected reaction, $Sr^{++} + 2\ NaX \rightleftharpoons 2\ Na^{+} + SrX_2$,

$$Q = \frac{[SrX_2]\ [Na^+]^2}{[Sr^{++}]\ [NaX]^2}$$

and

$$SF_{Na}^{Sr} = D_a^o(Sr)/D_a^o(Na) = \frac{[SrX_2]\ [Na^+]}{[Sr^{++}]\ [NaX]} = Q\ \frac{[NaX]}{[Na^+]}$$

where X represents the D2EHP anion, the quantities in brackets represent molar concentrations, and Q is the concentration equilibrium quotient. If Q were close to constant, as would be expected if molarities were satisfactory approximations to the activities in the organic phase, then at a given sodium nitrate concentration the separation factor should be directly proportional to the Na-D2EHP concentration, and $D_a^o(Sr)$ to its square. The simplest explanation for the failure of the system to conform to this relation is that (as suggested in sec. 1.2.1, and in ORNL-2172) the Na-D2EHP exists in the organic phase as stably dispersed aggregates or micelles of approximately constant activity. The observed decrease of the separation factor, and the increase of the distribution coefficient by a factor of 3 instead of 4, may then indicate that the nature of the aggregates changes to some extent with changing amount of diluent.

On the basis of constant Na-D2EHP activity over a range of nominal molarities, the separation factor should be inversely proportional to the aqueous sodium ion concentration. Plots of log SF vs log M $NaNO_3$ should be straight lines of slope -1. Plots for 0.1 and 0.4 M D2EHP and 10 and 1000 ppm strontium (Fig. 1.2) are somewhat flatter, but are close enough to support rather than to contradict the foregoing. The spread between the 0.1 and 0.4 M D2EHP lines illustrates the decrease in separation factor mentioned above. This spread was smaller in tests made with higher strontium concentrations (Fig. 1.3).

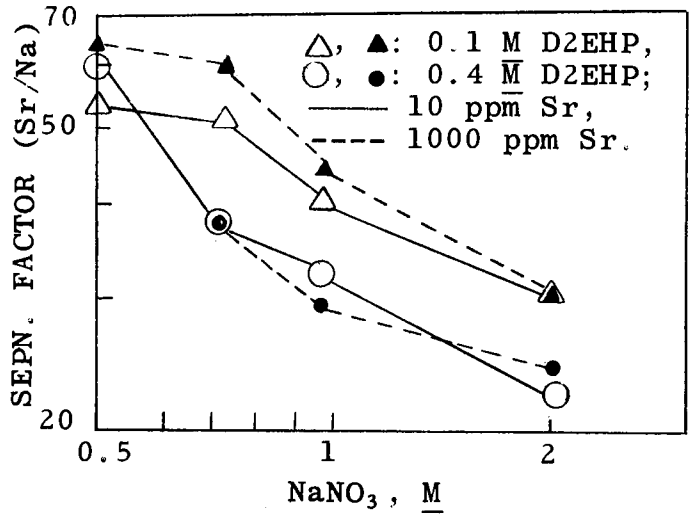


Fig. 1.2. Effect of Aqueous Sodium Nitrate Concentration on Separation Factor, $D_a^o(Sr)/D_a^o(Na)$.

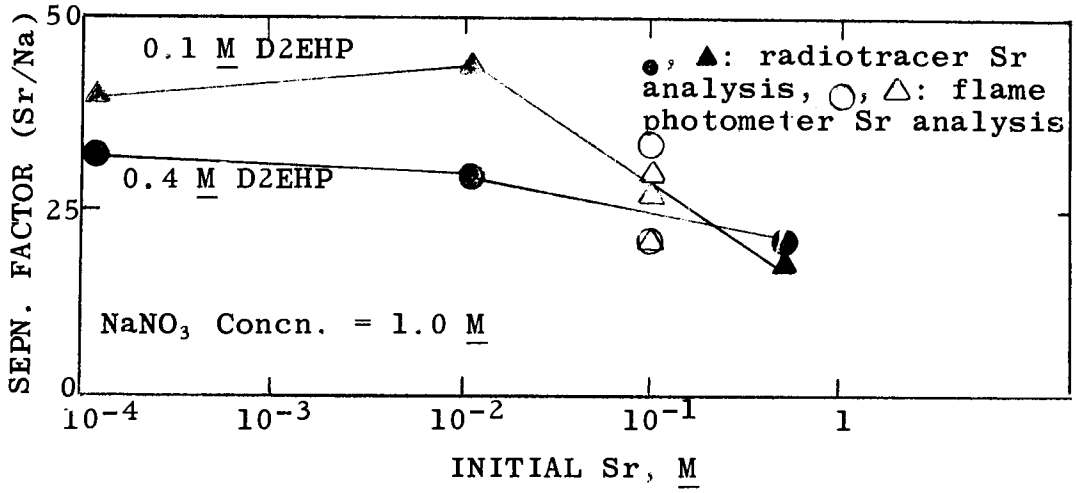


Fig. 1.3. Effect of Strontium Concentration on Separation Factor, $D_a^o(Sr)/D_a^o(Na)$.

Table 1.6 Strontium Distribution Between Sodium Di(2-ethylhexyl)-phosphate and Alkaline Sodium Nitrate Solutions

Diluent, Amsco 125-82, Amsco 123-15, or kerosene, modified with TBP to maintain miscibility of Na-D2EHP[a]

Aqueous pH 8-12, phase ratio 1/1, room temperature
Sr analyzed by counting Sr^{89} tracer, except as noted

Initial Concn., M			Distribution Coef. (o/a)		Separation Factor
Organic	Aqueous				
Na-D2EHP	Sr	Na	Sr	Na[b]	$D_o(Sr)/D_o(Na)$
0.1	$\sim 10^{-4}$	2.0	1.5	0.05	30[c]
		1.0	4.0	0.1	40[d]
		0.7	7.2	0.14	51[e]
		0.5	11	0.2	55[f]
	$\sim 10^{-2}$	2.0	1.3	0.043	30
		1.0	3.5	0.08	44
		0.7	6.7	0.11	60
		0.5	10	0.16	64
	0.10	1.0	0.6	0.25	25[g,h]
	0.25	1.5	0.22	0.010	22
	0.50	1.0	0.11	0.006	18
	0.75	0.5	0.075	-	-[i]
0.2	0.10	1.0	2.4	0.07	36[h]
0.4	$\sim 10^{-4}$	2.0	4.5	0.2	22[k]
		1.0	13.0	0.4	32[k]
		0.7	22	0.57	39[k]
	$\sim 10^{-2}$	2.0	4.5	0.19	24
		1.0	10.6	0.37	29
		0.7	20	0.52	39
	0.10	1.0	4.6	0.22	21[h]
			7.3		33[h]
	0.25	1.5	1.5	0.069	22
	0.50	1.0	0.6	0.029	20

Table 1.6 (Cont'd)

[a]The concentrations of TBP used, ~0.1 and 0.15 M with 0.1 and 0.4 M D2EHP, respectively, were sufficient to maintain miscibility in equilibrium with aqueous $NaNO_3$ concentrations down to 0.5 M, but third phases formed in tests with 0.2 M $NaNO_3$.

[b]Sodium distribution calculated from strontium distribution and material balance.

[c]Average of five results, 28-30; no systematic variation with pH (9-12) or diluent.

[d]Average of six results, 32-44; no systematic variation with pH (9-12) or diluent.

[e]Average of four results, 49-53; no systematic variation with pH (9-12) or diluent.

[f]Three results, each 55; pH 7.5-12.

[g]Average of three results, 21-29-27; no systematic variation with pH.

[h]Strontium analysis by flame photometer.

[i]Strontium in the organic (analysis by direct count) exceeded the theoretical equivalence of the D2EHP; hence the sodium distribution and separation factor could not be calculated from the material balance..

[j]Average of three results, 32-45-32; no systematic variation with pH.

[k]Average of two results agreeing within 4%; no systematic variation with pH.

Acidic Solutions. Strontium distributions to D2EHP from slightly acidified $NaNO_3$ solutions were measured, primarily to determine the minimum pH at which the dialkylphosphoric acid would be sufficiently ionized to have significant cation exchange capacity. The distribution coefficients dropped to low values in the region of pH 3 and below (Fig. 1.4). Instead of a simple drop-off from the alkaline-side values, however, the extraction coefficient rose to a maximum more than an order of magnitude higher in the region of pH 5. Only strontium was analyzed in these tests (as also in all the tests described above), and, since here the organic phase contained both Na^+ and H^+, material balance calculations were not sufficient to determine the distribution coefficients of either. Hence separation factors cannot yet be calculated, and only the distribution coefficients for strontium are shown in Fig. 1.4. It is obvious, however, since the Na^+ concentration was nearly constant in the aqueous phase, and must have decreased in the organic phase as the aqueous pH was changed from 8 to 5, that the strontium sodium separation factor increased even more than did the strontium distribution coefficient.

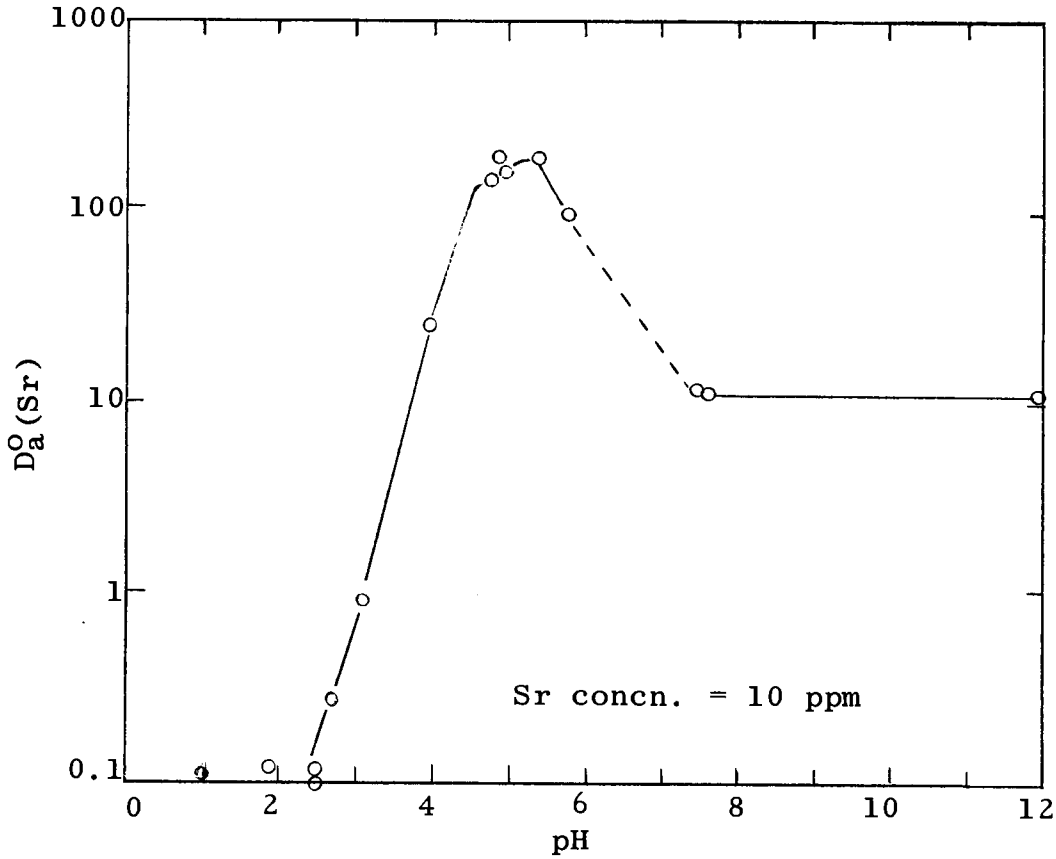
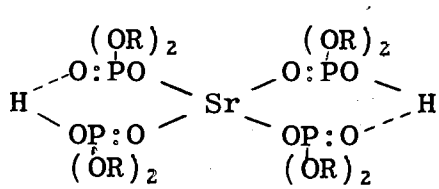


Fig. 1.4. Effect of Aqueous pH on the Distribution Coefficient of Strontium between ~0.5 M $NaNO_3$ aqueous solution and 0.1 M sodium di(2-ethylhexyl)phosphate solution in Amsco 125-82.

It is suggested that the high extraction power resulted from formation of a complex analogous to the $UO_2X_4H_2$ complex involved in uranyl extraction.* The structure might be



which is one of the structures suggested for the uranyl complex. The distribution behavior shown in Fig. 1.4 would then be explained as follows: The proportion of the chelate complex is highest at

*C. F. Baes, Jr., et al., "The Extraction of Uranium(VI) from Acid Perchlorate Solutions by Di(2-ethylhexyl)phosphoric Acid in n-Hexane," to be published in J. Phys. Chem., expected Jan., 1958.

pH ~5, with favorable concentrations of both ionized and un-ionized organic acid. At higher pH's there is less un-ionized organic acid available for formation of the hydrogen bonds, until in alkaline solution only the simple salt

$$(RO)_2\overset{O}{\overset{\|}{P}}O\text{-}Sr\text{-}O\overset{O}{\overset{\|}{P}}(OR)_2$$

can be formed. At lower pH's the direct competition by H^+ rapidly becomes important, until the organic acid is completely un-ionized. This hypothesis suggests that reagents of different acid strength might give high extraction of Sr^{++} and similar cations at other pH's, and that some bifunctional reagent might form a similar complex even in contact with alkaline solutions.

1.4 M^+-H^+ and M^{++}-H^+ Exchange in Monododecylphosphate (J. M. Schmitt)

Equilibrations of 0.5 N alkali and alkaline earth nitrate solutions with 0.1 M solutions of monododecylphosphoric acid (DDPA) in kerosene showed considerable extraction of those cations even at pH <2:

Cation	Final pH	Cation Concn. in Extract N	Cation Concn. in Extract % of Max.
Li^+	1.8	0.014	14
Na^+	1.7	0.020	20
K^+	1.7	0.018	18
Cs^+	1.9	0.021	21
Sr^{++}	1.5	0.025	25
Ba^{++}	1.5	0.031	31

These preliminary tests were made by equilibrating each neutral 0.5 N salt solution with an equal volume of 0.1 M DDPA in the acid form. The resulting pH of the aqueous phase was measured, and the normality of the extracted cation was determined by titration of the remaining free acid in the organic phase. The "maximum cation concentration in extract" referred to in this tabulation is 0.1 N for the 0.1 M DDPA; i.e., it is assumed that only the stronger of the two ionizable hydrogens was replaced to any significant extent.

While it has not appeared feasible to use monoalkylphosphoric acids diluted with hydrocarbons for cation exchange at high pH, since no suitable means has been found to prevent separation of a third phase, finding this degree of extraction at such low pH suggests that they may provide cation exchange over a useful range of slightly acidic solutions.

2.0 PROCESS DEVELOPMENT

2.1 Comparison of Uranium Extraction Isotherms (W. D. Arnold)

Isotherms were determined for extraction of uranium from synthetic Marysvale liquor with a new amine, Amberlite LA-2, submitted by Rohm and Haas and a new sample of di(tridecyl)amine which was from a pilot-scale batch produced by Carbide. The amines were tested at 0.10 M concentration in both kerosene and kerosene-tridecanol diluents (Table 2.1).

In comparison to Rohm and Haas 9D-178 amine (ORNL-2306, Table 2.1), LA-2 amine in kerosene diluent showed better selectivity with respect to ferric iron and approximately 20% higher uranium loading. Extraction coefficients, however, were lower by a factor of about 5 and phase separation was very sluggish, particularly in tests where the uranium loading of the solvent was low. Phase separation was considerably improved in 97% kerosene--3% tridecanol diluent, although still not rapid. Addition of the alcohol slightly increased the uranium extraction coefficients. This is in contrast to the performance of 9D-178 and S-24 amines where the presence of alcohol appreciably depresses uranium extraction (ORNL-2269, sec. 2.2).

Extraction results with di(tridecyl)amine in kerosene and 95% kerosene--5% tridecanol diluents were very similar to those obtained with the previous sample of di(tridecyl)amine (ORNL-2306, Table 2.2). In kerosene diluent the iron selectivity was relatively poor, but addition of 5% alcohol lowered the iron extraction to a level comparable to that of 9D-178 amine in kerosene. Uranium coefficients were appreciably increased, because of decreased competition by iron, and phase separation was improved by alcohol addition.

In preliminary tests both amine samples showed good compatibility with molybdenum liquors. The molybdenum compatibility tests are continuing.

2.2 Phosphate Content of Amex Vanadium Products (F. J. Hurst)

The phosphorus specification for commercial vanadium products is extremely low, i.e., <0.05% P based on contained V_2O_5. Since Western ore leach liquors ordinarily have a P/V_2O_5 ratio greatly in excess of this value, a useful vanadium recovery method must achieve a favorable separation from phosphate in the processing sequence. This problem is being investigated with respect to application of both Amex and Dapex to vanadium recovery. Preliminary results relating to the Dapex system were reported previously (ORNL-2399). Studies in the Amex system showed phosphate extraction at higher than the allowable amounts, but also showed sufficient separation in "red cake" precipitation to produce specification product.

Extraction of Phosphate with Amines. Phosphate was extracted by a 0.1 M solution of tri-iso-octylamine in 97% kerosene--3% tridecanol diluent from 0.5 M sulfate solutions (pH 1.8) containing 1, 2, and 5 g of phosphate per liter as follows:

Table 2.1 Uranium Extraction Isotherms

Aqueous: synthetic Marysvale liquor (0.15-3.0 g U, 5.8 g Fe(III), 3.3 g Al, 50 g SO_4, 2.0 g PO_4, and 1.7 g F per liter; pH 0.9)

a/o phase ratio = 2/1; 5 min contact time; 25°C

Amine (0.10 M)	Diluent	Phase Sep'n Time, sec	U, g/liter Head Liquor	U, g/liter Organic	U, g/liter Aqueous	Fe in Organic, g/liter	U Extraction Coefficient (E_a^o)
LA-2	Kerosene	>600	0.15	0.29	0.008	0.13	37
		>600	0.30	0.58	0.018	0.12	32
		240	0.60	1.15	0.045	0.10	26
		200	1.0	1.9	0.089	0.088	21
		120	1.25	2.4	0.126	0.068	19
		100	1.5	2.7	0.174	0.049	16
		85	2.0	3.7	0.32	0.037	12
		75	3.0	4.2	0.94	0.014	4
	97% kerosene--3% tridecanol	75	0.15	0.28	0.007	0.077	40
		90	0.30	0.57	0.016	0.070	36
		90	0.60	1.13	0.040	0.060	28
		90	1.0	1.8	0.077	0.047	23
		90	1.25	2.2	0.11	0.037	20
		90	1.5	2.7	0.16	0.031	17
		90	2.0	3.3	0.32	0.024	10
		70	3.0	4.2	0.91	-	5
Di(tridecyl) (compound 227B)	Kerosene	80	0.15	0.31	0.0040	1.1	77
		80	0.30	0.63	0.0087	0.90	73
		90	0.60	1.2	0.020	0.77	60
		85	1.0	2.0	0.043	0.55	47
		120	1.25	2.3	0.073	0.43	32
		120	1.5	2.9	0.099	0.31	29
		120	2.0	3.7	0.23	0.14	16
		100	3.0	4.3	0.90	0.03	5
	95% kerosene--5% tridecanol	70	0.15	0.32	0.0024	0.37	130
		45	0.30	0.63	0.0052	0.33	120
		55	0.60	1.2	0.011	0.26	110
		55	1.0	2.0	0.023	0.18	87
		60	1.25	2.4	0.045	0.13	53
		60	1.5	2.9	0.072	0.091	40
		75	2.0	3.6	0.20	0.038	18
		70	3.0	4.4	0.98	0.015	4

PO_4, g/liter			Phosphate Extraction Coefficient
Head Aqueous	Organic	Aqueous	(E_a^o)
1.0	0.017	1.0	0.017
2.0	0.036	2.0	0.018
4.9	0.073	3.0	0.015

a/o phase ratio = 3/1

Although the phosphate extraction coefficient was only about 0.015, the amounts of phosphate extracted were relatively large in terms of the amounts allowable.

With V(V) added to the system, much larger amounts of phosphate were extracted by both tri-iso-octyl and S-24 amines (Table 2.2). As expected, the P/V_2O_5 ratio in the extract increased with increase in phosphate content of the head solution. With the head solution containing 5 g of phosphate per liter, this ratio remained approximately constant at about 2.2 wt % (V/P mole ratio of about 15) over a fairly wide range of vanadium loadings. This suggests that the bulk of the phosphate was extracted as complex phosphovanadates. Complexes of the form $P(V_3O_4)_4^{7-}$ have been reported in the literature.*

Since phosphate forms complexes with Fe(III) and aluminum, less phosphate extraction might be expected from ore leach liquors than from the pure solutions used in the above tests. This was the case in tests in which the same amine solutions were used to extract vanadium from a synthetic leach liquor (0.5 M SO_4, pH 1.8) containing 3 g V(V), 3 g Fe(III), 3 g Al, and 1.1 or 2.2 g PO_4 per liter:

Amine	PO_4 in Head Aqueous, g/liter	V, g/liter		PO_4, g/liter		P/V_2O_5 in Extract, Wt %
		Organic	Aqueous	Organic	Aqueous	
S-24	1.1	7.1	0.55	0.074	1.1	0.19
	2.2	6.9	0.52	0.10	2.0	0.27
tri-isooctyl	2.2	7.4	0.43	0.10	2.0	0.24

a/o phase ratio = 3/1

Phosphate extraction from the leach liquors was a factor of 3-6 lower than from the pure vanadium solutions of comparable phosphate content. However, the P/V_2O_5 ratios of 0.19 wt % (1.1 g of phosphate per liter in the liquor) and ~0.25 wt % (2.2 g of phosphate per liter in the liquor) are still far above the specification limit.

*Freidheim and Michaelis, Z. Anorg. Chem. 5, 437 (1894).

Table 2.2 Extraction of Vanadium and Phosphate with Amines

Diluent: kerosene for S-24; 97% kerosene--3% tridecanol for tri-iso-octylamine
Aqueous: 3 g V(V)/liter, 0.5 M SO_4, indicated PO_4 concentration; pH 1.8
a/o phase ratio = 3/1; 15 min contact time

Amine (0.1 M)	Stage	PO_4 in Head Aqueous, g/liter	V, g/liter		PO_4, g/liter		Extract P/V_2O_5, wt %
			Organic	Aqueous	Organic	Aqueous	
S-24	1	1	7.4	0.56	0.23	0.94	0.6
	1	2	7.4	0.58	0.46	1.9	1.1
	1*	5	7.4	0.50	0.88	4.8	2.2
	2*	5	12.0	1.2	1.52	4.7	2.3
	3*	5	12.4	2.9	1.48	5.1	2.2
Tri-iso-octyl	1	1	7.2	0.40	0.40	0.92	1.0
	1	2	7.8	0.40	0.70	1.8	1.7
	1*	5	8.0	0.36	1.14	4.6	2.6
	2*	5	13.6	1.0	1.70	4.9	2.3
	3*	5	14.0	2.8	1.66	5.0	2.2

*Three-stage test in which organic was cascaded against three successive volumes of fresh aqueous (a/o = 3/1 in each contact).

Thus, it is apparent that, in treating liquors of this or higher phosphate content, some separation from phosphate must be achieved in operations subsequent to extraction.

The relative rates of vanadium and phosphate extraction from the synthetic liquor (1.1 g of phosphate per liter) were studied with 0.10 M S-24 amine in kerosene.

Contact Time,* min	V, g/liter		PO_4, g/liter		Extraction Coefficient (E_a^o)	
	Organic	Aqueous	Organic	Aqueous	V	PO_4
0.2	6.8	0.65	0.08	1.1	10	0.07
0.5	6.8	0.64	0.08	1.1	11	0.07
1	6.9	0.62	0.08	1.1	11	0.07
2	7.1	0.60	0.09	1.1	12	0.08
5	6.9	0.57	0.07	1.1	12	0.06
10	7.1	0.53	0.08	1.1	13	0.07
15	7.1	0.55	0.07	1.1	13	0.06

*Contacted by vigorous shaking in separatory funnels; a/o = 3/1.

Whereas extended contact times (~10-15 min) were required for maximum vanadium extraction, phosphate extraction apparently reached equilibrium in less than 0.5 min.

Scrubbing Phosphate from the Extract. Attempts to separate phosphate from vanadium by scrubbing the extract with dilute sulfuric acid were not very effective. Aliquots of an organic extract containing 7.9 g of V and 0.86 g of PO_4 per liter were scrubbed (o/a = 2/1) for 15 min with 1, 2, and 5% H_2SO_4 solutions and with 2% H_2SO_4--0.2 M $Fe_2(SO_4)_3$ solution. The last two solutions were the most effective but removed only about 25% of the phosphate from the solvent.

Separation from Phosphate During Product Precipitation. In the Amex vanadium process, the vanadium is stripped with sodium carbonate* solution and then recovered from solution by the conventional "red cake" precipitation. Any phosphate present in the extract reports to the strip solution along with the vanadium. To determine if some separation from phosphate would occur during precipitation of "red cake," a precipitation test was made with a strip solution obtained in a bench-scale continuous run. In this run 0.10 M S-24 amine in kerosene was used to extract vanadium from a synthetic liquor (0.5 M SO_4, pH 1.8) containing 3.5 g of V(V), 3 g of Fe(III), 3 g of Al, and 1.1 g of PO_4 per liter. The extract, which contained 9.1 g of V and 0.097 g of PO_4 per liter, was stripped with 0.35 M Na_2CO_3, yielding a pregnant strip solution with 37.8 g of V and 0.42 g of PO_4 per liter, i.e., P/V_2O_5 = 0.2 wt %. Approximately 15 ml of 6 M H_2SO_4 was added rapidly to

*Ammonium hydroxide has also shown promise as a stripping agent. However, this stripping method and methods for recovering vanadium from the strip solution have been only partially evaluated.

0.5 liter of strip solution at 90°C, lowering the pH to the isoelectric point (pH 2.3). The bulk of the vanadium precipitated immediately on addition of the acid. The precipitate was digested 2 hr at 90-95°C, during which time samples of the supernatant liquor were withdrawn and analyzed:

Time after Acid Addition, min	Analysis of Supernatant				Vanadium Precipitated, %
		g/liter			
	pH	V	PO_4	SO_4	
10	2.27	6.3	0.38	-	83
30	2.40	2.1	0.39	-	94
60	2.40	1.15	0.40	-	97
120	2.33	0.75	0.37	22	98

Vanadium continued to precipitate over the total digestion period, being 83% complete after 10 min and 98% complete after 2 hr. Very little phosphate was precipitated. The precipitate was filtered and washed* by repeatedly reslurrying in hot water and refiltering. Analyses of the wash filtrates showed:

Wash	Analysis of Filtrate			
		g/liter		
	pH	V	PO_4	SO_4
1	2.52	0.70	0.34	21.
2	2.72	0.32	0.17	9.6
3	2.90	0.18	0.11	5.4
4	3.10	0.11	0.08	3.1
5	3.40	0.07	0.05	1.5

Wash: 100 ml of hot water (~18 g of V in the precipitate); cake slurried for 10 min and filtered

The phosphate removed during washing was equivalent to 0.02% P (based on the V_2O_5 in the precipitate) and apparently was primarily that phosphate present in the solution occluded on the precipitate. The washed precipitate was calcined at 600°C, giving a product containing 92% V_2O_5 and 5% Na. Based on its V_2O_5 content, the product also contained 0.02% P and 0.04% S and thus met specifications for both phosphorus (<0.05%) and sulfur (<0.15%). Only about 10% of the phosphate in the strip solution carried through into the product.

Since the separation from phosphate during precipitation is favorable, it appears that, unless the phosphate concentration of the feed liquor is inordinately high, the Amex process should yield vanadium products of acceptable phosphorus content. Consequently, no further studies of this problem are planned.

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*Efficient washing is necessary in the "red cake" precipitation process to remove sulfate.

3.0 ENGINEERING STUDIES

3.1 Entrainment Studies of the Dapex Extraction Process (R. S. Lowrie)

The entrainment of solvent in raffinates obtained from the previously reported settler capacity measurements (ORNL-2306, -2399) was consistently less than 0.2 gal/1000 gal raffinate for water-in-oil type dispersions. For oil-in-water type dispersions it varied with the o/a phase ratio, decreasing from >2 gal/1000 gal at a ratio of 4/1 to 0.3 gal/1000 gal at 1/1.

The details of the equipment and operation were described in ORNL-2306 and -2399. The depth of each phase in the 6-in.-dia settler was approximately 8 in., resulting in a residence time of 5 min at a flow rate of 1 gpm/ft^2 for either phase. The depth of each phase in the 48-in.-dia settler was approximately 16 in., resulting in a residence time of 10 min at a flow rate of 1 gpm/ft^2. The initial method of measuring the solvent entrainment, which was used for the 48-in.-dia settler tests, was a modification of ASTM Standard Method D-322-35. A 1500-ml sample of the aqueous phase was steam distilled, and the solvent was collected in a calibrated condensate receiver. The method was suitable for measuring entrainment down to 0.2 gal of solvent/1000 gal of aqueous. As the studies progressed it was evident that the entrainment in many samples was too low to be accurately determined by the distillation method. A centrifugation method was developed and used for the 6-in.-dia settler tests. This method consisted of centrifuging 250-ml samples in a bottle with a neck calibrated in 0.01 ml per division. Tests with spiked samples indicated that the accuracy was $\pm$ 20% for samples containing as little as 0.04 gal of solvent per 1000 gal of aqueous. Aqueous entrainment in the solvent phase was determined by centrifugation of samples in calibrated cone-bottomed centrifuge tubes.

3.1.1 Solvent Entrainment in the 6-in.-dia Settler

In all water-in-oil type dispersions, at flow rates up to the flooding point of the settler, solvent entrainment was less than 0.04 gal/1000 gal of aqueous. For oil-in-water type dispersions solvent entrainment was low (<0.04 gal/1000 gal) at an a/o phase ratio of 1/1, but markedly higher at a phase ratio of 4/1:

Type of Dispersion	Phase Ratio (a/o)	Solvent Entrainment, gal/1000 gal
Oil in water	4/1	1.0
	1/1	<0.04
Water in oil	1/1	<0.04
	1/2	<0.04

The aqueous flow rate was 1.35 gpm/ft^2. Increasing the flow rate to flooding and raising the temperature from 25 to 50°C had no measurable effect on the entrainment except in the series with oil-in-water type dispersion at the higher a/o phase ratio of 4/1. Under these conditions, entrainment increased with increasing flow

rate at 25°C,

Aqueous Flow Rate, gpm/ft²	Solvent Entrainment, gal/1000 gal
1.35	1.0
2.70	2.2
4.35	3.8
5.40	6.2

and decreased with increasing temperature:

Temperature, °C	Solvent Entrainment, gal/1000 gal	
	1.35 gpm/ft²	4.35 gpm/ft²
15	2.0	5.6
25	1.0	3.8
35	0.6	2.6
50	0.4	1.6

For Dapex extraction of uranium from the average leach liquor, the cost of solvent lost by entrainment of 0.1 gal/1000 gal of raffinate would be less than 0.5¢ per pound of U_3O_8 processed. Thus, entrainment with the 6-in.-dia settler was significant only with the oil-in-water dispersions at the higher phase ratio.

3.1.2 Solvent Entrainment in the 48-in.-dia Settler

The solvent entrainment in the 48-in.-dia settler (Table 3.1) for water-in-oil type dispersions was consistently less than 0.2 gal/1000 gal of aqueous, which was the lower limit of the analytical method used. The entrainment for oil-in-water type dispersions was higher than the desired level of 0.1 gal/1000 gal, and was nearly independent of flow rate. It decreased with decreasing ratio of aqueous to organic, e.g., the average entrainment at a/o phase ratios of 4/1, 3/1, 2/1, and 1/1 was 2.2, 2.2, 1.4, and 0.3 gal/1000 gal, respectively.

In general the solvent entrainment data are in good agreement for the 6- and 48-in.-dia settlers. In both sizes the entrainment was less than 0.2 gal/1000 gal for water-in-oil type dispersions. For oil-in-water type dispersions the entrainment was dependent on the phase ratio, ranging from 0.1 to >2.0 gal/1000 gal as the a/o ratio was increased from 1/1 to 4/1.

3.1.3 Means of Recovering Entrained Solvent

Although the entrainment for oil-in-water type dispersions at an a/o phase ratio of 4/1 decreased with decreasing flow rate and increasing temperature, it still was greater than the desired goal of 0.1 gal/1000 gal. Preliminary tests indicated further recovery of the solvent from the aqueous raffinate as follows:

Prolonged Settling. In every case, additional static settling for 1.5 hr in a tank 18 in. deep reduced the entrainment to less than 0.1 gal/1000 gal.

Table 3.1 Solvent Entrainment in 48-in.-dia Settler

Phase Ratio (a/o)	Aqueous Flow Rate, gpm/ft^2	Solvent Entrainment, gal/1000 gal Oil-in-water Dispersion	Solvent Entrainment, gal/1000 gal Water-in-oil Dispersion
4/1	1.67	2.1	Not stable
	3.33	2.0	Not stable
	5.00	2.4	Not stable
3/1	1.25	2.3	< 0.2
	3.75	2.2	< 0.2
	5.00	2.2	< 0.2
2/1	1.67	1.1	< 0.2
	2.50	1.0	< 0.2
	3.33	1.7	< 0.2
	5.00	1.6	< 0.2
1/1	0.83	0.4	< 0.2
	1.25	0.3	< 0.2
	1.67	0.2	< 0.2
	2.08	0.5	< 0.2
	2.50	0.2	< 0.2
1/2	0.42	0.3	< 0.2

Wire Mesh Packing. It was previously shown (ORNL-2399) that wire-mesh packing* increased fourfold the capacity of a settler operating with water-in-oil type dispersion but had little effect on capacity with oil-in-water type dispersions. The solvent entrainment (Table 3.2) for oil-in-water type dispersions at an a/o ratio of 4/1 was significantly lower when wire mesh packing was used, although it was still above the desired level of 0.1 gal/1000 gal of aqueous. The entrainment was less in all other cases except the water-in-oil type dispersions when the dispersion stream entered in the center of the packing. In these tests the entering dispersion stream apparently impinged on the wire mesh with sufficient force to form numerous very small oil droplets, which were swept out of the settler in the aqueous stream. In all cases of high entrainment, subsequent static settling decreased the entrainment to the desired level or lower.

3.1.4 Aqueous Entrainment in the Solvent

The entrainment of aqueous solution in the solvent phase is not an important economic factor, but is of interest because carryover of entrained feed liquor in the extract stream (when not scrubbed) contaminates the stripping circuit and the uranium product.

*Yorkmesh mist eliminator, a woven stainless steel packing with 97% void volume and approximately 125 ft^2 surface area per cubic foot; manufactured by Otto H. York Co., East Orange, N. J.

Table 3.2 Effect of Wire Mesh Packing on Solvent Entrainment in 6-in.-dia Settler

Type of Dispersion	Phase Ratio (a/o)	Aqueous Flow Rate gpm/ft^2	Packing*	Solvent Entrainment, gal/1000 gal
Oil in water	4/1	5.4	None	6.2
		5.4	A	2.4
		5.4	B	2.5
	1/1	1.35	None	0.04
		1.35	A	0.04
		1.35	B	0.04
Water in oil	1/1	1.35	None	0.04
		1.35	A	0.04
		5.4	A	0.04
		1.35	B	0.24
		5.4	B	0.60
	1/2	1.35	None	0.04
		1.35	A	0.04
		2.70	A	0.04
		1.35	B	0.16
		2.70	B	0.20

*A: Two 3-in. sections of wire mesh positioned 4 in. apart with the dispersion stream entering the space between the sections.

B: One 6-in. section of wire mesh with the dispersion stream entering in the center.

In all tests the aqueous entrainment was less than 1 vol % of the solvent. For a typical installation where the ratio of feed liquor to extract is 4/1, an entrainment of 1 vol % would result in a ratio of each contaminant to uranium in the extract of 1/400 of that in the feed liquor. For the average mill liquors and the present uranium product specifications, this amount of contamination would be unimportant.

3.2 Effect of Liquor pH on Settler Capacity

The previously reported correlation of settler capacity with aqueous flow rates for the Dapex extraction system (ORNL-2399) was made with a uranium barren aqueous phase containing 70 g of sulfate per liter at a pH of 0.5. Since the pH of many leach liquors is about 1, the settler capacity was measured with a similar sulfate liquor at pH 1.0 (Table 3.3). There was virtually no difference in the settler capacity, as indicated by the dispersion band thickness, at the higher pH.

Table 3.3 Effect of Liquor pH on Settler Capacity

Type of Dispersion	Phase Ratio (a/o)	Aqueous Flow Rate gpm/ft^2	Dispersion Band Thickness, in. pH 1.0	pH 0.5*
Oil in water	4/1	1.35	0.3	0.3
		4.35	4.3	4.5
		5.4	7.8	7.8
	1/1	0.68	1.0	0.9
		1.35	5.0	4.6
Water in oil	1/1	1.35	2.3	2.0
		2.02	9.0	8.5
	1/2	1.35	2.5	2.8
		1.83	7.5	6.5

*From Fig. 3.1 in ORNL-2399.

4.0 FUNDAMENTAL STUDIES

4.1 Determination of Molecular Weights of Amine Species in Benzene Solution by Light Scattering (K. A. Allen)

In continued light-scattering measurements, a standard scattering ratio was measured for benzene, which is characteristic of the equipment under the exact conditions used for measurements on solutions. Previously, an individual value of this ratio was obtained for each series of measurements as the zero-concentration intercept (b) of the extrapolated scattering--vs.--concentration curve (ORNL-2380, p. 33). Use of carefully standardized equipment conditions and the corresponding precisely measured benzene scattering ratio should improve the accuracy of the molecular weight determinations, and may also permit further interpretation of those scattering curves which show changes of slope at some concentrations. The standard scattering ratio was evaluated by repeated light measurements at the 0, 90, 45, and 135° positions with a sample of benzene that was filtered initially and refiltered several times during the course of the measurements. The resulting set of 26 scattering ratios, i_{90}/i_0, averaged 0.8726 $\pm$ 0.0008 (90% deviation).

The light scattering by the normal sulfates of Amine S-24 (bis-(1-isobutyl-3,5-dimethylhexyl)amine) and methyldi-n-octylamine (MDOA) (Fig. 4.1) gave average molecular weights indicating aggregation numbers of, respectively, ~4 and 8-10:

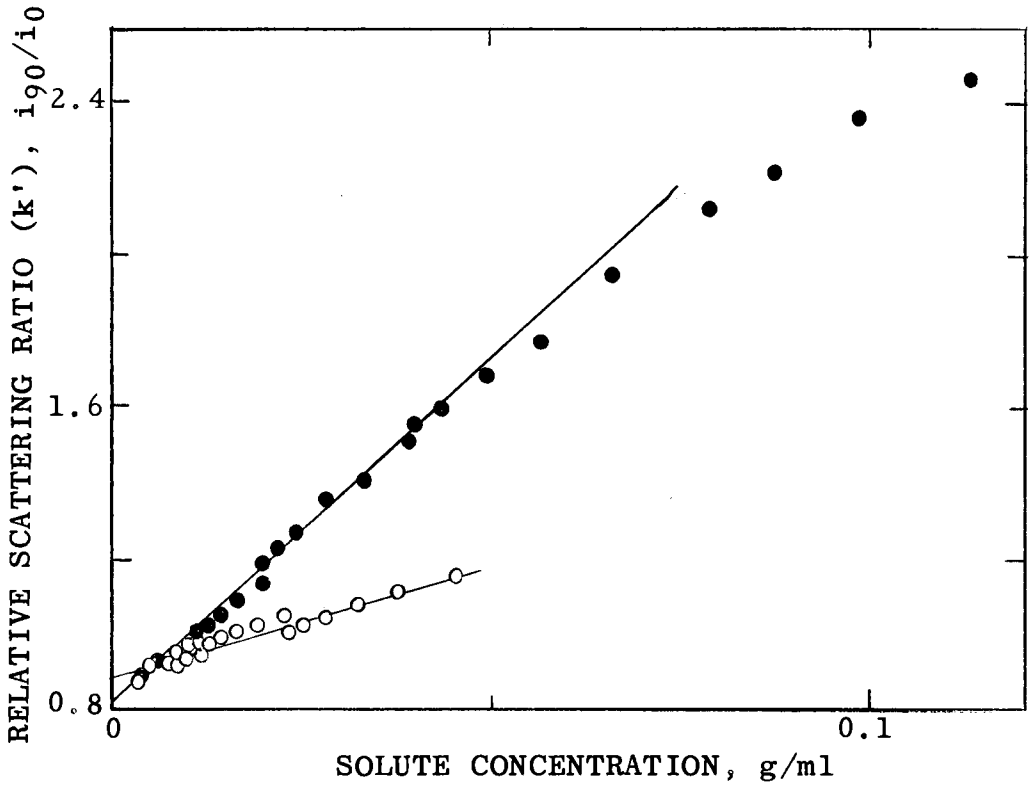

Fig. 4.1. Change of Relative Light Scattering with Change of Solute Concentration.

Solute:	S-24	MDOA
Monomeric weight	877	826
Moles H_2O/mole SO_4	2.7	~10
$\partial n/\partial c$	-0.0580	-0.0728
Slope (Fig. 4.1)	5.5	16-20
Depolarization	negl.	negl.
Molecular weight	3600	6800-8300
Aggregation No.	4	8-10

The monomeric weights were calculated from the experimental neutral equivalents (365 and 270 as compared with the nominal equivalent weights of 354 and 255) and the measured water contents (see below).

The previous evaluation of an aggregation number for N-benzylheptadecylamine normal sulfate was not confirmed in remeasurements, even within the large uncertainty reported (15-20). The uncertainty was due to the slope of the scattering curve (ORNL-2443, Fig. 4.4) being so low that a small error in measurement of the slope caused a large error in the estimated molecular weight. The subsequent measurements showed that the incremental

light scattering with this solute was too small relative to accidental variations for reproducible evaluation of the slope, and hence of the average molecular weight and the aggregation number.

The benzene solutions of some of the amine sulfates contain a considerable amount of water when prepared by equilibration with aqueous sulfuric acid. Water contents of the amine salt solutions previously examined were determined by Karl Fischer titration (corrected for the solubility of water in benzene, taken as constant). Both the monomeric molecular weights and the solute concentrations (c, g/ml) were recalculated for the amine salts previously reported. The average molecular weights were changed slightly by the correction, but the aggregation numbers were not changed since the changes in the monomeric molecular weights and in the average molecular weights came close to canceling each other. The water contents found, expressed as moles H_2O/mole SO_4, were approximately: di-n-decylamine sulfate, 2; tri-n-octylamine sulfate, 4; tri-n-octylamine bisulfate, 1; 1-(3-ethylpentyl)-4-ethyloctylamine sulfate, 8; bis(1-isobutyl-3,5-dimethylhexyl)amine sulfate, 3; methyldi-n-octylamine sulfate, 10; n-benzylheptadecyl-amine sulfate, 0.3.