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ORNL-2486
Technology-Raw Materials

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PROGRESS REPORT ON RAW MATERIALS

FOR DECEMBER, 1957

K. B. Brown

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Report Number: ORNL-2486

Contract No. W-7405, eng 26

CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT ON RAW MATERIALS FOR DECEMBER, 1957

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

DATE ISSUED
APR 17 1958

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ABSTRACT

Systematic Studies. In extraction of uranyl sulfate by kerosene solutions of N-benzylheptadecylamine (NBHA) from 1 M sulfate at pH 1, the extraction coefficient varied with a power between 1 and 1.5, and in extraction from 3 M sulfuric acid solution with the first power of the uncomplexed amine concentration. Extraction decreased with increasing sulfate concentration, but extraction coefficients were still high (>300 with 0.1 M NBHA) from 4 M $(NH_4)_2SO_4$-H_2SO_4 solutions when the H_2SO_4 content was 0.5 M or less, dropping to ~1 at 3 M. With 4 M H_2SO_4 the amine solutions separated into two phases.

In continued tests of strontium-sodium exchange between di(2-ethylhexyl)phosphate and aqueous solutions, the strontium extraction enhancement at pH ~5 over that at higher or lower pH's previously reported from nitrate solutions was also found from acetate solutions. An extraction isotherm from acetate buffer solution was consistent with the previously postulated complex formation, and showed that the enhancement is not limited to trace strontium.

Tracer cesium extractions confirmed the preferential extraction of sodium over cesium by D2EHP from nitrate solution at pH 4-11.

Process Development. In a continuous Amex run demonstrating the ammonium nitrate stripping flowsheet, >99.9% of the uranium and ~96% of the molybdenum were recovered from a synthetic leach liquor containing 3.5 g of uranium and 0.12 g of molybdenum per liter. Stripping of uranium was 99.9% complete, yielding a strip solution containing 30 g of uranium and 0.1 g of molybdenum per liter. Consumption of nitrate was 0.25 lb/lb of U_3O_8. Molybdenum, which tended to accumulate in the regeneration system, was sorbed from the uranium-barren ammonium nitrate solution (produced by regenerating the amine with ammonium hydroxide) on an ion exchange resin column; it was eluted with dilute caustic with difficulty. Control and physical operation of the regeneration system was satisfactory, although high entrainment of ammonium nitrate solution in the organic recycle stream is a potential process problem.

Molybdenum was recovered effectively from Amex nitrate strip solutions by adsorption on activated carbon, which was still far from saturation at a molybdenum loading of 220 g/kg of carbon. The molybdenum was readily eluted with dilute ammonium hydroxide, using 0.4 lb NH_3 per pound of molybdenum. Evaporation of the eluate and calcination gave a molybdenum product containing >99.9% MoO_3.

The rate of phase separation of amine solutions when contacted with leach liquors containing dissolved silica was dependent on a number of variables, including silica concentration, amine-diluent choice, amine concentration, liquor pH, temperature, and the type of mixing. When mixing was with the organic as the continuous phase, separation times were not appreciably affected by silica, but with aqueous-continuous mixing, separations slowed with increase in silica concentration, the effect being much more pro-

nounced for some amine-diluent combinations than for others. Of the amines tested, ditridecyl amine was affected least by the presence of silica. With 9D-178 amine (aqueous-continuous mixing), separation times decreased markedly with increase in temperature or decrease in solution pH but were not greatly affected by change in amine concentration in the range 0.0-0.1 M.

Engineering Studies. Phase separation in the extraction step of the Amex process (0.1 M Rohm and Haas Amberlite LA-1 in kerosene) was evaluated in 6- and 48-in.-dia gravity settlers. The flow capacity based on cross-sectional areas was the same for both sizes, demonstrating the feasibility of simple scaleup.

The nominal aqueous flow capacity for oil-in-water type dispersions was 0.8 gpm/ft^2 at a phase ratio of 1/1 and 2.9 gpm/ft^2 at 4/1. For water-in-oil type dispersions the aqueous flow capacity was 0.4. gpm/sq ft at a/o phase ratio of 1/1 and 1/2. Modification of the kerosene diluent with 3% tridecanol increased the flow capacity for water-in-oil type dispersions from 0.4 to 0.7 gpm/ft^2. No change was noted for oil-in-water type dispersions.

Entrainment of solvent in the aqueous phase after the primary break was low (0.04 to 0.1 gal/1000 gal) for water-in-oil type dispersions. For oil-in-water type dispersions the entrainment was 0.04-0.3 gal/1000 gal at an aqueous/organic phase ratio of 1/1 and was 1.0-3.0 at a ratio of 4/1.

In scouting tests to find methods of increasing the rate of phase separation dispersions were effectively coalesced by glass filter cloth, wire cloth, or application of an electrical potential.

Fundamental Studies. Isopiestic measurements of the concentration of solute particles in the di(2-ethylhexyl)phosphoric acid--tri-n-octylphosphine oxide--n-octane system gave qualitative corrobortion of adduct formation as previously reported on the basis of spectrophotometric data. The method appears suitable for quantitative testing of the formation constants previously derived.

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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¢)	July,	ORNL-2388	(75¢)
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March,	ORNL-2306	(25¢)	September,	ORNL-2443	($1.25)
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May,	ORNL-2366	(25¢)	November,	ORNL-2466	($1.00)
June,	ORNL-2380	($1.00)			

This is the last report in this series.

1.0 SYSTEMATIC STUDIES
Problem Leader: C. F. Coleman

1.1 Uranyl Sulfate Extraction with N-Benzylheptadecylamine (J. G. Moore)

Dependence of Extraction Coefficient on NBHA Concentration. As previously noted (ORNL-1922, -1959, -2099, -2380), N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine (N-benzylheptadecylamine, NBHA) and some other similar N-benzyl amines extract uranium from sulfate solutions with extraction coefficients an order of magnitude higher than those obtained with other amines. The resulting raffinate uranium concentrations are often too low for dependable analysis in extraction tests of the usual scale, so that a satisfactory measurement of the variation of extraction coefficient over a range of amine concentrations has not been available. The use of large volumes of aqueous solution permitted better calculation of the extraction coefficients in a series of batch equilibrations over the range 10^{-4} - 10^{-1} M amine, although there was still considerable experimental scatter.

The extraction coefficients from 1 M sulfate solution of pH 1 varied approximately linearly with the estimated uncomplexed amine concentration in kerosene (Fig. 1.1). Comparison of the experimental points with lines drawn at slopes 1 and 1.5 indicates that the power dependence was between those limits, i.e., $E_a^o \propto [\text{Amine}]^{1-1.5}$. The concentration of uncomplexed amine was calculated on the basis of six amines complexed with each uranium atom, which is the limiting ratio indicated at high uranium loadings and which also gave the best correlation throughout the range of the present tests. The scatter of the lower points in Fig. 1.1 resulted mainly from uncertainty in calculation of the very low uncomplexed amine concentrations by difference between larger numbers, while the scatter of the higher points resulted mainly from uncertainty in the very low raffinate analyses.

Coefficients for uranium extraction from 3 M H_2SO_4 solution fell close to a line drawn at slope 1. Since the extractions were much lower from this solution, there was no unusual degree of uncertainty in the calculation of either the extraction coefficients or the uncomplexed amine concentrations.

The unit slope lines correspond to linear equations for the uranium extraction coefficient, $E_a^o = 3\times10^5$ [M(uncomplexed amine) - 6 $M(U)_{org}$] from the 1 M sulfate, pH 1, solution and $E_a^o = 40$ [M(uncomplexed amine) - 6 $M(U)_{org}$] from the 3 M H_2SO_4 solution.

One liter of the 1 M sulfate solution at pH 1 was used in each extraction test, instead of the 10-25 ml generally used when there is no unusual analytical problem. The initial uranium concentration was varied from 10 to 100 mg/liter. The amine solution (0.001 to 0.1 M NBHA, pre-equilibrated with 1 M sulfate solution at pH 1) volumes, 20-1000 ml, were chosen to give three levels of uranium loading. The final amine/uranium ratios in the organic phases were near 6/1, near 12/1, and over 24/1. Uranium was stripped from the extracts with sodium carbonate solution for potentiometric or colorimetric analysis. Raffinates were filtered and extracted with

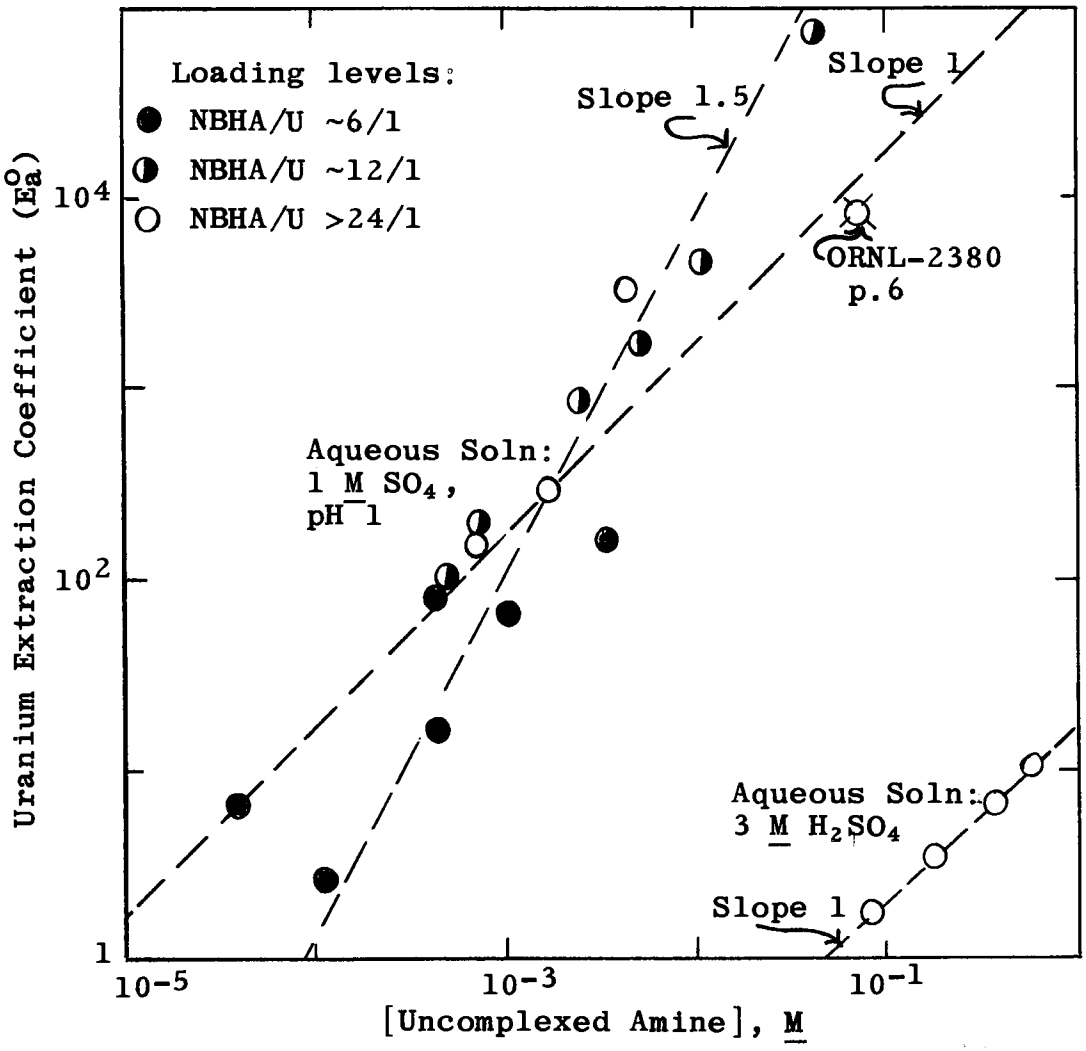

Fig. 1.1. Dependence of Uranium Extraction Coefficient on Concentration of Uncomplexed N-Benzylheptadecylamine in Kerosene.

NBHA, and the uranium was then stripped with nitrate solution, with an overall concentration factor of 100, for colorimetric analysis. All analytical discard solutions were checked for residual uranium by fluorimetric analysis.

No unusual extraction conditions were required for the extractions from 3 M H_2SO_4 solution.

Extraction from High Sulfate Solutions. Uranium extraction by amines from sulfate solution is impaired by both increasing sulfate concentration and increasing acidity. Extraction from, for example, 2 M H_2SO_4 solution is low with most of the available amines. In brief studies, extraction with NBHA from such solution showed useful extraction coefficients in the range up to 3 M H_2SO_4 and to at least 4 M sulfate.

Extraction coefficients with 0.1 M NBHA were high from 4 M ammonium sulfate--sulfuric acid solutions when the acid concentration was 0.5 M or less (Fig. 1.2). They dropped sharply at higher

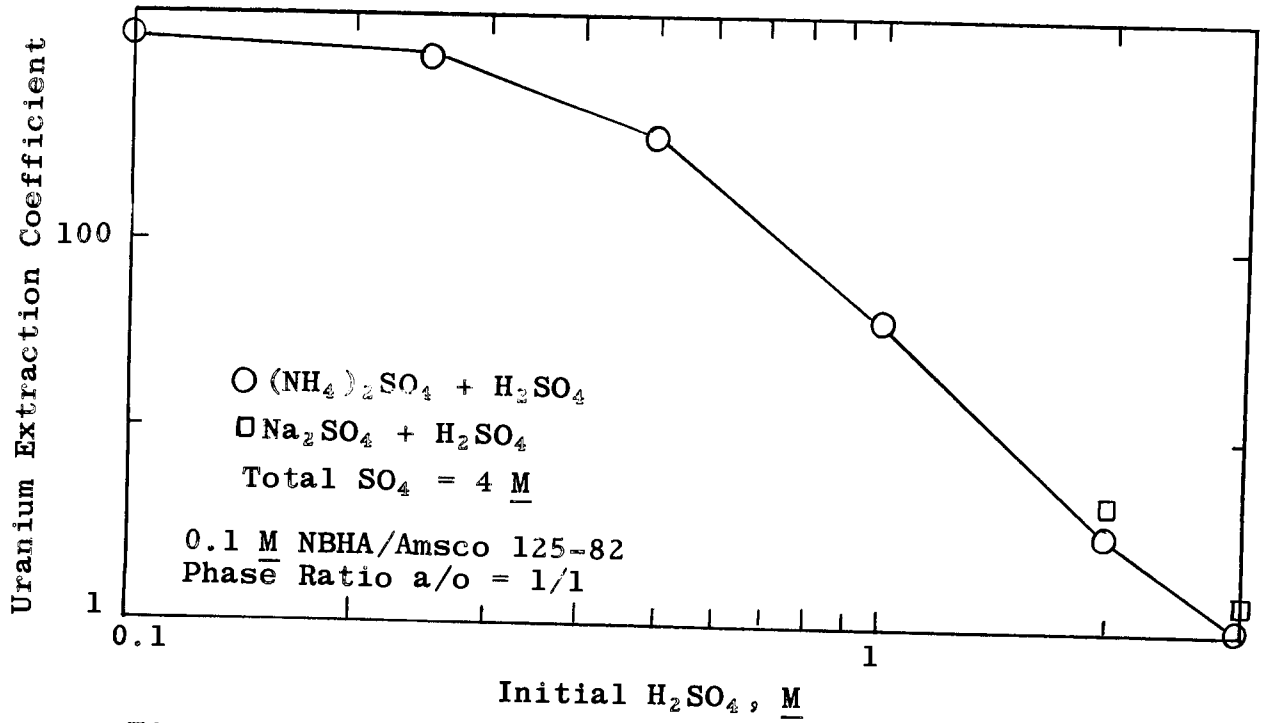

Fig. 1.2. Effect of Acidity on Uranium Extraction from 4 M Sulfate Solution by 0.1 M NBHA.

acidities, to ~1 at 3 M H_2SO_4. The extraction coefficients were about 50% higher when sodium instead of ammonium sulfate was used in combination with 2 and 3 M H_2SO_4.

The extraction coefficient with 0.1 M NBHA was 15 from 2 M H_2SO_4 without any added sulfate, and 2 from 3 M. A third phase separated on contact with H_2SO_4 at 4 M and higher. No third phase was found on contact with H_2SO_4 at 3 M or less even when the amine concentration was raised to 1 M (Amsco 125-82 diluent, phase ratio a/o = 1/1, room temperature). The organic phase was increasingly viscous at the higher concentrations, and phase separation was slow.

The extraction coefficients from 3 M H_2SO_4 solution increased from 2 at 0.1 M to 10 at 0.6 M initial NBHA concentration (see Fig. 1.1). Phase separation was rapid at 0.1 and 0.2 M but slow at 0.4 and 0.6 M amine. The conditions were an a/o phase ratio of 1/1 and room temperature.

1.2 Comparison of Tri-n-octylphosphine Oxide Batches (J. M. Schmitt, C. A. Blake)

Continuing the tests described in ORNL-2443, p. 9, three new batches (406, 407, 409) of tri-n-octylphosphine oxide from Distillation Products, Inc., were examined. Each new sample contained approximately 0.2% free acidity and had Karl Fischer titers of 0.02 eq/mole, but differed widely in combined acidity (Table 1.1). The high level of combined acidity is reflected in high uranium extraction coefficients, compared to those with batch OP 401, a reagent with low total combined and free acidity.

Table 1.1 Comparison of Tri-n-octylphosphine Oxide Batches

Physical Properties

Batch No.		Melting Point, °C	Acidity[a], %		Karl Fischer Titer, eq/mole	U Extraction Coefficient (o/a)[b]			
						Aq: 0.1 M NO_3, pH 1; Diluent CCl_4	Aq: 0.5 M SO_4, 0.3 M NO_3, pH 1		Aq: 1.4 M PO_4, 0.3 M NO_3, pH 1; Diluent CCl_4
ORNL	DPI		Free	Combined			Diluent CCl_4	Diluent Kerosene	
406	Lot 2	-	0.17	3.6	0.02	400	35	120	0.2
409	Lot 3	54.5-55	0.20	0.67	0.02	370	49	190	0.3
407	-	-	0.22	6.0	0.02	800	76	---	0.4
401		51.5-52	<0.02	<0.05	0.04	180	15	70	0.1

[a]Free acidity determined by titration with aqueous NaOH; combined acidity (material oxidizable and/or hydrolyzable to free acid) determined iodometrically (ORNL-1964, p. 106); both reported as dioctylphosphinic acid, $(C_8H_{17})_2PO_2H$.

[b]Uranium extraction coefficient by 0.1 M phosphine oxide in indicated diluent from aqueous phase containing 0.004 M U(VI). Aqueous/organic = 1/1 at room temperature.

Batch OP 406 will be purified further by the method described in ORNL-2399.

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

Strontium Extraction from Sodium Acetate Solution. High extraction of strontium by D2EHP from sodium nitrate solution in a narrow pH region near 5 was reported previously (ORNL-2466). Those tests were limited to low aqueous strontium concentrations, 10 mg/liter initially. In continuation of those tests at higher strontium concentrations, an extraction isotherm was measured at a pH near 5. A buffering anion was desired instead of nitrate for these tests in order to simplify the obtaining of identical equilibrium pH's in the separate extractions. Preliminary tests showed strontium extraction from sodium acetate solutions to be similar to that from nitrate solutions, with a maximum near pH 5. The distribution coefficients, D_a^o, decreased with increasing acetate concentration (suggesting an inverse cube dependence), but were sufficiently high from 1 M acetate or less for the comparative measurements.

Extraction Isotherm. Four extractions from 0.7 M sodium acetate--acetic acid solution at pH 5.1 with initial strontium concentrations from 0.01 to 5 mg/ml gave a typical extraction isotherm (Fig. 1.3), showing that the enhanced extraction power at

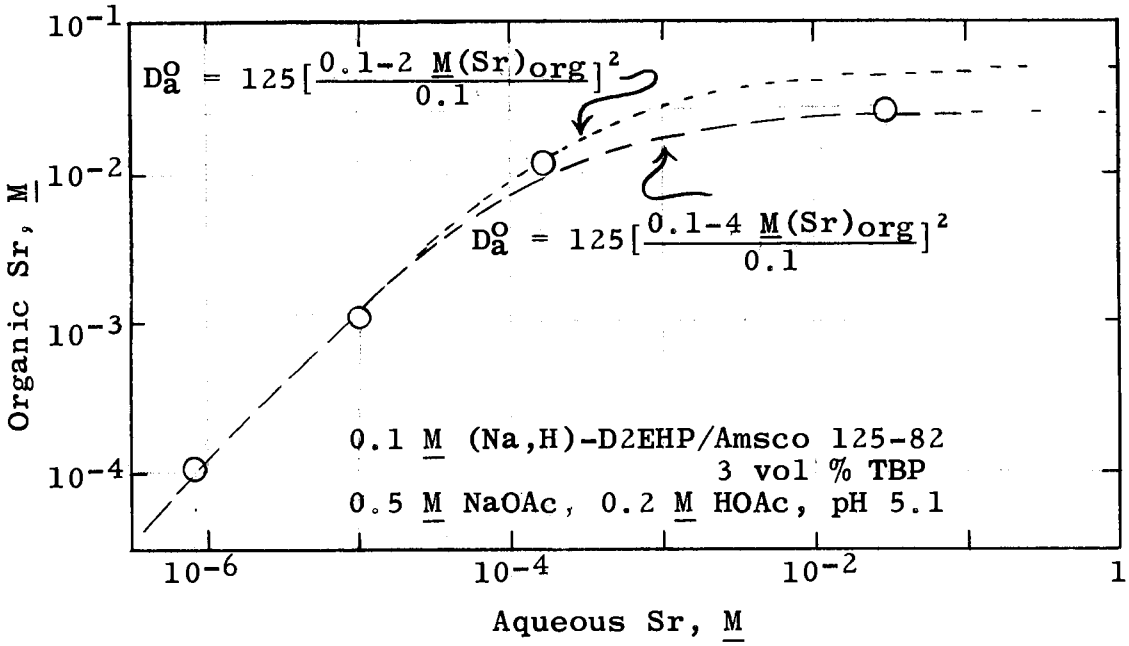

Fig. 1.3. Extraction Isotherm for Strontium by D2EHP from Acetate Solution.

this pH is not limited to trace levels of strontium. The difference between this curve and the theoretical curves expected on the basis of the alternate assumptions of SrX_2 and SrX_4H_2 as the strontium species in the organic phase is significant only at the highest point, which falls closer to the curve based on SrX_4H_2.

This is the formulation postulated in analogy to $UO_2X_4H_2$ to account for the occurrence of the extraction maximum (ORNL-2466). The initial organic phase in these extractions was 0.1 M Na-D2EHP in Amsco 125-82 modified with 3 vol % TBP. Conditions were 10 min mixing time, phase ratio a/o = 1/1, and room temperature.

Strontium Extraction from Ammonium Nitrate Solution. Strontium extraction was lower from nitrate solution when the competing cation was ammonium than when it was sodium, while similar in showing constant extraction at pH's above 7 and enhanced extraction at pH near 5:

Equilibrium pH	D_a^o(Sr) From 0.5 M $NaNO_3$	D_a^o(Sr) From 0.5 M NH_4NO_3	Equilibrium pH	D_a^o(Sr) From 0.5 M $NaNO_3$	D_a^o(Sr) From 0.5 M NH_4NO_3
2.5	0.16	0.14	5.0	180	29
3.5	4	4	5.5	160	16
4.5	85	21	7.5	11	7
4.7	120	24	9.2	11	7

The distribution coefficients for the sodium nitrate solutions are interpolated from the curve shown previously (ORNL-2466). Both sets used 0.1 M D2EHP in Amsco 125-82 modified with 3 vol % TBP and an initial aqueous strontium concentration of 10 mg/liter. Other conditions were 10 min mixing time, phase ratio a/o = 1/1, and room temperature.

Cesium Extraction from Sodium Nitrate Solution. In previously reported tests (ORNL-2451) with macro concentrations of cesium, extraction was low from 2 M nitrate solutions at pH 9 and above, with cesium/sodium separation factors less than unity. Results were similar in extraction of trace amounts of cesium, with a separation factor of 0.7 at pH 9 or 11 and decreasing cesium extraction at lower pH:

Equilibrium pH	D_a^o(Cs)	SF_{Na}^{Cs}	Equilibrium pH	D_a^o(Cs)	SF_{Na}^{Cs}
11.2	0.14	0.7	6.0	0.03	-
8.8	0.14	0.7	5.1	0.006	-
6.4	0.08	-	4.2	0.002	-

where $SF_{Na}^{Cs} = D_a^o(Cs)/D_a^o(Na)$; the sodium distribution was not measured in the tests at pH <7. The aqueous solutions contained initially 0.5 M $NaNO_3$ and 10 ppm cesium. The organic solutions contained 0.1 M D2EHP in Amsco 125-82 modified with 3 vol % TBP. Other conditions were 10 min mixing time, phase ratio a/o = 1/1, and room temperature. The sodium salt and acid forms of the reagent were used in varying proportions to give the range of equilibrium pH's shown.

2.0 PROCESS DEVELOPMENT
Problem Leader: D. J. Crouse

2.1 Evaluation of the Amex Nitrate Stripping Method in Continuous Operation (W. D. Arnold)

The nitrate stripping method, in batch tests, was shown to be very effective for stripping uranium from amines (ORNL-1734, -1959).

Estimated reagent costs were low, but some phase separation difficulties were encountered during stripping and amine regeneration,* particularly when the aqueous pH drifted near the neutral point. Further study of the system was desirable to develop suitable continuous methods for balancing the acid-base reactions and for removing molybdenum from the regeneration circuit. Using amine S-24 in kerosene as the extractant, a bench-scale test was recently completed successfully demonstrating nitrate stripping, amine regeneration, and molybdenum removal on a continuous basis.

2.1.1 Equipment and Operating Procedure

Three extraction, three stripping, and two regeneration mixer-settler stages were used (Fig. 2.1).

The synthetic leach liquor fed to the extraction system analyzed 3.8 g U, 0.1 g Mo, 1.0 g V(IV), 1.5 g Fe(II), 1.7 g Fe(III), 2.0 g Al, 2.1 g PO_4, and 44 g SO_4 per liter at pH 1.0. The organic (0.10 M amine S-24 in kerosene) and liquor flow rates were each 75 ml/min.

The solution used for stripping uranium (~8.8 ml/min) was prepared continuously by combining the make-up nitrate stream (1 M NH_4NO_3--0.3 M H_2SO_4, 1.3 ml/min) with the solution (~7.5 ml/min) of ammonium nitrate leaving the first regeneration stage. Make-up nitrate was equivalent to 0.25 lb/lb of U_3O_8.

The regeneration circuit which was designed to accomplish regeneration of the amine with approximately the stoichiometric amount of ammonium hydroxide consisted of an ammonium hydroxide reservoir and two mixer-settler stages. The reservoir, which had a liquid hold-up capacity (based on 7.5 ml flow) of approximately 100 min, was equipped with an agitator to ensure homogeneity of the contained solution. Prior to the start of the run the reservoir was filled with 0.6 M NH_4NO_3--0.4 M NH_4OH. Make-up ammonium hydroxide was provided by continuously dissolving ammonia gas in water, which was fed at a rate sufficient to maintain a constant liquid level in the reservoir. No ammonia gas reached the reservoir since the dissolution was completed in the water feed line. Solution was pumped from the reservoir to the second regeneration stage mixer at a rate (80-100 ml/min) slightly higher than that of the organic. The aqueous overflowing the settler gravity leg was recycled to the reservoir. Solution was pumped from the reservoir to the first regeneration stage mixer at a flow rate of 7.5 ml/min, or approximately 1/10 the organic flow rate. In operation, the system was controlled simply by regulating the ammonia flow at a rate sufficient to maintain the pH in the reservoir in the range 8.7-9.1 (corresponding to an NH_4OH concentration of 0.15-0.5 M). Such operation ensured that the solution

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*Regeneration of the stripped amine with ammonium hydroxide (or sodium carbonate) to the free base form prior to recycle is recommended since this recovers the relatively expensive nitrate for reuse and also avoids the loss in uranium extraction efficiency which would result from introduction of nitrate into the extraction system.

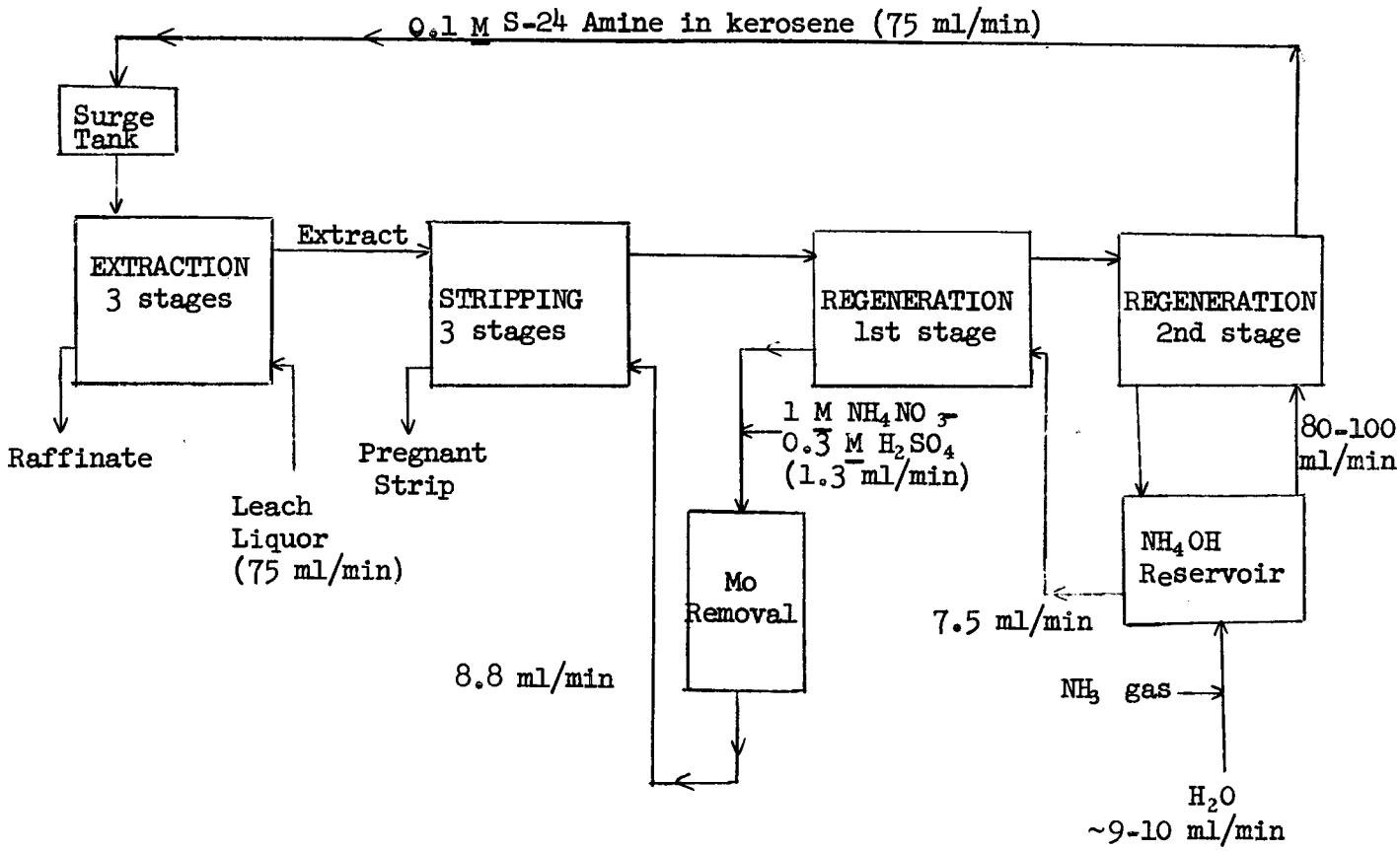

Fig. 2.1. Continuous Extraction--Nitrate Stripping--Regeneration System.

pumped to the first stage contained sufficient ammonium hydroxide to give only partial (15-50%) regeneration of the amine and hence that the ammonium nitrate solution leaving the regeneration system (for feed to the stripping system) would be slightly acidic. The ammonium hydroxide fed to the second regeneration stage, however, was always in sufficient excess to ensure completion of regeneration in that stage.

Molybdenum Removal. Preliminary scouting tests indicated that molybdenum, which is extracted strongly in the extraction and stripping circuits but removed from the solvent during regeneration would be trapped in the regeneration system and some provision would be necessary for removing it. A 1-in.-dia column containing a weak-base anion exchange resin (Amberlite IR-45 in the nitrate form) was inserted between the stripping and regeneration circuits for this purpose. A weak rather than a strong base resin was chosen since it was assumed that molybdenum could be eluted much more readily from the former. The wet-settled resin volume was ~145 ml and the solution flow was at the rate of about 25 gal/ft^2·hr.

2.1.2 Test Results

The system was operated for 7.5 hr, equivalent to 12 complete cycles of the organic phase. After 8 and 12 cycles, samples of

both phases were withdrawn from each settler for analysis (Table 2.1).

Based on the feed liquor and raffinate analyses, >99.9% of the uranium and 96-97% of the molybdenum were extracted.

Stripping of uranium was 99.9% complete. The pregnant strip solution contained ~30 g U and 0.1 g Mo per liter.

Both nitrate and molybdenum were completely stripped from the solvent in the regeneration circuit. At the times of sampling, the system was operating in such a way that approximately 20% of the nitrate was being removed in the first stage. The aqueous leaving the first stage contained about 0.8 M NH_4NO_3 and had a pH of ~4.5. The system for controlling the regeneration reaction and ammonium hydroxide make-up proved quite satisfactory and required very little attention.

One operational problem of potentially serious nature was encountered. Although the initial phase break in the regeneration settlers was satisfactorily rapid, the organic overflowing the settlers was extremely cloudy owing to excessive entrainment of the aqueous phase. This entrainment, which was estimated at times to be as high as 30 ml per liter of organic, was in part due to underdesign of the settlers and could have been decreased considerably by allowing a longer organic residence time in the settlers than the 1.5 min used. Some separation occurred (this separated aqueous was not returned to the regeneration system) in the organic surge tank preceding extraction but a large portion was carried into the extraction system. Most of the nitrate that entered the extraction system by this mechanism was extracted into the organic phase. Fortunately, flow rates were such that sufficient amine was available for extraction of both the uranium and nitrate and uranium extraction was not adversely affected. The loss of ammonium nitrate from the regeneration system by aqueous entrainment tended to upset the nitrate balance in the system. Thus, the ammonium nitrate solution produced for stripping was only 0.8 M in concentration, whereas a 1.0 M solution had been expected based on control of the organic/aqueous flow rates at 10/1. The nitrate entering the stripping system, which would otherwise have been insufficient for complete conversion of the amine to the nitrate form, was adequate only because nitrate was carried in by the extract. Thus, through a favorable combination of circumstances, results were good in both the extraction and stripping cycles in spite of the high entrainment. However, methods of minimizing the entrainment are being examined. Preliminary tests have shown that the entrainment can be readily controlled at a tolerable level by maintaining the aqueous as the continuous phase in the second regeneration stage mixer.

Molybdenum Removal. The resin column effectively removed molybdenum from solution, the effluent analyzing <0.05 g of molybdenum per liter throughout the run. Since the column feed at 8 and 12 cycles contained 0.3-0.4 g of molybdenum per liter, this corresponded to >80% molybdenum removal during this period. However, the run was not of sufficient duration to saturate the column with molybdenum (estimated loading was only 2-3 g of

Table 2.1 Stage Distribution Data for Continuous Run

Aqueous Feed: Synthetic leach liquor, pH 1.0, containing 3.8 g U, 0.1 g Mo, 1.0 g V(IV), 1.5 g Fe(II), 1.7 g Fe(III), 2.0 g Al, 2.1 g PO_4, and 44 g SO_4 per liter.
Organic: Amine S-24 in kerosene; concentration, initial 0.102 M, final 0.102 M.
Flow Rates: As shown in Fig. 2.1.

		After 8 Organic Cycles					After 12 Organic Cycles				
			Amount, g/liter			NH_4OH,		Amount, g/liter			NH_4OH,
Stage	Phase	pH	U	Mo	NO_3	M	pH	U	Mo	NO_3	M
Extraction											
1	Org	-	3.5	0.12	0.6	-	-	3.5	0.125	0.6	-
	Aq	0.95	0.33	0.024	-	-	0.95	0.24	0.024	-	-
2	Org	-	0.30	0.043	-	-	-	0.24	0.049	-	-
	Aq	0.95	0.003	0.007	-	-	0.95	0.002	0.007	-	-
3	Org	-	0.003	0.029	-	-	-	0.002	0.032	-	-
	Aq	1.2	<0.001	0.003	0.1	-	1.2	<0.001	0.004	0.1	-
Stripping											
1	Org	-	1.8	0.13	-	-	-	1.4	0.14	-	-
	Aq	1.2	30.6	0.09	1.8	-	1.2	30.5	0.01	1.9	-
2	Org	-	0.094	0.12	-	-	-	0.086	0.12	-	-
	Aq	1.2	-	0.26	-	-	1.2	11.2	0.34	-	-
3	Org	-	0.004	0.10	6.2	-	-	0.005	0.11	6.2	-
	Aq	1.2	0.40	0.13	-	-	1.2	0.46	0.13	-	-
Regeneration											
1	Org	-	0.002	0.14	5.0[a]	-	-	0.002	0.17	4.9[a]	-
	Aq	4.6	-	0.35[b]	48	-	4.5	-	0.45[b]	50	-
2	Org	-	<0.001	0.005	<0.01[a]	-	-	<0.001	0.005	<0.01[a]	-
	Aq	8.5	-	0.78	39	0.09	8.6	-	1.12	39	0.12
Reservoir		8.8	-	0.75	36	0.16	8.9	-	1.05	37	0.19
Mo Removal - IX Column											
Feed		-	-	0.30[b]	-	-	-	-	0.38[b]	-	-
Effluent		-	-	<0.05	-	-	-	-	<0.05	-	-

[a]Organic samples were filtered prior to analysis to remove entrained aqueous.
[b]Values calculated from a material balance.

molybdenum per liter) or to allow the molybdenum concentration in the regeneration system to reach a steady-state value. The amount of molybdenum which recycled between the first and second regeneration stages was much higher than had been anticipated on the basis of batch scouting tests, in which ~40% of the amine was regenerated in the first stage (rather than the ~20% in the continuous run) and essentially no molybdenum was re-extracted. It is assumed that, in the continuous run, the molybdenum build-up in the second regeneration stage could have been decreased by operating with a higher concentration of ammonium hydroxide in the reservoir, i.e., by increasing the extent of amine regeneration in the first stage.

At the end of the run, the molybdenum was eluted from the column with 0.75 M NaOH fed at a rate of ~25 gal/ft^2·hr. The molybdenum was eluted very slowly, the concentration in the eluate never going above 1.6 g per liter. Because of the low molybdenum loading on the column and the slow elution, consumption of caustic was excessive.

Further continuous tests of the nitrate stripping system are being made. The ion-exchange column has been replaced with an activated carbon column since molybdenum removal by the latter (Sec. 2.2) has shown more promise. In addition, the regeneration system has been simplified by enlarging the settlers and eliminating the ammonium hydroxide reservoir.

2.2 Recovery of Molybdenum from Amex Nitrate Strip Solutions by Adsorption on Activated Carbon (W. D. Arnold)

Molybdenum was effectively removed from solutions similar to those produced in the Amex nitrate stripping circuit (Sec. 2.1) by activated carbon. The successful use of activated carbon for removal of molybdenum from solutions of this type has previously been reported by the Bureau of Mines.*

Batch Tests. Isotherms for adsorption of molybdenum from a synthetic nitrate strip solution (1.0 M NH_4NO_3--0.05 M H_2SO_4, 1 g of Mo per liter, pH 1.2) were obtained for two samples of activated carbon (12-30 mesh Type BPL and 20-50 mesh Type OL) from the Pittsburgh Coke and Chemical Company (Fig. 2.2). Although adsorption of molybdenum was favorable for both samples, Type OL was the more effective with a molybdenum loading of 62 g/kg carbon when the molybdenum concentration in the aqueous phase was 0.7 g/liter. In other tests (results not shown), adsorption of molybdenum on Type OL carbon was negligible from a solution adjusted to pH 6. The isotherms were determined by stirring the solution with successive small portions of carbon (10-min contacts), the solution being sampled for molybdenum analysis after each contact. Carbon loadings were calculated on the basis of the changes in molybdenum content of the solution.

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*K. E. Tame, J. R. Ross, J. B. Rosenbaum, "Acid-CCD-Solvent Extraction Processing of White Canyon and Happy Jack Ores," U. S. Bur. Mines, Salt Lake City, RR-49.1 (March, 1957).

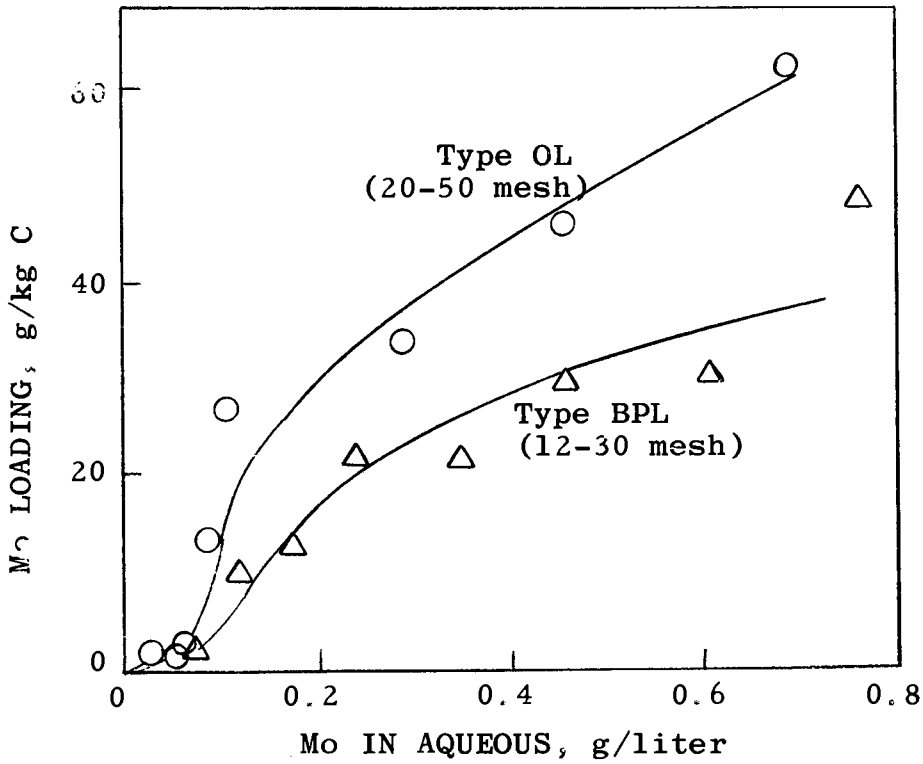

Fig. 2.2. Isotherms for Adsorption of Molybdenum on Activated Carbon. Head aqueous: 1 M NH_4NO_3--0.05 M H_2SO_4, 1.0 g Mo/liter, pH 1.2. Aqueous cascaded against small increments of fresh carbon, 10 min per contact.

Column Test. In further testing of type OL carbon, a synthetic strip solution (1.0 M NH_4NO_3--0.05 M H_2SO_4, 0.97 g of molybdenum per liter, pH 1.2) was passed at the rate of 8.5 ml/min (25 gal/ft^2·hr) through a 12-in.-long carbon bed in a 1-in.-dia glass column. The wet-settled carbon volume was approximately 155 ml. The effluent was collected in 500-ml increments (3.2 column volumes) which were analyzed for molybdenum (Fig. 2.3). The first 15 column volumes of effluent contained <0.001 g of molybdenum per liter. From this point the molybdenum began to break through slowly, increasing to 0.014 g/liter at 29-32 column volumes and to 0.036 g/liter at 95-97 column volumes (the end of the run). Since the latter figure corresponds to about 96% molybdenum recovery, the column was still far from saturation. Based on the aqueous feed and effluent analyses, 14.2 g of molybdenum was adsorbed on the 65 g of carbon in the column, which is equivalent to an average loading of ~220 g of molybdenum per kilogram of carbon. It should be noted that the efficiency of molybdenum adsorption was increased by the intermittent nature of the operation. Solution flow through the column was stopped for several days after 32 column volumes and overnight after 58 and 84 column volumes. In each case, the column appeared to "recuperate" on standing, resulting in an appreciable flattening of the overall breakthrough curve.

Elution of Molybdenum. Molybdenum was removed effectively from the carbon with dilute ammonium hydroxide at pH's above 6.

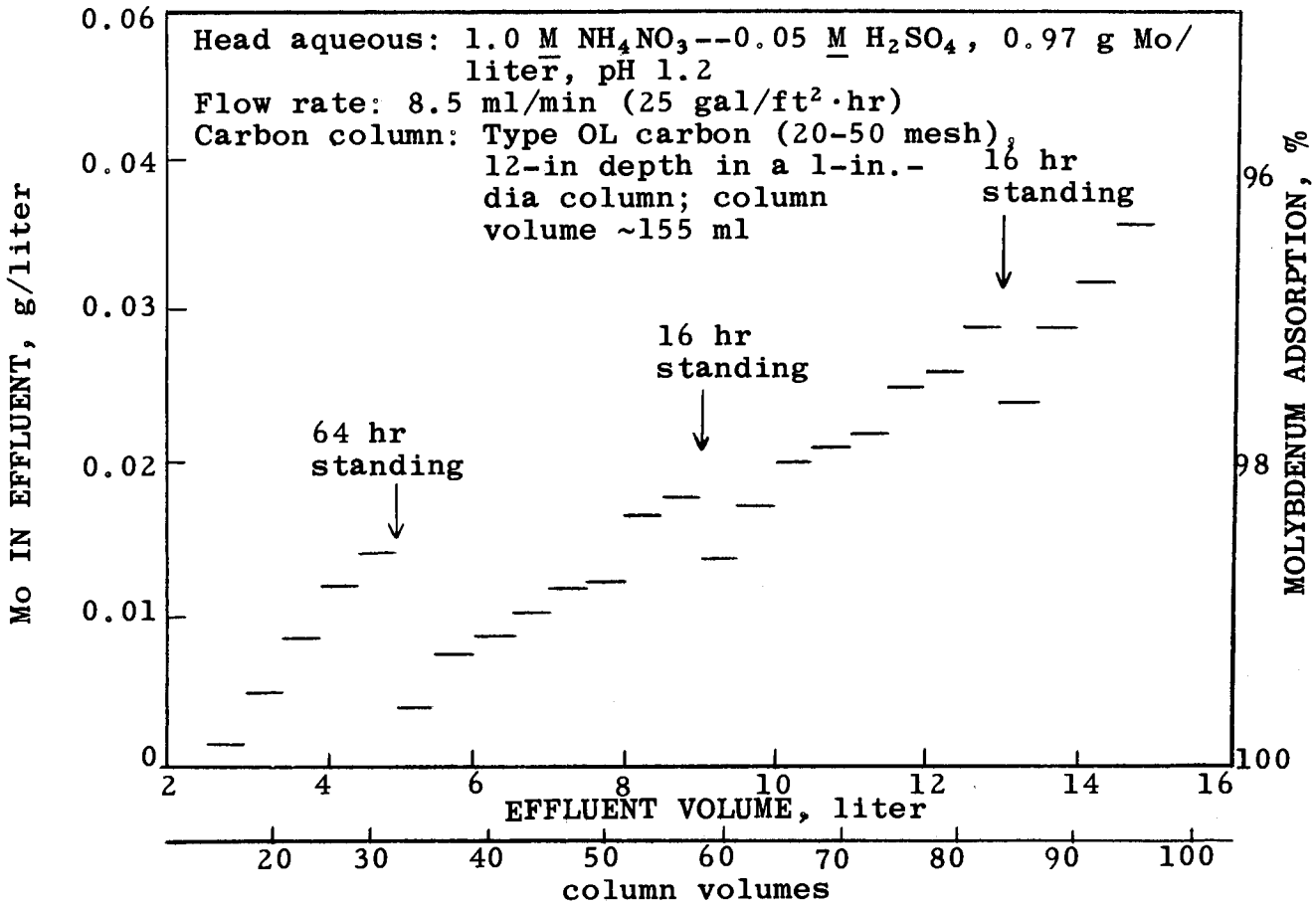

Fig. 2.3. Adsorption of Molybdenum on Carbon.

For the elution test, the column was drained of solution and the wet carbon was transferred to a beaker. It was stirred for 10 min with three successive 200 ml of water, the wash solutions being separated from the carbon by decantation. The amount of molybdenum removed by the washing was not significant:

Water Wash	pH	Mo in Wash Solution, g/liter
1st	1.5	0.083
2nd	1.8	0.067
3rd	2.0	0.060

After decantation of the third wash solution, 190 ml of water and 9 ml of 1.75 M NH_4OH were added and stirred with the carbon for 20 min. A 10-ml sample was then withdrawn for analysis, more ammonium hydroxide was added, and, after 20 min agitation, another aqueous sample was withdrawn. This procedure was repeated through a total of 13 additions of ammonium hydroxide. The molybdenum concentration of the eluate increased to about 33 g/liter:

1.75 M NH_4OH Added, ml		Agitation Time, min	Aqueous Sample		
Increment	Total		Volume, ml	pH	Mo, g/liter
9	9	20	10	2.8	0.25
7	16	20	10	3.3	0.63
9	25	20	10	4.2	1.6
4	29	20	10	4.8	3.1
4	33	20	10	5.1	5.3
5	38	20	10	5.4	7.5
6	44	20	5	5.6	11.2
5	49	20	5	5.7	12.9
50	99	10	10	6.2	22.3
25	124	10	10	6.5	27.6
25	149	10	10	7.3	33.1
15	164	10	10	8.1	33.9
25	189	10	260[a]	8.7	32.2

[a]The volume that could be removed by decantation.

After decantation of the pregnant eluate, the carbon was washed by stirring for 5 min with five 200-ml portions of water and decanting. A total of 13.5 g Mo was eluted from the carbon, ~95% of that adsorbed:

Wash	Aqueous	
	pH	Mo, g/liter
1st	8.6	11.2
2nd	8.6	4.2
3rd	8.6	1.3
4th	8.5	0.55
5th	-	0.36

Consumption of NH_3 was approximately 0.4 lb per pound of molybdenum eluted.

Evaporation of a portion of the eluate containing 32.2 g of molybdenum per liter and drying of the residue for 16 hr at 110°C produced an off-white solid analyzing 85.8% MoO_3 and 6.9% NH_3. Drying of this solid to constant weight at 110°C and 400°C resulted in a weight loss of 13.9 and 14.2%, respectively, indicating products containing 99.7 and >99.9% MoO_3. Although there were no metal impurities in the synthetic strip solution used in this test, it should be pointed out that none would be expected in actual operation since all extracted metals other than molybdenum would be removed from the solvent before it entered the regeneration circuit. Thus, it is anticipated that molybdenum of similar high purity could be recovered as a by-product of uranium recovery by the Amex process.

Tests are in progress to determine whether the carbon column will maintain its adsorption efficiency in cyclic operation.

2.3 Effect of Silica on Phase Separation in the Amex System (F. J. Hurst)

In prior Amex studies (ORNL-2034, -CF-54-4-79), stable emulsions were formed when liquors containing a high concentration of dissolved (or colloidally dispersed) silica, i.e., 2.5 g of silicon per liter, were treated. These liquors were processed successfully by maintaining the organic phase continuous (water-in-oil dispersion) during mixing, although it appeared that some provision would be required for intermittently removing (for external processing) stable emulsion which slowly accumulated at the interface in the settlers. Emulsion formation was completely avoided by operating with a small amount of decolorizing carbon dispersed in the organic phase.

In recent batch tests with liquors containing silica, the effect on phase separation of a number of variables including amine-diluent choice, amine concentration, temperature, and pH was examined. Each test involved stirring equal volumes of the organic and aqueous phases vigorously for 2 min in a baffled mixer, stopping agitation, and measuring the time for complete phase disengagement. The desired conditions of phase continuity during mixing were controlled by the start-up procedure previously described (ORNL-2172, p. 76).

2.3.1 Tests with Synthetic Leach Liquors

Effect of Silicon Content. The separation times of several amines from synthetic leach liquors containing 0.0, 0.2, and 0.8 g of silicon per liter did not vary appreciably with the silicon content when the organic was the continuous phase (Table 2.2). Separations were slow (2.5-6.5 min) for trilaurylamine in kerosene-tridecanol, 9D-178 in kerosene, and di(tridecyl)amine in kerosene, but reasonably rapid (1.3-2.0 min) for the other amine-diluent combinations. Addition of tridecanol to the diluent decreased separation times particularly for 9D-178 and di(tridecyl)amine. With aqueous continuous mixing, the results were approximately the same for no silicon and 0.2 g/liter but with 0.8 g/liter, separation times were prolonged for most of the amines. For example, with the tri-fatty and trilauryl amines, separation of the phases was still incomplete after 10 min and 9D-178 in kerosene or kerosene-tridecanol diluents required 7-7.5 min to separate. In comparison, di(tridecyl)amine in kerosene was not very sensitive to the presence of silica, the separation time with the liquor containing 0.8 g Si/liter being only 1.6 min compared to 1.2-1.3 min with the other two liquors. With S-24 amine in kerosene and S-24 or di(tridecyl)amine in kerosene-tridecanol, separation times with the high silica liquor were a factor of 2-3 longer than with the silica-free liquor, falling in the range 2.2-2.3 min.

Effect of Surface-active Agents. Of three surface-active agents tested with 0.1 M 9D-178 in 98% kerosene--2% tridecanol and the liquor containing 0.8 g of silicon per liter (aqueous-continuous mixing), two decreased the separation time by a factor of about 2, while the third resulted in formation of a permanent emulsion:

Table 2.2 Effect of Silica on Phase Separation

Organic: 0.1 M amine

Aqueous: Synthetic liquor with 0.5 g U, 0.5 g V(IV), 2 g Fe(III), 2 g Al, 75 g SO_4 and 0.0, 0.2, or 0.8 g Si per liter, pH 0.9; the silicon was added by spiking the liquors with a solution of sodium silicate.

Phase ratio: 1/1

Temperature: 23-26°C

Amine-Diluent	Separation Time, min					
	Organic Continuous			Aqueous Continuous		
	0.0 g Si/liter	0.2 g Si/liter	0.8 g Si/liter	0.0 g Si/liter	0.2 g Si/liter	0.8 g Si/liter
S-24 in kerosene	1.5	1.5	1.7	1.0	1.2	3.0
S-24 in 98% kerosene--2% tridecanol	1.4	1.3	1.3	1.0	1.2	2.2
9D-178 in kerosene	2.5	3.0	2.8	1.5	1.2	7.5
9D-178 in 98% kerosene--2% tridecanol	1.7	1.8	2.0	1.2	1.2	7.0
Di(tridecyl) in kerosene	6.5[a]	4.3	4.8	1.3[a]	1.2	1.6
Di(tridecyl) in 95% kerosene--5% tridecanol	1.8	1.4	1.9	1.5	1.2	2.5
Tri-fatty amine (General Mills) in 97% kerosene--3% tridecanol	2.0	2.0	2.0[a]	0.8	1.3	>10[a]
Trilauryl (Archer-Daniels-Midland) in 97% kerosene--3% tridecanol	5.5	5.0[a]	4.5[a]	2.0	1.5	>10

[a]A small amount of emulsion remained at the interface.

Surface Active Agent[a]	Separation Time, min
None	7
Lomar PW	3.3
Ninate 411	3.6
Victawet 12	Permanent emulsion

[a]50 ppm concentration in the liquor.

2.3.2 Tests with Kermac Pilot Plant Liquor

Analysis of the leach liquor produced by leaching ore from the Ambrosia Lake region (Holly mine) was:

Constituent	Amount, g/liter	Constituent	Amount, g/liter
U	1.33	Al	1.7
Si	0.92	Mo	0.039
Fe(III)	1.4	SO_4	31
Fe(II)	3.8	PO_4	0.4
V	0.07	Cl	0.2

The pH was 1.5.

Effect of pH. In a series of tests made with 9D-178, di(tridecyl), and tri-fatty amines and Kermac liquor adjusted to various pH levels in the range 1.0-2.1, phase separation times decreased with decrease in liquor pH:

Amine-Diluent	Final pH	Separation Time, min: Aqueous Continuous	Separation Time, min: Organic Continuous
0.1 M 9D-178 in 98% kerosene--2% tridecanol	1.8	4[a]	1.0
	1.5	3	-
	1.4	2.7	0.9
	1.2	2.3	0.9
	1.0	2.3	0.8
0.1 M di(tridecyl) in 95% kerosene--5% tridecanol	2.1	2.5	1.2
	1.5	1.5	-
	1.4	1.5	0.9
	1.2	1.3	0.9
0.1 M tri-fatty (General Mills) in 97% kerosene--3% tridecanol	1.5	>10	1.0
	1.2	7[a]	-

[a]A small amount of emulsion remained at the interface.

This effect was small when mixing with the organic phase continuous, the separations of each amine being rapid (0.8-1.2 min) at all pH levels tested. With aqueous continuous mixing, the tri-fatty amine separated very slowly. Separations of 9D-178 were more rapid but still relatively slow, whereas di(tridecyl)amine separated rapidly in all tests except the one at the highest pH. In all tests, the amine was converted to the chloride salt form to avoid excessive pH change during contacting.

Effect of Temperature. The phase separation rate of 0.1 M 9D-178 (chloride form) in 98% kerosene--2% tridecanol and Kermac liquor (aqueous continuous mixing) increased markedly with increase in temperature in the range 16-40°C:

Temperature, °C	Separation Time, min	Temperature, °C	Separation Time, min
16	6.5[a]	32	1.9
20	4.5[a]	40	1.5
26	2.5[a]		

[a]A small amount of emulsion remained at the interface.

Both phases, which were slightly turbid after separation at ambient or lower temperatures, were sparkling clear in the test at 40°C.

Effect of Amine Concentration. Tests with Kermac liquor at 3 different pH levels and 9D-178 (chloride form) in 98% kerosene--2% tridecanol diluent (aqueous continuous mixing) showed little variation in separation times with change in amine concentration in the range 0.0-0.10 M but somewhat slower separation in the range 0.05-0.07 M than at lower or at 0.10 M concentration:

Amine Conc. M	Final pH	Separation Time, min	Amine Conc. M	Final pH	Separation Time, min
0.10	1.8	4	0.00[a]	1.6	2.5
0.07	1.8	5	0.10	1.5	2.5
0.05	1.7	4.5	0.07	1.5	3.0
0.10	1.6	3.0	0.05	1.5	3.0
0.07	1.6	3.5	0.03	1.5	2.5
0.05	1.6	3.5	0.00[a]	1.5	2.2
0.03	1.6	3.0			

[a]Diluent alone; kerosene (without amine or tridecanol) also separated in 2.5 min.

With diluent alone the separation time was almost as long as with the 0.10 M amine solution. As before, the phase separation rate increased with decrease in solution pH.

Comparison of Diluents. In tests with Kermac liquor and with synthetic liquors containing 0.0 and 0.8 g of silicon per liter (aqueous-continuous mixing), Shell 140 and Amsco 123-15 (containing no amine) separated fairly rapidly from all three liquors. Separations of Gulf kerosene and Type T-2 solvent were very slow from the Kermac and silica-containing synthetic liquor although rapid from the silica-free synthetic liquor:

Liquor	pH	Separation Time, min			
		Kerosene[a]	Shell Flash 140 Naphtha[b]	British-American Type T-2 Aviation Kerosene[b]	Amsco 123-15[c]
Synthetic - no Si	0.8	1.0	0.8	1.1	1.0
Synthetic - 0.8 g Si/liter	0.8	3.0	1.0	6	1.3
Kermac	1.5	4.0	1.2	7	1.3

[a]From Gulf Refining Co.

[b]Samples received from Eldorado Mining and Refining, Ltd. in Ottawa, Canada.

[c]A highly refined aliphatic petroleum fraction.

The very rapid separation of Shell 140 from Kermac liquors was not duplicated when this solvent was combined with 9D-178 amine and tridecanol; in fact, the separation was much slower than that previously obtained with 9D-178 in kerosene-tridecanol. The separation of di(tridecyl)amine in Shell 140-tridecanol diluent was also slower than that obtained previously in kerosene-tridecanol:

Amine-Diluent	Final pH	Separation Time, min
0.1 M 9D-178 in 98% Shell 140--2% tridecanol	1.5	>10
0.1 M di(tridecyl) in 95% Shell 140--5% tridecanol	1.5	1.7

The amines were in the chloride form and mixing was aqueous-continuous.

3.0 ENGINEERING STUDIES
Problem Leader, A. D. Ryon

3.1 Continuous Flow Settler Tests of Amex Solvents (R. S. Lowrie, F. L. Daley)

Many of the factors necessary for mixer design and scale up of the Amex extraction system have been reported previously (ORNL-CF-56-4-79, -CF-56-8-30, and -2026). In further tests continuous-flow runs were made in 6- and 48-in.-dia settlers to determine scale up factors, flow capacity and entrainment values for the extraction section of the Amex process. The equipment and test procedures were the same as those used in studies of the Dapex process (ORNL-2306 and -2399) except that the 6-in.-dia settler was modified to permit a 27-in. liquid depth (20 in. of aqueous and 7 in. of solvent). The dispersion from the mixer was introduced at the interface. Entrainment values were obtained by the centrifugation method discussed in ORNL-2466.

The solvent was a 0.1 M solution of Rohm and Haas amine Amberlite LA-1 (formerly identified as 9D-178) in a kerosene diluent modified where noted with 3 vol % tridecanol. The aqueous feed was a uranium-barren sodium sulfate--sulfuric acid solution containing 70 g of sulfate per liter at pH 1.0, which had approximately the same primary break time as samples of actual plant liquors when mixed with the solvent. Physical properties of the phases at 25°C were:

Phase	Density, g/ml	Viscosity, centistokes	Interfacial Tension, dynes/cm	Primary Break Time in 12x12 in. tank at a/o of 1/1, sec	
				Oil-in-water	Water-in-oil
Unmodified solvent	0.82	3.0	6.0	180	440
Modified solvent	0.82	3.0	6.6	-	305
Aqueous feed	1.08	1.08	-	-	-

3.1.1 Correlation of Settler Sizes

At steady state a distinct band of dispersion existed at the interface which was of uniform thickness across the entire area of the settler. The excellent agreement of the phase separation data obtained in the 6- and 48-in.-dia settlers under these conditions, shown in Fig. 3.1, demonstrate that at constant aqueous flow rate per unit cross sectional area the thickness of the dispersion band is independent of settler diameter. (Note that the area of the 48-in.-dia settler is 60 times that of the 6-in.-dia settler.) Further, the slope of the family of nearly parallel lines resulting from the different phase ratios, dispersion type, and solvents tested indicate the thickness of the dispersion band increases approximately fivefold when the flow rate is doubled. Consequently, phase separation data obtained in small sized units may be used in scaling up the larger units, based on a constant flow per unit cross sectional area.

3.1.2 Comparison of Settler Capacities for Amex and Dapex Systems

The curves for the aqueous flow rate per unit cross sectional area vs. dispersion band thickness in the Amex systems are nearly parallel to similar curves for the Dapex system (ORNL-2399), but displaced toward lower flow rates for a given dispersion band thickness. Previously, the nominal aqueous flow capacity for the Dapex system had been determined in terms of the flow rate required to give a 5-in. dispersion band. Because the curves are nearly parallel, equally valid comparisons could be made at any band thickness. The nominal flow capacity for the two systems, read from Fig. 3.1, are:

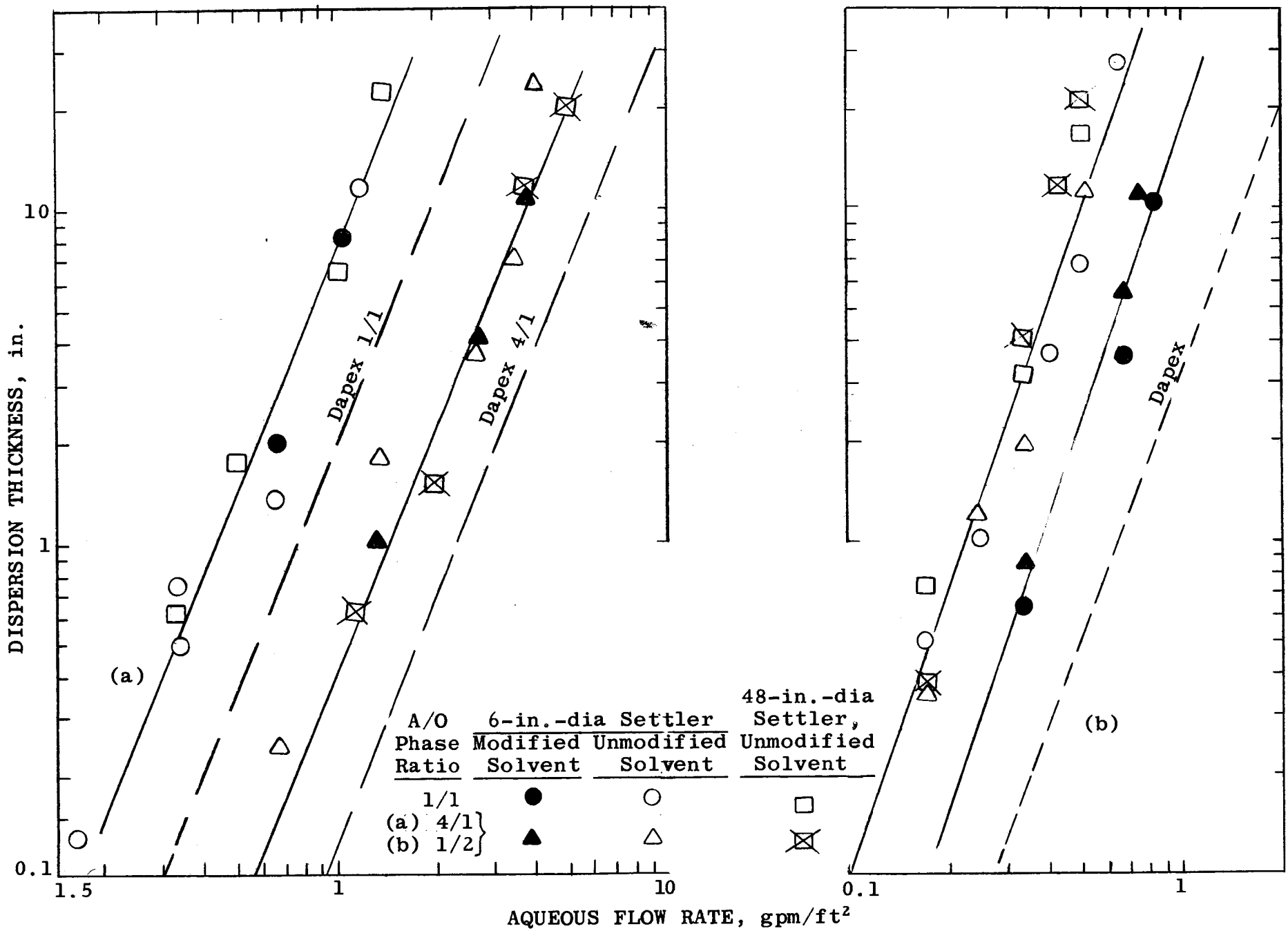

Fig. 3.1 Throughput Capacity of Settlers with (a) Oil-in-water and (b) Water-in-oil Type Dispersions.

Dispersion Type	Phase Ratio a/o	Aqueous Flow Rate, gpm/ft^2 Amex Solvents Unmodified	Amex Solvents Modified	Dapex Solvent
Oil-in-water	4/1	2.9	2.9	4.5
	1/1	0.8	0.8	1.4
Water-in-oil	1/1	0.4	0.7	1.1
	1/2	0.4	0.7	1.1

Note that increasing the a/o phase ratio from 1/1 to 4/1 with oil-in-water type dispersion increased the aqueous flow rate about 4 times, although decreasing the a/o phase ratio from 1/1 to 1/2 with water-in-oil type dispersion did not lower the aqueous flow rate. Modification of the Amex solvent by the addition of 3 vol % tridecanol increased the settler flow capacity about 75% with water-in-oil type dispersion but had no effect on oil-in-water type dispersions. In general, the nominal aqueous flow capacities with modified Amberlite LA-1 solvent were about 50% of those with Dapex solvent.

3.1.3 Entrainment

With water-in-oil type dispersions, solvent entrainment ranged from approximately 0.1 to <0.04 gal/1000 gal (Table 3.1). For Amex extraction of uranium from the average ore leach liquor, the cost of solvent lost by the entrainment of 0.1 gal/1000 gal of raffinate would be about 0.5¢ per pound of U_3O_8 product. Thus, the added cost of U_3O_8 due to solvent entrainment would not be significant for water-in-oil type dispersions.

Solvent entrainment for oil-in-water type dispersions at an a/o phase ratio of 1/1 were consistently less than 0.04 gal/1000 gal with the 6-in.-dia settler but ranged from <0.04 to about 0.3 gal/1000 gal with the 48-in.-dia settler, the lowest values being obtained with the thickest dispersion bands. Entrainment for oil-in-water dispersions at an a/o phase ratio of 4/1 was about 3 gal/1000 gal for both the 6- and 48-in.-dia settlers at the nominal flow capacity (2.9 gpm/ft^2). This would add about 15¢ per pound to the cost of U_3O_8 product, which justifies the investigation of methods for recovering entrained solvent.

The entrainment of aqueous in the solvent phase is of interest mainly in the extraction circuit, where carryover would contaminate the stripping circuit and the product. The highest entrainment of aqueous in solvent, obtained with water-in-oil type dispersions at an a/o phase ratio of 1/2 in the 48-in.-dia settler was about 30 gal/1000 gal. For a typical installation where the feed/solvent ratio is 3.5 to 1, this entrainment level would result in a ratio of 1/120 for each contaminant present in the entrained aqueous to the uranium in the solvent. For the average mill liquors, this amount of contamination would be less than the present uranium product specification although sufficiently high to warrant consideration of a scrub stage or holdup tank to lower entrainment.

Table 3.1. Summary of Settler Data

Phase Ratio (a/o)	Aq. Flow Rate, gpm/ft²	Dispersion Thickness, in. Solvent Unmod.	Dispersion Thickness, in. Solvent Modif.	Entrainment, gal/1000 gal Sol in Aq Unmod.	Entrainment, gal/1000 gal Sol in Aq Modif.	Entrainment, gal/1000 gal Aq in Sol Unmod.	Entrainment, gal/1000 gal Aq in Sol Modif.
6 in. dia, oil-in-water type dispersions							
4/1	0.68	0.25	---	0.9	-	1.4	-
	1.35	1.8	1.0	1.3	1.6	3.3	2.1
	2.70	3.8	4.3	2.1	2.0	6.7	1.6
	3.50	7.0	---	3.4	-	6.7	-
	3.78	-	10.3	-	1.6	-	0.9
	4.00	23.0	---	1.2	-	-	-
1/1	0.17	0.13	---	<0.04	-	2.1	-
	0.34	0.5	0.8	<0.04	<0.04	2.8	1.6
	0.68	1.4	2.0	<0.04	<0.04	4.2	1.4
	1.08	-	8.3	-	<0.04	-	1.9
	1.22	11.8	---	<0.04	-	3.5	-
6 in. dia, water-in-oil type dispersions							
1/1	0.17	0.5	---	<0.04	-	0.4	-
	0.25	1.0	---	<0.04	-	0.7	-
	0.34	-	0.6	-	<0.04	-	0.4
	0.41	3.8	---	<0.04	-	4.9	-
	0.51	6.8	---	<0.04	-	3.9	-
	0.63	27.0	---	<0.04	-	-	-
	0.68	-	3.6	-	<0.04	-	4.2
	0.81	-	10.8	-	<0.04	-	1.6
1/2	0.17	0.4	---	<0.04	-	2.1	-
	0.25	1.3	---	<0.04	-	5.0	-
	0.34	2.0	0.9	<0.04	<0.04	14.0	0.9
	0.51	12.0	---	<0.04	-	11.2	-
	0.68	-	5.0	-	<0.04	-	1.4
	0.74	-	11.8	-	<0.04	-	2.0
48 in. dia, oil-in-water type dispersions							
4/1	1.15	0.6		2.2		9.8	
	2.00	1.5		3.2		13.3	
	3.75	10.0		3.2		15.0	
	5.00	20.5		-		17.0	
1/1	0.34	0.6		0.19		12.3	
	0.50	1.8		0.16		14.0	
	1.00	6.5		0.28		15.4	
	1.40	22.8		<0.04		15.4	
48 in. dia, water-in-oil type dispersions							
1/1	0.17	0.8		0.10		1.4	
	0.33	3.3		0.13		5.3	
	0.50	16.5		<0.04		5.3	
1/2	0.17	0.4		0.08		11.2	
	0.33	4.0		0.13		22.4	
	0.42	11.5		0.08		24.5	
	0.50	22.5		<0.04		28.0	

3.1.4 Preliminary Coalescer Tests

The results reported in Sec. 3.1.2 show that the flow capacity of a gravity settler is less for the Amex solvent than for the Dapex.

Previously (ORNL-2399) it was shown that wire mesh packing (York Mesh Demistor) increases the flow capacity of the settler fourfold for water-in-oil type dispersions in the Dapex system. In similar tests of the Amex system the wire mesh packing had virtually no effect on the flow capacity. In other tests stainless steel wire cloth (40 and 200 mesh) and a coarse grade of glass filter cloth* packing and a commercial Selas coalescer were effective coalescers for the Amex system. Most of the tests were made with water-in-oil type dispersions at a phase ratio of 1/1. The flooding capacity (aqueous flow rate per unit area of coalescer) ranged from 1 gpm/ft^2 with the Selas unit to 5 gpm/ft^2 with the glass filter cloth. The pressure drop across the coalescer was less than 9 in. H_2O for the glass cloth and wire screens and approximately 60 in. for the Selas coalescer. Additional tests of coalescers are planned to determine the clogging effects of slime solids and colloidal matter such as silicic acid.

In addition to mechanical coalescers, in preliminary tests an electrical potential applied to a water-in-oil type dispersion rapidly coalesced the water droplets. In batch tests, application of an electrical potential reduced the break time of typical dispersions from 160 to 15 sec, and with certain amines which form stable dispersions with 5% H_2SO_4 the break time was reduced from several hours to a few minutes. In a few tests with continuous flow of dispersions through the electrical field a small electrical source coalesced about 4.6 gpm of dispersion.

4.0 FUNDAMENTAL STUDIES
Problem Leader: C. F. Coleman

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

In previous reports results of an infrared spectrophotometric investigation of di(2-ethylhexyl)phosphoric acid (A)--tri-n-octylphosphine oxide (B)--octane solutions were presented which indicated the formation of the adducts A_2B and AB, presumably as a result of hydrogen bonding. Preliminary isopiestic measurements confirm the existence of these adducts in octane solution (Table 4.1).

Isopiestic measurements are made by placing solutions of different nonvolatile solutes and a volatile solvent in an evacuated chamber, which is carefully thermostatted and gently agitated.

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*Fiberglas cloth, made by Owens-Corning Fiberglas Corp., Code N41A40.

Table 4.1 Isopiestic Equilibrations of n-Octane Solutions at 25°C

Concentration, molality					
Reference Solution, C_R	Solution of A and B			Unreacted A_2	Reacted A_2
	C_{A_2}	C_B	$C_{A_2}+C_B$	(C_R-C_B)	$[2(C_{A_2}-[A_2])]$
0.0794	0.0629	0.0641	0.1270	0.0153	0.0952
0.0793 $(C_6H_5)_3CH$	0.0385	0.0772	0.1157	0.0021	0.0728
0.1541	0.0797	0.1597	0.2394	0.0055	
0.1820	0.1545	0.0777	0.2322	0.1043	0.1004
0.1631 A_2	0.1143	0.1142	0.2285	0.0489	0.1308
0.2607	0.1698	0.2543	0.4241	0.0064	0.3268

The solvent distils among the various samples until all solutions have reached the same solvent vapor pressure; then the solution samples are removed and their concentrations determined. If it is assumed that Raoult's law applies to all the solutions, at equilibrium the total concentration of all solute species will be the same in all the samples.

In the table the samples labeled "reference solution" [either triphenylmethane or di(2-ethylhexyl)phosphoric acid in octane] were assumed to contain only one solute species [$(C_6H_5)_3CH$ or A_2, the dialkylphosphoric acid dimer], and their concentrations, C_R, by Raoult's law represent the total molarity of solute particles in the corresponding solution containing A and B. Since the sum of $C_{A_2} + C_B$ for these latter solutions is in every case greater than C_R, it appears that A_2 and B have interacted, decreasing the total number of particles in solution. This is consistent with the previously proposed reactions,

$$A_2 + B \rightleftharpoons A_2B \qquad (1)$$

$$A_2 + 2B \rightleftharpoons 2AB \qquad (2)$$

In the first, two species react to give one and in the second, three species react to give two. The total molarity of species in such a solution is

$$C_R = [A_2] + [B] + [A_2B] + [AB] \qquad (3)$$

which for present purposes may be simplified to

$$C_R = [A_2] + C_B \qquad (4)$$

The difference, C_R-C_B, by eq. 4, is equal to $[A_2]$, the concentration of unreacted dialkylphosphoric acid dimer. The resulting values are reasonable in all but one equilibration, wherein a small negative value was obtained. The quantity $2(C_{A_2}-[A_2])$, which represents the concentration of A in combination with B, was often greater than C_B. This is possible only if a species is present

which contains more than 1 mole of A per mole of B. This is a particularly significant feature of the present data since from the previously reported infrared measurements the species A_2B was less evident than was the species AB (its formation being assumed to explain the otherwise inconstant formation quotient for AB).

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