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PROGRESS REPORT ON RAW MATERIALS

FOR FEBRUARY, 1957

K. B. Brown
C. F. Coleman
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CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT ON RAW MATERIALS FOR FEBRUARY, 1957

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

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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¢)
March	ORNL-2306 to be published

ABSTRACT

Systematic Studies. Some new organophosphorus and organonitrogen compounds are described, together with some new batches of compounds previously tested. Uranium extraction power in standard tests is reported. Loss rates by distribution from organic to aqueous solutions is reported for some amines and for a quaternary ammonium compound (Rohm and Haas Quaternary B-104).

Process Development Studies. Batch tests of Amex extraction and stripping of uranium and molybdenum confirmed a considerable variation in tendency toward amine-molybdenum precipitation with choice of amine-diluent combination. The same tests also showed a strong dependence of precipitation on molybdenum concentration in the organic phase. Two continuous countercurrent tests were completed with no precipitation observed.

Rohm and Haas Experimental Quaternary B-104, dimethyldidodecenylammonium chloride (converted to carbonate before use), in Amsco G, Amsco G-tridecanol, or kerosene-tridecanol extracted uranium well from sodium carbonate and bicarbonate solutions. Extraction decreased with increasing total carbonate concentration and with increasing temperature, and increased with increasing tridecanol content through most of the range tested. Some long-chain alcohol content (e.g., 5% tridecanol) was required in the kerosene but not in the Amsco G to prevent third phase formation; the alcohol improved phase separation with both diluents. Stripping of the extracted uranium was highly effective with 1 M NaCl solution and was promising with 2 and 3 M NaOH solution.

Engineering Studies. Dapex uranium extraction rates in tank mixer batch tests at fairly low uranium loading levels were well represented by first-order rate constants,

$$K' = (1/t) \ln [(C_o - C_{eq})/(C_t - C_{eq})]$$

K' was somewhat larger (faster extraction) in a 12- than in a 6-in.-dia mixer, but was not significantly different between aqueous-continuous and organic-continuous dispersions. K' increased in proportion to turbine speed and to the cube root of power input, and doubled with approximately 15°C rise in temperature. The linear dependence on turbine speed indicates nearly linear dependence on interfacial area, and suggests rate control by reaction at the interface rather than by diffusion. The heat of activation was estimated from the temperature-dependence tests to be 8-9 kcal/mole, which is between the values expected for diffusion control (5 kcal) and reaction control (10-20 kcal).

1.0 SYSTEMATIC STUDIES

1.1 Screening of Organophosphorus Compounds (C. A. Blake, D. E. Horner, J. M. Schmitt)

Organophosphorus Acids. The purity of some new acids and of some batches of di(2-ethylhexyl)phosphoric acid, "D2EHPA," from new sources was assayed by potentiometric titration with sodium hydroxide in 70% aqueous ethanol (cf. ORNL-1903 pp. 100-105 and -2172 pp. 110-113):

Compound	Batch No.	Source[a]	Acid Assay, meq/g		
			Theo.[b]	"Strong"	"Weak"
Di(2-ethyl-4-methylpentyl)phosphoric acid	OP-340	E	3.11	2.97	0.15
	OP-344	-[c]		2.96	<0.1
Di(2-propyl-4-methylpentyl)-phosphoric acid	OP-341	E	2.86	2.72	0.25
	OP-345	-[c]		2.67	<0.1
Di(2-ethylhexyl)-dithiophosphoric acid	OP-323	L	2.82	2.22	<0.1
D2EHPA	OP-302	C	3.11	3.01	0.11
	OP-339	E		2.98	<0.1
	OP-366	V		2.94	0.11
Condensation product[d]	OP-326	L	-[d]	0.635	0.767

[a]E = Eastman Chemical Products, Inc., Kingsport, Tenn.
L = Lubrizol Corp., Cleveland 17, Ohio.
C = Carbide and Carbon Chemicals Co., New York.
V = Victor Chemical Works, Chicago.

[b]Theoretical acid assay of the reagents listed refer to "strong" acid only.

[c]Prepared from preceding batch by partitioning between ethylene glycol and petroleum ether.

[d]Phosphate derived from a diisobutylphenol-formaldehyde condensation product; equivalent weight reported by supplier as 544.

A "strong" acid assay lower than theoretical usually indicates neutral impurities, e.g., alcohols, and the presence of "weak" acid in a dialkylphosphoric acid usually indicates contamination with monoalkylphosphoric acid.

Uranium extractions by 0.1 M solutions of these compounds in kerosene (from 0.004 M uranium(VI) solutions, a/o phase ratio 1/1) were:

Compound	Batch No.	Uranium Extraction Coefficient (o/a)			
		0.5 M SO_4, pH 1	0.4 M PO_4, pH 1	1.4 M PO_4, pH 1	1.4 M PO_4, pH 2
Di(2-ethyl-4-methylpentyl)-phosphoric acid	OP-344	90	20	1.1	2.0
Di(2-propyl-4-methylpentyl)-phosphoric acid	OP-345	60	15	0.7	1.3
Di(2-ethylhexyl)-dithiophosphoric acid	OP-323	0.03			
D2EHPA	OP-302	90	20	1.1	1.8
	OP-339	90	20	1.1	2.2
	OP-366	90	20	0.9	1.9

With zinc di(4-methyl-2-pentyl)dithiophosphate (OP-330, Lubrizol Corp.) the $E_a^o(U)$ was <0.01, and with the condensation product (OP-326) at about 0.5 eq./liter the $E_a^o(U)$ was 220; both extractions were from 0.5 M SO_4, pH 1.

Phosphine Oxide. A sample of tri-n-butylphosphine oxide (OP-335, Arapahoe Chemicals, Inc., Boulder, Colo.) contained 15-18% water (supplier's analysis), 16% free acid, and 2.1% combined acid

calculated as dibutylphosphinic acid as received. The "combined acidity" was measured by an iodometric procedure (ORNL-1964 p. 106) and is considered to be dialkylphosphinous acid (or dialkylphosphine oxide), R_2HPO. In line with previous experience (ORNL-1964 p. 4), these contaminants showed high uranium extraction power from the usual test solutions at low uranium levels and obscured the performance of the phosphine oxide content of this new sample. Extraction tests at high uranium levels will follow.

Synergistic Extractants. Tests of synergistic uranium extraction combinations in which the acidic component is 0.1 M di(2-ethylhexyl)phosphoric acid (ORNL-2172 pp.10ff) have been extended to the following neutral organophosphorus compounds (0.1 M in kerosene, aqueous uranium(VI) concentration = 0.004 M, a/o phase ratio = 1/1):

Neutral Compound	Batch No.	Source[a]	U Extraction Coefficient (o/a) 0.5 M SO_4, pH 1 27°C	0.5 M SO_4, pH 1 50°C	1.5 M H_2SO_4 25-27°C	1.5 M H_2SO_4 50°C
None			110	55	3	
Phosphites						
Tri-n-butyl (83%)	OP-85	VC			12	4.5
Tri(2-ethyl-hexyl) (92%)	OP-83	VC	330		7	2.7
Di-n-hexyl[b]	OP-325	L			25	
Phosphates						
Tri-n-butyl	OP-338	CS	470		13	3.8
Tri(2-ethylhexyl)	OP-210	C	270		5	2.0
Tri-n-amyl	OP-378	ORNL[c]			10	3.7
Tricresyl	OP-333	ORNL[c]			2.4	1.5
Triphenyl	OP-322	ORNL[c]			5	3.1
Tri(terbutyl-phenyl)	OP-328	L			4	
Phosphonates						
Di-n-butyl n-butyl	OP-306	VC	1700		30	12
Di-n-hexyl n-hexyl	OP-329	L			40	
Di(2-ethylhexyl) 2-ethylhexyl	OP-162	VC	900		17	5.2
Di-n-butyl chloromethyl	OP-319	V			30	9
Di-n-butyl cyclohexyl	OP-347	S			9	
Di(2-ethylhexyl) chloromethyl	OP-318	V			20	6
Di-n-butyl benzene	OP-101	V			14	5
Diethyl 2-ethyl-1-hydroxyhexyl	OP-171	VC			11	

Neutral Compound	Batch No.	Source[a]	U Extraction Coefficient (o/a) 0.5 M SO_4, pH 1 27°C	0.5 M SO_4, pH 1 50°C	1.5 M H_2SO_4 25-27°C	1.5 M H_2SO_4 50°C
Phosphinates						
n-Butyl di-n-butyl	OP-93	ORNL[c]	3500		75	25
n-Butyl di-n-hexyl	OP-313	W	3500		75	25
Phosphine oxides						
Tri-n-butyl	OP-300-C	ORNL			120	
Tri(2-ethylhexyl)	OP-299	ORNL	650	240	12	4.4
Tri-n-octyl	OP-289	ORNL	3500		70	30
Tri-n-decyl	OP-292	ORNL			75	25
Other compounds						
n-Octylbis(dimethylamido)-phosphate	OP-336	P			30	
Tridecylbis(dimethylamido)-phosphate	OP-337	P			30	
Tri(2-ethylhexyl)-phosphonoacetate	OP-312	W			12	5

[a] C = Carbide and Carbon Chemicals Co., New York.
CS = Commercial Solvents Corporation, Terre Haute, Ind.
L = Lubrizol Corp., Cleveland, Ohio.
P = Pennsylvania Salt Manufacturing Co., Philadelphia.
S = Shea Chemical Corporation, New York.
V = Victor Chemical Works, Chicago.
VC = Virginia-Carolina Chemical Corp., Richmond, Virginia.
W = Westvaco Mineral Products Division, Carteret, New Jersey.

[b] Di-n-hexylphosphite, $(RO)_2POH$. The hydrogen is not ionized sufficiently to be titrated satisfactorily with 0.1 M NaOH in 70% aqueous ethanol.

[c] Supplied by W. H. Baldwin, Chemistry Division, ORNL.

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

The purity of some new compounds and of some new batches of compounds previously reported was examined by direct potentiometric titration with perchloric acid in nonaqueous medium to determine the apparent equivalent weights, and by differential titration as a measure of primary, secondary, and tertiary amine contents (Table 1.1). For description of procedures, and values found for previous compounds, see ORNL-1734 pp. 103ff, -1922 pp. 87 ff, and -2099 p. 63.

The uranium extraction from sulfate solution (0.004 M uranium(VI), 1 M SO_4, pH 0.9, a/o phase ratio = 1/1) in a series of diluents is shown in Table 1.2. For discussion of these

Table 1.1 New Organonitrogen Compounds

Compound	Batch No.	Source[a]	% by Differential Titration			Equiv. Wt.	
			Prim.	Secon.	Tert.	Theo.	Found
Primary amines							
1-Heptyloctyl	270A	A	99	<1	<1	227	238
1-Undecyldodecyl	272A	A	97	2	1	340	368
Amine 21F81, 1-(3-ethylpentyl)-4-ethyloctyl	120C	C	>99	-	-	254	255
Secondary amines							
Amine S-24, bis(1-isobutyl-3,5-dimethylhexyl)	30D	C	<1	98	2	355	364
"Secondary Rosin Amine"	277A	H					571
Tertiary amines							
Di(2-ethylhexyl)-n-hexyl	195A	C	1	10	89	326	319
Tri-iso-octyl	239A	C	5	2	93	354	357
	239B	GR	2	>1	>96		353
	239C	C	>1	9	>89		358
Tri-n-decyl	84D	B				438	477
Didodecenyl-n-butyl	253A	R	2	1	97	406	413
	253B	R	2	7	91		433
Other compounds							
Deriphat 150A, $CH_3(CH_2)_{11}NH(CH_2)_2CO_2Na$	278A	G	-	-	-	248	144
Alkylaniline C-5, $NH_2(C_6H_4)R$, $R \approx C_{12}$	254A	M	-	-	-	~168	179
Fatchemco DMO, $C_{17}H_{32}CONH(CH_2)_3N(CH_3)_2$	256A	U	-	-	-	365	349
Diamine 26, "Tallow"-$NH(CH_2)_3NH_2$	281A	G	-	-	-	-	189

[a]
A = Armour Chemical Division, Chicago
B = Bios Laboratories, New York
C = Carbide and Carbon Chemicals Co., New York
G = General Mills, Inc., Kankakee, Ill.
GR = Gulf Oil Corp., Pittsburgh, Pa.
H = Hercules Powder Co., Wilmington, Del.
M = Monsanto Chemical Co., St. Louis
R = Rohm and Haas Co., Philadelphia
U = Universal Chemical Corp., Lonsdale, R. I.

Table 1.2 Preliminary Tests of Uranium Extractions from Sulfate Solutions

Compound	Batch No.	Concn., M	% U Extracted and Extraction Coeff. (o/a) Kerosene %	Kerosene E	Chloroform %	Chloroform E	Benzene %	Benzene E	Benzene Prewashed %	Benzene Prewashed E	Phase Separation
Primary amines											
1-Heptyloctyl	270A	0.01	33		32		32		30		
		0.1	97[a]	25	99	65	97	30	96	25	Good
1-Undecyldodecyl	272A	0.01	20		23		31		21		
		0.1	97[a]	35	99	100	98	45	96	25	Good
Amine 21F81, 1-(3-ethylpentyl)-4-ethyloctyl	120C	0.01	32		39		33		32		
		0.1	96	25	98	65	97	30	96	25	Good
Secondary amines											
Amine S-24, bis(1-isobutyl-3,5-dimethylhexyl	30D	0.01	42		4		29		29		
		0.1	99	100	61	1.5	96	25	94	16	Good
Amine 9D-178	193G	0.01	31		8		34		32		
		0.1	99	70	75	3	98	55	97	30	Good
"Secondary Rosin Amine"	277A	0.1	74	3	89	8	94	15	93	14	Good
N-(p-sec-amylbenzyl)-1-isobutyl-3,5-dimethylhexyl	251B	0.01	28		13		29		29		
		0.1	99	140			98	90	98	70	Good
Tertiary amines											
Di(2-ethylhexyl)-n-hexyl	195A	0.1	31	0.4	37	0.6	51	1	25	0.6	
Tri-iso-octyl	239A	0.01	39				40		41		
		0.1	99[b]	100	38	0.6	99	100	99	70	Good

Table 1.2 (cont'd.)

Compound	Batch No.	Concn., M	% U Extracted and Extraction Coeff. (o/a) Kerosene %	Kerosene E	Chloroform %	Chloroform E	Benzene %	Benzene E	Benzene Prewashed %	Benzene Prewashed E	Phase Separation
Tertiary amines (cont'd.)											
Tri-iso-octyl	239B	0.01	42		0.5		40		40		
		0.1	99[c]	80	43	0.8	99	95	98	50	Good
	239C	0.01	39		2		37		39		
		0.1	98[c]	60	49	1	98	60	98	40	Good
Tri-n-decyl, prewashed[a]	84D	0.1			83	5	99	120			Good
Didodecenyl-n-butyl	253A	0.01	36		3		48		48		
		0.1	98[c]	70	77	3	99	130	99	100	Good
	253B	0.01	37		7		50		49		
		0.1	98[c]	60	77	3	99	140	99	100	Good
Other compounds											
Quaternary B-104, dimethyldidodecenyl-ammonium chloride	247A	0.01[d]	1.5		9		9		8		
		0.1[d]	39	0.6	40	0.7	44	0.8	46	0.8	Good
Deriphat 150A	278A	0.1	- - - - - - - - - - Insoluble - - - - - - -								
Alkylaniline C-5	254A	0.05	nil		9	0.1	3rd phase		nil		Good
Fatchemco DMO	256A	0.05	nil				nil		nil		Emulsions
Diamine 26	281A	0.1	ppt		36	0.6	ppt		<1		
N,N'-bis(1-heptyl-octyl)ethylene-diamine	271A	0.1	3rd phase		63	2	3rd phase		31	0.4	Poor

Table 1.2 (cont'd.)

[a]Chloroform and benzene solutions of tri-n-decylamine prewashed with 2% H_2SO_4 solution at 25[a]:1[o], then reconverted to free amine and adjusted to 0.1 M.

[b]Kerosene diluent modified by addition of 2 v % capryl alcohol (octanol-2).

[c]Kerosene diluent modified by addition of 3 v % mixed primary tridecanols.

[d]Initially containing some isopropyl alcohol, since compound was added as ~65% solution in isopropyl alcohol.

standardized tests and for extractions obtained with previous compounds, see ORNL-1734 pp. 6ff, -1922 pp. 4ff, and -2099 pp. 2ff.

Losses to Aqueous Solutions. The loss rates of several amines by distribution to aqueous solutions are shown in Table 1.3. For discussion of the measurements and for previously measured loss rates see ORNL-1734 pp. 45 ff, -1922 pp. 38 ff, and -2099 pp. 41ff. The fraction readily lost represents the content of titratable base that is considerably more water soluble than the principal component, e.g., amines of lower molecular weight. The steady-state loss (parts of amine per million parts of aqueous solution) is typically constant or nearly so over a wide range of aqueous/organic phase ratios, and is characteristic of the principal component or components. (The "steady state" loss of the quaternary ammonium chloride B-104 to water may not be so constant. The loss rate of about 1 g per liter of H_2O was at a/o phase ratios up to 50/1, but there was some indication that the distribution at higher a/o ratios might follow a normal distribution law.)

2.0 PROCESS DEVELOPMENT STUDIES

2.1 Amine-Molybdenum Precipitation (D. J. Crouse, W. D. Arnold A. D. Kelmers, R. S. Lowrie)

As previously reported, molybdenum is readily extracted along with uranium in the Amex process; both uranium and molybdenum are effectively stripped by sodium carbonate solutions, but only uranium by the usual chloride stripping solutions, offering a means for separation. Formation under certain conditions of amine-molybdenum precipitates, presumably heteropolymolybdates, has been observed in laboratory-scale studies (ORNL-1959, -2099, -2112). Two different general conditions of precipitation were reported: (1) during extraction from sulfate liquors when appreciable molybdenum was present together with vanadium(V) and phosphate, and particularly with Amine 9D-178 in unmodified kerosene diluent; (2) during chloride stripping in some tests when appreciable molybdenum was present together with phosphate or vanadium(V). The tendency toward precipitate formation varied considerably with choice of amine-diluent combination, and was especially noticeable with tri-iso-octyl- and tri-n-octylamine. The general tendency toward precipitation appeared to vary with diluents in the order kerosene > kerosene + alcohols > Amsco G > Esso Heavy Aromatic Naphtha. The precipitates usually formed quickly, but sometimes only after a lapse of several hours.

The previous batch tests at organic-phase molybdenum loadings in the range 1.1-1.5 g/liter (ORNL-2099, Table 9-12) were extended to cover a molybdenum range of ~0.1 to 3 g/liter for several amines in different diluents. The aqueous liquors used were identical except for the molybdenum concentration, 0.056-1.0 g/liter. Molybdenum was added as $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and the liquors were aged 3-8 days before the tests. The present tests

Table 1.3 Losses of Amine to Aqueous Solutions

Amine (Initially 0.1 M)	Batch No.	Diluent[a]	Aqueous Solution[b]	Loss of Amine: Fraction Readily Lost, % of initial	Loss of Amine: Steady-state Loss, Mg per liter Aq
Amine 21F81, 1-(3-ethylpentyl)-4-ethyloctyl	120C	Kerosene	Synthetic liquor	0	17
1-Heptyloctyl	270A	Kerosene + 3 v % TDA	Synthetic liquor	0	20
1-Undecyldodecyl	272A	Kerosene + 3 v % TDA	Synthetic liquor	8	<5
Amine S-24, bis(1-isobutyl-3,5-dimethylhexyl)	30C	Kerosene	Synthetic liquor	1.3[c]	10[c]
	30D	Kerosene	Synthetic liquor	1.1	14
Amine 9D-178	193D	Kerosene	0.33 M HNO_3, 0.67 M NH_4NO_3	6	2
Tri-iso-octyl	239B	Kerosene + 3 v % TDA	Synthetic liquor	1	20
	239C	Kerosene + 3 v % TDA	Synthetic liquor	3	14
Quaternary B-104, dimethyldido-decenylammonium chloride	247A	Kerosene + 5 v % TDA	Water		~1000
		Kerosene + 5 v % TDA	1 M HCl	0.6	3
		Kerosene + 5 v % TDA	1 M HNO_3	5	4
		Kerosene + 5 v % TDA	0.5 M Na_2CO_3	4	8

[a]"TDA" = mixed primary tridecanols.

[b]The synthetic liquor contained 5.8 g Fe(III), 3.3 g Al, 50 g SO_4, 2 g PO_4, and 1.7 g F per liter and had a pH of 0.8.

[c]Previously reported 3% initial loss, 6 ppm steady-state loss (ORNL-2099) from test over shorter range of phase ratios.

[d]Initially containing some isopropyl alcohol, since the compound was added as ~65% solution in isopropyl alcohol.

also differed from the previous in using three successive chloride strip stages instead of only one, followed as before by a regeneration stage with sodium carbonate.

If precipitation was seen at any point in the test procedure, the test was stopped and a sample of the organic phase was titrated for comparison of the amine concentration with that of the head organic. The first point of visible precipitation and the corresponding amine loss are noted in Table 2.1. The precipitates designated P were all amber to green, gummy solids. The material designated TP was white, much smaller in quantity, and possibly only an emulsion. It is not certain as yet whether this material contained amine. Titrations indicated 1 and 2% amine losses in some of the tests that showed "trace precipitation"; however, the analytical uncertainty in titration of the small samples used could amount to 2%.

It should be emphasized that precipitate formation or lack of formation was determined only by visual observation. Since the test samples were small, it is quite possible that trace amounts of solids could have been overlooked in some cases. This possibility will be checked by larger scale tests.

Tri-iso-octylamine in Kerosene and in Esso HAN: In kerosene-alcohol diluent, precipitation during the extraction cycle occurred at the highest molybdenum loading tested, ~3 g/liter organic. Amine loss in this case was severe, ~10%. No precipitation during extraction was observed even at this loading level when the amine was in Esso Heavy Aromatic Naphtha, with or without added alcohol.

In the chloride stripping cycle, the molybdenum tolerance of tri-iso-octylamine is quite low in kerosene-alcohol diluent, precipitation occurring in the third chloride stripping contact at a molybdenum loading of only about 0.5 g/liter organic. Precipitation was not observed in Esso Heavy Aromatic Naphtha at a loading of 0.6 g/liter, but was copious when the loading was increased to 1.2 g/liter.

Amine 9D-178 in Kerosene: Precipitation occurred during extraction at the highest molybdenum loading, ~3 g Mo/liter, but not during chloride stripping in any of the tests, with loadings up to 1.2 g Mo/liter. "Trace precipitation" occurred during regeneration, but titrations indicated no significant amine loss.

Amine S-24 in Kerosene: Precipitation occurred during extraction at the highest molybdenum loading, ~3 g Mo/liter, in unmodified kerosene, but not in kerosene modified with 2 v % tridecanol. "Trace precipitation" occurred in two of the chloride strip stages and one regeneration stage, but titrations indicated no significant amine loss.

Di(tridecyl P)amine in Kerosene: No precipitation occurred during any of the extraction or stripping stages. "Trace precipitation" occurred in some of the regeneration stages but titrations indicated no significant amine loss.

Table 2.1 Amine-Molybdenum Compatibility Tests

Amine solutions scrubbed with dilute sulfuric acid, sodium carbonate, and water and then adjusted to 0.1 M.

Head liquors (synthetic), 0.056 to 1.0 g Mo, 1 g U, 2 g Fe(III), 2 g Al, 1 g V(IV), 2 g PO_4 per liter, pH 1, aged 3-8 days.

Chloride strip, 1.0 M NaCl--0.05 M H_2SO_4

Regeneration, 3 w/v % Na_2CO_3

Procedure: Amine solution contacted with the liquor at a/o = 3/1, stripped by three successive contacts with the chloride strip solution at a/o = 2/1, and finally regenerated to the free base form at a/o = 4/1; each contact was for 5 min with 0.5 hr standing between contacts for observation of precipitate formation

Amine (0.1 M)	Diluent	Mo concn, g/liter		Observations[a]					Amine Loss, % of initial
		Head Liquor	Extract	Extr. Stage	Chloride Strip Stages 1st	2nd	3rd	Regen. Stage	
Tri-iso-octyl	95% kerosene--5% TDA[b]	0.056	0.12	NP	NP	NP	NP	TP	<1
		0.11	0.29	NP	NP	NP	NP	TP	1
		0.22	0.56	NP	NP	NP	P	--	3
		0.40	0.87	NP	P	--	--	--	7
		1.0	3[c]	P	--	--	--	--	10
Tri-iso-octyl	92% kerosene--8% TDA[b]	0.056	0.087	NP	NP	NP	NP	NP	<1
		0.11	0.24	NP	NP	NP	NP	TP	<1
		0.22	0.46	NP	NP	NP	P	--	4
		0.40	0.71	NP	P	--	--	--	8
		1.0	3[c]	P	--	--	--	--	10
Tri-iso-octyl	Esso HAN[d]	0.056	0.16	NP	NP	NP	NP	NP	<1
		0.11	0.31	NP	NP	NP	NP	NP	<1
		0.22	0.62	NP	NP	NP	NP	NP	2
		0.40	1.23	NP	NP	P	--	--	7
		1.0	3.0	NP	P	--	--	--	20
Tri-iso-octyl	98% Esso HAN[d]--2% TDA[b]	0.056	0.15	NP	NP	NP	NP	NP	<1
		0.11	0.31	NP	NP	NP	NP	NP	<1
		0.22	0.59	NP	NP	NP	NP	NP	<1
		0.40	1.22	NP	NP	P	--	--	6
		1.0	3.1	NP	P	--	--	--	20

Table 2.1 (cont'd.)

Amine (0.1 M)	Diluent	Mo concn, g/liter Head Liquor	Mo concn, g/liter Extract	Observations[a] Extr. Stage	Observations[a] Chloride Strip Stages 1st	Observations[a] Chloride Strip Stages 2nd	Observations[a] Chloride Strip Stages 3rd	Observations[a] Regen. Stage	Amine Loss, % of initial
9D-178	Kerosene	0.056	0.16	NP	NP	NP	NP	TP	<1
		0.11	0.28	NP	NP	NP	NP	TP	1
		0.22	0.60	NP	NP	NP	NP	TP	<1
		0.40	1.01	NP	NP	NP	NP	TP	2
		1.0	3[c]	P	--	--	--	--	3
9D-178	98% kerosene-- 2% TDA[b]	0.056	0.13	NP	NP	NP	NP	TP	<1
		0.11	0.26	NP	NP	NP	NP	TP	1
		0.22	0.56	NP	NP	NP	NP	TP	2
		0.40	1.17	NP	NP	NP	NP	TP	2
		1.0	3[c]	P	--	--	--	--	6
S-24	Kerosene	0.056	0.13	NP	NP	NP	NP	NP	<1
		0.11	0.30	NP	NP	NP	NP	NP	<1
		0.22	0.61	NP	NP	NP	TP	--	<1
		0.40	1.19	NP	NP	NP	TP	--	<1
		1.0	3[c]	P	--	--	--	--	3
S-24	98% kerosene-- 2% TDA[b]	0.056	0.13	NP	NP	NP	NP	NP	<1
		0.11	0.29	NP	NP	NP	NP	NP	<1
		0.22	0.60	NP	NP	NP	TP	--	<1
		0.40	1.20	NP	NP	NP	TP	--	1
		1.0	3.0	NP	NP	NP	NP	TP	2
Di(tri-decyl P)	Kerosene	0.056	0.14	NP	NP	NP	NP	NP	<1
		0.11	0.30	NP	NP	NP	NP	NP	<1
		0.22	0.59	NP	NP	NP	NP	TP	<1
		0.40	1.20	NP	NP	NP	NP	TP	<1
		1.0	3.0	NP	NP	NP	NP	TP	<1
Di(tri-decyl P)	98% kerosene-- 2% TDA[b]	0.056	0.14	NP	NP	NP	NP	NP	<1
		0.11	0.30	NP	NP	NP	NP	NP	<1
		0.22	0.59	NP	NP	NP	NP	TP	<1
		0.40	1.20	NP	NP	NP	NP	TP	<1
		1.0	3.0	NP	NP	NP	NP	TP	<1

Table 2.1 (cont'd.)

[a]NP = no precipitate observed
P = amber to green, gummy precipitate
TP = trace of white material at interface, possibly a precipitate

[b]TDA = mixed primary tridecanols

[c]Molybdenum concentration expected if precipitation had not occurred during extraction

[d]HAN = Esso Heavy Aromatic Naphtha (scrubbed before use with acid and sodium carbonate solution).

These results confirm the previously noted orders of susceptibility to this precipitation, and in addition show a strong dependence on the molybdenum concentration in the organic phase. It should also be noted here that the effects observed were from extraction of a liquor of particular composition under set conditions. In other tests, as might be expected, variations in residence time and in liquor composition other than the molybdenum level (e.g., concentrations of phosphate and vanadium and of metals which complex phosphate, such as iron(III)) have been important. More quantitative data on these variables will be reported later.

The molybdenum extraction coefficients obtained in the foregoing tests (see also section 2.2) followed the same unusual pattern observed previously (ORNL-2099 p. 38), i.e., the extraction coefficients as usually calculated increased instead of remaining constant or decreasing as the molybdenum concentration increased in the organic phase. At each level, the extraction coefficient was decreased somewhat by addition of alcohol to the solvent.

Continuous Countercurrent Tests. No precipitation was observed in either of two continuous countercurrent tests, with Amine S-24 and Amine 9D-178, of an Amex process for recovery of molybdenum by-product from a uranium liquor containing relatively high concentrations of molybdenum and phosphate. The synthetic feed liquor for these tests contained 0.3 g U, 0.3 g Mo, 15 g Fe(III), 5 g Al, 10 g PO_4, and 160 g SO_4 per liter at pH 1. Uranium and molybdenum were extracted together by 0.1 M S-24 or 9D-178 in kerosene, the loading being approximately 2 g U and 2 g Mo per liter. The uranium was selectively stripped in four stages with 0.9 M NaCl--0.1 M HCl, and then the molybdenum was stripped in three stages with 10 w/v % sodium carbonate. The flow ratios of head liquor/organic/chloride strip/carbonate strip were 30/4/1/1.

Sodium Carbonate Stripping. It was noted in connection with the previously reported tests (ORNL-2099 p. 25) that small amounts of precipitate sometimes formed during carbonate stripping of solvents containing large amounts of molybdenum. In subsequent studies on direct carbonate stripping of molybdenum and uranium together, precipitates occurred under conditions where little or no excess sodium carbonate above stoichiometric was present, but not when reasonable quantities of excess carbonate were present. It is not certain that these precipitates contained amine.

The general study of amine-molybdenum precipitation is continuing. On the basis of present knowledge, it appears that process problems arising from this source can be avoided with little difficulty when handling low-molybdenum liquors by proper choice of amine, diluent, and stripping method. With high-molybdenum liquors the compatibility requirements are considerably more severe. A more quantitative knowledge of these requirements is needed and this will be the objective of future work.

2.2 Effect of Alcohol on Extraction and Stripping

The extraction and stripping coefficients from the compatibility tests (Table 2.1) show the extent to which the extraction power of each of the amine-diluent combinations used is depressed by the addition of a long-chain alcohol (Table 2.2). These results are in general agreement with previous measurements of the effects of added alcohols (ORNL-1959 p. 23, -2099 p. 8), but show more effect on Amine 9D-178 and Amine S-24 than has previously been noted with other amines.

For tri-iso-octylamine in kerosene-tridecanol, the uranium coefficient decreased by a factor of about 3 as the alcohol concentration was increased from 5 to 8 v %. The addition of only 2 v % tridecanol to the kerosene diluent had a fairly strong adverse effect on the uranium coefficients of the secondary amines with branching in close proximity to the nitrogen, i.e., Amine S-24 and Amine 9D-178. In contrast, addition of 2 v % increased the uranium extraction coefficients with di(tridecyl P)amine, in which branching is more distant from the nitrogen. This is ascribed at least in part to the marked depression by the alcohol of iron(III) extraction, so that uranium extraction benefited from decreased competition. The molybdenum extraction coefficients were shifted in the same directions as those of uranium by the addition of alcohol, but to a somewhat less extent.

The uranium stripping coefficients found in these tests emphasize the previously noted (ORNL-1959 pp. 42, 51) differences in effectiveness of chloride stripping of various amine-diluent combinations:

	S_o^a		S_o^a
Tri-iso-octylamine		Amine S-24	
95% kerosene--5% TDA	30	kerosene	400
92% kerosene--8% TDA	80	98% kerosene--2% TDA	650
Esso HAN	15		
98% HAN--2% TDA	30	Di(tridecyl P)amine	
		kerosene	15
Amine 9D-178		98% kerosene--2% TDA	25
kerosene	300		
98% kerosene--2% TDA	350		

The chloride stripped uranium much more effectively from Amine 9D-178 and Amine S-24 than from tri-iso-octylamine and di(tridecyl P)amine. As expected, the presence of alcohol improved the stripping. The coefficients listed are from the tests starting with 0.056 g/liter molybdenum liquor (Table 2.1); the uranium stripping in the other tests was similar.

Table 2.2 Extraction Coefficients from Compatibility Tests

(See Table 2.1)

Amine and Diluent	Uranium Extraction Coefficient				
	A*	B	C	D	E
Tri-iso-octyl					
95% kerosene--5% TDA	85	90	80	60	ppt
92% kerosene--8% TDA	25	25	25	20	ppt
Esso HAN	200	220	190	140	80
98% HAN--2% TDA	120	120	120	95	45
9D-178					
kerosene	100	95	70	65	ppt
98% kerosene--2% TDA	55	55	50	35	ppt
S-24					
kerosene	140	150	130	110	ppt
98% kerosene--2% TDA	30	45	45	40	20
Di(tridecyl P)					
kerosene	70	70	60	55	30
98% kerosene--2% TDA	95	95	85	65	30
	Molybdenum Extraction Coefficient				
Tri-iso-octyl					
95% kerosene--5% TDA	8	20	30	45	ppt
92% kerosene--8% TDA	3	8	15	20	ppt
Esso HAN	25	45	85	155	300
98% HAN--2% TDA	15	35	60	120	230
9D-178					
kerosene	10	15	30	45	ppt
98% kerosene--2% TDA	6	12	20	40	ppt
S-24					
kerosene	15	30	55	90	ppt
98% kerosene--2% TDA	10	20	30	70	140
Di(tridecyl P)					
kerosene	15	30	50	75	150
98% kerosene--2% TDA	15	25	--	65	110

*A = 0.056 g/liter initial molybdenum concentration
B = 0.11
C = 0.22
D = 0.40
E = 1.0

2.3 Solvent Extraction of Uranium from Carbonate Solutions (F. J. Hurst)

Early tests (ORNL-1922) showed that certain quaternary ammonium compounds extract uranium from solutions of sodium carbonate. The uranium extraction coefficients of the more favorable extractants, while low, were possibly of useable magnitude, but diluent limitations were severe, the practicable aromatic or aliphatic hydrocarbon solvents appearing unsuitable. However, initial results (ORNL-2099) with one compound (Rohm and Haas experimental compound Quaternary B-104, dimethyldidodecenylammonium chloride) were encouraging in that uranium extraction was significant and phase separation rates were reasonable when the aromatic petroleum product Amsco G was used as diluent. This quaternary compound has been further evaluated with regard to (1) effects of liquor composition, temperature, and choice of diluent on extraction, (2) stripping methods, and (3) determination of losses of extractant through distribution to aqueous solutions.

Solutions Used. Rohm and Haas Quaternary B-104 was supplied as about a 65% solution in isopropyl alcohol. This solution was diluted with either kerosene or Amsco G. Prior to use for extraction tests the organic solutions were contacted alternately with 0.5 M Na_2CO_3 and 0.5 M HCl (o/a = 1/3), twice each, to remove most of the isopropyl alcohol and possibly other impurities. The extractant was then converted to the carbonate form by five to eight contacts with fresh volumes of 0.5 M Na_2CO_3 solution (o/a = 1/3) until no chloride could be detected in the aqueous phase. Modification of the kerosene diluent with ~5 v % of a long-chain alcohol was necessary to prevent formation of a third phase during contact with the carbonate solutions. This was not necessary with the Amsco G diluent but did improve the rate of phase separation. A few experiments were made with 0.5 N amine, but phase separation was considerably faster with 0.1 N, and 0.1 N was used in all the tests reported here.

Two methods were used to determine the extractant concentration: (1) complete conversion to the chloride salt by contacting with successive volumes of 0.5 M HCl, followed by stripping with 1 M HNO_3 and analysis of the stripped chloride, and (2) direct potentiometric titration of a sample dissolved in chloroform with a standard solution of perchloric acid in dioxane. With the second method, best results were when the nitrate salt was titrated. Agreement between the two methods of analysis was good.

The aqueous solutions used in extraction tests were prepared by dissolving sodium uranyl tricarbonate in a solution of sodium carbonate, sodium carbonate plus sodium bicarbonate, or sodium bicarbonate to give a uranium concentration of approximately 1 g/liter.

Effect of Carbonate Concentration. A strong dependence on aqueous carbonate concentration of the uranium extraction by 0.1 N B-104 carbonate in three different diluents (95% kerosene--

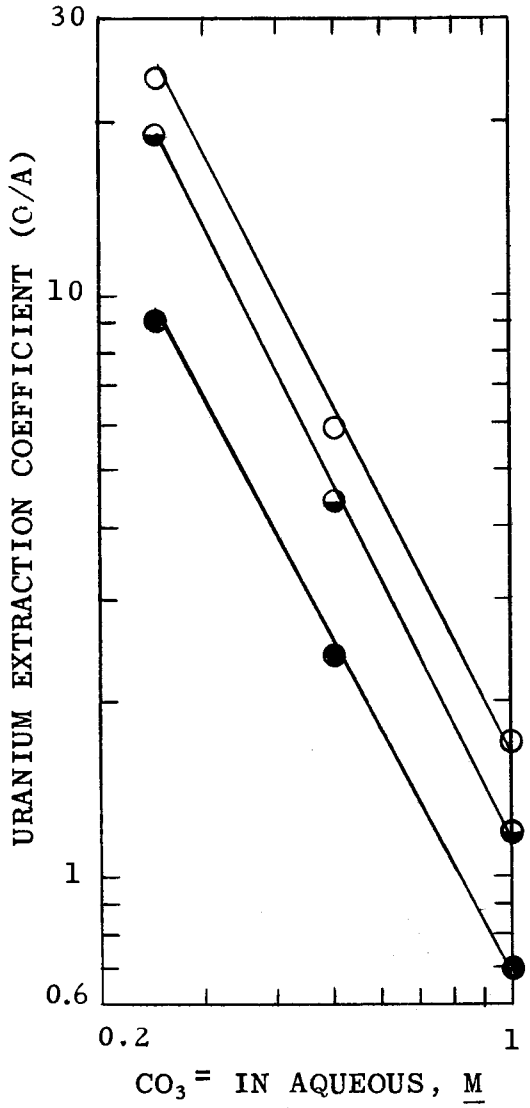

Fig. 2.1 Effect of Carbonate Concentration on Extraction of Uranium from Sodium Carbonate Solution with 0.1 N Quaternary B-104 Carbonate. Initial Uranium in Aqueous, 1 g/liter; phase ratio, 1/1; contact time, 5 min.

DILUENT
- ● Amsco G
- ◒ 97% Amsco G--3% tridecanol
- ○ 95% kerosene--5% tridecanol

5% tridecanol, Amsco G, and 97% Amsco G--3% tridecanol) was shown (Fig. 2.1), $E_a^o(U) \propto (CO_3^=)^{-2}$, as expected for tetravalent-divalent anion exchange. Considerable difference in uranium extraction with these different diluents was also shown, the highest being with the 95% kerosene--5% tridecanol diluent. The addition of 3 v % tridecanol to the Amsco G diluent improved the coefficients considerably over those with Amsco G alone.

Phase separations were extremely slow when the sodium carbonate concentration was 1 M. For example, with 97% Amsco G--3% tridecanol (which gave the fastest separation of the diluents tested) and 1 M Na_2CO_3, the phases separated in approximately 0.5 hr in contrast to 4 and 3.5 min with 0.25 M and 0.5 M Na_2CO_3, respectively.

Effect of Bicarbonate:Carbonate Ratio. Variation of the aqueous bicarbonate concentration from 0 to 97.5% of the total

carbonate concentration, with the total concentration held constant at 0.50-0.51 M initial concentration, had little effect on uranium extraction by 0.1 N B-104 (o/a phase ratio 1/1, 5 min contact time):

Initial Bicarbonate, mole % of Total Carbonate	Final pH	Uranium Extraction Coefficient (o/a)		
		Amsco G Diluent	Amsco G + 3% TDA Diluent	Kerosene + 5% TDA Diluent
0	11.3-11.5	2.4	4.4	5.9
20	10.7-10.8	2.3	4.5	5.7
50	10.2-10.3	2.7	4.6	6.3
97.5	9.4- 9.6	2.2	3.3	5.5

It should be noted that relative bicarbonate concentration is expected to be more important at higher total carbonate concentrations, since $E_a^o(U) \propto (HCO_3^-)^{-4}$ is expected for the tetravalent-monovalent anion exchange.

Effect of Temperature. Increase of temperature caused an appreciable but not prohibitive decrease in extraction of uranium from 0.5 M Na_2CO_3 solution by 0.1 N B-104, while the rate of phase separation was virtually unaffected:

Diluent	Temp., °C	Uranium Extraction Coefficient (o/a)	Phase Separation Time, min
Amsco G	27	2.4	7
Amsco G	50	1.8	6
Amsco G + 3% tridecanol	27	4.4	3.5
Amsco G + 3% tridecanol	50	2.8	3.5

Effect of Alcohol Modification of the Diluent. Since the foregoing tests showed an improvement in uranium extraction power and phase separation rate upon addition of 3-5 v % tridecanol to the diluent, additional extraction tests were made in which the tridecanol concentration in both kerosene and Amsco G diluents was varied over a wide range (0.1 N B-104, 0.5 M Na_2CO_3, o/a phase ratio 1/1, 5 min contact time):

Diluent	Uranium Extraction Coefficient (o/a)	Phase Separation Time, min
Amsco G	2.4	7
97% Amsco G, 3% tridecanol	4.4	3.5
95% Amsco G, 5% tridecanol	7.1	6
90% Amsco G, 10% tridecanol	12	4.5
85% Amsco G, 15% tridecanol	17	3
75% Amsco G, 25% tridecanol	30	2.5
68% Amsco G, 32% tridecanol	18	2

(cont'd. on p. 24)

(cont'd. from p. 23)

Diluent	Uranium Extraction Coefficient (o/a)	Phase Separation Time, min
95% kerosene, 5% tridecanol	5.9	10
95% kerosene, 5% tridecanol	5.7	15
90% kerosene, 10% tridecanol	14	8
85% kerosene, 15% tridecanol	21	6
75% kerosene, 25% tridecanol	30	4

The extraction coefficient drop to 18 at 32% tridecanol in Amsco G suggests a maximum in extraction power around 25% tridecanol.

The phase separation rate improved considerably with increase in alcohol concentration but was still not rapid (~2 min) even at the highest alcohol level.

Extraction Isotherms. Complete extraction isotherms (Fig. 2.2) were determined for 0.1 N B-104 in Amsco G diluent, containing 3, 15, and 25 v % tridecanol. The organic solutions were cascaded against successive volumes of a 0.5 M Na_2CO_3 solution containing 1 g of uranium per liter, and the phases were sampled after each contact. The beneficial effect of tridecanol is again obvious.

Stripping Tests. A few preliminary uranium stripping tests on another quaternary ammonium compound (Hyamine 10X in chloroform diluent) were reported in ORNL-2099. As expected from analogy to strong-base anion-exchange resins, uranium was effectively stripped with solutions of HCl, HNO_3, HCl-NH_4Cl, and HNO_3-NH_4NO_3, nitrate being much more effective than chloride. Some stripping was also accomplished, by direct precipitation, with a solution of sodium hydroxide.

In preliminary studies on stripping of uranium from 0.1 N B-104 in 75% Amsco G--25% tridecanol (loaded to 3.5 g of uranium per liter) 1 M NaCl solution was extremely effective, with a stripping coefficient, S_o^a, >1000. Phase separation was very rapid. However, in spite of the effectiveness of uranium stripping with neutral chloride solutions, use of a chloride stripping flowsheet does not appear attractive since the extractant would probably have to be reconverted to the carbonate form prior to recycle to the extraction circuit. As indicated in the preliminary treatment of the reagent (above), displacing of chloride with carbonate is difficult. For this reason the present emphasis is being placed on basic stripping.

With the same organic extract the stripping coefficient with 1 M $NaHCO_3$ was approximately 2. With 1 M NaOH stripping was not complete even after several successive contacts with fresh NaOH solution, and a fairly large percentage of the uranium stripped from the organic did not precipitate but remained in solution. Stripping was much more efficient with 2 M and 3 M NaOH:

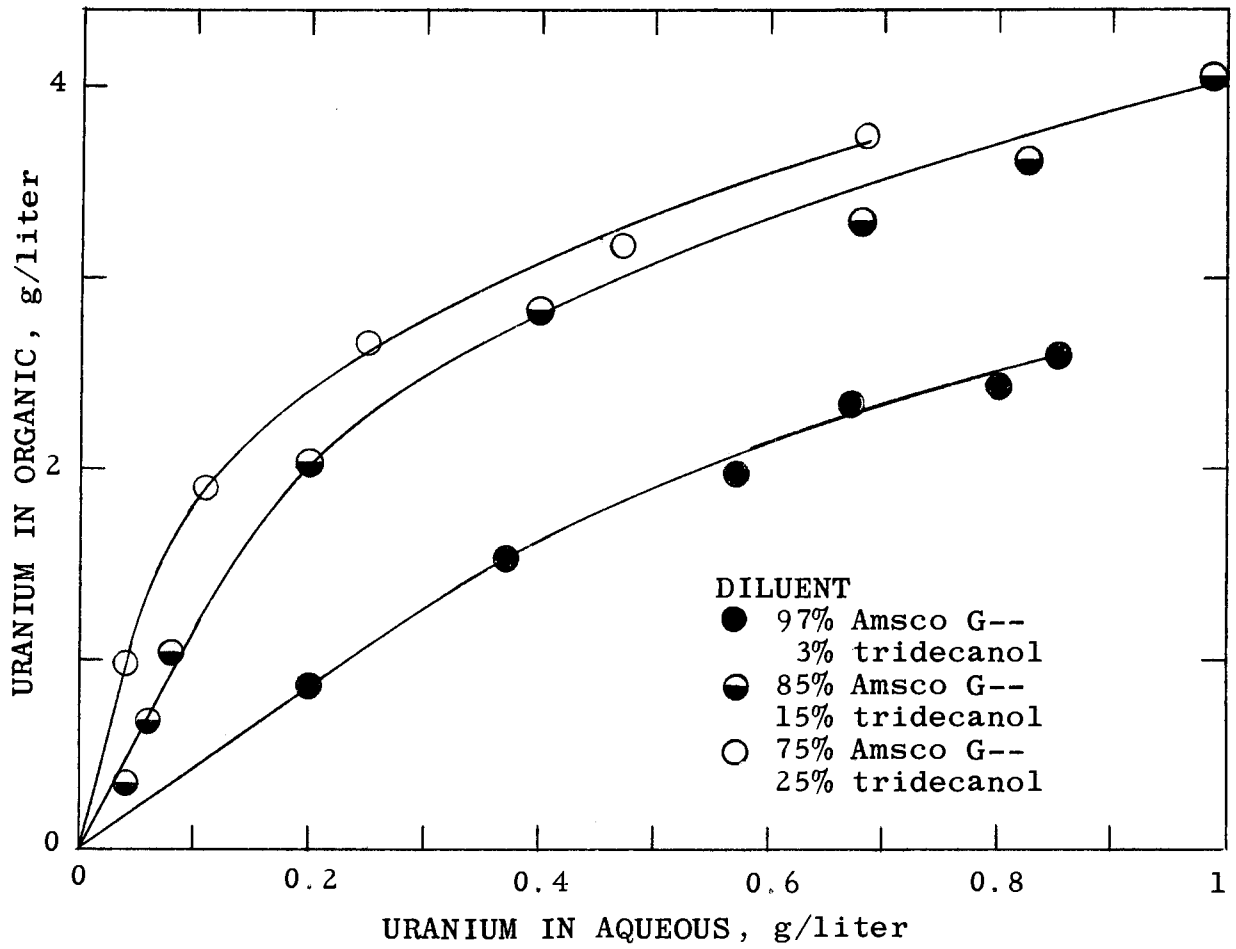

Fig. 2.2 Uranium Extraction Isotherms from 0.5 M Sodium Carbonate Solution with 0.1 N Quaternary B-104 Carbonate. Organic phase cascaded against fresh volumes of aqueous; contact time, 5 min per stage.

NaOH Concn., M	No. of Contacts	U Stripped, % of total
1	1	69
	4	91
2	1	84
	2	99
3	1	83
	2	99

The precipitate that formed on stripping with NaOH showed little tendency to collect at the organic interface or to cause emulsions but settled fairly readily in the aqueous phase.

Loss of Extractant to Aqueous Solutions. Losses of Quaternary B-104 chloride to aqueous solutions are shown in

Table 1.3. The loss rate of about 1 g/liter into water, in contrast to loss rates of only a few milligrams per liter into the acid and carbonate solutions, indicates that contact of the organic phase with water or very dilute aqueous solutions should be avoided in process use.

The laboratory-scale development of uranium extraction from carbonate solutions is continuing with major emphasis on stripping and on the behavior of other metals (e.g., vanadium, molybdenum) which could be of importance in a uranium process. Tests have also been started on extraction of tungsten, tantalum, and niobium from alkaline solutions.

3.0 ENGINEERING STUDIES

3.1 Batch Kinetic Studies of Dapex Extraction (A. D. Ryon, F. L. Daley)

The extraction kinetics of a high uranium-vanadium liquor were studied with a Dapex type extractant in tank mixers. Extraction rate constants were determined to establish orders of magnitude and also to correlate with data from dynamic kinetic studies. The mixing power, temperature, choice of continuous phase, and liquor source were varied independently.

Two mixers were used: a 6-in.-i.d. baffled tank with a 3-in. four-bladed turbine impeller (illustrated and described in ORNL-2213) and a similar 12-in.-i.d. tank with a 4-in. six-bladed impeller. The extractant was 0.16 M di(2-ethylhexyl)-phosphoric acid in kerosene plus 35 g of tributyl phosphate per liter. A synthetic liquor was used in most of the tests, but two plant liquors were tested for comparison:

	110 (Synthetic)	C-13 (Plant)	C-15 (Plant)
U g/liter	5.2	5.9	6.1
ΣV	4.8	4.7	4.8
V(V)	3.4	4.3	3.9
Fe(III)	0.52	0.60	0.4
Al	2.6	2.5	2.5
Mo	0.02	0.02	0.02
Ti	None	0.077	0.05
Si	None	0.006	0.06
SO_4	89	116	97
PO_4	3.0	3.4	3.6
Cl	1.0	1.4	1.4
F	0.28	-	-
pH	0.32	0.15	0.20

Equal volumes of feed liquor and organic phase were used in all tests. One phase was made continuous by adding the other phase to it while the turbine was running. Instantaneous samples were dipped from the mixer at timed intervals without interruption of mixing.

Treatment of Data. In ORNL-2213 it was shown that the equation for a first-order reaction gives a useful rate constant:

$$K' = \frac{1}{t} \ln \frac{C_o - C_{eq}}{C_t - C_{eq}} \tag{1}$$

where C_o = original concentration of uranium in aqueous phase
C_t = concentration of uranium at time t
C_{eq} = concentration of uranium at equilibrium

Let E = extraction efficiency = $\frac{C_o - C_t}{C_o - C_{eq}}$; then

$$1 - E = \frac{C_t - C_{eq}}{C_o - C_{eq}} \tag{2}$$

Substitution in eq. 1 gives

$$K' = \frac{1}{t} \ln \frac{1}{1 - E} = - \frac{1}{t} \ln (1-E)$$

$$\ln (1-E) = -K't \tag{3}$$

Hence, a plot of ln (1-E) against mixing time t should give a straight line of slope -K'.

The experimental values of ln (1-E) plotted against t do fall on a straight line, but it does not go through the expected intercept, ln (1-E) = 0 at t = 0. It is known that extraction occurs during the separation of the phases after the samples are taken; therefore, the actual contact time is longer than the indicated sample time by Δt. On the assumption that the extraction during phase separation has the same driving force as during mixing, the line was shifted to pass through ln (1-E) = 0, t = 0 without changing the slope. This is equivalent to the assumption that Δt was essentially constant for all the samples in any one series, which is supported by the observation that the time to achieve the primary break was constant. The values of Δt so obtained were similar to tests made under similar conditions.

Results and Discussion. The aqueous uranium concentrations found at the indicated sampling times, together with the resulting values of K' (eq. 3), and the values of Δt required to shift the ln (1-E) vs. t lines to the point ln (1-E) = 0, t = 0 , are summarized in Table 3.1.

Table 3.1 Uranium Concentration in Raffinates after Various Mixing Times

Test No.	Uranium Concentration in Raffinate, g/liter										K', min^{-1}	Δt, sec
	0 sec	5 sec	10 sec	20 sec	30 sec	45 sec	60 sec	120 sec	240 sec	480 sec		
89	5.2	--	2.30	1.85	1.44	1.07	0.68	0.35	0.23	0.23	1.57	22.2
91	5.2	--	1.67	1.21	0.81	0.54	0.37	0.21	0.20	0.21	2.58	18.0
93	5.2	--	0.99	0.63	0.39	0.28	0.23	0.22	0.23	0.23	4.35	15.0
95	5.2	--	1.05	0.54	0.34	0.23	0.20	0.20	0.22	0.23	5.77	9.0
121	5.2	3.25	2.80	2.10	1.68	1.17	0.86	0.36	0.22	0.22	1.76	12.0
123	5.2	2.40	1.95	1.32	0.93	0.60	0.43	0.24	0.23	0.23	2.70	12.6
7*	6.1	--	2.6	1.7	1.1	0.60	0.42	0.29	0.29	0.29	3.57	4.2
9**	5.9	--	2.6	1.8	1.2	0.68	0.50	0.36	0.35	0.36	3.37	6.0
125	5.2	1.86	1.31	0.73	0.46	0.32	0.26	0.23	0.23	0.26	4.35	11.5
127	5.2	1.90	1.13	0.57	0.42	0.29	0.28	0.25	0.27	--	5.36	12.0
111	5.2	--	3.25	2.45	1.89	1.52	1.07	0.47	0.26	0.25	1.72	9.0
103	5.2	--	1.71	1.27	0.87	0.64	0.46	0.26	0.23	0.25	2.44	19.8
105	5.2	--	1.55	0.90	0.61	0.41	0.29	0.24	0.24	0.25	3.65	12.6
107	5.2	--	1.56	0.93	0.57	0.39	0.32	0.24	0.24	0.24	4.00	9.6
109	5.2	--	0.92	0.50	0.35	0.27	0.24	0.23	0.24	0.27	5.83	10.2
115	5.2	3.70	3.10	2.65	2.20	1.64	1.26	0.55	0.19	0.14	1.13	18.6
113	5.2	3.30	2.70	1.99	1.60	1.13	0.84	0.32	0.20	0.19	1.64	16.2
117	5.2	2.75	2.10	1.36	0.97	0.63	0.46	0.34	0.36	0.38	3.37	6.9
119	5.2	2.15	1.46	0.93	0.76	0.63	0.60	0.61	0.63	0.65	6.45	5.5
15	5.3	--	1.80	1.20	0.74	0.44	0.32	0.16	0.15	0.15	3.00	6.6
13	5.3	--	0.64	0.44	0.46	0.45	0.44	0.43	0.46	0.51	9.84	12.6

*Plant liquor C-15 instead of synthetic liquor 110.

**Plant liquor C-13 instead of synthetic liquor 110.

Tests with three different liquors under mixing conditions which were identical except for some uncertainty in temperature showed no more difference in K' than might be attributed to the possible temperature differences (aqueous continuous, 6-in. mixer, 600 rpm, 0.020 hp/gal):

Run No.	Liquor	Temp., °C	K', min^{-1}
7	C-15 (plant)	25-28	3.57
9	C-13 (plant)	25-28	3.37
123	110 (synthetic)	25	2.70

At a given mixing speed, there was no significant difference in K' whether the aqueous phase or the organic phase was continuous:

Mixer dia, in.	Turbine Speed, rpm	Power Input, hp/gal	Organic Continuous		Aqueous Continuous	
			Run No.	K', min^{-1}	Run No.	K', min^{-1}
6	400	0.0059	89	1.57	121	1.76
	600	0.020	91	2.58	123	2.70
	900	0.067	93	4.35	125	4.35
	1350	0.220	95	5.77	127	5.36
12	323	0.0025	111	1.72		
	430	0.0059	103	2.44		
	647	0.020	105	3.65	107	4.00
	970	0.067	109	5.83		

Correlation of these rates with turbine speed and with power input are shown in Figs. 3.1 and 3.2.

The parallel lines for the 6- and 12-in.-dia tank data in Fig. 3.1 indicate the same relative effect of turbine speed in each. The slope of unity shows that K' is proportional to the first power of turbine speed. A rate controlled by diffusion through viscous layers would be expected to be proportional to a higher power of turbine speed (e.g., third or fourth). A rate controlled by a reaction at the interface would be expected to be directly proportional to the interfacial area, and recent measurements in tank mixers have reported the interfacial area to be proportional to nearly the first power of turbine speed (i.e., the 0.72* or the 1.2 power**). Thus the present results suggest rate control by reaction at the interface rather than by diffusion.

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*W. A. Rodger, "Interfacial Area in Liquid-Liquid Dispersions Related to Fluid Motion in Mixing Vessels," ANL-5575 (June 1956).

**G. E. Langlois, G. M. Williams, T. Vermeulen, "Interfacial Area in Liquid-Liquid and Gas-Liquid Agitation," Chem. Eng. Progr., 51: 81F (1955).

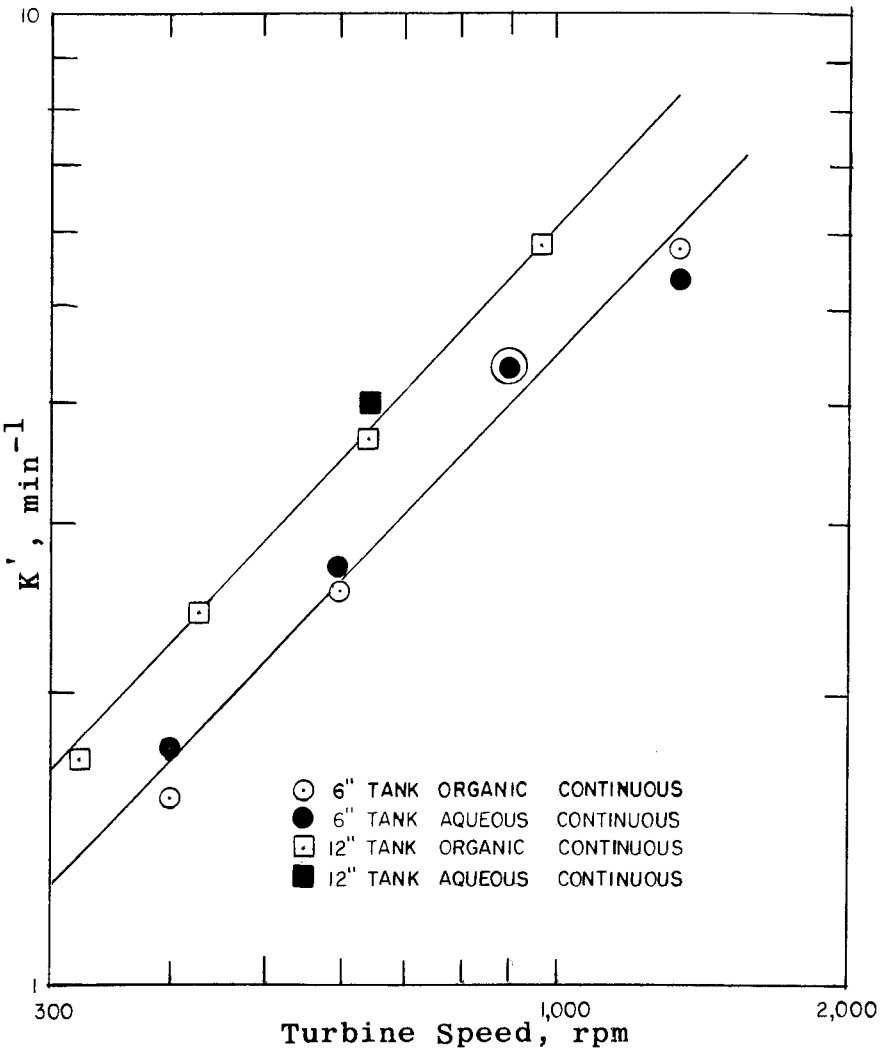

Fig. 3.1. Correlation of Extraction Rate with Turbine Speed.

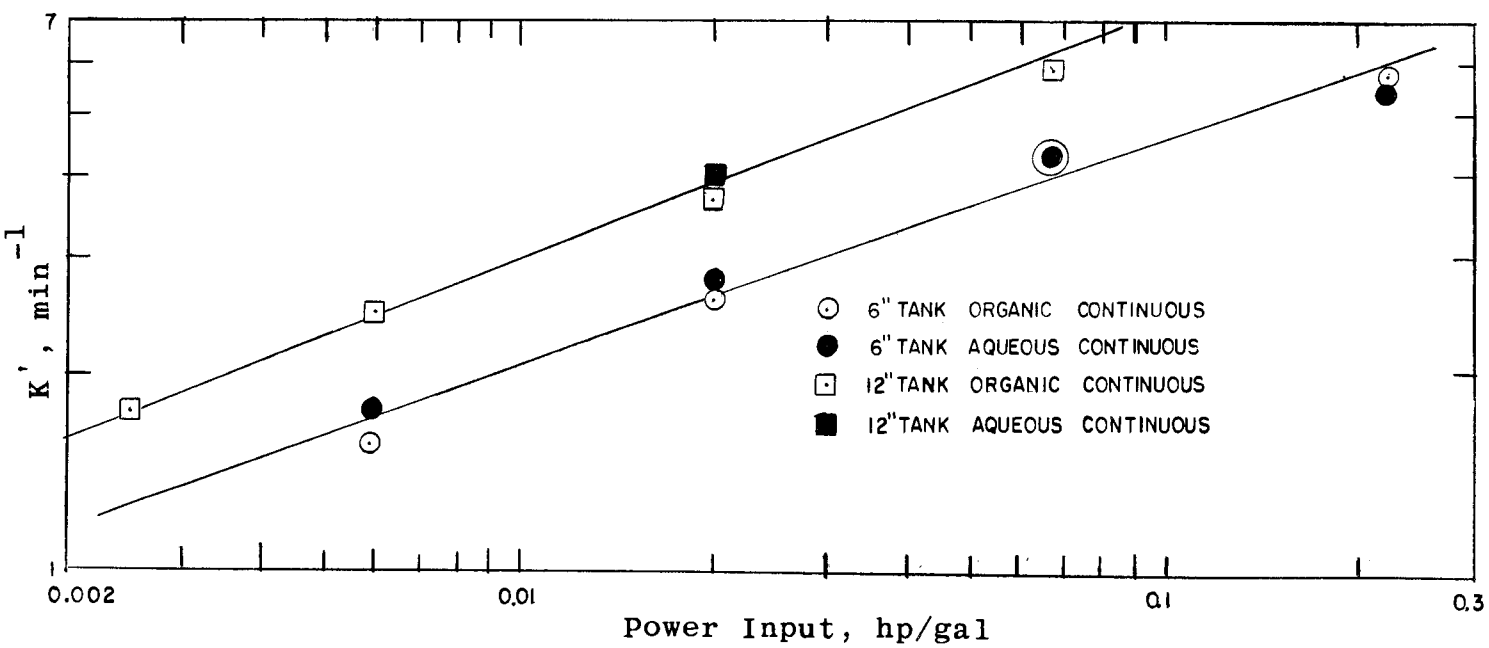

Fig. 3.2. Correlation of Extraction Rate with Power Input

The correlation of extration rate with power input (Fig. 3.2) shows straight lines of slope 1/3, in conformance with the dependence of power input on the cube of turbine speed. However, the lines for the two mixers still do not coincide (higher rate in the larger mixer at a given power input), showing that power input alone is not a sufficient parameter to define the rate even in these tanks of similar geometry.

The extraction rate increased with rising temperature, K' approximately doubling with a 15° rise in the range 15-55°C (synthetic liquor, 6-in.-dia mixer):

Run No.	Cont. Phase	Temp., °C	Turbine Speed, rpm	Power Input, hp/gal	K', min^{-1}
115	o	15	400	0.0059	1.13
113	o	25	400	0.0059	1.64
117	o	40	400	0.0059	3.37
119	o	55	400	0.0059	6.45
15	a	20	600	0.020	3.00
13	a	49	600	0.020	9.84

The heat of activation, ΔH_A, was calculated from these rate-vs-temperature data by means of the integrated form of Arrhenius' equation,

$$\log \frac{K_2}{K_1} = \frac{\Delta H_A}{2.303\ R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$$

By means of Rodger's correlation referred to above, (interfacial area) $\propto$ (turbine speed)$^{0.72}$, the interfacial area in the aqueous-continuous tests was calculated to be 1430 sq ft/cu ft at 20° and 1470 at 49°C. Since the two log plots of K' vs the reciprocal of absolute temperature (Fig. 3.3) are parallel, it was assumed that in the organic-continuous tests also the change in interfacial area with temperature was small and could be ignored. ΔH_A was calculated to be 8950 cal/mole from the organic-continuous runs and 7920 cal/mole from the aqueous-continuous runs. For diffusion processes, ΔH_A is usually around 5000 cal/mole, while for most chemical reactions it is 10,000 to 20,000 cal/mole; hence at this stage the heats of activation appear inconclusive between rate control by reaction and by diffusion.

Further study of the kinetics of this extraction system is in progress with the major emphasis on the effects of phase ratio and mixer geometry.

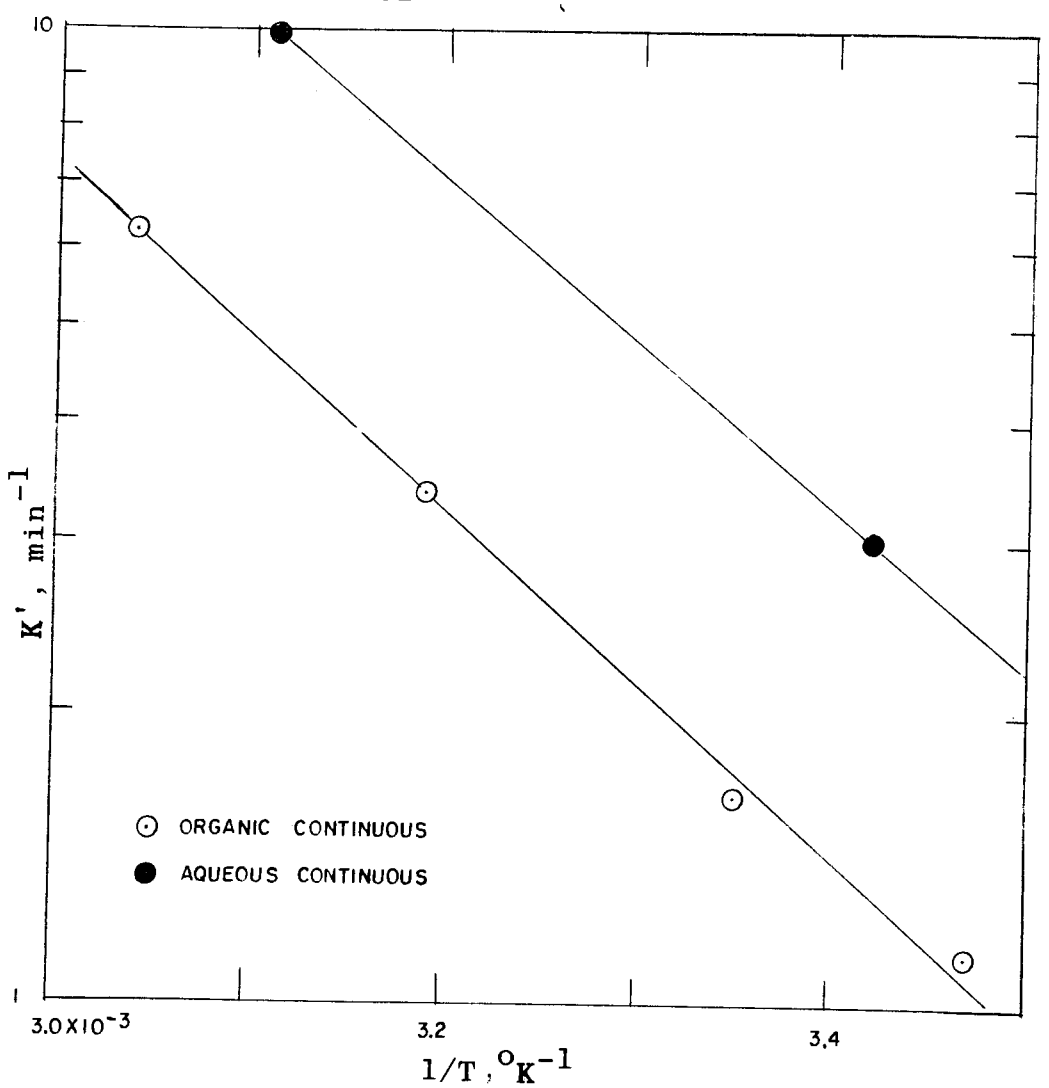

Fig. 3.3. Temperature Dependence of Extraction Rate