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PROGRESS REPORT ON RAW MATERIALS

FOR APRIL, 1957

K. B. Brown
C. F. Coleman
D. J. Crouse
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CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT ON RAW MATERIALS

FOR APRIL, 1957

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

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

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

OTHER REPORTS IN THIS SERIES

Preliminary, ORNL-2268 (20¢)
February, ORNL-2269
March, ORNL-2306

ABSTRACT

Systematic Studies. The enhanced uranium extraction coefficients obtained with synergistic combinations of di(2-ethylhexyl)phosphoric acid (D2EHPA) and trialkylphosphate, dialkyl alkylphosphonate, or trialkylphosphine oxide reach maxima at characteristic concentrations of the neutral components which appear to be essentially independent of the D2EHPA concentration. The coefficients vary with D2EHPA concentration and with pH and sulfate concentration of the aqueous solution in the same way as in extractions with D2EHPA alone.

In brief examination of extractions of some metals other than uranium by amines, alkylphosphoric acids, and phosphine oxides, strong extraction of thorium was found with D2EHPA, and potential separations were indicated between rare earths, hafnium-zirconium, and cobalt-nickel.

Process Development Studies. Aqueous slurries of several different commercial magnesias stripped uranium effectively from tri-n-octylamine in kerosene plus 3% alcohol. Stripping of Amine 9D-178 in kerosene was more rapid at 38°C than 28°C although stripping results were favorable at both temperatures. The presence of molybdenum in the amine extracts decreased the rate of uranium stripping. Molybdenum was stripped more slowly than uranium.

Engineering Studies. Studies were made of the mixing requirements for stripping uranium from the Dapex type solvent with sodium carbonate. Stage efficiency was greater than 90% with a residence time of 0.38 min and a power input of 0.01 hp/gal.

1.0 SYSTEMATIC STUDIES

In addition to the studies described below, systematic studies during the month have included (1) testing of new amines

and organophosphorus compounds as uranium extractants, (2) preparation and purification of long chain monoalkylphosphoric acids, (3) solubility loss rates of amines and of monoalkylphosphates, and (4) testing of dialkyl alkylphosphonates as neutral extractants and as synergistic components in Dapex extraction.

1.1 Synergistic Uranium Extraction Systems (C. A. Blake, J. M. Schmitt, D. E. Horner)

The nature and the importance of synergistic uranium extractant combinations were described in ORNL-2268, Sec. 3.3, and in references cited therein. As pointed out there, the high extraction power at low uranium levels provides more efficient reduction of the raffinate uranium level in a small number of stages, permits higher uranium loading from dilute liquors, and extends the usefulness of the Dapex process to liquors otherwise difficult to extract.

The extraction variables important to the effectiveness of the synergistic extractants have been found to include the choice of the acid and neutral components and their concentration, the choice of diluent, the uranium loading level, the temperature, and the composition of the aqueous phase. In studying these variables (except the last) it has been expedient to extract from 1.5 M sulfuric acid solution, instead of from solutions more like the leach liquors of interest (e.g., 0.5 M sulfate, pH 1), since extraction coefficients from the latter are often too high for valid intercomparison. While many synergistic components have been tested (ORNL-2269, Sec. 1.1; see also below), most of the systematic investigation of the extraction variables has utilized di(2-ethylhexyl)phosphoric acid (D2EHPA), tributylphosphate (TBP), dibutyl butylphosphonate (DBBP), and tributylphosphine oxide (TBPO).

Neutral Component. In combination with D2EHPA, the synergistic enhancement increases TBP < DBBP < TBPO (Fig. 1.1). With each of these, at a constant D2EHPA concentration (e.g., 0.1 M in Fig. 1.1), the extraction coefficient first rises with increasing concentration of neutral reagent, passes through a maximum, and then falls. The concentration giving the maximum enhancement appears to be characteristic for each class of compound, i.e., about 0.15 M phosphate, 0.08 M phosphonate, 0.05 M phosphine oxide. Surprisingly, and as yet unexplained, the concentration of neutral component for maximum enhancement varies little if any with concentration of D2EHPA, as shown for DBBP in Fig. 1.2. The E vs. (DBBP) curves are raised by increase of (D2EHPA) without significant change of shape; the same was found with the other neutral components examined. A dependence on the reagent/uranium ratio was suspected, but extraction of a tenfold lower uranium concentration (from 0.004 to 0.0004 M (uranium in the organic) showed only the expected small rise of E due to decreased loading (see below), with no shift of the enhancement maximum.

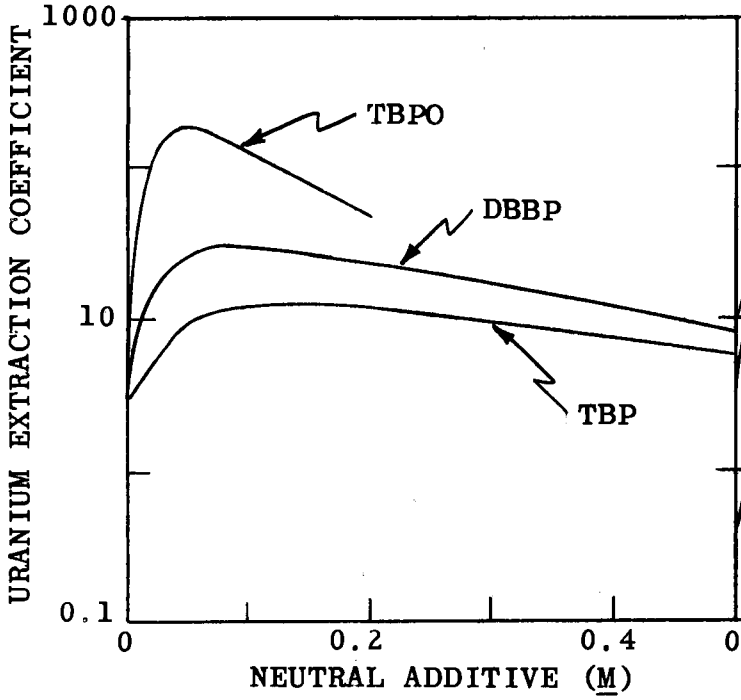

Fig. 1.1 Uranium Extraction with Combinations of Several Neutral Reagents with 0.1 M D2EHPA

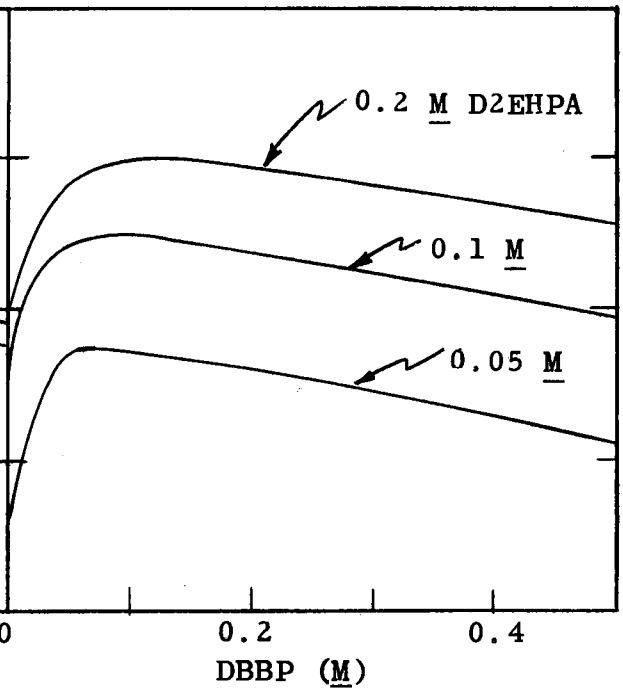

Fig. 1.2 Effect of Reagent Concentrations on Synergistic Uranium Extraction

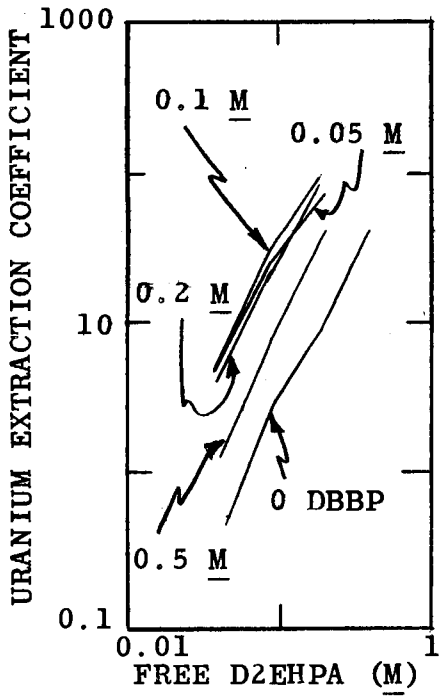

Fig. 1.3 Extraction as a Function of Free D2EHPA Concentration at Various DBBP Levels

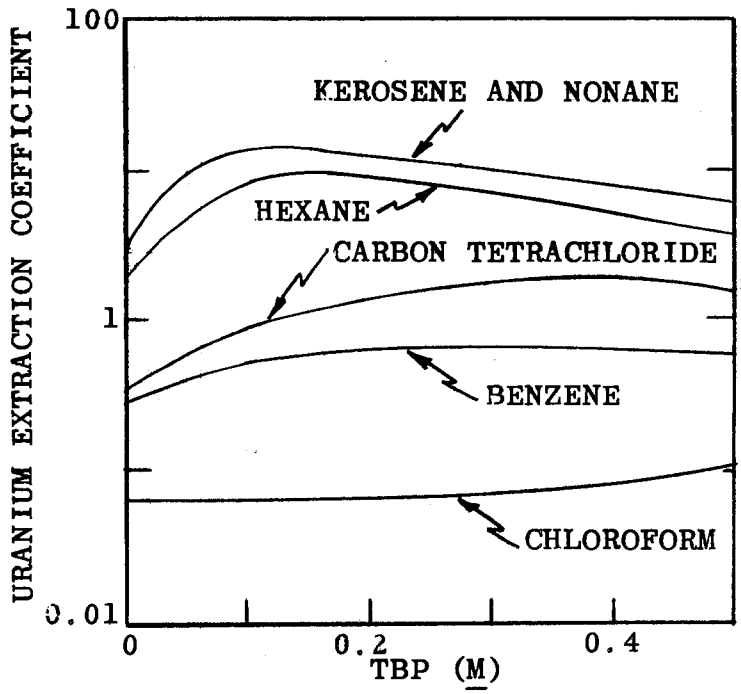

Fig. 1.4 Effect of Diluent on Synergistic Uranium Extraction with TBP and 0.1 M D2EHPA

D2EHPA Concentration. At a given concentration of the neutral component, the extraction coefficient increases as the square of the uncomplexed D2EHPA concentration (Fig. 1.3). This is the same behavior as shown by D2EHPA alone. The free D2EHPA was calculated assuming four molecules of D2EHPA (two dimers) bound by each uranium*, although here, with ~0.004 M uranium, the correction was small.

Choice of Diluent. The diluents best for extraction with D2EHPA alone (ORNL-1903, p. 6) were also best for the synergistic combinations, so that kerosene is the diluent of choice on the basis of extraction power as well as on the basis of cost and availability. As shown in Fig. 1.4 for varying TBP concentration, the steeper curves (i.e., those with the more favorable diluents) also reached and passed the maximum at lower concentrations of TBP, so that this group of curves superficially resembles the group in Fig. 1.1. This behavior has not been explained, but it is obvious that the diluent is not truly "inert" in these extractions.

Uranium Loading Level. When the concentration of uranium in the organic phase increases significantly, the effective concentration of the extractant decreases, and the extraction coefficient as usually measured decreases. Uranium extraction isotherms contrasting the behavior of D2EHPA alone, D2EHPA-TBP, and D2EHPA-DBBP were shown in ORNL-2172, p. 14. Whereas the curve for D2EHPA alone was of the usual shape, those of the synergistic combinations were initially much steeper and straighter, then began to bend more abruptly than is usual and continued to rise only slightly. The resulting pronounced "knee" in each curve was in the region of a uranium/D2EHPA mole ratio of 1/4, suggesting that enhanced stability of a 1-to-4 complex (e.g., 1 uranium to 2 acid dimers) might be involved in the enhanced extraction power.

Temperature. The extraction coefficient decreased by about 50% with a 15°C rise in temperature (25° to 40°C). This is a somewhat larger temperature effect than was found with D2EHPA in kerosene modified with alcohol, i.e., a decrease by about 25% over the same temperature range (ORNL-1903, p. 18).

Aqueous Composition. The effects of sulfate concentration and of pH on synergistic extraction with 0.1 M D2EHPA-0.12 M DBBP were about the same as on extraction with 0.1 M D2EHPA alone (kerosene diluent):

---

*C. F. Baes, Jr., R. A. Zingaro, and C. F. Coleman, "The Extraction of Uranium(VI) from Acid Perchlorate Solutions by Di(2-ethylhexyl)phosphoric Acid in n-Hexane," presented at ACS Meeting, Miami, April, 1957.

Aqueous Solution		U E_a^o	
$SO_4^=$ (M)	pH	D2EHPA	D2EHPA-DBBP
1.5	(H_2SO_4)	3	30
1.5	0.5	7	85
1.5	1	15	280
1.5	2	250	4600
0.5	(H_2SO_4)	7	100
0.5	1	110	4000

As with D2EHPA alone, extraction was best when the principal aqueous anion was nitrate, decreasing in the order NO_3 > Cl > SO_4 > PO_4. The factor of enhancement of each synergistic combination tested over D2EHPA alone was about the same with each of the following aqueous anions:

	U E_a^o	
1.5 M Acid	0.1 M D2EHPA	0.1 M D2EHPA-0.11 M TBP
HNO_3	70	200
HCl	15	70
H_2SO_4	3	12
H_3PO_4	0.5	2.5

Relation to the Dapex Process. As described in ORNL-2268, Sec. 3.1, the Dapex process consists typically of countercurrent extraction with a dialkylphosphoric acid solution, stripping of the extracted value (e.g., uranium) with sodium carbonate solution, and recycle of the extractant. Besides the extraction power, selectivity of extraction is important. The selectivity for uranium (ORNL-2172, p. 15) is not impaired and is sometimes improved by use of the synergistic extractants.

Alkaline stripping requires modification of the kerosene diluent to avoid separation of the alkali dialkylphosphate as a third liquid phase. The neutral components of the synergistic extractants are effective modifiers for this purpose. The quantities required of several have been reported (ORNL-2306, Sec. 1.1), e.g., 0.09 M TBP or 0.06 M DBBP with 0.1 M D2EHPA, and 0.13 M TBP or 0.10 M DBBP with 0.3 M D2EHPA. Fortunately, these concentrations are compatible with maximum extraction enhancement (Figs. 1.1 and 1.2). However, for some special applications, a balance might be required between the increased extraction power obtainable by increasing the D2EHPA concentration and the resulting increased modifier requirements in order to avoid losing synergistic enhancement.

Other Organophosphorus Acids. The synergistic enhancement of uranium extraction has been obtained only with dialkylphosphoric acids. Dialkylphosphinic acids in combination with TBP showed little or no change in extraction ability from that of the acid reagents alone. Monoalkylphosphoric acids and alkylphosphonic acids, on the other hand, showed considerable antagonistic effects. Addition of 0.1 M TBP to several of the reagents, also at 0.1 M, caused decreases of an order of

magnitude below the coefficients with the acid reagents alone:

	$U\ E_a^o$			
	0.5 M SO_4, pH 1		1.5 M H_2SO_4	
0.1 M Acid Reagent in Kerosene	Alone	With 0.1 M TBP	Alone	With 0.1 M TBP
Monoalkylphosphonic acids				
n-Octyl			27	11
3,5,5-Trimethylhexyl			28	8
Diisobutylmethyl			13	1.4
2,6,8-Trimethylnonyl-4	650	55	7	1
4-Ethyl-1-isobutyloctyl	600	60	8	1
3,9-Diethyltridecanol-6	550	60	7	1
Dialkylphosphinic acids				
n-Hexyl			2.8	2.6
2-Ethylhexyl			1.5	1.3
Alkylphosphonic acid				
2-Ethylhexyl			29	3

1.2 Extraction of Other Metals (J. G. Moore, C. A. Blake, J. M. Schmitt)

Besides extraction of uranium from sulfate solutions, which has been the primary interest in this laboratory, each class of extractants studied has also shown potential in extractions and separations of other metal ions. Some of these have been studied and reported in relation to uranium extraction, particularly vanadium in the Amex and Dapex processes, and molybdenum and thorium in the Amex process (see ORNL-2268). At the same time, some survey tests and limited systematic investigations have been made with a few other metals. Results with thorium, rare earths, zirconium-hafnium, and cobalt-nickel are summarized in this section.

In addition to these tests, analytical applications of trialkylphosphine oxides and of D2EHPA are being developed in the ORNL Analytical Chemistry Division.*

a. Extraction of Thorium with D2EHPA

Thorium is effectively extracted from dilute acidic sulfate liquors by di(2-ethylhexyl)phosphoric acid (D2EHPA). Extraction is stronger at the lower sulfate concentrations and at relatively high pH:

*ORNL-2161, ORNL-CF-56-9-18, -56-10-86, -57-1-5, -57-2-37.

SO_4 (M)	Initial pH	Final pH and Th E_a^o 0.1 M D2EHPA pH	0.1 M D2EHPA E_a^o	0.1 M D2EHPA-0.1 M TBP pH	0.1 M D2EHPA-0.1 M TBP E_a^o
0.25	0.75	0.7	10	0.8	4
	1.0	0.9	35	1.0	10
0.52	0.6	0.5	1.4	0.5	0.6
	1.0	1.0	20	1.0	6
	1.8	1.8	2000	1.7	>400
1.04	0.3	0.3	0.2	0.25	0.05
	0.9	0.8	3	0.8	1
	1.8	1.7	1000	1.7	>400

The diluent in these extractions was kerosene, the initial thorium concentration in the aqueous solutions was 2 g/liter and the aqueous/organic ratio was 1/1. In contrast to the synergistic enhancement of uranium(VI) extractions, the addition of tributylphosphate decreased the extraction of thorium. The increase of extraction with increase of pH from 1 to 1.8 was greater than the decrease caused by both increasing the sulfate concentration and adding TBP, suggesting that useful extraction from a wide variety of solutions can be obtained by pH adjustment. In addition, while only 0.1 M reagent has been tested, it is expected that extraction coefficients will increase considerably with increase of reagent concentration.

An extraction isotherm from 0.37 M sulfate solution at pH 2.1 with 0.1 M D2EHPA in kerosene showed the thorium loading leveling off at about 6 g/liter, which is at a D2EHPA/thorium mole ratio close to 4:

Initial Th (g/liter)	Phase Ratio, a/o	Final Th (g/liter) Aq	Final Th (g/liter) Org	D2EHPA (moles/ per mole Th)
1.47	2	<0.002	2.9	8.0
1.47	10	1.0	5.1	4.5
7.35	1	1.7	5.5	4.2
7.35	5	5.8	6.3	3.7
7.35	10	6.5	6.1	3.8

The first point indicates an extraction coefficient from this solution of 1500 or more, even though the thorium loading was already relatively high and probably at least half the reagent was already bound by the extracted thorium.

b. Rare Earths

Extraction and Separation with Amines. Qualitative and semiquantitative tests with 0.1 M tri-n-octylamine in kerosene modified with tridecanol indicated extraction of yttrium earths with separation from yttrium. In these tests extraction increased with increasing nitrate concentration and

decreasing free acid concentration. Extraction was very low with as much as 0.5 M free HNO_3, as determined by titration to the methyl red endpoint. At the same time, rare earths were hydrolytically precipitated when too much nitric acid was extracted. Hence, for these laboratory tests, it was expedient to pre-equilibrate the amine solutions with acidic nitrate solutions approximating the rare earth head solutions.

Even under the more favorable conditions tested with 0.1 M amine, the RE_2O_3 loading in the extract was low, e.g., 0.5-0.8 g/liter (1 mole of rare earth per 20-30 moles of amine) from aqueous solutions containing up to 230 g/liter. In the subsequent extractions with 1 M amine in benzene, the loading reached ~20 g/liter (1 mole of rare earth per ~8 moles of amine) from similar aqueous solutions.

Tri-iso-octyl- and tri-n-octylamine (1 M in benzene) gave about the same percent extractions and separations, while extraction with the substituted tertiary di-2-ethylhexyl(β-hydroxyethyl)amine was somewhat lower:

	Tri-iso-octyl-amine		Tri-n-octyl-amine		Di-2-ethylhexyl-(β-hydroxyethyl)-amine	
	(%)	SF/Y	(%)	SF/Y	(%)	SF/Y
Y_2O_3	6	---	5	---	4	---
Gd_2O_3	17	3.4	17	3.7	10	3.2
Dy_2O_3	23	5.1	20	4.5	9	2.9
Ho_2O_3	22	4.7	21	4.6	10	3.2
Er_2O_3	14	2.8	12	2.4	7	2.0
Yb_2O_3	4	0.6	4	0.7	3	0.9
ΣRE_2O_3	8.4	---	8.6	---	5.4	---
Loading (g of oxide/liter organic phase)	19.9		20.4		12.9	

where the separation factor from yttrium, SF/Y = $\frac{(RE_2O_3)_{org}/(RE_2O_3)_{aq}}{(Y_2O_3)_{org}/(Y_2O_3)_{aq}}$. In corresponding tests the extraction was very low with the primary 1-(3-ethylpentyl)-4-ethyloctylamine (0.4%), the secondary Amine S-24, bis(1-isobutyl-3,5-dimethylhexyl)amine (<0.1%), and a diamine, N,N'-bis(1-heptyloctyl)-ethylenediamine (<0.1%). These tests were single-stage batch equilibrations, with an aqueous/organic ratio of 1/1 and 5 min contact time at room temperature. For analysis, the extracted rare earth was stripped with water, precipitated as oxalate, and ignited for weighing, and then analyzed spectrographically.* The head solutions for these and for the subsequent tests were prepared from Lindsay 75% Y_2O_3 with

*Spectrographic analyses were made by John Norris of the ORNL Stable Isotopes Division.

Gd_2O_3 added to give, typically, 75% Y_2O_3, 8-10% Gd_2O_3, 52% Dy_2O_3, 1.5% Ho_2O_3, 4% Er_2O_3, 2.5% Yb_2O_3, and smaller amounts of the other heavy rare earths.

No systematic difference was found in the percentage of total rare earth oxide extracted by 1 M tri-n-octylamine in benzene at contact times from 5 to 60 min, and there was little if any systematic difference in extraction of the individual elements:

	RE_2O_3 Extraction (% of initial)					
	5 min			15 min	30 min	60 min
Y_2O_3	5	5	6	6	6	5
Gd_2O_3	17	16	15	18	15	19
Dy_2O_3	20	20	20	22	22	24
Ho_2O_3	21	18	17	20	17	20
Er_2O_3	12	12	11	14	12	13
Yb_2O_3	4	4	4	4	4	4
ΣRE_2O_3	8.6	8.3	8.1	8.3	8.2	8.2

The initial aqueous RE_2O_3 concentration was ~240 g/liter; extraction conditions were similar to those of the preceding tests.

When the nitrate concentration was decreased from >5 to ~0.6 M by changing the initial aqueous total rare earth oxide concentration from ~230 to ~23 g/liter, with no other salts present and with the free nitric acid maintained constant at 0.1 M, the extraction dropped too low to be measured. Addition of 5 M NH_4NO_3 gave nearly 20% extraction:

Initial NO_3 (M)	NH_4NO_3 (M)	RE_2O_3 Extracted (% of initial)
0.6	0	<0.1
5.6	5	18.5

The free nitric acid concentration (by titration to methyl red endpoint) was 0.1 M. With the free nitric acid increased only to 0.16 M, at close to the same total nitrate concentration, extraction was very low. Extraction was improved but still low when equivalent aluminum nitrate was substituted for the ammonium nitrate (total nitrate 5.5 M):

NH_4NO_3 (M)	$Al(NO_3)_3$ (M)	H_2SO_4 (M)	RE_2O_3 Extracted (% of initial)
4.8	0	0	1.0
4.8	0	0.02	0.8
0	1.6	0	6.2
0	1.6	0.02	4.4

However, in view of the indicated high sensitivity to free acid content, this difference could be due to a very small

difference in free acid instead of to a real difference in effect between aluminum and ammonium. The small amount of sulfate acid in two of the extractions, added to test for possible favorable complexing, appeared to have a slight adverse effect.

Individual extractions, in the three of the foregoing tests that provided enough extracted rare earths for analysis, gave separation factors from yttrium following the same pattern but lower than those obtained in the extractions from the higher aqueous RE_2O_3 concentration:

	0.5 M NH_4NO_3 - 0.1 M HNO_3		1.6 M $Al(NO_3)_3$ - 0.16 M HNO_3		0.02 M H_2SO_4 - 1.6 M $Al(NO_3)_3$ - 0.16 M HNO_3	
	(%)	SF/Y	(%)	SF/Y	(%)	SF/Y
Y_2O_3	16	---	5	---	3	---
Gd_2O_3	24	1.7	12	2.7	8	2.5
Dy_2O_3	28	2.2	11	2.5	10	3.3
Ho_2O_3	27	2.0	13	3.0	11	3.4
Er_2O_3	22	1.5	8	1.8	6	1.9
Yb_2O_3	13	0.8	2	0.4	2	0.6
ΣRE_2O_3	18.5	---	6.2	---	4.4	---
Loading (g of oxide/liter organic phase)	4.4		1.5		1.1	

The lower selectivity is probably due to the lower loading of the extractant with rare earths, i.e., to the higher equilibrium concentration of uncomplexed amine.

Extraction and Separation with Alkylphosphoric Acids. The relatively few tests made with mono- and dialkylphosphoric acids allow some characterization of the behavior of these compounds. The monoalkylphosphoric acids showed higher extractions than the dialkyl reagents:

Reagent, 0.1 M in kerosene	RE_2O_3 Extracted (% of initial)					
	La	Pr	Nd	Sm	Gd	Y
Dialkylphosphoric acids						
3,5,5-trimethylhexyl	25	57	--	Ppt[a]	Ppt[b]	Ppt[c]
2-ethylhexyl	1	7	9	24	50	84
di-isobutylmethyl	3	5	2	9	6	6
Monoalkylphosphoric acids						
3,5,5-trimethylhexyl	62	95	96	97	--	98
2-ethylhexyl	70	93	91	90	88	96
di-isobutylmethyl	57	88	85	88	--	82
2,6,8-trimethylnonyl-4	45	67	68	74	--	69

[a] 54% Sm removed from aqueous phase, 25% reporting to organic phase.

[b] 90% Gd removed from aqueous phase.

[c] 90% Y removed from aqueous phase.

These tests were single-stage batch equilibrations, with an aqueous/organic ratio of 1/1, and 10 min contact time at room temperature. Each aqueous phase contained one of the rare earth oxides at 2 g/liter, ~0.2 M nitrate, and pH 1.

As in the case of uranium extractions (ORNL-1903, -2172), the effect of structure is reflected in the decreased extraction ability of the compounds having more branching in the substituent alkyl chains. The dialkyl acids tend to precipitate rare earths/reagent ratios (e.g., ~1.6 g of rare earth oxides/liter in 0.1 M D2EHPA, mole ratio ~1/8). The tendency toward precipitation decreases with increased reagent branching, as was also found in the precipitation of aluminum by some of the reagents (ORNL-1903, p. 31). Recent tests showed that di(2-propyl-4-methylpentyl)phosphoric acid permits higher loadings with little or no precipitation under conditions that yield voluminous precipitates with D2EHPA (2.2 g of rare earth oxides per liter of 0.1 M reagent from solution 0.5 M in chloride and pH of 2). Proportionately higher loadings without precipitation can be reached with higher reagent concentrations (see below).

D2EHPA in kerosene extracts yttrium earths better than cerium earths. There is a gradual decrease from ytterbium to lanthanum, and yttrium is extracted with a coefficient intermediate to those of holmium and erbium. Separation factors between adjacent elements are indicated to be 1.5 and higher:

	1 M HCl		0.5 M HCl		0.5 M HCl	
	(%)	SF/Y	(%)	SF/Y	(%)	SF/Y
Gd_2O_3	--	---	11	0.1	15% of the oxides ppt'd, 66% extracted into organic	
Dy_2O_3	10	0.3	35	0.4		
Ho_2O_3	12	0.4	50	0.7		
Y_2O_3	23	---	58	---		
Er_2O_3	25	1.0	70	1.6		
Yb_2O_3	72	8.3	96	16		
Initial pH	<0		0.54		1.0	
Final pH	<0		0.52		0.9	
Loading (g of oxide/liter organic phase)	1.6		1.2		1.3	

	0.5 M H_2SO_4		0.5 M SO_4		0.5 M SO_4	
	(%)	SF/Y	(%)	SF/Y	(%)	SF/Y
Gd_2O_3	--	---	18	0.1		
Dy_2O_3	9	0.2	34	0.2		
Ho_2O_3	19	0.4	58	0.5		
Y_2O_3	35	---	74	---		
Er_2O_3	43	1.3	83	1.6		
Yb_2O_3	92	20	99	27		
Initial pH	0.55		1.1		2.1	
Final pH	0.49		1.1		1.8	

	0.5 M H_2SO_4		0.5 M SO_4		0.5 M SO_4	
	(%)	SF/Y	(%)	SF/Y	(%)	SF/Y
Loading (g of oxide/liter organic phase)	0.8		1.4		1.3	

The extractions were made with 0.1 M D2EHPA in kerosene from the aqueous solution containing approximately 2 g of rare earth oxides per liter. The oxides were obtained from the Lindsay 75% Y_2O_3 described above. (The Gd_2O_3 content was 0.8%, whereas more Gd_2O_3 was added in the amine extractions tests described above.) The contact time was 10 min and the aqueous/organic ratios were 1/1. Contact times of 16 hr showed no further extraction from the hydrochloric and sulfuric acid solutions.

The extractions from chloride solutions were higher at the lower chloride and higher pH levels. Extractions from the sulfate solutions increased with pH. Extractions from 0.5 M HCl were higher than those from 0.5 M H_2SO_4.

Precipitation occurred at the highest pH levels in both chloride and sulfate solutions. The 0.1 M D2EHPA had extracted and held a total of about 1.2-1.6 g of oxides per liter when precipitation took place. The precipitates contained 3 moles of D2EHPA for each mole of the rare earth elements. Loadings were higher without precipitation with D2EHPA concentrations higher in kerosene (e.g., 13 g/liter in 1 M D2EHPA), and also in 1.0 M D2EHPA in brief tests with diluents other than kerosene, e.g., 19 g/liter in trichloroethylene, 17 g/liter in chloroform. No difficulty in phase separation was observed at these levels.

Extraction and Separation with Trialkylphosphine Oxides. Trialkylphosphine oxides extract rare earth elements from chloride and nitrate solutions. Extractions increase with increasing atomic weight of the elements from lanthanum to about samarium or gadolinium, pass through a maximum in about this range, and then continue to decrease throughout the series of yttrium earths:

Rare Earth Oxide Extracted (% of initial)					
La	Pr	Nd	Sm	Gd	Y
26	45	49	58	52	30

These tests were single-stage batch equilibrations with an aqueous/organic ratio of 1/1, and 10 min contact time at room temperature. The organic phase was 0.1 M trioctylphosphine oxide in kerosene and each aqueous phase contained one of the rare earth oxides at 2 g/liter, ~0.2 M nitrate, pH 1.

The general decrease is also shown in extractions with 0.1 M trioctylphosphine oxide in kerosene from the yttrium earth mixture described above:

	1 M HNO_3		0.5 M HNO_3		0.2 M NO_3, pH 1	
	(%)	SF/Y	(%)	SF/Y	(%)	SF/Y
Gd_2O_3	28	2.1	55	3.3	57	4.0
Tb_2O_3	20	1.3	48	2.4	--	---
Dy_2O_3	24	1.7	54	3.1	54	3.5
Ho_2O_3	19	1.3	44	2.1	47	2.7
Er_2O_3	15	1.0	39	1.7	40	2.0
Tm_2O_3	11	0.6	31	1.2	--	---
Yb_2O_3	2	0.01	26	1.0	30	1.3
Y_2O_3	16	---	27	---	25	---

The extraction of total rare earth increased as the acidity and nitrate concentration decreased, while the apparent position of yttrium in the extraction order shifted from near erbium toward and beyond ytterbium. Further tests in which aluminum nitrate was added and the free acid was kept low showed substantially increased rare earth extraction.

Extraction with 0.1 M trioctylphosphine oxide from a concentrated rare earth solution (100 g of rare earth oxides per liter) in low excess nitric acid (0.2 M) showed limited loading of the organic phase with RE_2O_3 at about 3 g/liter. This corresponds to approximately 4 moles of phosphine oxide for each mole of rare earth extracted. Correspondingly higher concentrations would be expected at higher reagent concentrations in the organic phase, up to the solubility limit of the reagent itself (e.g., 0.4 M trioctylphosphine oxide in kerosene at 30°C; ORNL-1964, p. 54).

c. Zirconium-Hafnium

Extraction and Separation with Amines. Strong extraction of zirconium from sulfate solutions by primary, secondary, and tertiary amines was reported in connection with the selectivity of uranium extraction (ORNL-1734, p. 37; -2099, p. 35). In the following tests several amines were compared in extraction of zirconium and hafnium (separately) from sulfuric acid and sulfate solutions. The results suggested choice of tri-n-octylamine for exploratory tests of separations, the extractions being high but still showing significant differences:

	Zr or Hf Extracted (% of initial)			
	1 M H_2SO_4		1 M SO_4, pH 1	
Amine, 0.1 M in benzene	Zr	Hf	Zr	Hf
1-(3-Ethylpentyl)-4-ethyloctyl	>99	>97	>99	>97
N-Benzyl-1-(3-ethylpentyl)-4-ethyloctyl	>99	>97	>99	>97
Dibenzyl	<1	<15	11	15
Tribenzyl	<1	<15	<1	<15
Tri-n-octyl	>99	93	99	>97
Tri-iso-octyl	>99	>97	>99	>97

The initial aqueous concentrations of zirconium and of hafnium were 1 and 0.4 g/liter, respectively, with an organic/aqueous

ratio of 1/1 and 30 min contact time. Chloroform as the diluent showed no advantage. Tri-n-octylamine in 97% kerosene--3% tridecanol gave >99% extraction of zirconium and 90% extraction of hafnium from the 1 M H_2SO_4 solution, and this extractant combination was used for subsequent tests.

The extraction isotherms of zirconium and hafnium (separately) from 1 M H_2SO_4 with 0.1 M tri-n-octylamine in 97% kerosene--3% tridecanol showed initial extraction coefficients for zirconium and hafnium of >100 and ~10:

Phase Ratio, a/o	Zr (g/liter), Aq Head, 0.91		Hf (g/liter), Aq Head, 1.15	
	Aq	Org	Aq	Org
1/5	<0.001	0.18	0.03	0.23
1/2	0.003	0.44	0.12	0.53
1/1	0.04	0.82	0.27	0.89
2/1	0.14	1.52	0.48	1.32
5/1	0.53	1.85	0.82	1.71

The contact time was 5 min. The zirconium curve rose steeply to 1.5 g/liter organic, but had leveled off considerably at the highest point reached, 1.85 g/liter or 0.02 M (five moles of amine per mole of zirconium).

Extractions and separations were compared from a series of solutions varying in sulfate concentration and acidity. Extractions decreased with increasing sulfuric acid concentration and increased with increasing pH, so that they were nearly the same from a 0.6 M H_2SO_4 solution (pH 0.2) and a 1 M SO_4 solution adjusted to pH 0.7:

ZrO_2 + HfO_2 (g/liter)							
0.6 M H_2SO_4		1 M H_2SO_4		2 M H_2SO_4		1 M SO_4, pH 0.7	
Aq	Org	Aq	Org	Aq	Org	Aq	Org
0.33	2.14	0.48	1.85	0.93	0.94	0.38	2.04
1.05	2.85	1.05	2.55	1.26	1.22	1.05	2.74
1.37	2.91	1.34	2.68	1.36	1.30	1.35	2.85
1.39	2.94	1.38	2.73	1.39	1.31	1.39	2.87

Separation as measured by the percentage of hafnium remaining in the extracted zirconium appeared slightly better from the former, but was nearly the same from all four solutions:

% Hf in Extracted Zr			
0.6 M H_2SO_4	1 M H_2SO_4	2 M H_2SO_4	1 M SO_4, pH 0.7
0.19	0.20	0.22	0.24

These were cascade extractions, the organic solution contacting fresh aqueous solution with an aqueous/organic ratio of 2/1, in each of four stages. The contact time was 5 min; the extractant

was 0.1 M tri-n-octylamine in 97% kerosene--3% tridecanol; and the head aqueous solution contained 1.38 g of ZrO_2 and 0.020 g of HfO_2 per liter (i.e., there was initially 1.4% HF in the Zr). The resulting isotherm from 1 M H_2SO_4 is in fair agreement with that presented above for extraction of zirconium alone. The extraction isotherms from 0.6 M H_2SO_4 and from 1 M SO_4, pH 0.7 reached zirconium loadings of 0.024 and 0.023 M (4.2 and 4.3 amines per Zr), and suggest a limiting ratio of 4 amines per Zr.

Doubling the concentration of tri-n-octylamine increased the zirconium extraction coefficient only by about half:

	Zr		Hf	
Amine	0.1	0.2	0.1	0.2
Aq/org ratio	1	2	1	2
Loading (g/liter)	0.82	0.84	0.89	0.90
E_a^o	22	33	3.3	4.5

The hafnium extraction coefficient increased relatively less, suggesting better separation at the higher amine concentration; this has not yet been checked by extraction from a mixture. These were separate extractions, from the same aqueous solutions as used for the separate extraction isotherm (above). Contact time was 5 min; the results were almost identical when the extractions were repeated with 60 min contact time.

The effect of contact time was also tested in extractions from a mixture. The results appeared contradictory, one series, a/o phase ratio of 3/1, showing essentially no change from 5 min to 4 hr and the other, a/o phase ratio of 8/1, showing a definite increase in total extraction and decrease in separation:

Contact Time (min)	A/O = 3/1			A/O = 8/1		
	Loading (g/liter)	Extraction (%)	SF	Loading (g/liter)	Extraction (%)	SF
5	2.04	63	5.0	2.61	29	6.1
15	2.09	63	5.3	2.66	30	3.6
30	2.11	62	6.0	2.82	32	3.0
60	1.95	60	4.9	3.16	34	2.8
240	2.11	64	5.2	3.10	35	2.4

The separation factor SF = $E_a^o(Zr)/E_a^o(Hf)$, and is approximately equal to (initial % Hf)/(final % Hf). "Loading" and "extraction" are given in terms of total oxide, ZrO_2 + HfO_2. The head solution contained 1.10 g of ZrO_2 and 0.02 g of HfO_2 per liter (initially 1.4% Hf in the Zr); the extractant was 0.1 M tri-n-octylamine in 97% kerosene--3% tridecanol. Finding the slow increase in total extraction only at the higher phase ratio may not actually be a contradiction, but might be due to the higher loading, which came very close to the limit suggested by the extraction isotherms. However, there is no obvious reason that the relatively slower equilibration of hafnium than of zirconium (if that is real) should occur only at high loading.

Extraction and Separation with D2EHPA. A few tests with zirconium and hafnium (separately) in 1 M sulfate solutions showed strong extractions, and indicated high separation factors:

0.1 M D2EHPA in	pH	Zr or Hf Extracted (% of initial) Hf	Zr	Separation Factor, Hf/Zr
Kerosene	<0*	>99	75	>15
	1	>99	73	>15
Benzene	<0*	73	23	10
	1	>99	47	>40
Chloroform	<0*	33	17	2.5
	1	87	33	15

*Unbuffered in 1 M H_2SO_4.

Extractions were better at the higher pH levels and were best when the diluent was kerosene. However, useful separation factors were indicated in all three diluents. The initial aqueous solutions contained either 1 g of zirconium or 0.4 g of hafnium per liter. The contact time was 30 min and the aqueous/organic phase ratio was 1/1.

d. Cobalt-Nickel

Extraction and Separation with Amines. Amine extraction of cobalt and of nickel from several aqueous solutions was surveyed briefly to outline the conditions for extraction and possibly for separation. The aqueous solutions tested were mineral acid solutions containing 1 g of either cobalt or nickel per liter (0.017 M) but no other salt. Cobalt extractions with 0.1 M amines were significant from 6-10 M HCl, but not from 1-3 M HCl or from 1 or 6 M HNO_3 or H_2SO_4. Nickel extractions were too low to be measured (E_a^o <0.002) in all the corresponding tests, suggesting effective separation unless interaction (as possibly formation of mixed polynuclear complexes) occurs in mixtures. The cobalt extraction was maximum at about 8 M HCl:

Amine (0.1 M) and Diluent	Co Extracted (% of initial) 1 M HCl	3 M HCl	6 M HCl	8 M HCl	10 M HCl
Tri-n-octyl in 95% kerosene--5% tridecanol	<1	<1	39	68	50
Di(tridecyl P) in kerosene	<1	<1	33	70	64

The organic/aqueous ratio was 1/1 and the equilibration time 5 min.

Of the amines tested, cobalt extraction from 6 M HCl was best with the tertiaries tri-n-octyl- and tri-iso-octylamine, somewhat less with di(tridecyl P)amine, less but still measurable (10 to 3%) with several other secondary amines,* and too low to be measured (<0.5%) with the only primary tested, Primene JMR. The tertiary amines performed better in the aromatic diluents benzene, Amsco G, and Esso Heavy Aromatic Naphtha (HAN) (69-75% with tri-n-octylamine, under the same test conditions as above) than in alcohol-modified kerosene (39%), while extraction was very low in chloroform (<1%). About 5% tridecanol was needed to prevent third-phase formation with these amines in kerosene. Di(tridecyl P)amine, in contrast, performed better in kerosene than in HAN. Alcohol was not required for miscibility of di(tridecyl P)amine chloride in kerosene, and was not tested.

The foregoing tests all used an arbitrary 5 min equilibration time. The rate of equilibration was checked with tri-n-octylamine in 95% kerosene--5% TDA only. Cobalt extractions from 6 M HCl were all between 38 and 40% after equilibration times ranging from 2 to 240 min without suggesting any systematic trend. The corresponding nickel extractions after 5- to 240-min equilibrations were all <0.1% (E_a^o <0.001).

The effect of cobalt loading on extraction with tri-n-octyl-, tri-iso-octyl-, and di(tridecyl P)amine was examined by means of extraction isotherms (Fig. 1.5). The diluent was HAN. As indicated above, a little higher extraction would be expected with di(tridecyl P)amine in kerosene, but still rather lower than with the tertiaries. The initial slopes of the curves for the latter indicate extraction coefficients, essentially unaffected by loading, of 3-4 from 6 M and about 12 from 8 M HCl. These curves do not extend far enough to establish the asymptotic loading limits, but do suggest that they are more than 1.5 g/liter from the 6 M HCl and 2 g/liter or more from the 8 M HCl. A stoichiometric loading limit of 2 g/liter (0.034 M Co) in 0.1 M amine would correspond to as association of three moles of amine per mole of cobalt. It is of interest to note that the upper curve in Fig. 1.5 can be fairly closely reproduced on the assumption of an average association of 2.7 moles of amine per mole of cobalt.**

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*N-(p-sec-amylbenzyl)-1-isobutyl-3,5-dimethylhexylamine, N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine, N-benzyl-1-isobutyl-4-ethyloctylamine, N-(α-methylbenzyl)-2-ethylhexylamine, and Amine 9D-178.

**The corresponding E_a^o value for 0.1 M uncomplexed amine required in the calculation is 13.5, in good agreement with the initial slope of about 12. It is also assumed for this calculation that $E_a^o \propto$ M (uncomplexed amine), in analogy with the extraction of uranium, etc., which is probably reasonable unless the cobalt extraction involves complications such as polynuclear complexes.

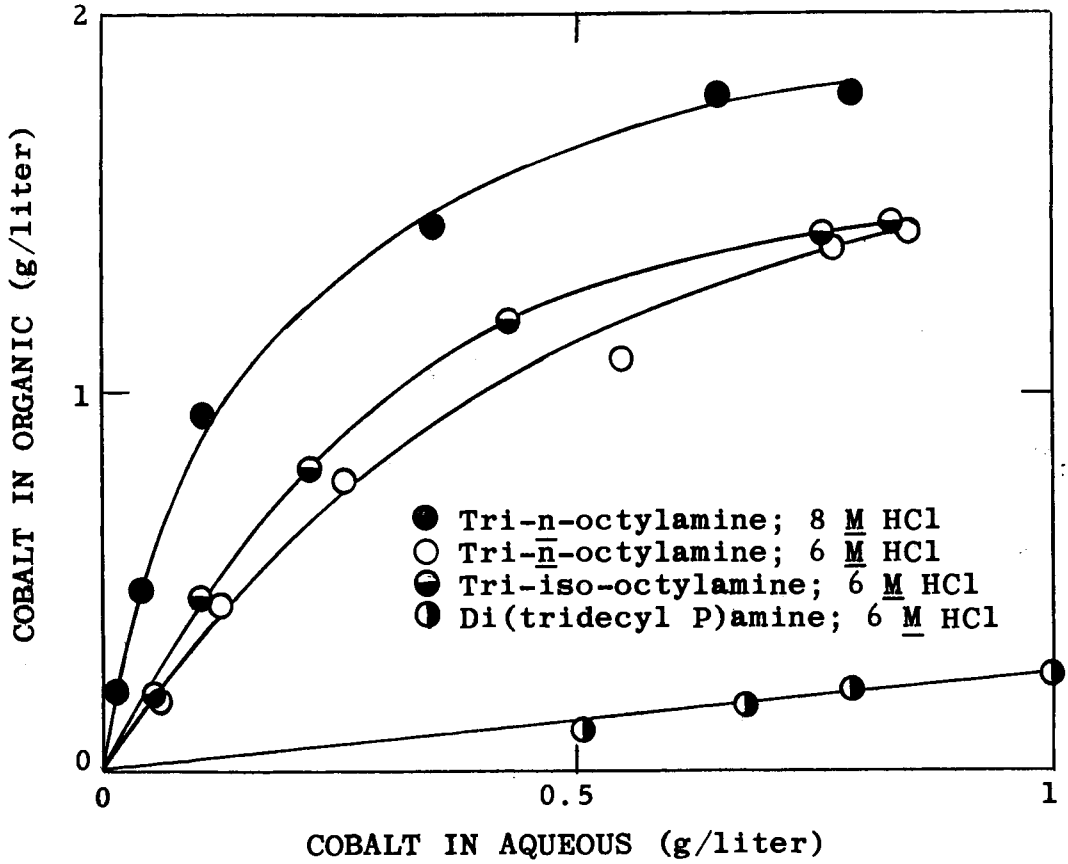

Fig. 1.5 Extraction Isotherms of Cobalt with 0.1 M Amines in Esso Heavy Aromatic Naphtha from 6 and 8 M HCl Solutions Containing Initially 1.03 g of Cobalt per Liter.

Phase separation was reasonably clean and rapid in all the foregoing tests, requiring usually less than 1 min, and about 2 min at the slowest.

No more than this brief survey is planned at present. Some further tests may be made to compare the behavior at higher amine concentrations (to permit higher cobalt loadings) and to check whether the suggested degree of separation from nickel is attainable.

2.0 PROCESS DEVELOPMENT

In addition to the studies described below, process development projects during the month included (1) further studies on the Dapex vanadium process, (2) further studies on the Amex vanadium process, (3) control of phosphate contamination of vanadium products, (4) compatibility of amines with molybdenum-contaminated liquors, and (5) thorium recovery from carbonate strip solutions.

2.1 Stripping Amines with Magnesium Oxide Slurries (W. D. Arnold)

Batch and continuous tests previously reported (ORNL-2099, -2173) demonstrated recovery of uranium from amine extracts by direct precipitation with an aqueous slurry of magnesium oxide. Emulsion formation due to the presence of solids was avoided by maintaining organic-continuous contacting conditions in the mixer. The uranium precipitate settled rapidly in the aqueous phase and filtered readily.

Recent tests at this laboratory* have been concerned with comparison of several commercial magnesias as stripping agents and with study of the effect of temperature on the uranium stripping efficiency. Effects from the presence of molybdenum in the extract have also been briefly studied. All the tests were batch experiments conducted in a baffled mixer, with an organic/aqueous phase ratio of 5/1. The quantity of magnesium oxide supplied to the system was 5-10% in excess of the stoichiometric amount required for neutralization of the amine salt (assuming no bisulfate to be present) and precipitation of the uranium (see equations, ORNL-2099, p. 53). To ensure organic-continuous mixing conditions, the organic extract was placed in the mixer first, and agitation was begun before the slurry was added.

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*The possibilities of magnesium oxide stripping are also being examined on a laboratory and pilot scale by Eldorado Mining and Refining Ltd. at Port Hope and Port Radium and by the Canadian Department of Mines and Technical Surveys at Ottawa (meeting at Ottawa in January, 1957, between representatives from Eldorado Mining and Refining Ltd., the Canadian Department of Mines and Technical Surveys, and ORNL).

a. Comparison of Commercial Magnesias

Several commercial magnesias in the price range $82-120 per ton (carload lots) have proved effective for stripping uranium from 0.1 M tri-n-octylamine in 97% kerosene--3% tridecyl alcohol (Table 2.I) More than 99.5% of the uranium was stripped in 5 min and 99.9% in 20 min with Calcined Magnesite No. 2665 (Westvaco), Calcined Magnesites Nos. 5 and 15 (Michigan Chemical Corp.), and Synthetic Magnesite Calcined L-2-65 Hammermilled (Dow Chemical Co.). Results were also favorable with Calcined Magnesite No. 2663 (Westvaco) although stripping was slightly slower than with the others. Only about 25% of the uranium was stripped in 5 min contact time with U-99 Magnesite (International Minerals and Chemical Corp.). Results were not improved by increasing the stirring speed from 400 to 600 rpm. This magnesia, because of its high density, could not be kept in suspension, which may account in part for the relatively poor results. Because of the physical difficulties encountered in handling the U-99 slurries, tests which were planned at contact times longer than 5 min were suspended pending receipt of more reactive magnesias from this source. Methods of activating the dense magnesia may be tested.

Phase separation in all the above tests was rapid, the primary break between the organic and slurry phases occurring in 20-30 sec. The precipitates settled rapidly and little or no precipitate or emulsion was present at the organic-aqueous interface.

b. Effect of Temperature

Increasing the temperature from 28 to 38°C increased the rate of stripping of Amine 9D-178 in kerosene (loaded to 3.3 g U/liter from a synethetic liquor) with calcined Magnesite No. 15. The improved efficiency was more noticeable after a short contact time (5 min) since stripping was practically complete at both temperatures in 10-20 min:

Temp (°C)	Agitation Time (min)	U in Stripped Organic (g/liter)	Uranium Stripped (% of total)
28	5	0.110	96.5
28	10	0.012	99.6
28	20	0.007	99.8
38	5	0.031	99.1
38	10	0.007	99.8
38	20	0.006	99.8

The conditions were 0.10 M amine, 10% excess MgO, 400 rpm stirring speed.

c. Effect of Molybdenum

The presence of molybdenum in the amine extract adversely affected the efficiency of uranium stripping with magnesium

Table 2.1 Comparison of Commercial Magnesias for Stripping Uranium

Organic: 0.1 M tri-n-octylamine in 97% kerosene--3% tridecyl alcohol loaded to 4.9 g U/liter from a synthetic leach liquor

$MgO-H_2O$ Slurry: 5-10% excess MgO

Organic/slurry: 5/1

Stirring speed: 400 rpm

Temperature: Room

Magnesia	Pulp Density[a] (lb/ft^3)	Agitation Time (min)	U in Stripped Organic (g/liter)	Uranium Stripped[b] (% of total)
Calcined Magnesite No. 2665 (Westvaco)	31	5	0.014	99.7
		10	0.006	99.9
		20	0.001	99.9
Calcined Magnesite No. 2663 (Westvaco)	33	5	0.050	99.0
		10	0.020	99.6
		20	0.020	99.6
Calcined Magnesite No. 5 (Michigan Chemical Corp.)	28	5	0.018	99.6
		10	0.010	99.8
		20	0.004	99.9
Calcined Magnesite No. 15 (Michigan Chemical Corp.)	24	5	0.010	99.8
		10	0.004	99.9
		20	0.004	99.9
Synthetic Magnesite Calcined L-2-65 Hammermilled (Dow Chemical Co.)	20	5	0.016	99.7
		10	0.008	99.8
		20	0.004	99.9
U-99 Magnesite (International Minerals)	75-80	5	3.65	25
		5[c]	3.75	23

[a]Data from the manufacturer.

[b]Based on the extract and stripped organic analyses.

[c]600 rpm stirring speed.

oxide. Comparison of Tables 2.1 and 2.2 shows uranium stripping of tri-n-octylamine with three different magnesias to be slower when the extract contained 0.21 g Mo/liter than when no molybdenum was present. The molybdenum was stripped at a slower rate than the uranium. With 10% excess Calcined Magnesite No. 2665, 99.7% of the uranium and 97% of the molybdenum was removed in 20 min contact time. Under the same conditions, Nos. 2663 and 15 Calcined Magnesites stripped only 92-93% of the uranium and 45-55% of the molybdenum. Increasing the excess magnesium oxide from 10 to 20% considerably improved the results with Calcined Magnesite No. 15, uranium removal being 99.9% and molybdenum removal 97% complete in 20 min. In this test the molybdenum content of the extract was 0.37 g/liter. A major part of the stripped molybdenum remained with the uranium product after filtration and washing. This molybdenum was removed effectively from the uranium by digesting the filter cake with 1% sodium hydroxide (0.2 lb NaOH/lb U_3O_8) for 20 min at room temperature.

3.0 ENGINEERING STUDIES

In addition to the studies described below, the rate of uranium extraction by Dapex-type solvent was investigated.

3.1 Continuous-flow Mixer Studies of Uranium Stripping from Dapex-type Solvent (R. R. Wiethaup)

Previously (ORNL-2213) the rate of uranium stripping with sodium carbonate was studied batchwise in a 6-in. mixer to determine the effect of power input and stripping agent excess. With the batch data as a guide, continuous flow tests were made in the same size mixer to determine the effect of residence time and power input on the stripping efficiency. A two-stage stripping circuit was simulated by first contacting loaded organic with 1 M sodium carbonate and subsequently contacting the partially stripped organic with fresh sodium carbonate.

The mixer was a 6- by 12-in. baffled tank (liquid volume, 0.73 gal) with a 3-in. 4-bladed turbine in the center. The loaded organic phase and sodium carbonate were metered into the bottom of the mixer, and flowed out through a side nozzle 6 in. above the bottom. At steady state, the exit stream was sampled, the phases were separated, and the uranium content of the organic phase was determined as a basis for calculation of mixer efficiency.

The organic solvent contained 0.16 M di(2-ethylhexyl)-phosphoric acid (D2EHPA) and 35 g of TBP per liter in kerosene. The solvent was loaded with uranium by contacting with a synthetic leach liquor containing U, Fe, Al, V(IV), PO_4, and SO_4. The stripping solution was 1 M Na_2CO_3. The ratio of flow rates of the solvent and stripping solution was such that the carbonate was supplied in 45% excess over stoichio-

Table 2.2 Effect of the Presence of Molybdenum on Magnesium Oxide Stripping

Organic: 0.10 M tri-n-octylamine in 97% kerosene--3% tridecyl alcohol loaded with 4.3 g of uranium and 0.21 g of molybdenum per liter from a synthetic leach liquor

$MgO-H_2O$ Slurry: 10% excess MgO[a]

Organic/slurry: 5/1

Stirring speed: 400 rpm

Temperature: room

Magnesia	Agitation Time (min)	U in Stripped Organic (g/liter)	Mo in Stripped Organic (g/liter)	U Stripped (% of total)	Mo Stripped (% of total)
Calcined Magnesite No. 2665 (Westvaco)	5	0.55	0.150	87	30
	10	0.16	0.062	96	70
	20	0.010	0.005	99.7	97
Calcined Magnesite No. 2663 (Westvaco)	5	0.55	0.125	87	40
	10	0.40	0.125	91	40
	20	0.32	0.115	93	45
Calcined Magnesite No. 15 (Michigan Chemical Corp.)	5	0.55	0.185	87	9
	10	0.50	0.185	88	9
	20	0.36	0.095	92	55
	20[b]	0.005[b]	0.010[b]	99.9[b]	97[b]

[a]Excess magnesium oxide was calculated ignoring the presence of molybdenum.

[b]20% excess MgO, 0.37 g of molybdenum per liter in extract.

metric.* In all tests the mixing was controlled so that organic-continuous dispersions were formed and the temperature was maintained at 24 to 30°C.

The efficiency of the mixer was calculated as Murphree efficiency based on uranium concentrations in the organic phase. The operating data are in Table 3.1 and the results are summarized in the following table:

Turbine Speed (rpm)	Power (hp/gal)	Stripping Efficiency, %			
		1.5 min residence		0.38 min residence	
		1st stage	2nd stage	1st stage	2nd stage
200	0.0007	93(89)*	94	--	--
300	0.0022	98	99	73	96
400	0.0053	99	99	82	98
600	0.018	99(100)*	99	95	98
900	0.060	100	--	98	98

*Carbonate excess was 21%, compared with 45% for other runs.

Greater than 90% efficiency was readily attained in both stages. With a residence time of 1.5 min in the mixer, the efficiency was greater than 90% at the lowest turbine speed tested, which was equivalent to a power input of 0.0007 hp per gallon of total mixer content. At a residence time of 0.38 min, the power required for 90% efficiency was 0.01 hp/gal in the first stage and 0.002 in the second. A conservative basis for scale-up would be a residence time of 1 min and a power input of 0.01 hp per gallon of total mixer content.

*The stoichiometric equivalent was assumed to be 3 moles of Na_2CO_3 per mole of uranium plus 0.5 mole per mole of free D2EHPA estimated on the basis of 2 D2EHPA for each uranium; i.e., 13 and 15 g of Na_2CO_3 per liter of the 0.16 M D2EHPA solution containing 5.4 and 7.1 g U/liter, respectively.

Table 3.1 Dapex Uranium Stripping Data

Run No.	Flow Rates (gpm) Organic	Flow Rates (gpm) Aqueous	Uranium Conc. (g/liter) Organic in	Uranium Conc. (g/liter) Organic out	Turbine Speed (rpm)	Efficiency (%)
			First Stage			
603	0.43	0.083	5.4	0.62	200	93
604	0.43	0.083	5.4	0.36	300	98
605	0.43	0.083	5.4	0.35	400	99
606	0.43	0.083	5.4	0.34	600	99
611	1.8	0.33	5.4	1.71	300	73
612	1.8	0.33	5.4	1.25	400	82
613	1.8	0.33	5.4	0.60	600	95
614	1.8	0.33	5.4	0.42	900	98
625*	0.46	0.082	7.1	1.00	200	89
626*	0.46	0.082	7.1	0.44	600	100
			Second Stage			
607	0.43	0.079	0.43	0.042	200	94
608	0.43	0.079	0.43	0.022	300	99
609	0.43	0.079	0.43	0.021	400	99
610	0.43	0.079	0.43	0.021	600	99
615	1.7	0.34	1.0	0.086	300	96
616	1.7	0.34	1.0	0.066	400	98
617	1.7	0.34	1.0	0.058	600	98
618	1.7	0.34	1.0	0.058	900	98

*Carbonate excess was 21%, compared with 45% for other runs.