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PROGRESS REPORT ON SEPARATION AND RECOVERY OF URANIUM AND THORIUM FROM SULFATE LIQUORS BY THE AMEX PROCESS

D. J. Crouse
K. B. Brown
W. D. Arnold

OAK RIDGE NATIONAL LABORATORY
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Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

ORNL-2173
Chemistry

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section C

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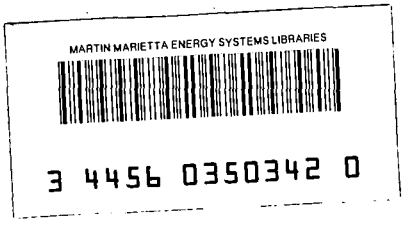

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0.0 ABSTRACT

The amine extraction (Amex) process can be used effectively for the extraction and separation of uranium and thorium from sulfate liquors in which these metals coexist. With proper choice of reagents, either uranium or thorium can be extracted first and the other extracted in a second cycle. Reagent costs are estimated to be low for both the uranium and thorium recovery cycles.

1.0 INTRODUCTION

Extensive studies on the recovery of uranium and other metals from acid liquors by extraction with long chain amines in hydrocarbon diluents (Amex process) have been reported previously.[1-6] The present report describes further studies on the Amex process with regard to its application for the separation and recovery of uranium and thorium from sulfuric acid ore leach liquors in which these two elements coexist.

Since the known occurrences of thorium in appreciable concentration in domestic uranium ores are relatively rare, the processes used or being developed for domestic application have not been faced as yet with the problem of separating and recovering both metals. This problem, on the other hand, is of considerable importance in the processing of certain Canadian ores. Large bodies of uranium-thorium ores, recently discovered in the Blind River district, are now being treated by a process which includes sulfuric acid leaching, countercurrent decantation and filtration to obtain a clear leach liquor, and sorption of uranium on anion exchange resins in columns.[7] The sulfuric acid leaching step dissolves almost all the uranium and an appreciable amount of thorium from the ore. The anion exchange step is effective for achieving complete uranium recovery from the leach liquors, but it is not efficient in separating the uranium from the thorium. The thorium content of the uranium concentrate is sufficiently high to cause serious problems in existing refining plants where these products are further processed into pure uranium compounds and metals.[8] Also, provision for recovering thorium as a valuable, or potentially valuable, by-product from the Blind River ores has not been made.

In the course of previous studies on the Amex process, the extractions of numerous metals, including thorium from

sulfate solutions were investigated. It was found that certain amines which possessed high uranium extraction power had negligible extraction power for thorium. Also, it was found that certain other amines were effective extractants for thorium, the extraction coefficients being higher, in some cases much higher, than those for uranium. The variation in extraction performance of the different amines could be correlated with variations in the compound type and structure. On the basis of these observations a promising process was developed for the recovery of thorium and uranium from sulfuric acid digests of monazite sand.[3] Preliminary studies were also made on liquors of the composition that might be derived from Blind River type ores, and effective thorium-uranium separations were demonstrated.[2]

The intent of the present studies has been to evaluate more closely the feasibility and economics for applying the amine extractants to the recovery and separation of uranium and thorium from liquors of the Blind River type. Two general process possibilities have been considered: (1) the extraction of uranium in a first cycle with subsequent extraction of thorium and (2) extraction of thorium in the primary cycle with subsequent extraction of uranium. The results from this work may also be used in evaluating a combination of solvent extraction with present ion exchange practice wherein thorium is recovered from the liquor prior to or after the uranium separation step.

Several amines which were expected from earlier work to possess favorable properties for the intended application were selected for study along with, for purposes of comparison, several compounds which were expected to give relatively poor performance. Numerous batch extraction tests were made to compare the extraction abilities of the different reagents and to evaluate the importance of several process variables. Since samples of uranium-thorium ores or plant liquors were not available, all tests were made on synthetic leach solutions. Preliminary evaluations of three different methods for stripping thorium from the organic extracts were also made by batch testing. Uranium stripping was not examined since several effective methods have been developed in previous work.[1,4,6] Finally, a bench-scale run was made in small mixer-settler equipment to demonstrate a two cycle Amex process for thorium and uranium recovery under conditions of continuous countercurrent operation. Reagent consumptions for both the uranium and thorium cycles were estimated from the data obtained.

Discussions of several topics of general pertinence to the use of amines as extraction agents have not been within the scope of this report, e.g., availability of different reagent types, reagent stability, diluent compatibilities, extraction selectivities with regard to other metals, probable reactions taking place during extraction and stripping, phase

separation, etc. These topics have been treated in considerable detail in previous reports.[1,2,4,6] It is suggested that these reports be reviewed as background material for the present discussions.

2.0 SUMMARY

Preliminary bench-scale studies have been completed on the use of the amine extraction (Amex) process for the recovery and separation of uranium and thorium from sulfuric acid ore leach liquors in which these two elements coexist.

In batch extraction tests on a liquor of typical thorium or uranium content, excellent separation of uranium from thorium was achieved by selectively extracting the uranium with a tertiary amine such as tri(iso-octyl)- or tri-n-octylamine. If scrubbing stages were provided, or if the organic phase was loaded to near saturation with uranium, good separations could also be obtained with secondary amines in which the alkyl chains were branched in close proximity to the nitrogen. Of the secondary amines tested, Amine S-24 was superior in performance.

Thorium was efficiently recovered from uranium-barren liquors by extracting with a branched chain primary amine or a secondary amine with branching at a distance from the nitrogen. For example, Primene JM-T (primary) and di(tridecyl P)-amine (secondary) were effective extractants in this respect, with the latter reagent preferred because of lower losses to the aqueous liquors and greater selectivity with regard to other metals such as iron(III). Extractions of thorium with these reagents would be equally possible from liquors that had been processed previously for uranium recovery either by Amex or anion exchange. Complete thorium extraction isotherms were determined for typical liquors with 0.1 M di(tridecyl P)amine in kerosene as the extracting solvent. At this reagent concentration, the indicated maximum loading of the solvent was approximately 3 g Th per liter.

The possibility of first separating thorium from the original leach liquor, leaving uranium for subsequent recovery, was investigated with two amines which had demonstrated greater than average thorium extraction power, i.e., Primene JM-T and di(tridecyl P)amine. Favorable separations were not obtained with the latter reagent, the ratio of thorium to uranium extraction coefficients being too low for the desired purpose. However, with Primene JM-T, reasonably effective separation and recovery of thorium were shown to be possible. Thus, analysis of batch test data in terms of a continuous countercurrent process indicated that essentially complete

thorium recovery and adequate separation from uranium could be accomplished by operating under conditions which would load the organic phase to near saturation with thorium. Similar end results should be attainable when operating at lower loadings by scrubbing the solvent with dilute sulfuric acid.

Thorium can be stripped from the organic extract by methods similar to those developed earlier for uranium processing.[4] For example, 1.0 M solutions of nitrate or chloride salts containing 0.05 M sulfuric acid have given efficient removal of thorium, providing pregnant strip liquors containing 20-30 g of thorium per liter. Sodium carbonate has also shown promise as a stripping reagent.

Using data from the batch experiments as a guide, a continuous countercurrent test of the Amex process for separation and recovery of uranium and thorium was made in bench-scale mixer-settler equipment. The composition of the synthetic leach liquor used in this test was, in grams per liter, 1.2 U, 0.2 Th, 1.0 Fe(III), 1.0 Fe(II), 40 SO_4; pH 0.9. Recovery of greater than 99.9% of the uranium and greater than 99% of the thorium was achieved in a two-cycle operation. In the first cycle, uranium was recovered by extracting in 3 mixer-settler stages with 0.1 M tri-n-octylamine in kerosene plus 3 v % tridecyl alcohol. The uranium was stripped from the extract with an aqueous slurry of magnesium oxide, yielding a product containing only 0.03 - 0.05% ThO_2. In the second cycle, thorium was extracted from the raffinate of the uranium recovery operation in 3 mixer-settler stages with 0.05 M solution of di(tridecyl P)amine in kerosene. The thorium was stripped from the extract with 1.0 M NaCl - 0.05 M H_2SO_4 solution and precipitated with ammonia. The product precipitate thus obtained contained only small amounts of other metal impurities. Based on the data from the continuous countercurrent test, it was estimated that total reagent costs might be as low as $\sim$7¢/lb U_3O_8 for uranium recovery and $\sim$13¢/lb ThO_2 for thorium recovery.

Continuous tests have not been made on recovery of thorium and uranium in reverse order to that described above, e.g., recovery of thorium by extracting with a reagent such as Primene JM-T and subsequent recovery of uranium by one of several suitable amine reagents.[4,6] Since excellent separations are so easily obtained by extracting uranium with a tertiary amine in the first cycle, it is believed that this reverse sequence would be a less favorable process arrangement. On the other hand, mills using anion exchange resins for uranium recovery from uranium-thorium liquors are already in existence. Installation of a primary thorium recovery cycle in these mills should be profitable since it would eliminate the problem of thorium contamination in present ion exchange uranium concentrates and produce, at the same time,

a valuable thorium by-product. Further attention will be given to this possibility as a part of a continuing development program on applications for the Amex process.

Although the experiments described in this report were made with liquors of a particular composition (~1.2 g U and ~0.2 g Th per liter) and the continuous tests have been restricted thus far to one of several process arrangements, the data obtained can be extrapolated to considerations of other liquors and process modifications. Also, only a limited number of specific amine reagents were selected for study. It would be expected, however, that other reagents generally similar in type and structure to those tested would give similar performance.

3.0 BATCH TESTS

3.1 Extraction of Uranium and Thorium

3.1.1 Separation of Uranium from Thorium by Selective Uranium Extraction. The extraction of uranium (and thorium) from a 0.5 M sulfate solution at pH 0.9 containing 1 g U and 0.5 g Th per liter was investigated with four different amines, i.e., Amine S-24*, tri(iso-octyl)amine, R&H Amine 9D-178*, and tri-n-octylamine. Uranium-thorium separations with the latter two compounds from sulfate solutions containing 1 g U and 1 g Th per liter have been reported previously.[2] Extractions were performed at two different phase ratios to determine in a preliminary manner the degree to which uranium-thorium separations might be improved with the various amines by increasing the uranium loading in the solvent.

Very effective separation of uranium from thorium was achieved with tri-n-octyl and tri(iso-octyl) amines (Table 1). In all tests with these compounds, even in those with lower uranium loadings, the thorium reporting to the organic phase was below the limit of detection by the analytical methods used. Appreciable amounts of thorium were extracted by the two secondary amines when the uranium loading was relatively low ($3^a/1^o$). However, when the uranium loading was increased ($6^a/1^o$), thorium contamination of the extract was only 0.5% of the uranium content using Amine S-24 and 2% using R&H 9D-178 amine. More effective thorium decontamination would

*Structures given in Appendix B.

TABLE 1. URANIUM-THORIUM EXTRACTION WITH AMINES FROM 0.5 M SULFATE SOLUTION

Aqueous: 1 g U and 0.5 g Th per liter; 0.5 M SO_4; pH 0.9
Organic: 0.1 M amine
Contact time: ~2 min
Temperature: Room

Organic*	Phase Ratio (a/o)	Final Concentration, g/liter				Extraction Coefficient (E_a^o)		Thorium Decontamination Factor**
		Aqueous		Organic				
		U	Th	U	Th	U	Th	
R&H 9D-178 Amine in kerosene + 2 v % capryl alcohol	3	0.047	0.41	2.8	0.25	60	0.6	6
	6	0.29	0.46	3.7***	0.072	13	0.16	26
Amine S-24 in kerosene	3	0.024	0.41	3.0	0.26	125	0.63	6
	6	0.26	0.50	4.5	0.021	17	0.04	110
Tri-n-octylamine in kerosene + 2 v % capryl alcohol	3	0.011	0.47	2.8	<0.02	250	<0.05	>70
	6	0.13	0.40***	4.5	<0.02	35	<0.05	>110
Tri(iso-octyl)amine in kerosene + 3 v % tridecyl alcohol	3	0.019	0.49	2.8	<0.02	150	<0.05	>70
	6	0.18	0.51	4.8	<0.02	27	<0.05	>110

*Amine structures are given in Appendix B.

**$\frac{\text{Th/U in head liquor}}{\text{Th/U in organic}}$

***Poor material balances. This does not have an important effect on the significance of the data, however, since both phases were analyzed for uranium and thorium.

be expected at still higher uranium loadings.* Further decontamination might also be obtained by scrubbing the organic extract with dilute sulfuric acid. In process practice, the scrub solution thus produced would be recycled to some suitable point in the process stream.

The differences observed in the effectiveness of uranium and thorium separation with the different amines are in agreement with those anticipated from earlier studies on the selectivity of amines for uranium over other metals as a function of amine type and structure. As stated in ORNL-1959, "the efficiency with which uranium can be separated by amine extractants from the various metal contaminants is dependent on a number of factors. The type and structure of the extractant is of primary importance, the primary amines being generally the least selective and the symmetrical tertiary amines** generally the most selective of the reagents tested. With secondary amines, branching of the alkyl chains on the carbon adjacent to the nitrogen improves the selectivity over that of amines with no branching or with branching farther removed from the nitrogen. Thus, compounds such as C&C 16F27 (now Amine S-24) and R&H 9D-178 amine, are superior in selectivity to compounds such as dilauryl, di(2-butyloctyl) and di(tridecyl P) amines. Also, it has appeared that C&C 16F27 (Amine S-24), in which both chains are branched at the first carbon, has somewhat better selectivity properties than R&H 9D-178, in which only one chain is branched at the first carbon."

Primary amines and secondary amines with no branching or branching distant from the nitrogen were not included in the tests shown in Table 1. As suggested above, the preferential extraction of uranium with these compounds would have been poor. As a matter of fact, as described below and as also

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*It should be noted, however, that at a phase ratio of $6^a/1^o$ uranium loading of the organic phase was not far from the maximum loading achievable with this liquor. Also it should be noted that, in a countercurrent extraction system, loading is increased at the expense of increasing the number of extraction stages required for complete uranium recovery. In addition, and possibly more important, operation of the system in such a manner as to accomplish essentially maximum uranium loading of the organic phase requires extremely careful control. The organic and aqueous feed rates must be accurately measured and the uranium content of the feed liquor and the amine concentration accurately known. In view of these considerations the more selective tertiary amines described above would be operationally superior for this application.

**Unsymmetrical tertiary amines with three alkyl chains of reasonable length should behave similarly. For more complete discussions of effects of reagent structure see ORNL-1734, -1922, -1959, and -2099.

indicated by previously reported thorium coefficients,[1] some amines of these types can be used effectively as extractants for thorium from the sulfate liquors after the uranium has been removed. In addition, primary amines may be used to separate thorium selectively from liquors containing both uranium and thorium. Such separations are described in Sec. 3.1.3 for sulfate liquors and have been previously described in ORNL-1859 for sulfate-phosphate liquors obtained by sulfuric acid digestion of monazite sand.

3.1.2 Extraction of Thorium from Synthetic Sulfate Liquors. Extraction of thorium from synthetic leach liquors containing 0.2 g Th per liter by three different secondary amines and one primary amine has been studied at pH 0.6 and 1.0. The results (Table 2) show that effective extraction of thorium ($E_a^o > 130$) was achieved with the primary amine (Primene JM-T) and with di(tridecyl P)amine at both pH values. Extraction coefficients with Armeen 212, although somewhat lower, were still sufficiently high for potential practical application. As expected, much weaker thorium extraction was observed with R&H 9D-178 amine (branching close to the nitrogen). Had they been tested, still weaker extractions would have been shown by secondary amines with even greater branching close to the nitrogen (e.g., Amine S-24) and tertiary amines such as tri-n-octyl and tri(iso-octyl).

The extraction efficiency of Armeen 212 and R&H 9D-178 amines decreased markedly at increased aqueous acidity. In the tests with Primene JM-T and di(tridecyl P) amines no dependable data on the effect of pH change was obtained since, in all cases, the concentration of thorium remaining in the aqueous phase was either close to or below the limit of determination by the analytical methods used.

Appreciable amounts of iron were extracted by di(tridecyl P)amine at pH 1.0 and still greater amounts by Primene JM-T at both pH levels. In tests with Armeen 212 and R&H 9D-178, iron extractions were relatively low. These data are in conformance with previous data[1,2,4] on the dependence of Fe(III) extraction on reagent type and structure.* From a process utilization standpoint, it should be pointed out that the thorium loading of the extract in all the tests in Table 2 was low, and consequently the iron extraction approximated that which would be expected in the raffinate end of a countercurrent extraction system. In regions of high thorium loading (extract end of the system) the amount

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*As described in previous reports[2,4,6] the presence of alcohol in the diluent markedly decreases extraction of ferric iron. Thus the selectivity with respect to iron exhibited by Armeen 212 in these tests is better than would be expected.

TABLE 2. EXTRACTION OF THORIUM FROM A SYNTHETIC LEACH LIQUOR WITH AMINES

Aqueous: 0.20 g Th, 1.1 g Fe(II), and 0.9 g Fe(III) per liter; A, 0.4 M SO_4, pH 0.9; B, 0.6 M SO_4, pH 0.5
Organic: 0.1 M amine in kerosene
Phase ratio: $2^a/1^o$
Contact time: 5 min
Temperature: Room

Amine*	Aqueous	Final pH	Th, g/liter		Fe in Organic, g/liter	Thorium Extraction Coefficient (E_a^o)
			Aqueous	Organic		
R&H 9D-178	A	1.0	0.027	0.34	0.11	13
Armeen 212**	A	1.0	0.004	0.40	0.03	100
Di(tridecyl P)	A	1.0	0.003	0.42	0.35	140
Primene JM-T	A	1.0	<0.003	0.39	0.91	>130
R&H 9D-178	B	0.60	0.097	0.19	0.026	2
Armeen 212**	B	0.60	0.014	0.36	0.016	26
Di(tridecyl P)	B	0.60	<0.003	0.40	0.047	>130
Primene JM-T	B	0.60	<0.003	0.39	0.81	>130

*Amine structures are given in Appendix B.

**Diluent was kerosene modified with 5 v % tridecyl alcohol.

of iron in the extract would be expected to be considerably lower.*

This expectation is borne out by the isotherms for extraction of thorium at pH 0.5 and 0.9 by 0.106 M di(tridecyl P)amine (Fig. 1). Data from which the isotherms were plotted, including analyses for the amount of iron extracted into the organic phase, are presented in Tables 3 and 4. At both pH levels very high thorium extraction coefficients were observed with this reagent even at relatively high thorium loadings in the organic phase. The isotherms indicate a maximum thorium loading from these solutions of about 3 g per liter, corresponding to about 8 moles of amine per mole of thorium. Slightly higher thorium loadings were indicated at pH 0.5 than at pH 0.9, but it seems possible that the small difference could be attributed to analytical uncertainties. As noted previously, the amount of iron extracted with this amine was low at pH 0.5. At pH 0.9, although iron extraction was appreciable at low thorium loadings (Table 4), only relatively small amounts of iron were present in the organic phase when it was loaded to near saturation with thorium.

3.1.3 Separation of Thorium from Uranium by Selective Thorium Extraction. The possibility of selectively extracting thorium from a synthetic sulfate liquor containing 1.2 g U and 0.2 g Th per liter was studied with kerosene solutions of Primene JM-T and di(tridecyl P)amine. Both these amines have previously been shown to be good extractants for uranium[1,2,4]. Thus, achievement of an effective separation of thorium from uranium, out of a liquor in which the uranium concentration is appreciably higher than that of the thorium, requires that the thorium extraction power of the reagent be extremely high, i.e., considerably higher than for uranium. If this condition is met, it should be possible to keep the uranium extraction at a low level by loading the solvent to near saturation with thorium. To determine the degree to which separations would be affected by thorium loading in these particular solvents, the extraction tests were carried out at several different phase ratios.

With di(tridecyl P)amine the uranium and thorium separations obtained were quite poor even under the most favorable experimental conditions, the ratio of thorium to uranium coefficients evidently being too low for the desired purpose (Table 5). With Primene JM-T, however, effective separations and recoveries were shown to be possible (Table 5 and Fig. 2). For example, in a single stage contact, 90% of the thorium could be extracted while removing at the

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*Iron extraction can also be prevented by reducing to the non-extractable ferrous state.[1]

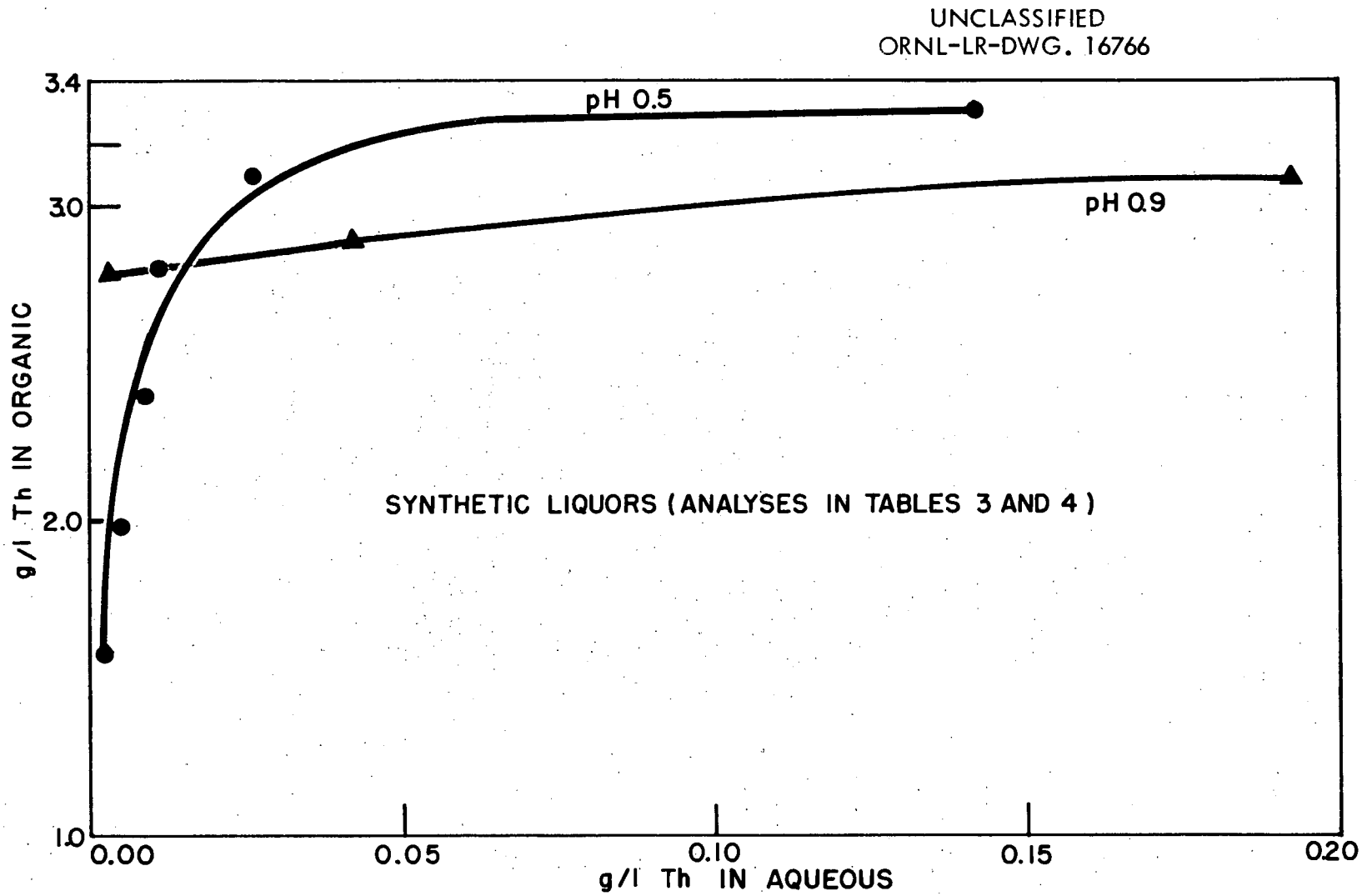

FIGURE 1. THORIUM EXTRACTION ISOTHERMS FOR 0.1M DI(TRIDECYL P) AMINE IN KEROSENE

TABLE 3. DATA ON EXTRACTION OF THORIUM FROM A SYNTHETIC LEACH LIQUOR AT pH 0.5 BY DI(TRIDECYL P)AMINE

Aqueous: 0.20 g Th, 1.1 g Fe(II), 0.9 g Fe(III) per liter; 0.6 M SO_4; pH 0.5
Organic: 0.106 M di(tridecyl P)amine in kerosene

Procedure: Organic cascaded against fresh volumes of liquor and phases sampled after each contact; phase ratio was $2^a/1^o$ on all contacts except the last which was $5^a/1^o$

Contact time: 2 min per stage

Cascade No.	Final Aqueous pH	Th, g/liter		Fe in Organic, g/liter	Thorium Extraction Coefficient (E_a^o)
		Aqueous	Organic		
1*	0.6	<0.002	0.40	0.076	>200
2*	0.5	<0.002	0.80	0.052	>400
3	0.5	<0.002	1.23	0.046	>600
4	0.5	0.002	1.58	0.033	800
5	0.5	0.004	1.99	0.026	500
6	0.5	0.008	2.4	0.036	300
7	0.5	0.011	2.8	0.019	250
8	0.5	0.026	3.1	0.014	120
9	0.5	0.142	3.3	0.009	23

*Phase separation was very slow (5-10 min) in the first two contacts.

TABLE 4. DATA ON EXTRACTION OF THORIUM FROM A SYNTHETIC LEACH LIQUOR AT pH 0.9 BY DI(TRIDECYL P)AMINE

Aqueous: 0.20 g Th, 1.1 g Fe(II), 0.9 g Fe(III) per liter; 0.4 M SO_4; pH 0.9
Organic: 0.106 M di(tridecyl P)amine in kerosene

Procedure: Organic cascaded against fresh volumes of liquor and phases sampled after each contact; phase ratio was $2^a/1^o$ on all contacts except the last which was $5^a/1^o$

Contact time: 2 min per stage

Cascade No.	Final Aqueous pH	Th, g/liter		Fe in Organic, g/liter	Thorium Extraction Coefficient (E_a^o)
		Aqueous	Organic		
1	1.0	<0.002	0.40	0.36	>200
2	0.9	<0.002	0.80	0.28	>400
3	0.9	<0.002	1.2	0.22	>600
4	0.9	<0.002	1.6	0.20	>800
5	0.9	<0.002	2.1	0.17	>1000
6	0.9	<0.002	2.4	0.13	>1200
7	0.9	0.003	2.8	0.092	930
8	0.9	0.042	2.9	0.030	70
9	0.9	0.193	3.1	0.019	16

TABLE 5. SELECTIVE EXTRACTION OF THORIUM FROM A SYNTHETIC LEACH LIQUOR

Aqueous: 1.35 g U, 0.20 g Th, 1.0 g Fe(III), 1 g Fe(II), and 45 g SO_4 per liter; pH 0.90

Contact time: 5 min

Temperature: Room ($\sim 24^{o}C$)

Organic	Phase Ratio (a/o)	Concentration, g/liter					Extraction Coefficient (E_a^o)		Uranium Decontamination Factor*
		Organic Phase			Aqueous Phase				
		Th	U	Fe	Th	U	Th	U	
0.046 M Primene JM-T in kerosene	5	1.0	0.117	0.030	<0.003	~1.3	>330	0.090	60
	6	1.2	0.078	---	0.007	~1.3	170	0.065	100
	7	1.3	0.056	0.007	0.028	~1.3	46	0.047	140
	8	1.3	0.042	0.006	0.046	~1.3	28	0.035	190
	9	1.3	0.033	0.006	0.062	~1.3	21	0.027	230
	10	1.3	0.033	0.003	0.072	~1.3	18	0.027	230
	11	1.3	0.028	0.003	0.084	~1.3	15	0.023	280
0.05 M di(tridecyl P)-amine in kerosene	7	0.61	1.21	0.004	0.116	~1.2	5.3	~1.0	3.0
	8	0.58	1.20	0.004	0.124	~1.2	4.7	~1.0	2.9
	9	0.58	1.23	0.005	0.131	~1.2	4.4	~1.0	2.8
	10	0.61	1.21	0.004	0.139	~1.2	4.4	~1.0	3.0
	11	0.61	1.19	0.003	0.144	~1.2	4.2	~1.0	3.1

*Uranium decontamination factor = $\frac{\text{U/Th in head liquor}}{\text{U/Th in organic}}$.

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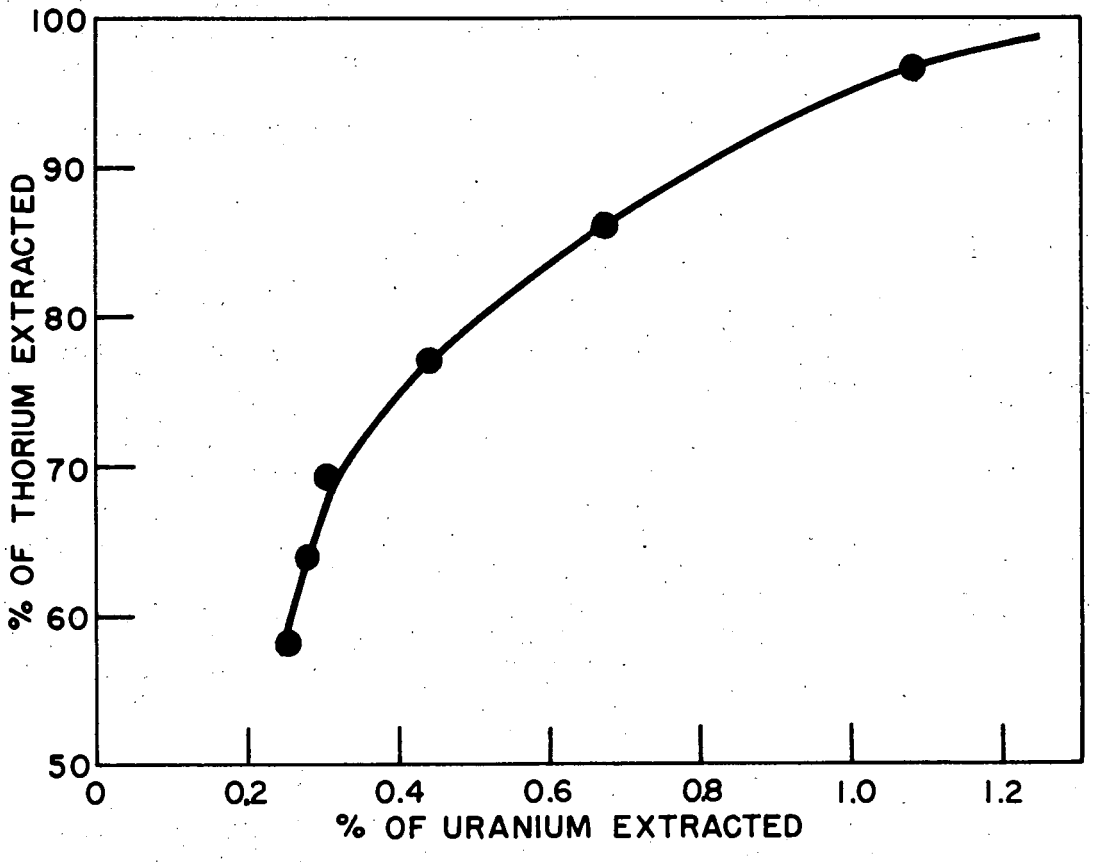

FIGURE 2. SELECTIVE EXTRACTION OF THORIUM WITH PRIMENE JM-T IN KEROSENE

same time only about 0.8% of the uranium. In single stage contacts under conditions of higher loading of thorium in the extract* (lower thorium recovery) the uranium extraction was reduced to < 0.3%. By proper operation of a multistage countercurrent system, very high recoveries of thorium and very low extractions of uranium could be achieved simultaneously.

A process of this type might be useful for removal and recovery of thorium from uranium-thorium liquors prior to uranium recovery in instances where the existing uranium recovery method does not give satisfactory uranium-thorium separations, e.g., the ion exchange plants operating on Blind River ores. Several different arrangements of extraction, stripping, and scrubbing operations could be used in a process of this nature and some of these will be examined in bench-scale countercurrent tests. Preliminary results have shown that certain stripping methods might give thorium-uranium separation in addition to that obtained in the extraction system, and further studies along these lines are indicated.

3.2 Thorium Stripping

3.2.1 Stripping with Nitrate or Chloride Salt Solutions. Experimental results on stripping of thorium from pregnant di(tridecyl P)amine - kerosene solvent with acidic chloride and nitrate solutions are presented in Table 6.** In conformance with previous studies on uranium,[1,4] effective removal of thorium from the organic phase was obtained with both stripping solutions, the stripping efficiency being, as expected, considerably higher when nitrate rather than chloride was used as the stripping anion. The data of Table 6 are presented in the form of stripping isotherms in Fig. 3. Using 1.0 M NaCl - 0.05 M H_2SO_4, the maximum loading of thorium into the aqueous phase is indicated to be approximately 20 g per liter. The indicated maximum thorium loading with the 0.1 M HNO_3 - 0.9 M NH_4NO_3 strip solution is of the order of 30 g per liter.

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*In tests at organic/aqueous phase ratios above 6/1, the loading of the organic phase was close to maximum in all cases. The small changes in loading that occurred at increased ratios above this point were not detectable from analyses of the organic phase and can best be followed by observing the thorium concentration in the aqueous phase.

**Tests on the stripping of thorium from Primene JM-R with sodium carbonate, sodium hydroxide, nitric acid, and nitric acid-ammonium nitrate solutions were described in ORNL-1859.

TABLE 6. STRIPPING THORIUM WITH ACIDIC NITRATE AND CHLORIDE SOLUTIONS

Organic: 0.05 M di(tridecyl P)amine in kerosene loaded to 1.6 g Th per liter from a synthetic leach liquor

Contact time: 2 min

Temperature: Room (28°C)

Stripping Solution	Phase Ratio (o/a)	Final pH	Phase Separation Time, sec	Th, g/liter		Stripping Coefficient (S_o^a)
				Aqueous	Organic	
0.1 M HNO_3 - 0.9 M NH_4NO_3	1	1.20	50	1.6	<0.005	>280
	4	1.25	60	6.1	<0.005	>1200
	8	1.30	60	12.5	0.028	450
	12	1.40	65	18.2	0.072	250
	15	1.50	75	22.4	0.100	220
	20	1.45	40	30.2	0.20	150
	25	1.45	70	30.3	0.52	60
1.0 M NaCl - 0.05 M H_2SO_4	1	1.15	45	1.5	0.08(?)	19(?)
	5	1.25	45	7.3	0.11	65
	10	1.35	55	13.6	0.23	60
	15	1.40	65	17.3	0.44	40
	20	1.40	55	19.0	0.67	28

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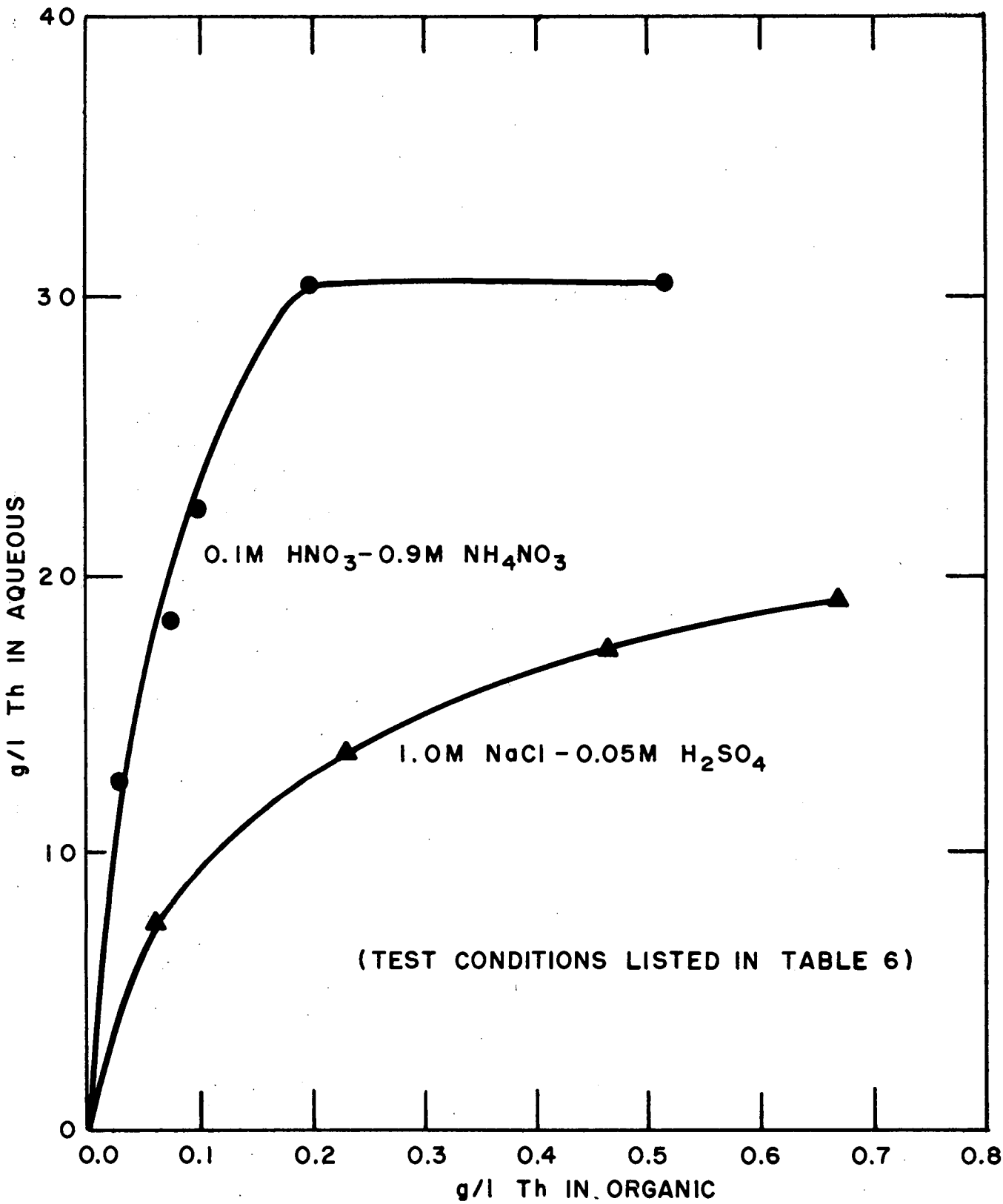

FIGURE 3. ISOTHERMS FOR STRIPPING THORIUM FROM 0.05M DI(TRIDECYL P) AMINE WITH NITRATE AND CHLORIDE SOLUTIONS

3.2.2 Stripping with Sodium Carbonate Solutions. Preliminary studies have been made on thorium stripping with sodium carbonate solutions. In the tests described in Table 7, a thorium loaded di(tridecyl P)amine - kerosene solvent was contacted with 8 w/v %* sodium carbonate at various phase ratios.

At a phase ratio of $9^o/1^a$, 95% of the thorium was stripped after 2 min contact time and 99% after 10 min contact time, yielding in each case a clear aqueous strip solution. At higher organic/aqueous phase ratios, i.e., higher thorium loading in the aqueous and a smaller excess of sodium carbonate, thorium removal from the organic phase was less complete but there was some indication that better recoveries might have been realized with longer contact times.** Precipitation of thorium occurred in all these latter experiments, the amount of precipitate formed increasing with increased contact time. Over the range of conditions studied in these particular tests the degree of precipitation varied from 7 to 99.9% of the total thorium stripped. In tests where precipitation occurred, the phase separation was, nevertheless, rapid and clean with all the precipitate settling into the aqueous phase.

As a result of these preliminary batch studies it is believed that sodium carbonate stripping could be operated successfully in a multistage system where more efficient utilization of the stripping agent would be achieved. Further tests will be made to better define the optimum combination of such conditions as sodium carbonate concentration, flow ratios, contact time, temperature, etc.

4.0 CONTINUOUS COUNTERCURRENT TESTS

Preliminary demonstration of the applicability of the Amex process for separation and recovery of uranium and thorium from sulfate leach liquors has been made in continuous countercurrent bench scale equipment. The design of the equipment was generally similar to that used in Dapex process tests which are described in Appendix A of ORNL-2172 with the exception that pumps were not used for transferring the organic phase from stage to stage. Instead, advantage was taken of the hydraulic head developed by the mixer impellers to provide interstage flow of organic. The synthetic leach liquor treated in these tests (see Table 7) contained uranium,

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*8 w/v % sodium carbonate = 80 g Na_2CO_3 per liter.

**Better recoveries might also be obtained at higher temperatures.

TABLE 7. STRIPPING THORIUM WITH SODIUM CARBONATE SOLUTIONS

Organic: 0.05 M di(tridecyl P)amine in kerosene loaded to 1.6 g Th per liter from a synthetic liquor

Strip solution: 8 w/v % Na_2CO_3 solution

Temperature: Room (28°C)

Phase Ratio (o/a)	Contact Time, min	Final pH	Phase Separation Time, sec	Th, g/liter		Thorium Stripped** (% of total)	Thorium Precipitated (% of stripped)
				Aqueous	Organic		
9	2	8.8	10	13.3	0.072	95	0
9	10	8.0	40	15.1	0.018	99	0
11	2	8.4	10	14.4*	0.19	88	7
13	2	8.3	<10	8.8*	0.31	81	48
13	10	7.7	<10	1.5*	0.082	95	92
15	2	8.4	<10	6.0*	0.48	70	64
18	2	8.4	<10	6.1*	0.65	59	64
18	10	---	<10	0.024*	0.44	72	99.9

*Thorium precipitation occurred; aqueous phase was filtered before analysis.

**Based on the extract and stripped organic analyses.

thorium, iron, and sulfate at concentration levels approximating those which have been obtained by leaching ores from the Blind River district of Canada.[7] A two-cycle extraction process employing tri-n-octylamine for uranium recovery and di(tridecyl P)amine for thorium recovery was utilized. The overall flow diagram for uranium-thorium recovery is shown in Fig. 4.

4.1 Uranium Recovery Cycle

Operating conditions for the uranium recovery cycle are listed in Table 8. Uranium was extracted in three mixer-settler stages with 0.10 M tri-n-octylamine in 97% kerosene - 3% tridecyl alcohol diluent at a phase ratio of $4^a/1^o$. Stripping of the extract was accomplished in a single stage using an aqueous slurry of magnesium oxide* at a phase ratio of $5^o/1^a$ ($\sim$12% excess MgO over calculated stoichiometric requirements - see ORNL-2099). A description of the design and method of operation of the magnesium oxide stripping system is presented in Appendix A.

Results from the uranium recovery cycle, showing the distribution of uranium between the aqueous and organic phases in the extraction system and the concentration of uranium in the stripped organic phase at various periods throughout the run, are listed in Table 9. The run proceeded for 7 hr, which was equivalent to approximately seven complete cycles of the organic phase. Based on the raffinate analysis, uranium recovery was essentially complete (>99.9%). The thorium content of the uranium-loaded extract was below the limit of the analytical determinations (i.e., <0.005 g Th per liter, or <0.1% Th based on uranium).

Uranium stripping from the loaded extract was incomplete, with the stripping efficiency falling in the range 94-99%. However, in spite of the relatively high recycle of uranium to the extraction system, uranium recovery results were not substantially affected owing to the very favorable uranium distribution occurring in the bottom extraction stage. Some of the stripping inefficiency in this run is attributed to a decrease in the amount of magnesium oxide supplied to the stripping system during one period as the result of partial clogging of the slurry feed line. When this situation was remedied, the stripping efficiency improved but was never greater than 98-99%. Failure to achieve more efficient stripping was somewhat surprising since batch tests with the

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*Other stripping agents would also be suitable. Various methods for stripping uranium from amines have been discussed in previous reports.[1,3,4,6] Previous information relating to the magnesium oxide stripping method is presented in ORNL-2099.

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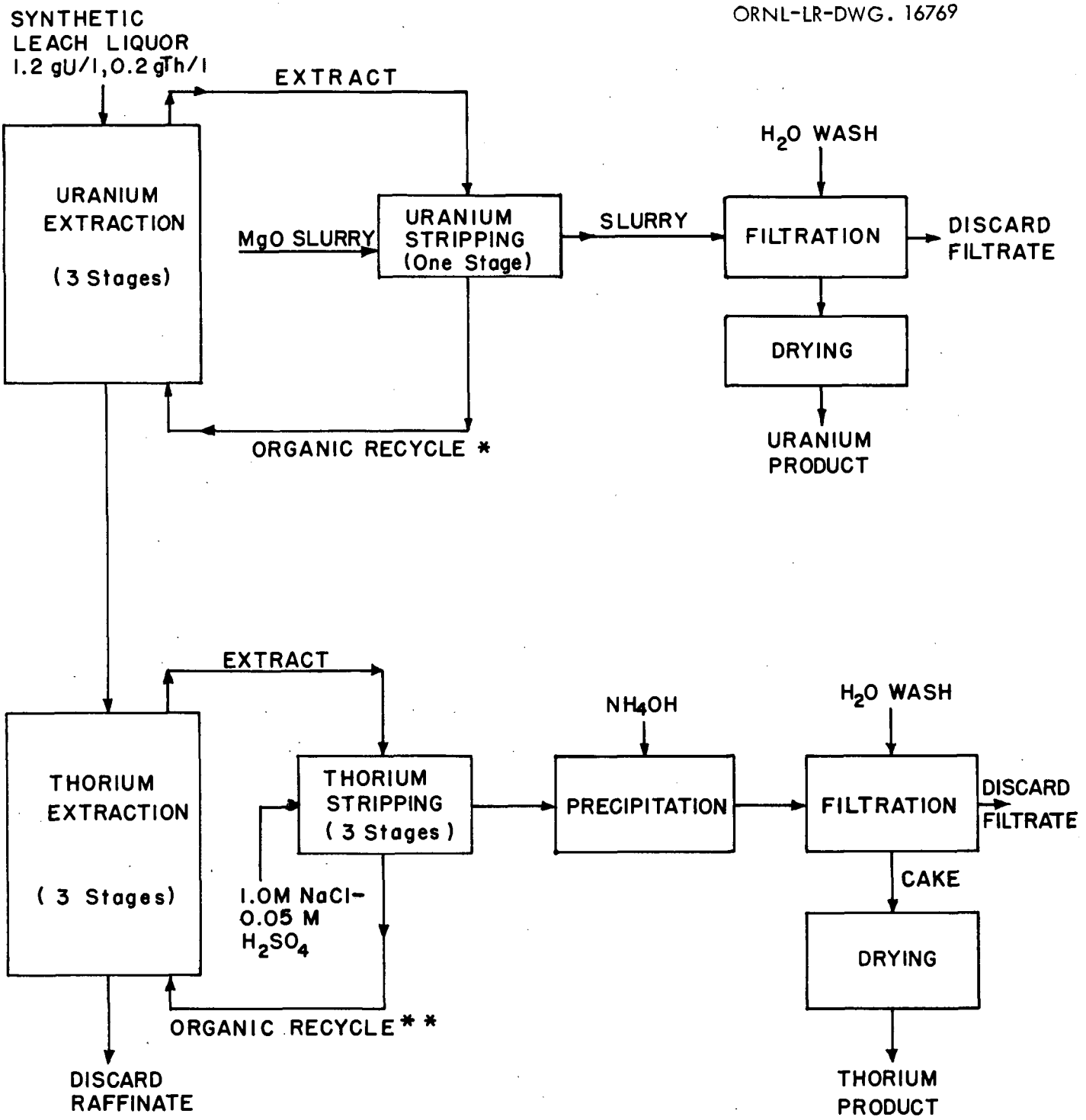

* 0.1M TRI-n-OCTYLAMINE IN 97% KEROSENE — 3% TRIDECYL ALCOHOL.
** 0.05 M DI(TRIDECYL P) AMINE IN KEROSENE.

FIGURE 4, URANIUM — THORIUM RECOVERY WITH AMINES

TABLE 8. OPERATING CONDITIONS FOR THE URANIUM RECOVERY CYCLE

Extraction System

Number of mixer-settler stages: 3

Organic phase: 0.10 M tri-n-octylamine in 97% kerosene - 3% tridecyl alcohol

Leach liquor: Synthetic liquor with 1.2 g U, 0.2 g Th, 1.0 g Fe(II), 1.0 g Fe(III), and 40 g SO_4 per liter; pH 0.9

Feed rate: Aqueous 100 ml/min
Organic 25 ml/min

Residence time in each mixer: 1.6 min

Residence time in each settler: Aqueous 1.5 min
Organic 6 min

Stripping System (see Appendix for further information)

Number of stripping stages: 1

Stripping agent: Aqueous slurry of Michigan Chemical Co. No. 15 calcined magnesite, 0.467 M MgO*

Feed rate: Extract 25 ml/min
MgO slurry 5 ml/min

Operating temperature: Room (32°C)

Residence time in each of two cocurrent mixers: 10-12 min

Residence time in settler: Aqueous (single pass) 7.5 min
Organic 14 min

*A sample of the slurry was titrated with acid thus giving the total base strength of the slurry which is expressed here as equivalent MgO.

TABLE 9. URANIUM RECOVERY CYCLE DATA

Material Sampled	Time of Sampling,* hr	U, g/liter		Th in Organic, g/liter	Uranium Extraction Coefficient (E_a^o)
		Aqueous	Organic		
Extraction System					
Stage 1	2	0.36	5.0	<0.005	14
Stage 2		0.016	1.9	<0.005	120
Stage 3		0.0017	0.47	<0.005	280
Stage 1	7	0.23	4.9	<0.005	21
Stage 2		0.008	1.0	<0.005	120
Stage 3		0.0006	0.11	<0.005	170
Total raffinate collected		0.0011	--	--	---
Stripping System					
Stripped organic	2	--	0.055	--	---
	4.5	--	0.31**	--	---
	5	--	0.24	--	---
	6	--	0.10	--	---
	7	--	0.11***	--	---

*One complete cycle of the organic phase required approximately 1 hr.

**A decrease in the MgO slurry flow rate occurred owing to a partial clogging of the feed line. The line was purged and the run continued.

***A sample of organic taken from the first of the two cocurrent mixers at the same time had a uranium concentration of 0.38 g/liter. Hence, about 92% stripping was accomplished in the first mixer and the balance ($\sim$6%) in the second mixer during this particular period of operation.

same magnesium oxide-organic combination had resulted in essentially complete (>99.8%) stripping using similar contacting conditions. A longer contact time and/or more vigorous mixing would probably have given improved efficiency. Also, other tests (results not presented) have shown that increasing the temperature of the stripping system by as little as 10°C appreciably increases the rate of reaction over that observed at room temperature. Further study of the magnesium oxide stripping method is being made in a two-stage countercurrent system as contrasted to the single stage operation used in these tests. The importance of mixing variations, contact time, temperature, and excess magnesium oxide will be evaluated.

Physical operation of the extraction and stripping circuits with respect to phase separation, etc. was satisfactory throughout the run. The organic overflow from the stripping settler was clear and completely devoid of precipitate. It should be emphasized that the residence times in the extraction and stripping mixers and settlers as shown in Table 8 are not meant to represent those that would be used in actual process practice. The particular conditions used in this test resulted from a choice of convenient flow rates as dictated by the size of the contacting equipment and pumps available. Other work on the Amex process by the Process Test Section has shown that much lower residence times, particularly in the mixer,* are possible with proper optimizing of the mixing variables.(9)

The magnesium "diuranate" slurry discharged from the stripping system was collected in three increments, which were filtered, washed with water, and dried at 400°C. Filtration rates for all these samples were rapid. The uranium content of the filtrate (not including the wash solution) was 0.008 g per liter, equivalent to 99.95% recovery of the contained uranium in the product precipitate. The U_3O_8 content ranged from 75-78% and the ThO_2 content was only 0.03 - 0.05% (Table 10).

Measurement of the amount of organic entrained** in the uranium precipitate slurry discharged from the organic

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*As described above, this does not necessarily apply to the mixers in the magnesium oxide stripping system where an increase in residence time would presumably have been beneficial. Even here, however, more efficient mixing might be used as an alternate to increased residence time or might permit a decrease in time.

**The organic content of the slurry was determined by scrubbing a volume of the slurry exhaustively with benzene, evaporating the benzene scrub solution to a relatively small volume, and titrating its amine content. Previous studies (unreported)

TABLE 10. ANALYSIS OF URANIUM PRODUCTS

Product Fraction	Analysis, %					Loss on Ignition at 1000°C, %
	U_3O_8	MgO	CO_3	SO_4	ThO_2	
1st	78.3	11.8	0.56	0.05	0.04	6.4
2nd	74.8	14.3	0.40	0.05	0.03	7.7
3rd	77.0	12.8	0.28	0.05	0.05	6.4

recovery chamber (see Appendix A) showed a loss of 0.002 lb of amine and 0.007 gal of diluent per pound of U_3O_8. Such losses would be unimportant costwise. Since the slurry discharge from the settler contained 0.019 lb of amine and 0.067 gal of diluent per pound of U_3O_8, the recovery efficiency in the organic recovery chamber was about 90%. In process practice the operation of the organic recovery chamber may not be necessary since these losses also would not be prohibitive. Furthermore, it is probable that some of the organic entrained in the slurry could be recovered from the filtrate following product filtration.

4.2 Thorium Recovery Cycle

Thorium was recovered from the raffinate of the uranium recovery cycle using di(tridecyl P)amine as extraction agent. This amine was selected since it provides a favorable combination of high thorium extraction power (see Tables 2, 3, and 4) and low amine distribution loss to the aqueous phase.*

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have indicated that there is no preferential adsorption of amine on the uranium precipitate. Thus, determination of the amine content of the slurry offers a convenient method for estimating the volume of organic entrained.

*The loss of amine through distribution to the aqueous phase on a lb amine/lb Th basis is inversely proportional to the thorium content of the head liquor. Hence, since the thorium content of this liquor was low ($\sim$ 0.2 g per liter) it was particularly important to choose an amine with a low distribution loss. The steady state distribution loss of di(tridecyl P)amine to a 0.5 M sulfate liquor at pH 1 has been measured to be about 5 ppm.[2] The loss of Primene JM-R (redistilled Primene JM-T), the only other amine of those tested thus far which showed comparative thorium extraction power, was measured to be about 50 ppm (not previously reported).

Operating conditions for the run are listed in Table 11. The thorium was extracted with 0.05 M di(tridecyl P)amine in kerosene, using three extraction stages and an aqueous/organic feed ratio of 7/1. Thorium was stripped from the extract with an acidic chloride solution (1.0 M NaCl - 0.05 M H_2SO_4) in three stages.* The run proceeded for 8 hr, which was equivalent to about 5.5 complete cycles of the organic phase. Here again, as in the uranium recovery cycle described above, the residence times of the aqueous and organic phases in the system (Table 11) have no relation to those that might be possible in actual practice. The conditions chosen for this test were simply those that were convenient to use in the available small bench-scale equipment.

Samples of the organic and aqueous phases from the settler of each stage were taken after approximately 3, 4, and 5 complete cycles of the organic phase. The thorium content of the final raffinate was <0.002 g per liter (Table 12), and thus thorium recovery was greater than 99%. Although an appreciable amount of iron was extracted in the bottom extraction stage, most of this iron was rejected from the organic phase as it loaded to a higher level with thorium, so that the final iron contamination was unimportant.

Thorium stripping was not complete in this test, with the recycled organic phase containing 0.08 - 0.10 g per liter. Nevertheless, as just described, this level of thorium was sufficiently low to allow essentially complete thorium recovery in the extraction system.

The pregnant strip solution contained 18.1 g Th and 0.1 g Fe per liter. Thorium was precipitated from this solution by raising the pH to 7.0 with ammonium hydroxide. Ammonia requirements were approximately 0.24 lb NH_3 per pound ThO_2. The precipitate, which filtered readily, was washed with water and dried at 110°C. The thorium product analyzed 65.5% ThO_2, 0.22% Fe, 0.07% Cl, and 24% SO_4. Weight losses after ignition at 200, 500, and 1000°C were 7.9, 11.6, and 31.8%, respectively. The high sulfate content of the product may be undesirable, and methods, other than calcining, for eliminating sulfate are being studied.

Physical operation of both the extraction and stripping circuits was satisfactory throughout the run.

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*As suggested earlier for uranium, other stripping methods could also be used as outlined in previous reports and other sections of this report.

TABLE 11. OPERATING CONDITIONS FOR THE THORIUM RECOVERY CYCLE

Extraction System

Number of mixer-settler stages: 3

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

Leach liquor: raffinate from uranium recovery cycle + synthetic uranium-barren liquor;* approximate composition, g/liter, 0.2 Th, 1.0 Fe(II), 1.0 Fe(III), 0.0004 U, 40 SO_4; pH 0.95

Feed rate: Aqueous 160 ml/min
Organic 22.5 ml/min

Residence time in each mixer: 1.3 min

Residence time in each settler: Aqueous 0.7 min
Organic 5 min

Stripping System

Number of mixer-settler stages: 3

Stripping agent: 1.0 M NaCl - 0.05 M H_2SO_4

Feed rate: Extract 22.5 ml/min
Strip solution 1.7 ml/min

Residence time in each mixer: 10 min

Residence time in each settler: Aqueous 16 min
Organic 8.5 min

*A larger volume of liquor for thorium recovery was desired for the tests than was available as raffinate from the uranium recovery cycle. Hence, additional uranium-barren synthetic liquor was prepared with similar composition. This was combined with the raffinate from the uranium recovery to give the desired volume of feed liquor for the thorium recovery cycle.

TABLE 12. THORIUM RECOVERY CYCLE DATA

Material Sampled	Time of Sampling,* hr	Aqueous pH	Th, g/liter		Fe in Organic, g/liter	Thorium Coefficients	
			Aqueous	Organic		Extraction (E_a^o)	Stripping (S_o^a)
Extraction System							
Stage 1	5	0.90	0.18	1.57	0.005	8.7	--
Stage 2		0.92	0.041	1.55	0.015	38	--
Stage 3		0.95	<0.002	0.57	0.063	>280	--
Stage 1	6.5	0.90	0.18	1.55	0.004	8.6	--
Stage 2		0.92	0.035	1.45	0.021	41	--
Stage 3		0.95	<0.002	0.44	0.065	>220	--
Stage 1	8	0.90	0.12	----	0.006	--	--
Stage 2		0.92	0.01	1.02	0.048	100	--
Stage 3		0.95	<0.002	0.16	0.075	>80	--
Stripping System							
Stage 1	5	1.45	16.3**	0.90	--	--	18
Stage 2		1.25	7.1	0.26	--	--	27
Stage 3		1.10	1.1	0.098	--	--	11
Stage 1	6.5	1.45	20.6**	1.10	--	--	19
Stage 2		1.25	9.5	0.34	--	--	28
Stage 3		1.10	1.9	0.098	--	--	19
Stage 1	8	1.45	22.6**	0.97	--	--	23
Stage 2		1.25	9.6	0.26	--	--	37
Stage 3		1.10	2.1	0.08	--	--	26

*One complete cycle of the organic phase required approximately 1.5 hr.

**Precipitate formed on standing overnight.

5.0 ESTIMATED REAGENT COSTS

Using the data from the continuous countercurrent runs described above, reagent costs have been estimated for recovery of uranium and thorium from these sulfate liquors with amine extractants. The following assumptions were made:

1. The uranium and thorium contents of the head liquor are the same as in the liquor tested, i.e., 1.2 g U and 0.2 g Th per liter.

2. The loss of the organic phase through entrainment and spillage is 0.05% of the raffinate volume. This estimate is based on results of process tests by the Process Test Section which have actually indicated lower losses. However, this particular source of reagent cost might vary considerably in large-scale operation and would best be checked in a pilot plant which is operating continuously on the actual liquors to be treated.

3. Loadings of the extract and the strip solutions are exactly the same as obtained in the countercurrent tests.

It should be emphasized that the estimates made here are for only one set of process circumstances. Other processing arrangements are possible, for example, choice of different stripping methods or type of liquor treated, which could lead to different costs than those presented.

5.1 Uranium Recovery Cycle

The estimated total reagent costs (Table 13) for the uranium recovery cycle are about 7¢ per pound of U_3O_8 recovered. Approximately half this cost is for the magnesium oxide utilized for stripping and the balance for losses of the amine and diluent.

5.2 Thorium Recovery Cycle

For the thorium recovery cycle, the total reagent costs, including the cost of ammonia for product precipitation, are estimated (Table 14) to be about 13¢ per pound of ThO_2 recovered. Fifty-four percent of this cost is contributed by estimates of entrainment and spillage losses of the organic solvent, the amounts being relatively greater for thorium than for uranium owing to the lower concentration of thorium in the head liquor. The sensitivity of overall costs to these losses with dilute liquors again points up the need for pilot-scale studies of this factor. It would be equally important to determine whether the actual losses might be higher than estimated or whether they could be held lower by, e.g., providing sufficient hold-up time for the raffinate prior to discard.

TABLE 13. ESTIMATED REAGENT COSTS FOR URANIUM RECOVERY

Chemical	Consumption	Consumption, lb/lb U_3O_8	Unit Cost, ¢/lb	Cost, ¢/lb U_3O_8
MgO	Uranium precipitation	0.66	5.5	3.6
Tri(iso-octyl)amine*	Distribution to raffinate (~25 ppm)	0.017	80	1.4
Total organic phase	Entrainment and spillage**	0.043 gal/lb U_3O_8	45¢/gal***	1.9
			Total	6.9

*Tri-n-octylamine, rather than tri(iso-octyl)amine, was actually used for the demonstration run. However, since the supply potential[4] of tri(iso-octyl)amine appears considerably better than that of tri-n-octylamine, and since the extraction performance of these two compounds have proved to be almost identical, the use of tri(iso-octyl)amine was postulated for this estimate. The listed cost of the amine (80¢/lb) is an estimate by the manufacturer of a reasonable selling price for the compound, assuming that it would be produced in large quantities. At the present time it is available only in experimental lots, and until quantity production is realized, cost of the amine would, of course, be substantially higher. However, it is evident that assumption of a cost even double the above value, i.e., $1.60/lb, would not raise the estimated cost of the amine loss to a prohibitive value.

**Organic loss by entrainment and spillage estimated at 0.05% of the raffinate volume.

***Based on kerosene cost of 14¢/gal and tridecyl alcohol cost of 23¢/lb. No charge is made for the tridecyl alcohol lost through distribution to the aqueous phase. The loss of tridecyl alcohol from di(2-ethylhexyl)phosphoric acid - kerosene solvent has been measured to be <10 ppm[10], suggesting that the loss from the amine-kerosene solvent is also very low and negligible costwise.

TABLE 14. ESTIMATED REAGENT COSTS FOR THORIUM RECOVERY

Chemical	Consumption	Consumption, lb/lb ThO_2	Unit Cost, ¢/lb	Cost, ¢/lb ThO_2
NaCl	Thorium stripping	2.9	0.8	2.3
H_2SO_4	Thorium stripping	0.25	1.5	0.4
NH_3	Thorium precipitation	0.24	5.8	1.4
Di(tridecyl P)amine	Distribution to raffinate (5 ppm)	0.022	80*	1.8
Organic phase	Entrainment and spillage**	0.26 gal/lb ThO_2	27¢/gal***	7.0
			Total	12.9

*Di(tridecyl P)amine is now available only in experimental quantities. As with tri(iso-octyl)amine (see footnote, Table 13), the selling price of the compound would be sensitive to the level of production. The price listed is that estimated by the manufacturer for large-quantity production.

**Organic loss by entrainment and spillage estimated at 0.05% of the raffinate volume.

***Based on kerosene cost of 14¢/gal.

6.0 REFERENCES

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7. Meeting at Oak Ridge with Messrs. Rabbitts and Grimes of Eldorado Mining and Refining, Ltd., and Messrs. Ingles and Simard of the Canada Department of Mines and Technical Surveys, Nov. 2, 1955.

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9. "Raw Materials Process Testing Program - Semiannual Progress Report, July 1, 1954 to December 31, 1954," ORNL-1914 (July 13, 1955).

10. Blake, C. A., D. J. Crouse, C. F. Coleman, K. B. Brown, and A. D. Kelmers, "Progress Report: Further Studies of the Dialkylphosphoric Acid Extraction (Dapex) Process for Uranium," ORNL-2172 (Sept. 6, 1956).

APPENDIX A

Design and Operation of the Magnesium Oxide Stripping System

The magnesium oxide stripping system used for the uranium recovery cycle (see p.21) consisted of two cocurrent baffled mixers, a settler, and an organic recovery chamber connected together as shown in Fig. A-1. In operation, the organic extract and the magnesium oxide slurry were fed to the first mixer (A) from which they passed to the second mixer (B) and then to the settler (C). Residence time in each mixer was approximately 12 min. The stripped organic phase overflowed from the settler and was recycled to the extraction system. The settler was provided with a very slow-turning stirrer, which aided in disengagement of organic from the slurry. The magnesium "diuranate" slurry was pumped from the bottom of the settler and fed to the top of the organic recovery chamber (D). Slurry was pumped from the bottom of the organic recovery chamber to a filter. Both the C and D chambers were equipped with conical-shaped bottoms to ensure proper discharge of the slurry solids. Slurry was pumped from C to D at a considerably faster rate than it was pumped from D. Operation in this manner allowed continuous overflow of aqueous* (and recovered organic) from D which was recycled to C. The level of the interface in C was controlled by the rate at which slurry was pumped from D.

Success in avoiding emulsion formation while contacting the magnesium oxide slurry with the extract depends on maintaining the organic phase continuous in the mixers. Since the organic/aqueous feed ratio to the system is high, i.e., $\sim$5/1, this condition is not difficult to maintain, although some care should be taken in start-up to ensure that the opposite condition, i.e., aqueous phase continuous, does not result. This is best accomplished by filling the mixers with the organic phase and starting the stirrers before beginning feed of the magnesium oxide slurry.

The magnesium oxide slurry used in this run was prepared by dispersing Michigan No. 15 calcined magnesite** in water.

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*Since the uranium precipitate settled fairly rapidly in D, the aqueous overflow contained essentially no solids.

**The source of the magnesium oxide used for stripping uranium from amines can be an important variable since various samples have shown different degrees of reactivity for this purpose. In addition to No. 15 calcined magnesite (Michigan Chemical Co.), other commercial magnesium oxide samples in the same price range which have given satisfactory stripping results include No. 5 calcined magnesite (Michigan Chemical Co.), calcined magnesite No. 2665 (Westvaco), and synthetic magnesite calcined L-2-65 (Dow Chemical Co.).

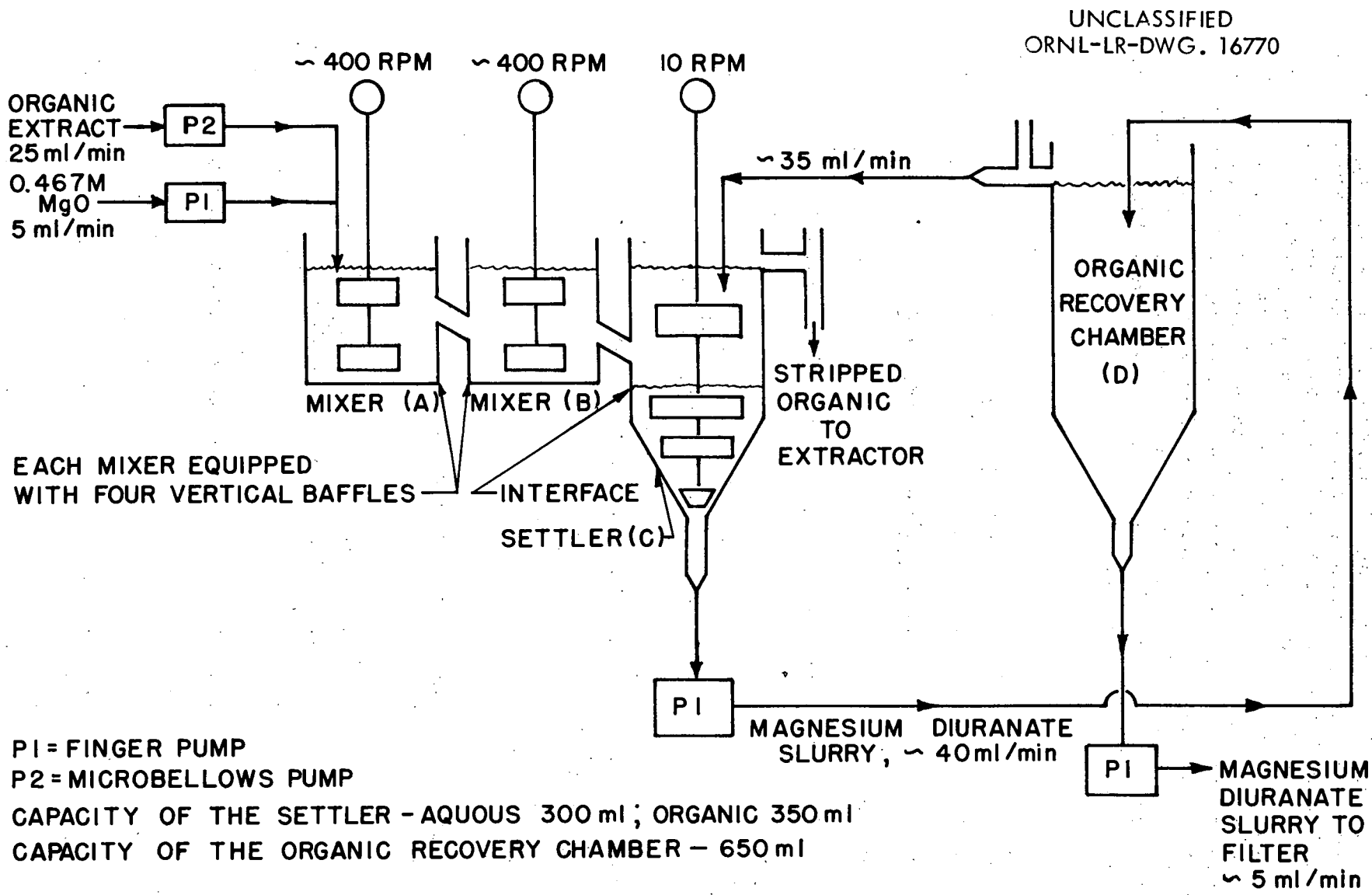


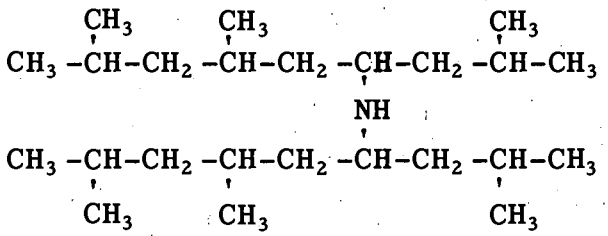
FIGURE A-1. MAGNESIUM OXIDE STRIPPING SYSTEM

Prior to use the slurry was "homogenized" in a Waring blender. This procedure was adopted since, in preliminary tests, some difficulty had been encountered in pumping a uniform slurry because of settling out of the larger sized particles in the feed line. The problem of pumping a uniform slurry is undoubtedly much more difficult in the small-scale experimental equipment used where the slurry feed rate is only 5 ml/min than it would be in plant-scale equipment where the flow velocity in the feed line would be much higher. In large scale operation, it is doubtful that "homogenization" of the slurry would be necessary.

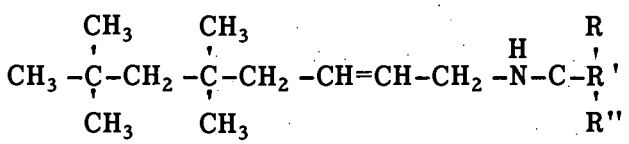
APPENDIX B

Description of Reagents

Amine S-24: bis(1-isobutyl-3,5-dimethylhexyl)amine

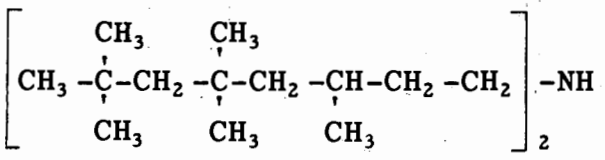


Amine 9D-178: dodecenyl Primene 81

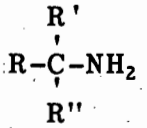


where R + R' + R" = 11-14 carbon atoms

Di(tridecyl P)amine: alkyl group derived from tetrapropylene



Primene JM-T: mixture of primary amines



where R + R' + R" = 15-21 carbon atoms

Armeen 212: mostly dilaurylamine; structure self-evident

Tri-n-octylamine: structure self-evident

Tri(iso-octyl)amine: branching reported to be no closer to the nitrogen than the third carbon

For further information on sources of the reagents, their purity levels, their potential availability, etc., see ORNL-1734, p. 103 (AECD-4142, p. 103), and ORNL-1922, pp. 65 and 87.