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ORNL-2388
Technology-Raw Materials

PROGRESS REPORT ON RAW MATERIALS

FOR JULY, 1957

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

K RIDGE NATIONAL LABORATORY
OPERATED BY
UNION CARBIDE NUCLEAR COMPANY
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Printed in USA. Price 75 cents. Available from the

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

Report Number: ORNL-2388

Contract No. W-7405, eng 26

CHEMICAL TECHNOLOGY DIVISION

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

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OCT 28 1957

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CONTENTS

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

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February,	ORNL-2269 (25¢)	May,	ORNL-2366 (25¢)
March,	ORNL-2306 (25¢)	June,	ORNL-2380 ($1.00)

ABSTRACT

Systematic Studies. Three new amine samples, tris(tridecyl)-, N-(1-undecyldodecyl)dodecyl-, and N-(1-nonyldecyl)-dodecylamine, showed good uranium extraction performance and low losses to aqueous liquors. Tests with a new batch of trilaurylamine continued to show the potential utility of this reagent. The purity of the new sample was lower than for previous batches, however, and the phase separations during extraction were slower. Tests with tri(n-octyl)phosphine oxide and 2-phenylvinyl(dioctyl)phosphine oxide showed the latter to be the poorer extractant.

In further tests of synergistic reagent systems for uranium extraction, diamyl amylphosphonate (DAAP) was shown to be a promising reagent for process use. The compound is potentially available in commercial quantities at a price lower than that of dihexyl hexylphosphonate (DHHP). Uranium extraction performance and losses to aqueous liquors are similar to those for DHHP.

Process Development. The coefficients for extraction of uranium with tri-n-octylamine in kerosene-alcohol diluent were approximately equivalent with capryl alcohol, mixed decanols, or tridecanol in concentrations of 0.04-0.20 M alcohol. The coefficients decreased markedly when the alcohol concentration was increased to 0.3 and 0.5 M. With 0.10 M nonylphenol or 0.04 dinonylphenol added to the

solvent, coefficients were similar in magnitude to those obtained with 0.04-0.20 M alcohol modifier. Addition of nonylphenol or dinonylphenol in concentrations as high as 0.2 M, however, severely depressed uranium extraction.

The effect of small concentrations of chloride and nitrate on thorium recovery by the Amex process from uranium-barren Blind River liquors was evaluated. The chloride or nitrate enters the liquor during ion-exchange recovery of uranium. The presence of chloride depressed thorium extraction but not sufficiently to interfere seriously with process performance. Nitrate interference, on the other hand, was severe, indicating that special provisions would be necessary for treating uranium-barren raffinates where nitrate elution is used in the ion-exchange process. Nitrate was extracted effectively, suggesting the possibility of nitrate recovery from the liquor prior to thorium extraction. In addition, a process for simultaneous recovery of thorium and nitrate by the Amex process appears economically attractive and is being given further study.

Engineering Studies. The rate of uranium extraction from two synthetic sulfuric acid leach liquors by the Dapex solvent was proportional to the cube root of power input in mixers of three different sizes. The rate was nearly independent of the particular combinations of uranium concentration, phase ratio, and solvent strength. Scale-up of mixers by constant power input per unit mixer volume was demonstrated to be slightly conservative for 6-, 12-, and 20-in. baffled tank mixers which are geometrically similar.

1.0 SYSTEMATIC STUDIES

In addition to the studies described below, systematic studies during the month have included (1) preliminary study of the applicability of amine and organophosphorus extractants to separations in fuel reprocessing and waste disposal, (2) screening new organophosphorus and organonitrogen compounds as uranium extractants, (3) comparison of base strengths of amine diluent combinations, and (4) measurements of solubility distribution of organophosphorus extractant to aqueous solution.

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

Three new amine samples, tris(tridecyl P)-, N-(1-undecyldodecyl)-dodecyl-, and N-(1-nonyldecyl)dodecylamine, showed good extraction properties (Table 1.1) in tests of the type described previously. (ORNL-1734, p. 6; cf. ORNL-2269). The branched chain tris(tridecyl) amine showed an advantage over straight chain tertiary amines in being compatible with unmodified kerosene. As expected, the loss rate to a sulfate liquor from unmodified kerosene was low, < 5 mg/liter (Table 1.2). In view of its excellent extraction characteristics, further tests are being made to study the selectivity properties and the compatibility of this reagent

Table 1.1 Preliminary Tests of Uranium Extractions from Sulfate Solutions

Compound	Batch No.	Concn., M	U Extracted and Extraction Coeff. (o/a) Kerosene %	Kerosene E	Benzene %	Benzene E	Benzene Prewashed %	Benzene Prewashed E	Phase Separation
Secondary amines									
N-(1-nonyldecyl)-dodecyl	309A	0.01	41	-	56	-	62	-	Good
		0.1	99	121	99	117	99	102	
N-(1-undecyldodecyl)-dodecyl	308A	0.01	35	-	39	-	34	-	Poor in kerosene
		0.1	99	127	99	89	98	54	
Benzylisopropyl	307A	0.1	nil	-	nil	-	nil	-	Good
Tertiary amines									
Armeen 3-12	86C	0.01	39	-	44	-	43	-	Poor
		0.1	98[a]	63[a]	99	143	99	103	
Tris(tridecyl P)	310A	0.01	34	-	32	-	32	-	Good
		0.1	99[b]	145[b]	98	64	98	46	
RD2805B[c]	300A	0.1	nil	nil	1	0.01	nil	nil	Poor
RD2807B[c]	301A	0.1	nil	nil	0.5	0.005	nil	nil	Good
RD2807B[c]	302A	0.1	nil	nil	3rd phase		16	0.19	Good
RD2808B[c]	303A	0.1	3rd phase		93	12	88	7.5	Poor in benzene

[a] In 97% kerosene--3% tridecanol, 99% extraction, E_a^o of 75, poor phase separation.

[b] In 97% kerosene--3% tridecanol, 97% extraction, E_a^o of 31, good phase separation.

[c] Alkyl(di-isopropoxy)amines.

Table 1.2 Losses of Amine to Aqueous Solutions

Aqueous = synthetic sulfate liquor containing (g/liter):
~6 Fe(III), 3.3 Al, 50 SO_4, 2 PO_4, and 1.7 F; pH 0.8

Conc. of amine = 0.1 M

Maximum aqueous/organic ratio examined = 500/1

Amine	Batch No.	Diluent	Loss of Amine: Fraction Readily Lost, % of Initial	Loss of Amine: Steady-state Loss, mg per liter Aq
N-(1-nonyldecyl)dodecyl	309A	Kerosene	<1	<5
N-(1-undecyldodecyl)dodecyl	308A	Kerosene	11[a]	<5[a]
Armeen 3-12 (trilauryl)	86C	Kerosene + 3 v % tridecanol	≤3	≤5
Tris(tridecyl P)	310A	Kerosene	<1	<5

[a] <5 mg/liter loss rate after 300/1 aqueous/organic ratio.

with liquors containing molybdenum.

Both the new secondary amines gave good uranium extractions. The extraction coefficients in unmodified kerosene were higher than those with Amine 9D-178 (ORNL-2380) or S-24 (ORNL-1922). Some differences were noticeable between these two samples. The N-(1-nonyldecyl)dodecylamine gave better phase separation than the other. It also was of higher purity (Table 1.3), and required less scrubbing to remove the more soluble fractions. Both compounds had low loss rates to a sulfate liquor from kerosene, < 5 mg/liter; however, the N-(1-undecyldodecyl)dodecylamine did not reach a constant level until the 300/1 aqueous/organic phase ratio was reached. These two compounds are experimental chemicals and at present there is no indication of further production.

A new batch of trilaurylamine (Armeen 3-12) gave extraction coefficients nearly the same as those obtained with the previous batches (ORNL-1734 and ORNL-2380). Phase separation, however, was slower. The apparent equivalent weight, 600 (Table 1.3), was much higher than the previous batch (542) or the theoretical weight (522), indicating the presence of inert impurities. These could account for the slower phase separations and for difficulty encountered in dissolving this material in kerosene and kerosene modified with 3 v % tridecanol. The loss rate to a sulfate liquor from alcohol-modified kerosene was low, ≤ 5 mg/liter, which is the same as that found for the previous batch (ORNL-2380).

Other experimental amines submitted for evaluation included a series of alkyl(di-isopropoxy)amines (RD-2805B - RD-2808B), benzylisopropylamine, and alkyl ether amines No. 1, 3, and 4. None of these was satisfactory. The alkyl ether amines produced emulsions that could not be broken, and the other compounds gave very poor uranium extractions.

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

2-Phenylvinyl(dioctyl)phosphine oxide. The structure of this compound, prepared by Dr. G. M. Kosolapoff of Auburn University, was chosen to give increased electron density in the vicinity of the P-O group in the expectation that this might increase the uranium extraction. However, tests in both kerosene and carbon tetrachloride diluent showed the reagent to be inferior to tri(n-octyl)-phosphine oxide (ORNL-1964):

Aqueous phase	Phase Ratio (a/o)	Diluent	Extraction Coefficient: 2-phenylvinyldioctyl-phosphine oxide	Extraction Coefficient: Tri-n-octyl-phosphine oxide
0.1 M NO_3	2	CCl_4	60	310
	2	Kerosene	375	1250
0.5 M SO_4, 0.3 M NO_3	1	CCl_4	6	20
	1	Kerosene	18	110
0.4 M PO_4, 0.3 M NO_3	1	CCl_4	1	2

Table 1.3 New Organonitrogen Compounds: Assay by Direct and Differential Titration

Compound	Batch No.	Source[a]	% by Differential Titration			Equiv. Wt.	
			Prim.	Secon.	Tert.	Theo.	Found
Primary amines							
Alkyl ether amine No. 1 $R{\cdot}O{\cdot}(CH_2)_n{\cdot}NH_2$	304A	ADM	--	--	--	240-260[b]	285
Alkyl ether amine No. 3 $R{\cdot}O{\cdot}(CH_2)_n{\cdot}NH_2$	305A	ADM	--	--	--	310-330[b]	384
Alkyl ether amine No. 4 $R{\cdot}O{\cdot}(CH_2)_n{\cdot}NH_2$	306A	ADM	--	--	--	310-330[b]	369
Secondary amines							
N-(1-nonyldecyl)dodecyl	309A	A	6	92	2	452	450
N-(1-undecyldodecyl)dodecyl	308A	A	17	81	2	508	513
Benzylisopropyl	307A	S	--	--	--	149	155
Tertiary amines							
Armeen 3-12 (trilauryl)	86C	A	7	3+	89+	522	600
Tris(tridecyl P) $(C_{13}H_{27})_3N$ with the alkyl groups derived from tetrapropylene	310A	C	2	1	97	564	566
RD-2805B $RN\begin{smallmatrix}\nearrow[CH_2CH(CH_3)O]_x\\ \searrow[CH_2CH(CH_3)O]_y\end{smallmatrix}$ where x + y = 2	300A	A	--	--	--	-	341
RD-2806B where x + y = 5	301A	A	--	--	--	-	368
RD-2807B where x + y = 8.5	302A	A	--	--	--	-	635
RD-2808B where x + y = 15	303A	A	--	--	--	-	1060

[a] A = Armour Chemical Division, Chicago.
C = Union Carbide Chemical Co., New York.
S = Sumner Chemical Co., Inc., New York.
ADM = Archer-Daniels-Midland Co., Minneapolis, Minn.

[b] Furnished by vendor.

The reagent, 0.1 M in the diluent, was contacted with an aqueous solution containing 0.004 M U(VI) for 10 min at 26°C. The reagent tended to supersaturate in kerosene, and, although these tests were run without trouble at the 0.1 M level, some of the phosphine oxide precipitated about 3 hr later. The synergistic behavior of this reagent is described below.

Synergistic Extractants. The synergistic enhancement of D2EHPA uranium extraction by some new neutral organophosphorus compounds, including samples of new sources of compounds previously examined, were closely in line with the performances of similar compounds previously tested (ORNL-2172 pp. 10ff, ORNL-2269 p. 6, ORNL-2306 p. 5).

Neutral Compound	Batch No.	Source[a]	U Extraction Coeff. (o/a) 0.5 M SO_4, pH 1	1.5 M H_2SO_4
None			110	3
Tributylphosphate	343	E	550	13
Tri-isobutylphosphate	342	E	450	9
Tri-isobutylphosphate	368	V	400	9
Tri(2-methylbutyl)phosphate	397	E	400	10
Triallylphosphate	351	S	600	12
Trioctylchlorophosphate	369	V	110	3
Diamyl amylphosphonate		S	2000	50
Didecyl decylphosphonate		S	600	40
Tetra(2-ethylhexyl) trimethylenediphosphonate	25	VC	1350	30
Tetra(2-ethylhexyl) ethylenediphosphonate	168	VC	1000	20
Tetrabutyl propylenediphosphonate	272	K	1000	20
Tetrabutyl ethylenediphosphonate	273	K	1200	30
2-Phenylvinyl(dioctyl)phosphine oxide	398	K	4000	80

[a] E Eastman Chemical Products, Inc., Kingsport, Tenn.
V Victor Chemical Works, Chicago
S Shea Chemical Corp., New York
VC Virginia-Carolina Chemical Corp., Richmond, Va.
K Prepared by Dr. G. M. Kosolapoff, Auburn Univ.

The neutral compound and the D2EHPA were used at 0.1 M in kerosene, the aqueous U(VI) concentration was 0.004 M, a/o phase ratio = 1/1, temperature 25-27°C.

The trialkylphosphates behaved similarly, with some indication that branching of the butyl group decreased extraction slightly. The triallylphosphate compared favorably with TBP, but the chlorophosphate was much less effective.

Diamyl amylphosphonate was as effective as dihexyl hexylphosphonate (ORNL-2306, p. 5) but the decyl derivative was inferior.

The 2-phenylvinyl(dioctyl)phosphine oxide showed about the same enhancement observed previously with trioctylphosphine oxide.

The diphosphonates behaved similarly and were about as effective as dibutyl butylphosphonate.

1.3 Dialkyl alkylphosphonates (C. A. Blake, D. E. Horner, J. M. Schmitt)

Samples of diamyl amylphosphonate (DAAP) and didecyl decylphosphonate (DDDP) were received from Shea Chemical Corporation, 114 E. 40th St., New York 16, N. Y. These compounds are described as having potential commercial availability at prices somewhat lower than those previously quoted for dihexyl hexylphosphonate (DHHP) (ORNL-2306, p. 4). The extraction behavior of these compounds is being examined.

Synergistic Enhancement of Uranium Extraction. Comparison of extraction coefficients in tests similar to those previously described (ORNL-2306, p. 5) shows that the synergistic enhancement of uranium extraction by 0.1 M D2EHPA is nearly the same with DAAP and DHHP. Although enhancement with DDDP is lower, the coefficients are still higher than those obtained with TBP.

Neutral Compounds	Batch No.	Uranium Extraction Coefficients (o/a)	
		0.5 M SO_4, pH 1	1.5 M H_2SO_4
None		110	3
TBP	338	470	13
DHHP	383	2200	45
DAAP		2000	50
DDDP		600	40

Each reagent was used at 0.1 M concentration, with 0.1 M D2EHPA, in kerosene diluent. The initial aqueous uranium concentration was 0.004 M (~ 1 g/liter) and the phase ratio was 1/1.

Diluent Modification for Miscibility. The minimum reagent concentrations required in use of 10% Na_2CO_3 stripping solution in modification of D2EHPA at 30°C are given by the following linear functions:

w/v %* DAAP = 1.3 + 4.6 M D2EHPA, or M DAAP = 0.045 + 0.16 M D2EHPA
w/v % DDDP = 5.2 + 5.8 M D2EHPA, or M DDDP = 0.104 + 0.12 M D2EHPA

For comparison, the requirements at two specific D2EHPA concentrations are

	0.1 M D2EHPA	0.3 M D2EHPA
DAAP	1.8 w/v %	2.7 w/v %
DDDP	5.8	6.9
DHHP	2.0	2.7

Thus the concentrations required of DAAP and DHHP are about equal while more than twice as much DDDP is needed.

---

* w/v % = g/100 ml.

Loss to Aqueous Phase. The loss rate of DAAP by distribution to 0.5 M sulfate solution at pH 1, measured by titration to the critical miscibility point (ORNL-2172, p. 17) was less than 5 mg/liter aq. In extraction from a similar liquor containing, e.g., 1 g U_3O_8 per liter, this would correspond to < 0.005 lb/lb U_3O_8. The same limit on loss rate has already been reported for DHHP, and, since the price of DAAP is predicted to be lower than that of DHHP, the charges incurred from reagent loss should be correspondingly lower.

Extraction from Nitrate Solutions. Apart from their use in synergistic combinations, phosphonates may be useful extractants in their own right. Some tests have been made in nitrate solutions to determine the effect of the aqueous composition on uranium extraction with commercially available DHHP.

The effect of nitric acid concentration was examined on DHHP in comparison with TBP. Extractions with the former were about an order of magnitude higher than with TBP, (Fig. 1.1). Both have maximum extractions in the vicinity of 4 M HNO_3. The tests were for 0.1 M reagent in kerosene in contact for 10 min at 25° with the aqueous phase containing 0.004 M U(VI). The phase ratio was 1/1.

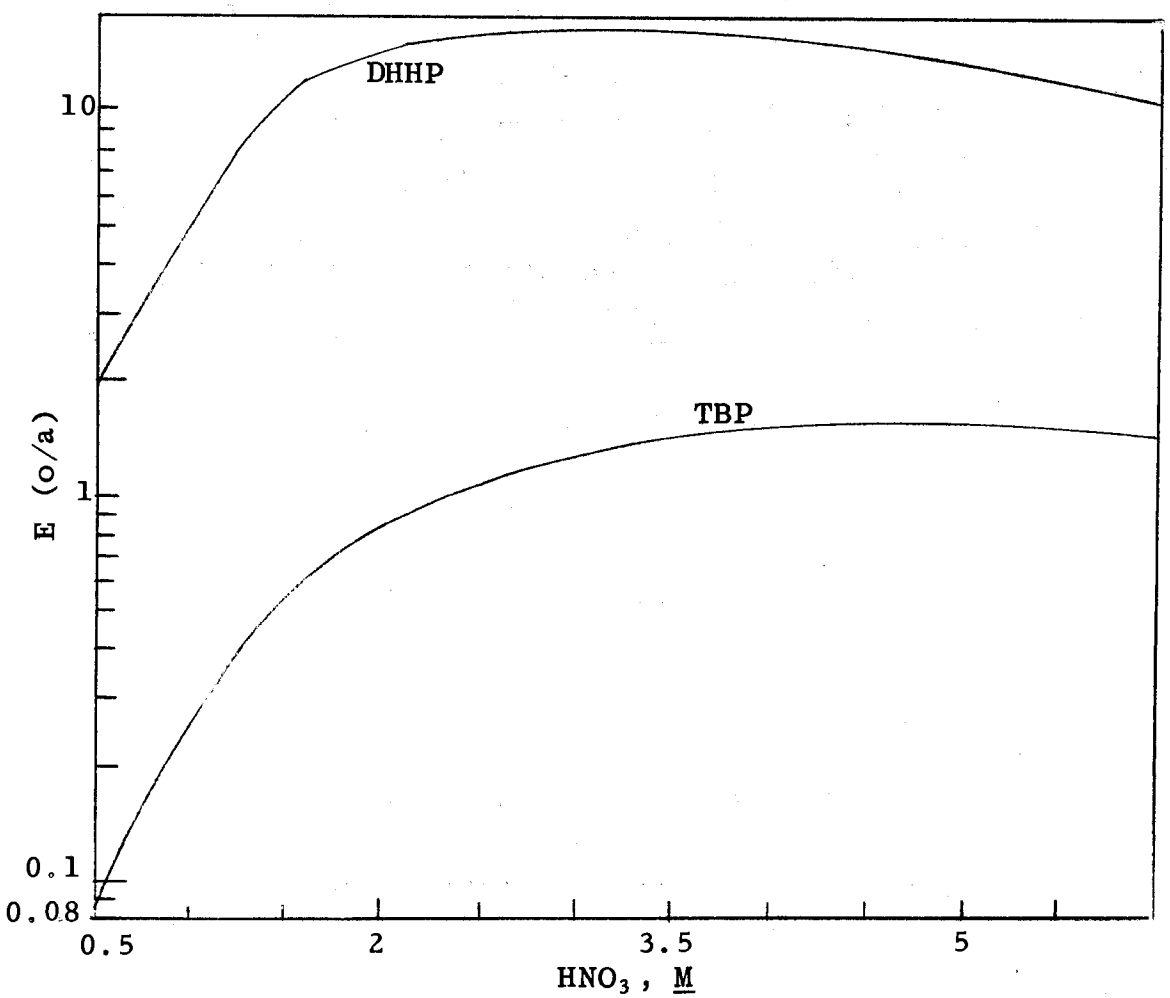

Fig. 1.1 Variation in Extraction of Uranium with Nitric Acid Concentration by DHHP and TBP.

Increasing the pH had a greater effect on extractions with DHHP than on TBP:

pH of 4 M NO_3 Solution	Extraction Coefficient (o/a) DHHP	TBP
<0	15	1.5
0.75	270	6
1.5	270	6

The tests were with 0.1 M reagent in kerosene and the uranium concentration was 0.004 M.

1.4 Commercial Monoalkylphosphoric Acid

A sample of DOWSOL-12, a commercial mono(2,6,8-trimethylnonyl-4)phosphoric acid (DDPA) was obtained from Dow Chemical Company for comparison with DDPA previously examined (ORNL-2380). The reagent is the product of the reaction in kerosene of phosphorus pentoxide and 2,6,8-trimethylnonanol-4 followed by subsequent hydrolysis with hydrochloric acid. The product as received was titrated with 0.1 M NaOH, and contained 0.92 meq/ml strong acid and 0.83 meq/ml weak acid. Since pure DDPA would have equivalent strong and weak acid content, the difference of 0.11 meq/ml represents by-product material, possibly the corresponding dialkylphosphoric acid, pyro compounds, or polymeric compounds. A 0.1 M solution (based on the weak acid content was prepared by dilution with kerosene and tested for uranium extraction ability.

Extraction coefficients were higher with this reagent than with the corresponding DDPA prepared at ORNL (ORNL-2346). As with other reagent samples, the addition of TBP or of decanol markedly depressed the uranium extraction:

Aqueous Solution	Additive	E (o/a)
1.5 M H_2SO_4	None	10
	0.1 M TBP	1.9
	5 v % decanol	0.8
0.5 M SO_4, pH 1	None	770
	0.1 M TBP	70
	5 v % decanol	30

2.0 PROCESS DEVELOPMENT

In addition to the studies described below, process development projects during the month included (1) continued study of the compatibility of different amines with liquors containing molybdenum, (2) evaluation in continuous equipment of the nitrate stripping method for recovery of uranium from amines, (3) stripping of uranium from amines with magnesium oxide slurries, (4) further evaluation of the Amex process for vanadium recovery, and (5) control of phosphate contamination of vanadium products as obtained in both the Dapex and Amex processes.

2.1 Effect of Diluent Modifiers on Uranium Extraction with Tri-n-octylamine in Kerosene (W. D. Arnold)

Diluent modifiers such as long-chain alcohols are commonly used in the Amex process to improve the diluent compatibility of those amines whose salts have limited miscibility in kerosene. These amine salts tend to separate from the kerosene as a third liquid phase or as a precipitate when no modifier is present (ORNL-1734, -1922, -1959, -2099).

With 0.1 M tri-n-octylamine in kerosene, addition of 2-3 v % alcohol is usually sufficient to ensure miscibility during uranium extraction from sulfate liquors of usual composition. Larger amounts of alcohol (4-6 v %) are required with sulfate liquors of unusually high acidity (owing to formation of larger amounts of amine bisulfate) or with the chloride or nitrate salt stripping cycles.

The addition of these large amounts of alcohol decreased the uranium extraction power. Consequently, a systematic study is being made to determine whether any important limitation might be imposed on the Amex process through alcohol addition.

Table 2.1 shows recent results of uranium extractions from a sulfate solution (0.5 M SO_4, pH 0.9) with 0.1 M tri-n-octylamine containing varying amounts of diluent modifiers. Third phase formation, which occurred with no modifier present, was avoided by adding as little as 0.04 M capryl alcohol, mixed primary decanols, tridecanol, nonylphenol, or dinonylphenol. However, extracted uranium increased the miscibility of the amine salt, and somewhat higher concentrations of modifier might be required to ensure miscibility in a countercurrent extraction system where the uranium concentration in the bottom stages would be relatively low. The uranium extraction coefficients were practically constant in the range 0.04-0.20 M alcohol concentration but decreased appreciably as the alcohol concentration was raised to 0.3 and 0.5 M. However, even with 0.5 M alcohol, the coefficients were sufficiently high, i.e., 30-70, for process use.

With nonyl phenol the uranium coefficient increased from 180 at 0.04 M to 220 at 0.1 M concentration and then decreased severely as the modifier concentration was increased to 0.20 M (4.6 v %). The extraction pattern was somewhat similar with dinonylphenol, although in this case the highest coefficient, i.e., 250, was observed at 0.04 M concentration. Increasing the concentration to 0.10 M and 0.20 M lowered the coefficients to 130 and 4, respectively.

Phase separation was rapid (50 sec or less) in all tests with some variations, depending on the modifier used and its concentration.

Table 2.1 Effect of Diluent Modifiers on Uranium Extraction by Tri-n-octylamine in Kerosene

Organic: 0.10 M tri-n-octylamine in kerosene + indicated diluent modifier

Aqueous: 1.0 g U/liter, 0.5 M $SO_4^=$, pH 0.90
Phase ratio (a/o): 2/1
Contact time: 10 min
Temperature: 25°C

Modifier	Modifier Concentration M	Modifier Concentration v %	U g/liter Organic	U g/liter Aqueous	Uranium Extraction Coefficient, E_a^o
None	--	-	-	0.014	a
Capryl alcohol	0.04	0.6	2.0	0.010	200
	0.10	1.6	2.0	0.008	250
	0.15	2.4	2.0	0.008	250
	0.20	3.2	2.0	0.008	250
	0.30	4.8	2.1	0.016	130
	0.50	8.0	2.0	0.029	70
Mixed primary decanols	0.04	0.8	2.0	0.009	220
	0.10	1.9	2.0	0.008	250
	0.15	2.9	2.0	0.009	220
	0.20	3.8	2.0	0.009	220
	0.30	5.7	2.0	0.026	80
	0.50	9.5	1.9	0.068	28
Tridecanol	0.04	1.0	2.0	0.009	220
	0.10	2.4	2.0	0.009	220
	0.15	3.6	2.0	0.009	220
	0.20	4.8	2.0	0.009	220
	0.30	7.2	2.0	0.023	90
	0.50	12.0	1.9	0.058	33
Nonylphenol	0.04	0.9	2.0	0.011	180
	0.10	2.3	2.0	0.009	220
	0.15	3.5	2.0	0.019	100
	0.20	4.6	1.9	0.060	32
Dinonylphenol	0.04	1.5	1.9	0.008	240
	0.10	3.7	1.8[b]	0.014	130
	0.15	4.6	1.6[b]	0.063	25
	0.20	7.4	1.3	0.325	4

a
A third liquid phase formed since the miscibility of the amine salt in kerosene was exceeded.

b
Poor uranium material balance.

2.2 Effect of Chloride and Nitrate on Thorium Extraction with Amines from Blind River Ion Exchange Effluents (W. D. Arnold, A. D. Kelmers)

The Amex process has been proposed for application to the separation and recovery of uranium and thorium from sulfate liquors of the type produced by leaching ores from the Blind River District of Canada (ORNL-2173). When the uranium is recovered by ion-exchange methods, as in existing Blind River mills, thorium recovery from the uranium-barren liquors by the Amex process is also a possibility.

In the latter case the liquor would contain small amounts of the eluting anion (both the chloride and nitrate elution methods are used in Blind River mills). Consequently, studies were made of the effect of these anions, both of which are effective stripping agents for amines, on the thorium extraction process. The extraction and recovery of nitrate in combination with thorium was also examined, since recycle of the relatively expensive nitrate might be an attractive possibility.

The amounts of chloride or nitrate expected in the uranium-barren liquor discharged from the ion-exchange circuit can be estimated from knowledge of the head-liquor uranium concentration and the resin loading. For Blind River liquors containing 1.0 g U_3O_8/liter and a resin of 1.0 equivalent capacity per liter wet settled resin loaded to 60 g U_3O_8/liter w.s.r., the average concentration of chloride or nitrate in the effluent would be ~0.6 g and ~1 g/liter, respectively. The concentration would not be uniform but would peak during the initial period of the loading cycle and decrease to concentrations considerably lower than average for the rest of the loading cycle.

Effect of Chloride. Extraction of thorium from a synthetic Blind River liquor (uranium-barren) containing 0.2 g Th/liter and chloride in the range 0-2.0 g/liter was studied with 0.05 M di-(tridecyl P)amine in kerosene (Table 2.2). This amine was the most favorable of those previously examined for thorium recovery from Blind River liquors.

As expected, thorium coefficients were depressed by addition of chloride to the system. For example, at a thorium loading of about 1 g/liter, the coefficient decreased from >500 to 90 as the chloride concentration was increased from 0 to 2.0 g/liter. However, at a chloride concentration of 0.6 g/liter, which is the approximate average concentration expected, thorium coefficients were sufficiently high that essentially complete thorium recovery and excellent thorium loading (1.5 g/liter) would be obtainable in only 2-3 countercurrent stages. Even with a chloride concentration of 2.0 g/liter in the liquor, stage requirements could be kept at the same level by operating at slightly lower thorium loadings, i.e., 1.2-1.3 g/liter.

To avoid large fluctuations in the chloride content of the thorium process feed, a surge tank could be provided between the

Table 2.2 Effect of Chloride on Thorium Extraction from Sulfate Liquors with Di(tridecyl P)amine in Kerosene

Organic: 0.05 M di(tridecyl P)amine in kerosene

Aqueous: synthetic Blind River liquor (uranium barren) containing 0.2 g Th, 1.1 g Fe(III), 1.0 g Fe(II), 1.5 g Al, 24 g SO_4, and 0-2.0 g Cl^- per liter at pH 1.4

Contact time: 5 min

Cl^- in Liquor[a], g/liter	Phase Ratio (a/o)	Th, g/liter		Thorium Extraction Coefficient, E_a^o
		Organic	Aqueous	
0.0	2	0.4	<0.002	>200
	5	1.0	<0.002	>500
	10	1.5	0.046	33
0.6	2	0.4	--	-
	5	1.0	0.006	170
	10	1.5	0.051	29
1.0	2	0.4	<0.002	>200
	5	1.0	0.006	170
	10	1.5	0.054	28
1.6	2	0.4	0.002	200
	5	1.0	0.010	100
	10	1.3	0.070	19
2.0	2	0.4	0.003	130
	5	0.9	0.010	90
	10	1.3	0.084	15

[a] Added as NaCl.

uranium and thorium circuits with a capacity sufficient to give effective "averaging" of the chloride concentration. If this were done, the effect of the chloride would be of almost negligible importance in the thorium recovery process.

Effect of Nitrate. Extractions of thorium and nitrate from a synthetic Blind River liquor containing 0.5-1.1 g NO_3 per liter was investigated with 0.05 M solutions of di(tridecyl P), S-24, 9D-178, and tri-iso-octylamines (Table 2.3). Extractions of thorium by the first three amines were severely depressed owing to the strong competition for the amine by nitrate. For example, with a nitrate concentration of 1.1 g/liter in the liquor, which is approximately the average concentration expected in the ion-exchange plant effluents, thorium extractions by S-24 and 9D-178 amines were negligible and the extraction coefficient for di(tridecyl P)amine was only 2.3. Tri-iso-octylamine extracted nitrate fairly effectively but, as expected from previous studies (ORNL-2173), did not extract thorium.

It is evident that effective recovery of thorium from a liquor containing nitrate at the expected average nitrate concentration could not be accomplished in the usual arrangement of the Amex flowsheet. However, the results suggest that, with appropriate flowsheet modification, recovery of both thorium and nitrate should be possible either simultaneously, in a single-cycle process, or separately in a two-cycle process.

Single-cycle Process. A single-cycle process is currently being evaluated in bench-scale continuous equipment. In the proposed process (Fig. 2.1), thorium and nitrate are extracted simultaneously with 0.05-0.10 M amine, the thorium is stripped with ammonium nitrate solution, and the nitrate with ammonium hydroxide. A portion of the recovered nitrate salt is recycled to the thorium stripping operation and the balance is sent to the uranium ion-exchange elution circuit. Di(tridecyl P) amine, which has exceptionally strong thorium extraction power, adequate nitrate extraction power, and very low distribution loss to the aqueous phase, is a favorable amine for use in such a circuit. Use of an amine mixture combining a strong thorium extractant and a strong nitrate extractant, e.g., di(tridecyl P) and S-24 amines, is also being considered. Preliminary estimates indicate that, allowing a credit of 6¢ per pound of nitrate returned to the uranium elution circuit, reagent costs for thorium recovery would be lower than those previously anticipated for processing a nitrate-free effluent.

Two-cycle Process. In a two-cycle process, nitrate would be removed from the liquor in the primary extraction cycle. Of the amines examined, S-24 showed the highest nitrate extraction coefficients ($E_a^o > 7$) and appears to be a suitable amine for selective nitrate extraction. In equilibrium with an aqueous solution containing 0.5 g of nitrate per liter, nitrate loading of S-24 (0.05 M) was 2.8 g/liter, equivalent to about 90% conversion of the amine to the nitrate salt. Both S-24 and 9D-178 amines extracted some thorium at low nitrate loadings but extractions were negligible at the higher nitrate loadings. In contrast, extractions of thorium

Table 2.3 Extraction of Thorium and Nitrate by Amines

Organic: 0.05 M amine

Aqueous: Synthetic Blind River liquor (uranium barren) containing, g/liter, 0.1 Th,[a] 1.1 Fe(III), 1.0 Fe(II), 1.5 Al, 18 SO_4, and 0.5-1.1 NO_3^-; pH 1.4

Phase Ratio (a/o): 5/1

Contact time: 5 min

Amine	Diluent	NO_3^- in liquor, g/liter	Amount, g/liter				Extraction Coefficient, E_a^o	
			Th		NO_3			
			Org	Aq	Org	Aq	Th	NO_3
Di(tridecyl P)	Kerosene	0.5	0.45	0.006	1.2	0.3	75	4
		1.1	0.16	0.069	2.4	0.6	2.3	4
S-24	Kerosene	0.5	0.18	0.061	-	<0.2	2.9	>7
		1.1	<0.005	0.095	2.8	0.5	<0.05	5.5
S-24	98% kerosene--2% TDA[b]	0.5	0.015	0.094	1.4	0.2	0.16	7
		1.1	<0.005	0.099	2.4	0.6	<0.05	4
9D-178	Kerosene	0.5	0.15	0.068	1.3	0.3	2.2	4.5
		1.1	0.01	0.097	2.2	0.7	0.10	3
Tri-iso-octyl	95% kerosene--5% TDA	0.5	<0.005	0.098	0.9	0.3	<0.05	3
		1.1	<0.005	0.095	1.7	0.7	<0.05	2.5

a Owing to an error in preparation of the liquor, the thorium concentration was only half the desired concentration of 0.2 g/liter, which is more typical of Blind River liquors.

b TDA = tridecanol.

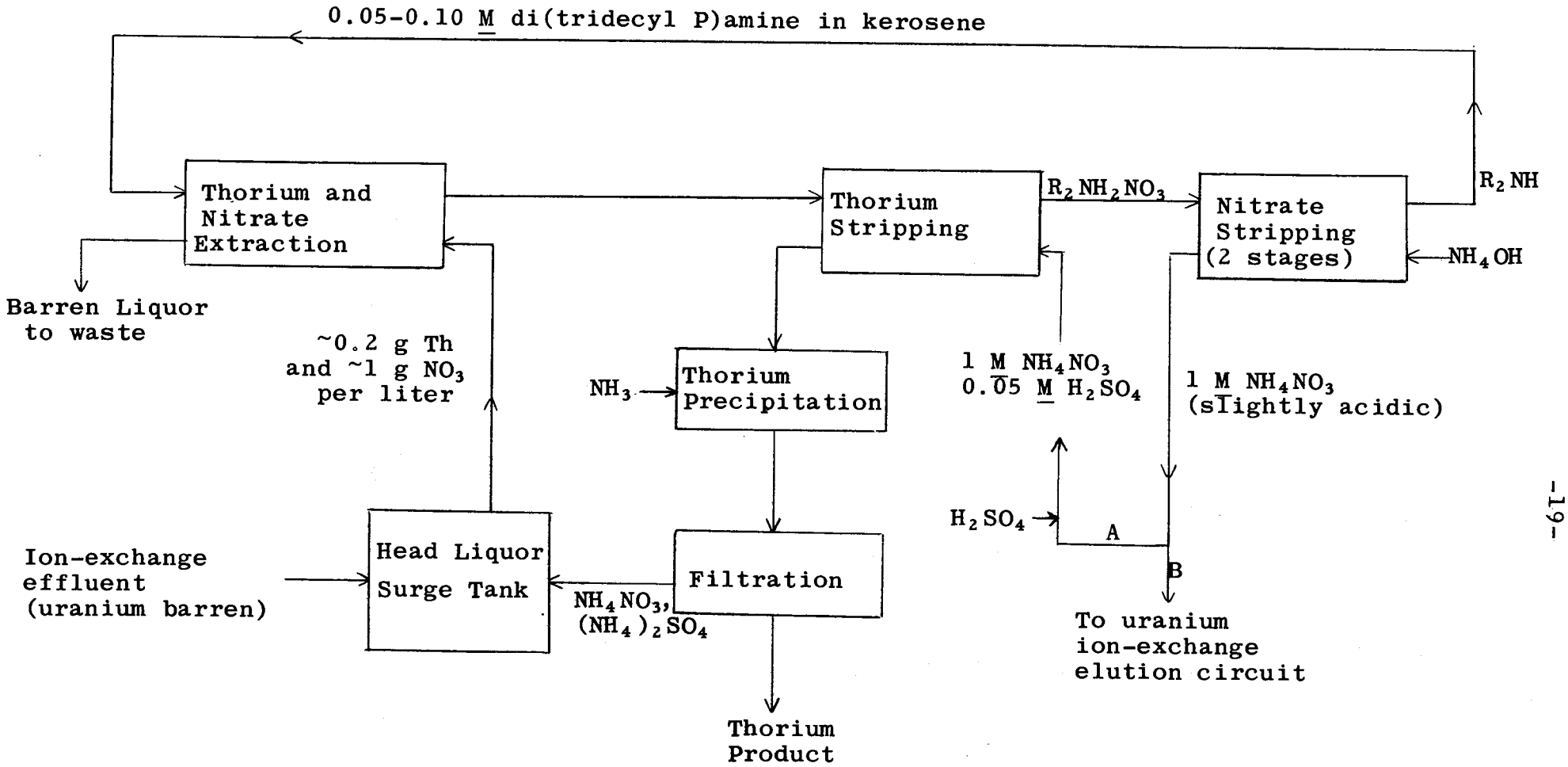

Fig. 2.1 Proposed Amex Process for Simultaneous Recovery of Thorium and Nitrate by Amex

by di(tridecyl P) amine were sufficiently strong that selective extraction of nitrate with this amine does not seem feasible unless the nitrate/thorium ratio is appreciably higher than average. As indicated previously, selective collection of the high nitrate fraction of the effluent should be advantageous. This fraction could be processed for nitrate recovery and then combined with the low nitrate fraction for thorium recovery. If nitrate recovery is not desired, the high nitrate fraction could be discarded and thorium recovered only from the low nitrate fraction. Quantitative information is needed on the distribution of nitrate and thorium in the effluent over the period of the uranium ion-exchange cycle in order to determine the relative merit of these alternatives.

Still another possibility for nitrate recovery has been proposed by workers at Rohm and Haas. In this proposal, nitrate is extracted by amines from sulfate-nitrate solutions produced in ion-exchange systems where the resin, after the elution cycle, is converted from the nitrate to the sulfate form in preparation for the loading cycle (Rohm and Haas Circular SP-69). Their studies showed amine 9D-178 to be useful for this purpose. If such a processing step were incorporated in the Blind River plants, the ion-exchange effluents would be free of nitrate and thorium could be recovered by Amex in the usual manner.

3.0 ENGINEERING STUDIES

In addition to the studies described below, engineering studies during the month have included (1) continuation of continuous flow evaluation of a 12-in. mixer for uranium extraction with Dapex solvent, (2) kinetics of vanadium extraction in the Dapex process, (3) phase separation and entrainment studies in the Dapex process, (4) bench scale studies of the compatibility of certain amines for extraction of uranium from liquors containing molybdenum.

3.1 Batch Kinetic Studies of Dapex Uranium Extraction (F. L. Daley)

Previously, the kinetics of uranium extraction was studied batchwise in 6- and 12-in. baffled tank mixers (ORNL-2269 and -2366). The results of additional tests (Tables 3.1 - 3.3) in a 20-in. mixer are reported here and are compared with previous data to show the dependence of the rate of uranium extraction on power input and mixer size for two types of sulfuric acid leach liquors, one containing a high concentration of uranium (5 g/liter) and the other a lower concentration (1.2 g/liter), more typical of that encountered in most Colorado Plateau mills.

The aqueous/organic ratio for each system was arbitrarily set to load the organic to about 80% of the maximum concentration obtainable for the particular feed liquor in an infinite number of extraction stages. For the high-uranium liquor (system A) the ratio was 1/1 and for the typical liquor (system B), 4/1.

The mixers were geometrically similar baffled tanks agitated

Table 3.1 Composition of Organic and Aqueous Feed Solutions

	System A	System B
Organic		
Di(2-ethylhexyl)phosphoric Acid, M	0.16	0.10
TBP, g/liter	35	30
Diluent	Kerosene	Kerosene
Aqueous, g/liter		
U	5.2	1.2
Fe^{+3}	0.52	0.33
Al	2.6	2.8
V (total)	4.8	0.94
V^{+4}	1.4	0.94
SO_4	89	51
PO_4	3.0	1.9
Cl	1.0	-
pH	0.32	1.1

Table 3.2 Uranium Concentration in Raffinate vs. Time

Test No.	Uranium Concentration in Raffinate, g/liter												
	0 sec	5 sec	10 sec	20 sec	30 sec	45 sec	60 sec	75 sec	120 sec	240 sec	480 sec	960 sec	K', min^{-1}
165	5.4	2.70	--	1.16	0.73	0.44	0.32	0.27	0.24	0.24	0.26	0.27	3.64
173	5.4	--	3.15	2.20	1.52	1.02	0.70	0.52	0.31	0.25	0.25	0.27	2.19
163	5.4	1.50	0.93	0.45	0.29	0.24	0.22	0.24	0.26	0.27	0.30	0.23	7.19
139	1.16	--	--	--	--	0.42	0.34	0.26	0.14	0.11	0.12	0.14	1.75
137	1.16	0.69	0.58	0.42	0.31	0.20	0.15	0.12	0.10	0.10	0.12	0.13	2.58
133	1.16	0.68	0.56	0.40	0.26	0.18	0.14	0.12	0.089	0.094	0.13	0.16	2.90
171	1.25	--	--	0.93	0.82	0.58	0.48	0.39	0.19	0.12	0.12	0.11	1.23
169	1.27	0.97	0.84	0.65	0.52	0.39	0.30	0.25	0.16	0.11	0.12	0.14	1.61
135	1.16	0.53	0.50	0.35	0.23	0.16	0.12	0.11	--	--	0.13	0.14	3.49

Table 3.3 Rate of Uranium Extraction in 20-in.-dia Mixer

Test No.	System	Turbine Dia, in.	Turbine Speed, rpm	Power Input, hp/1000 gal	K', min^{-1}	K'[a] for D/T = 1/3
173	A	6	370	5.9	2.19	2.09
165	A	4	1140	24	3.64	3.10
163	A	6	1140	170	7.19	6.87
171	B	6	290	2.5	1.23	1.18
139	B	3	1140	5.8	1.75	1.42
169	B	6	440	10	1.61	1.54
137	B	4	1140	24	2.58	2.20
133	B	5	1140	73	2.90	2.61
135	B	6	1140	170	3.49	3.34

[a] Value of K' for D/T = 1/3 was calculated from the dependence of K' on D/T in 12-in. mixer tests (ORNL-2366).

by 6-bladed flat-blade turbines located in the center of the tanks. The liquid depth was equal to the tank diameter. Samples were dipped from the mixer at timed intervals without interruption of mixing. The rate constant, K', was obtained graphically from ln-(1-E) = -K't where E is the fractional approach to equilibrium of aqueous samples at time t (ORNL-2269). In order to compare the extraction rates for systems at different phase ratios, the rate constant was based on the volume fraction of aqueous phase, that is, K'R/V where K' is the measured rate constant and R is the volume of aqueous phase present in the total volume, V, of mixed phases in the mixer. For the high uranium liquor R/V was 1/2 and for the typical liquor, 4/5. The rate constants for both systems and the three mixers are shown in Fig. 3.1 for a constant ratio of turbine to tank diameter (D/T) of 1/3. Included in the correlation are data obtained at different D/T ratios. These data were normalized to a D/T ratio of 1/3 by use of results showing the effect of D/T on K' in the 12-in. mixer tests (ORNL-2366).

The correlation of extraction rate with power input shows straight lines of average slope of 1/3 over a range of power input from 2.5 to 200 hp per 1000 gal of mixer volume. With the same mixing conditions the rate constant was slightly greater for the high-uranium liquor than for the typical liquor. At the same power input, the rate increased slightly (less than 10%) with increased mixer size, showing that scale-up by constant power input per unit mixer volume is conservative for uranium extraction by the Dapex process over the ranges of uranium concentration, phase ratio, and organic concentration investigated.

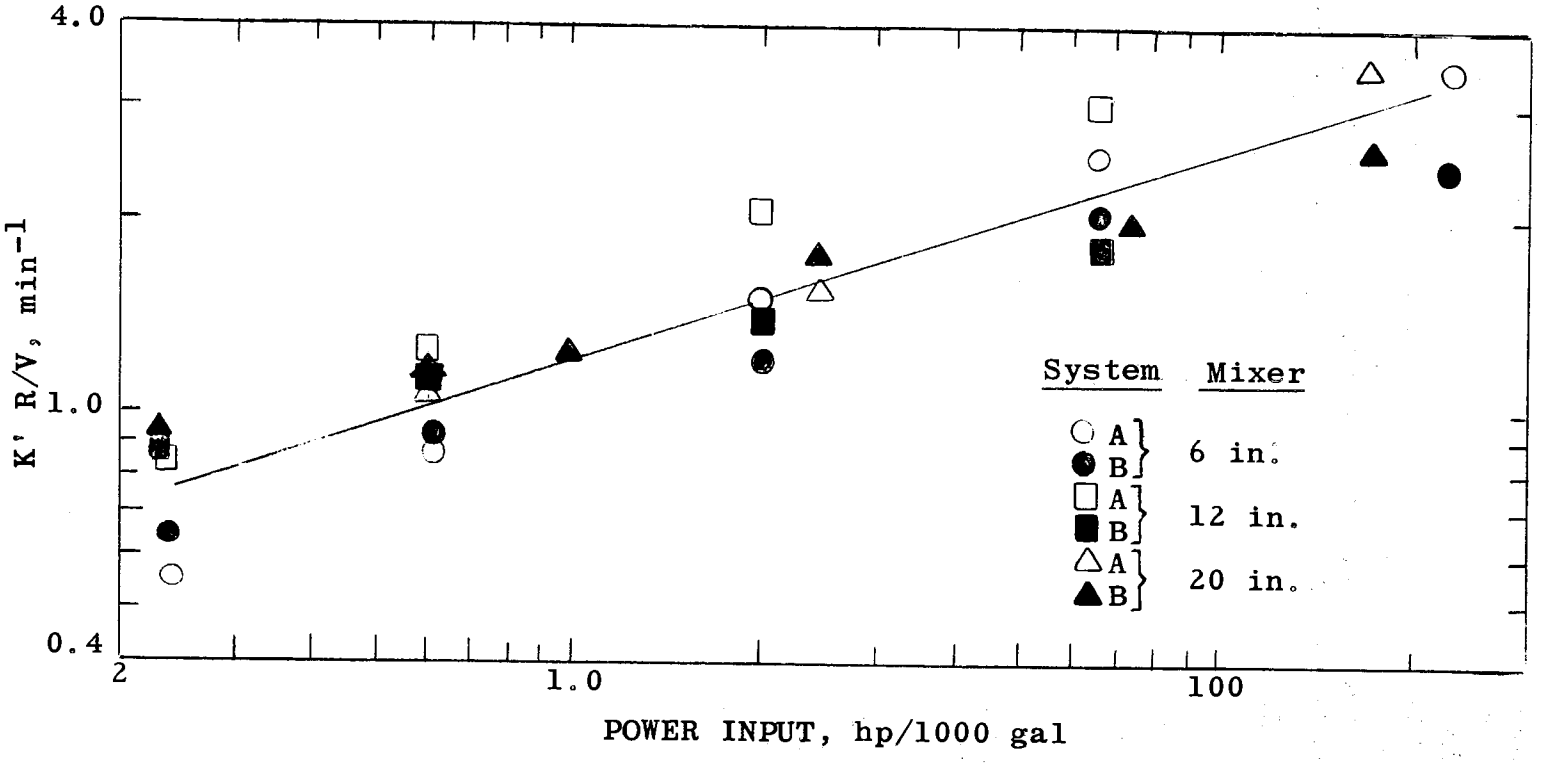

Fig. 3.1 Correlation of Rate of Uranium Extraction with Mixer Power