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SOLVENT EXTRACTION OF URANIUM
FROM CARBONATE SOLUTIONS

F. G. Seeley
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OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

A process for recovering uranium from carbonate leach liquors by extraction with quaternary ammonium compounds was developed and evaluated in bench-scale continuous equipment with synthetic liquors. Uranium was recovered from the solvent by direct precipitation with sodium hydroxide—sodium carbonate solution. Results with relatively pure synthetic carbonate liquors were favorable, but attempts to treat a highly contaminated leach liquor from a western mill were relatively unsuccessful owing to interference from sulfate, chloride, thiocyanate, molybdenum, vanadium, and organic matter present. The process is therefore not considered competitive with the precipitation process used in several western carbonate-leach mills.

CONTENTS

1.0 SUMMARY

Of 15 quaternary ammonium compounds tested, only Quaternary B-104 and Aliquat 336 had both adequate extraction power and reasonable phase separation properties. The uranium extraction power was directly proportional to the quaternary concentration, inversely proportional to the square of the carbonate concentration, and almost independent of the carbonate/bicarbonate ratio in the aqueous phase. Uranium extraction was depressed slightly by increasing the temperature from 27 to 50°C and severely by adding small amounts of nitrate or chloride to the system. Interference from sulfate was much weaker. Addition of tridecanol to the kerosene diluent dramatically improved phase separation and uranium extraction power. With Aliquat 336 in kerosene, results were optimum with a tridecanol/quaternary mole ratio of ~5. Both vanadium and molybdenum were extracted relatively strongly and were replaced by uranium only with difficulty. Selectivity for uranium over vanadium was improved by increasing the aqueous pH.

Uranium was stripped from the solvent extremely effectively with neutral nitrate or chloride solution, but reconversion of the quaternary salt to the carbonate form for recycle was difficult. Basic stripping agents showed more promise, best results being obtained with sodium hydroxide—sodium carbonate solutions, which precipitated the uranium directly from the solvent.

In several runs with synthetic liquors in continuous equipment, using Aliquat 336 as the extractant and 0.5-1 M NaOH—0.5 M Na_2CO_3 solution for stripping, physical performance in both the extraction and stripping circuits was satisfactory but separation from vanadium was not adequate. Consumption of caustic for the stripping-precipitation step was ~0.7 lb per pound of U_3O_8 recovered.

Batch extractions from a carbonate liquor received from a western mill were relatively unsuccessful owing to interference from sulfate, chloride, thiocyanate, molybdenum, vanadium, and organic matter in the liquor. Because of the difficulties in the batch tests, this liquor was not processed in continuous equipment.

Although interference by contaminants with the extraction process can be controlled to some extent by adjustment of conditions for the ore leaching and solvent extraction operations and by addition of extra processing steps, it was concluded that the quaternary solvent extraction process for treating ore carbonate liquors shows little promise of becoming competitive with the caustic precipitation process currently used in western uranium mills.

2.0 INTRODUCTION

This report describes development of a solvent extraction process for recovering uranium from ore carbonate leach liquors with quaternary ammonium compounds as extractants.

In the carbonate leach—caustic precipitation process (Fig. 2.1), which is used in several mills in the western United States for treating uranium ores, the ore is leached at elevated temperatures with sodium carbonate—sodium bicarbonate solution. The pregnant liquor is filtered from the residue and treated with excess caustic to precipitate sodium polyuranate. The precipitation filtrate is recarbonated and recycled, by way of the filtration-wash circuit, to the leaching step. The precipitation and recarbonation steps could be eliminated by the use of a solvent extraction process.

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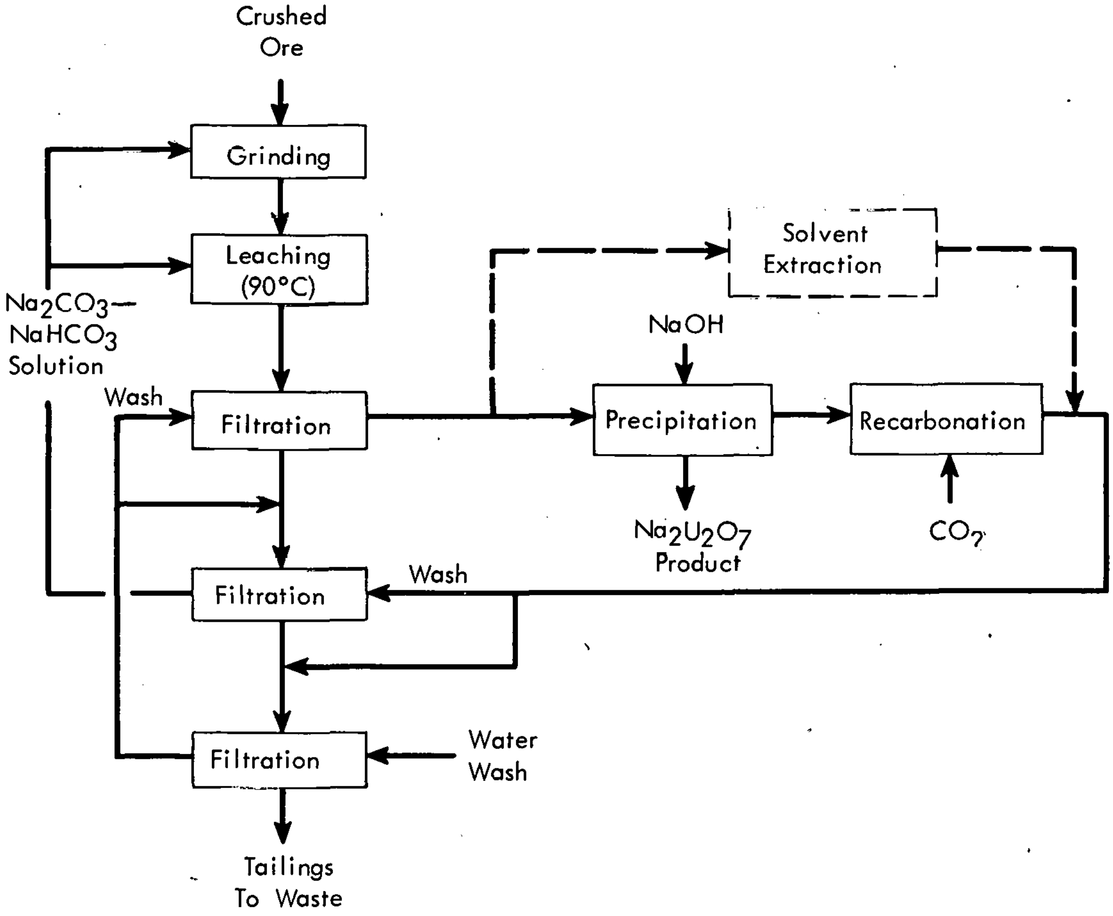

Fig. 2.1. Carbonate leach--caustic precipitation process for uranium ores.

From the outset of the solvent extraction studies it was evident that the potential gain in substituting solvent extraction for precipitation in the carbonate leach process was much less than in the acid leach process for uranium. However, the caustic precipitation method for treating carbonate liquors, although generally successful, does have some disadvantages. For example, separation from vanadium in the precipitation step is poor and further treatment of the precipitate is often required to meet vanadium specifications for uranium concentrates. In addition, accumulation of dissolved organic matter in the recycled carbonate liquor prevents complete precipitation of uranium, resulting in some uranium loss when the precipitation filtrate is recycled to the filtration-wash circuit. Consequently, it appeared that, if a simple, economical solvent extraction flowsheet could be devised which circumvented these problems, some economic advantage could be realized.

Although some of the quaternary ammonium compounds examined initially[1,2] extracted uranium, process studies with these compounds were impossible owing to their exceptionally poor phase separation characteristics and lack of compatibility with practicable diluents. After some time, an experimental compound (Quaternary B-104) was obtained which had sufficiently favorable phase separation properties to permit evaluation[3,4] of the effects of numerous extraction variables and brief examination of the stripping cycle. Still later, a commercial compound (Aliquat 336) with good phase separation properties was obtained and process studies[5,6] were completed with this compound. After batch examination of the extraction and stripping cycles, a process was demonstrated in continuous countercurrent equipment with synthetic carbonate leach liquors and was evaluated in batch tests with an actual leach liquor from a western mill. This report summarizes data obtained in the course of this work, including data previously[2-6] reported. Information on the structure and source of supply of the quaternary ammonium compounds studied is given in Sec. 3.0 and the Appendix.

The authors are indebted to John G. Moore who performed many of the initial extraction tests.

3.0 EXPERIMENTAL MATERIALS AND TECHNIQUES

Except for the preliminary extraction tests described in Sec. 4.1a, all tests were made with Quaternary B-104 or Aliquat 336 as the extractant and kerosene or Amsco G (high-boiling aromatic petroleum product) as diluent. A diluent modifier, usually tridecanol (TDA), was added in most tests to prevent third-phase formation or to improve phase separation, which was extremely sluggish with no modifier present.

Quaternary B-104 (dimethyldidodecenylammonium chloride), an experimental compound from Rohm and Haas, was supplied as a 65% solution in isopropyl alcohol. Aliquat 336 (methyltrialkylammonium chloride, alkyl groups being mixed n-octyl and n-decyl), which is now commercially available from General Mills, was received as a 75% active solution. Except for the tests described in Sec. 4.1a, the diluted solutions of the quaternaries were scrubbed with 0.5 M Na_2CO_3 solution prior to use in order to remove aqueous-soluble impurities from the solvent which might influence extraction results, and to convert the quaternary to the carbonate salt form. The solvent was scrubbed until essentially no chloride could be detected in the aqueous phase, this usually requiring ~10 contacts at an aqueous/organic phase ratio of 1/1 for Aliquat 336. From data obtained in scrubbing this compound, the ratio of distribution coefficients, chloride/carbonate, was estimated to be ~35.

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

The aqueous solutions studied in the extraction tests were synthetic leach liquors, an actual leach liquor from an operating mill, and "pure" solutions of individual metals. Compositions of the solutions used in each set of experiments are given with the experimental data.

Batch extraction tests were made by contacting the organic and aqueous phases in separatory funnels, vigorous agitation being supplied by a Burrell wrist-action shaker. Continuous countercurrent extraction tests were made in bench-scale mixer-settlers. Description of the continuous equipment is given in the Appendix.

4.0 EXTRACTION FROM CARBONATE SOLUTIONS

The chemical behavior of the primary, secondary, and tertiary amines, which are useful extractants from acid solutions (Amex process[1,7,8]) but ineffective extractants from basic solutions, is analogous to that of weak-base anion exchange resins. Similarly, there appears to be a close analogy between extraction with quaternary ammonium compounds and sorption by strong-base anion exchange resins. Extraction of uranium from carbonate liquors can be represented as an anion exchange reaction, the uranyl tricarbonate complex anion displacing carbonate (or chloride if the quaternary is initially in the chloride form) from the solvent phase:

$$\underline{2(R_4N)_2CO_3} + UO_2(CO_3)_3^{4-} \rightleftharpoons \underline{(R_4N)_4UO_2(CO_3)_3} + 2CO_3^{=} \qquad (1)$$

where the dotted underlines represent species in the organic phase.

4.1 Uranium

a. Preliminary Tests. In extractions from 0.5 M sodium carbonate solution with 14 different quaternary ammonium compounds in chloroform and benzene diluents, only Quaternary B-104 and Aliquat 336 showed both significant uranium extraction power and reasonable phase separation properties (Table 4.1). Results were better in chloroform than in benzene diluent for some compounds but poorer for others. All the compounds were in the form of the halide salt when received and were used as such in the first tests. Since, analogous to ion exchange resins, the quaternary extractants have a strong affinity for chloride, the extractions were undoubtedly affected adversely by the presence of chloride (Sec. 4.1g). On the assumption that interference from sulfate would be less, most of the tests were repeated with the quaternary converted to the sulfate form, but this improved results only slightly. The solubility of many of the compounds in benzene diluent was limited, and saturated solutions were used in all cases where limited solubility prevented preparation of ~0.1 M solutions. The amount of reagent in the organic solvent was determined by evaporating a known volume to a constant weight. This method was also used to obtain an indication of the amount of reagent remaining in the solvent after contact with the aqueous liquor.

One other quaternary (N-benzyl-N-N-dimethyl-1-undecyldodecylammonium chloride), which was received late in the studies, was tested as an extractant but only after conversion to the carbonate form. At 0.04 N concentration in kerosene—tridecanol (TDA) diluent it showed good extraction power but extremely slow phase separation:

TDA Conc, vol %	Uranium Analysis, g/liter Organic	Uranium Analysis, g/liter Aqueous	Uranium Extraction Coefficient (E_a^o)	Phase Separation Time, hr
4	1.60	0.37	4.3	>1.5
10	1.55	0.31	5.1	>1.5

The above extractions were from 0.4 M Na_2CO_3—0.1 M $NaHCO_3$ solution containing 2 g of uranium per liter at an aqueous/organic phase ratio of 1/1. In both tests the extraction coefficients shown were severely limited by near saturation of the quaternary with uranium.

Table 4.1. Extraction of Uranium from Carbonate Solution

Aqueous: ~ 0.5 $\underline{M}$ Na_2CO_3, ~ 1 g of uranium per liter
Phase ratio, a/o: 1/1
Contact time: 5 min

	Halide Salt				Sulfate Salt						
	Chloroform		Benzene		Chloroform			Benzene			
Compound[a]	Init. Reagent Conc., g/liter	E_a^o	Init. Reagent Conc., g/liter	E_a^o	Reagent Conc., g/liter Init.	Final	E_a^o	Reagent Conc., g/liter Init.	Final	E_a^o	Phase Sepn.
Quaternary S	41.1	0.03	39.2	0.03	52.4	40.5	nil	1.7	2.2	nil	Poor
Quaternary O	40	nil	39.6	0.03	47	43	0.17	1.7	2.9	nil	Poor
Quaternary C	35.5	nil	38.3	nil	47.9	18.2	nil	1.3	1.8	nil	Fair
Hyamine 10X	44.7	2.9	1.4	0.03	52.5	54.1	4.5	1.8	0.9	nil	Poor
Hyamine 1622	42.8	2.2	0.4	nil	51.6	49.1	3.1	0.6	1.2	nil	Poor
Trimethylphenylammonium chloride	18.2	nil	0	nil	1.6	1.8	nil	0	1.1	nil	-
Cetyldimethylethylammonium bromide	48.4	nil	19.5	nil	56.2	12.7	nil	-	3.8	nil	-
Cetyltrimethylammonium bromide	38.2	0.26	1.7	0	42.0	12.1	0.01	1.7	2.9	nil	Poor
Cetyldimethylbenzylammonium chloride	38.3	1.3	35.7	Third Phase	42.8	42.0	3.5	40.2	5.4	0.008	Fair
Cetylpyridinium chloride	34.2	0.002	5.5	0.001	43.8	6.8	nil	4.6	4.0	0.002	Poor
Laurylpyridinium chloride	27.8	nil	0.4	nil	31	2.6	nil	0.6	1.0	nil	Fair
Tributyllaurylammonium bromide	41.3	nil	23.1	nil	41.6	28.9	nil	23.3	19.0	nil	Good
Quaternary B-104	~50	1.0	~50	2.0[b]	-	-	-	-	-	-	Fair
Aliquat 336	40	0.2	40	3.3	-	-	-	-	-	-	Good

[a] Structure and source of supply for each compound are listed in the Appendix.

[b] Coefficient was 4.3 in Amsco G (high-boiling aromatic petroleum product) diluent.

b. Effect of Carbonate Concentration. As would be expected from eq. 1, the extraction coefficient for uranium was approximately inversely proportional to the square of the aqueous carbonate concentration (Fig. 4.1). These extractions were from 0.3-1.0 M Na_2CO_3 with 0.1 N Quaternary B-104 carbonate in three different diluents (kerosene + 5 vol % TDA, Amsco G, and Amsco G + 3 vol % TDA). Considerable difference in uranium extraction with the different diluents was shown, the highest coefficients being obtained with kerosene + 5 vol % TDA and the lowest with Amsco G.

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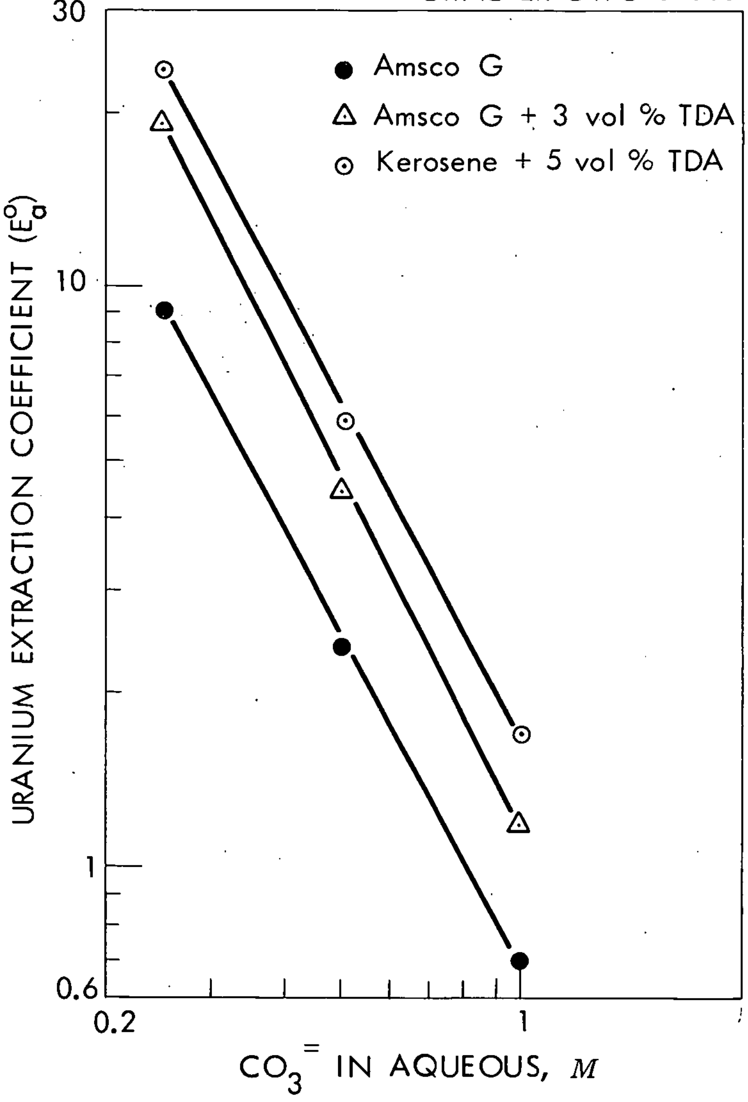

Fig. 4.1. Effect of carbonate concentration on extraction of uranium from sodium carbonate solution with 0.1 N Quaternary B-104 carbonate. Initial uranium in aqueous, 1 g/liter; phase ratio, 1/1; contact time, 5 min. Various diluents.

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

c. Effect of Carbonate/Bicarbonate Ratio. Variation of the aqueous bicarbonate concentration from 0 to 97% of the total carbonate concentration, with the total concentration held constant at ~0.5 M, had little effect on extractions with 0.1 N Quaternary B-104 carbonate:

Initial Bicarbonate, mole % of total carbonate	Final pH	Uranium Extraction Coefficient (E_a^o) Amsco G Diluent	Amsco G + 3% TDA Diluent	Kerosene + 5% TDA Diluent
0	11.3-11.5	2.4	4.4	5.9
20	10.7-10.8	2.3	4.5	5.7
50	10.2-10.3	2.7	4.6	6.3
97	9.4- 9.6	2.2	3.3	5.5

Conditions: 1 g of uranium per liter in initial aqueous, phase ratio 1/1, 5 min contact

d. Effect of Temperature. Increase in temperature from 27 to 50°C caused an appreciable but not prohibitive decrease in extraction of uranium from 0.5 M Na_2CO_3 solution by 0.1 N Quaternary B-104, while the rate of phase separation was virtually unaffected:

Diluent	Temp, °C	Uranium Extraction Coefficient (E_a^o)	Phase Separation Time, min
Amsco G	27	2.4	7
	50	1.8	6
Amsco G + 3 vol % TDA	27	4.4	3.5
	50	2.8	3.5

Conditions: 1 g of uranium per liter in head aqueous, phase ratio 1/1, 5 min contact

e. Effect of Diluent Modifiers. Since the foregoing tests showed an improvement in uranium extraction power and phase separation rate on addition of 3-5 vol % tridecanol (TDA) to the diluent, additional studies were made with 0.1 N Quaternary B-104 carbonate in which the TDA concentration in both Amsco G and kerosene diluents was varied over a wide range (Table 4.2). With the former diluent the uranium extraction coefficient reached a maximum of 30 at 25 vol % TDA (~10 moles of TDA per mole

Table 4.2. Effect of Tridecanol Concentration on Extraction with Quaternary B-104

Head aqueous: 0.5 M Na_2CO_3, 1 g of uranium per liter
Phase ratio: 1/1
Contact time: 5 min

Diluent	Uranium Extraction Coefficient (E_a^o)	Phase Separation Time, min
Amsco G	2.4	7
Amsco G + 3 vol % TDA	4.4	3.5
+ 5 vol % TDA	7.1	6
+ 10 vol % TDA	12	4.5
+ 15 vol % TDA	17	3
+ 25 vol % TDA	30	2.5
+ 32 vol % TDA	18	2
kerosene + 5 vol % TDA	5.9,5.7	10,15
+ 10 vol % TDA	14	8
+ 15 vol % TDA	21	6
+ 25 vol % TDA	30	4

of Quaternary) and then decreased to 18 at 32 vol % TDA. In kerosene the highest coefficient, 30, again was obtained at 25 vol % TDA, but higher concentrations were not tested. The phase separation rate improved considerably with increase in alcohol concentration but still was not rapid (~2 min) even at the highest alcohol level.

Further data showing the effect of TDA concentration on uranium extraction is shown in the form of extraction isotherms for 0.1 N Quaternary B-104 (Fig. 4.2) and for 0.021-0.083 N Aliquat 336 (Fig. 4.3). With the former in Amsco G—TDA diluent, the extraction power over the total range of the isotherm was improved by increase in TDA concentration from 3 to 25 vol %. With Aliquat 336 in kerosene—TDA diluent, however, extractions at higher alcohol concentrations were appreciably depressed in regions of high uranium loadings although efficient at low loadings. For example, the indicated maximum uranium loading for 0.083 N extractant was decreased from ~3.5 to ~2.7 g per liter by increasing the TDA concentration from 5 to 15 vol %. Since, in the dilute uranium region, the effect of alcohol concentration is masked by convergence of the isotherms, the data are replotted in Fig. 4.4. At two different extractant concentrations, the uranium extraction coefficient reached a maximum at an alcohol/quaternary ratio of about 5/1, i.e. 10 vol % TDA for 0.083 N Aliquat 336 and 5 vol % TDA for 0.042 N Aliquat 336. The rate of phase separation was reasonably rapid (2 min or less) in all tests with Aliquat 336 but was appreciably faster with alcohol/quaternary mole ratios of 5 or greater than with a ratio

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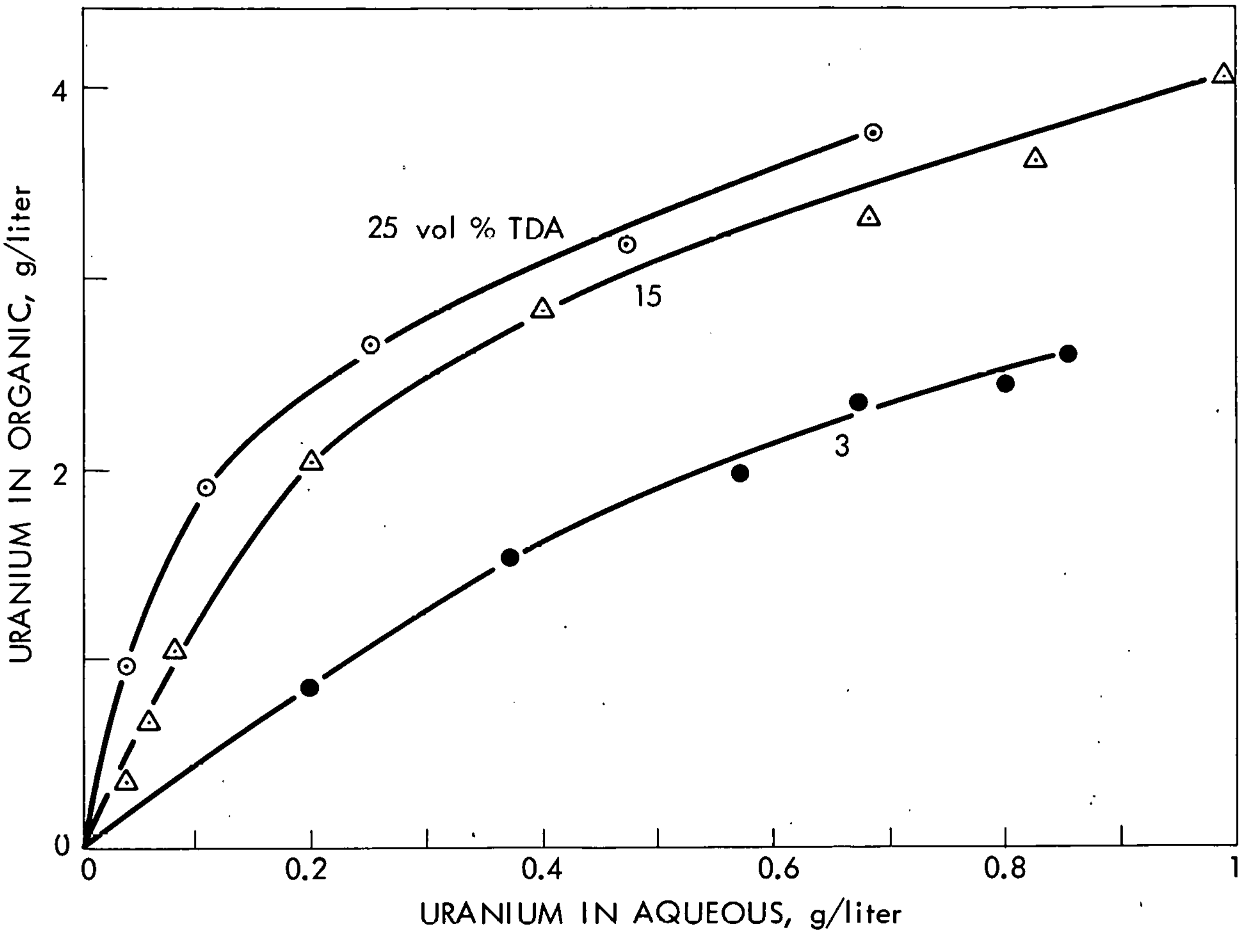

Fig. 4.2. Uranium extraction isotherms from 0.5 M sodium carbonate solution with 0.1 N Quaternary B-104 carbonate in Amsco G—TDA diluent. Organic phase cascaded against fresh volumes of aqueous; contact time, 5 min per stage.

of 2.5. For example, the times (average of 5 tests) for complete disengagement of the phases with 0.083 N Aliquat 336 were 1.5, 0.9, and 0.9 min with alcohol/quaternary ratios of 2.5, 5, and 7.5, respectively. On the basis of the extraction and phase separation results, an alcohol/quaternary ratio of ~5 appears to be optimum for Aliquat 336 in kerosene diluent.

Comparison of uranium extraction coefficients at constant alcohol/quaternary ratios showed a near linear dependence of extraction power on quaternary concentration, at least in the range 0.04-0.1 N.

Extraction of Aqueous. In preparing organic solutions, it was noticed that a small amount of aqueous separated from the

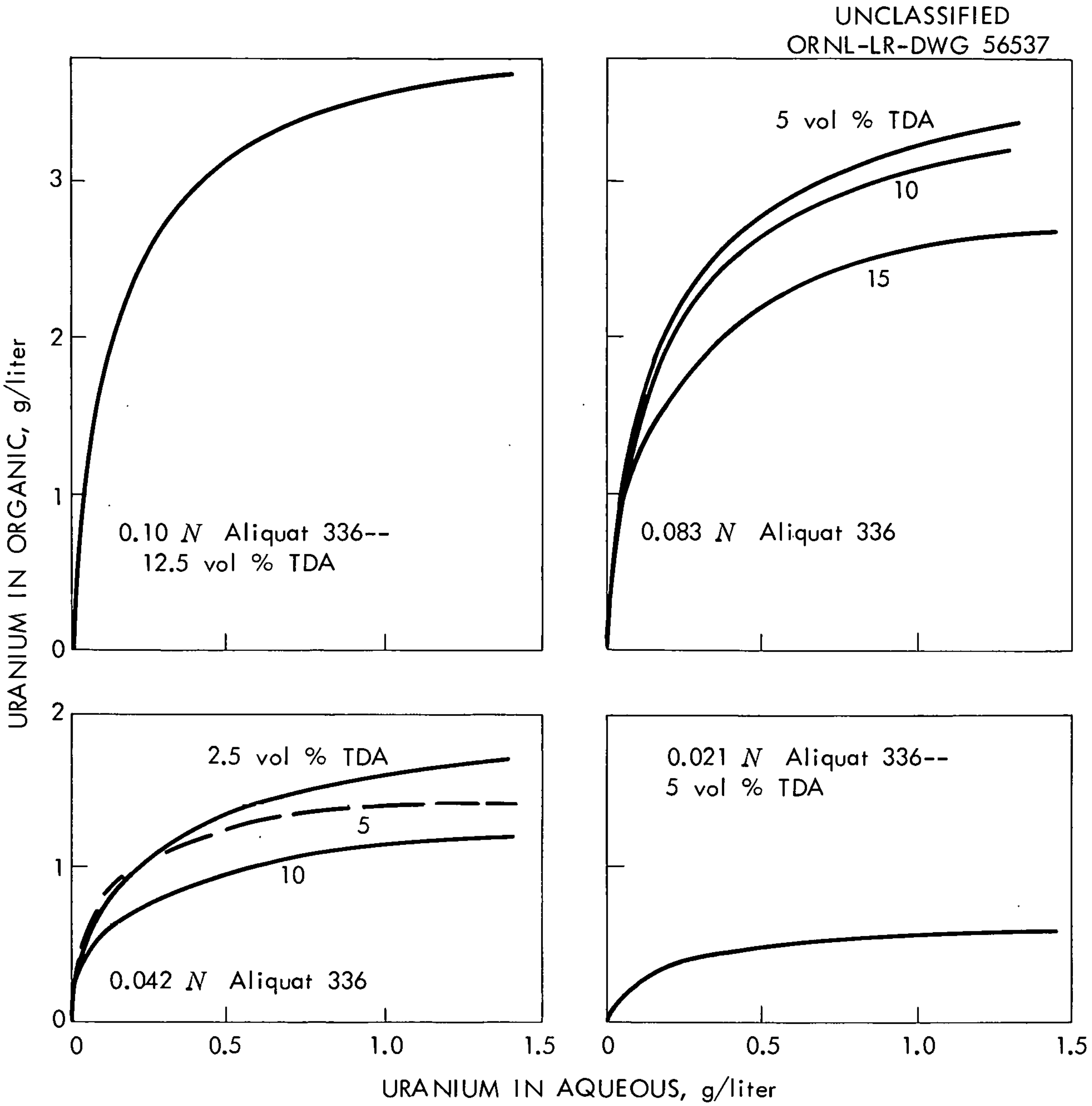

Fig. 4.3. Isotherms for extraction of uranium from carbonate solution with Aliquat 336 (carbonate form) in kerosene--TDA diluent. Initial aqueous: 0.4 M Na_2CO_3--0.1 M $NaHCO_3$, 1 g of uranium per liter, pH ~10. Organic cascaded against fresh volumes of aqueous; 5-min contacts.

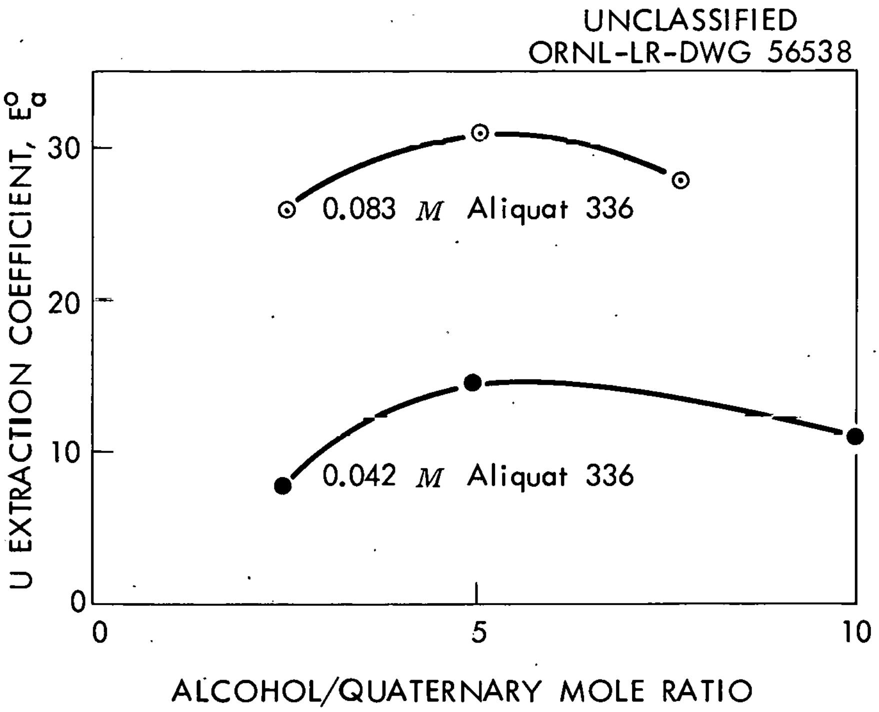

Fig. 4.4. Effect of tridecanol concentration on uranium extraction at low loading. Aqueous: 0.4 M Na_2CO_3—0.1 M $NaHCO_3$. Organic: Aliquat 336 in kerosene—TDA diluent; solvent ~15% loaded with uranium.

quaternary carbonate—diluent solution on addition of TDA. In one test with Quaternary B-104 carbonate in Amsco G, this separated phase was analyzed and found to contain 0.45 M carbonate at pH 11, which was the approximate composition of the aqueous phase (0.5 M Na_2CO_3) last contacted prior to addition of the TDA. Analyses of the solvent in several other cases showed carbonate appreciably in excess of that equivalent to the quaternary carbonate, again suggesting that aqueous takeup by the solvent was due to extraction of sodium carbonate solution rather than to hydration of the quaternary carbonate salt. Estimation of the amount of aqueous extracted by analyzing the solvent (Aliquat 336 carbonate in kerosene—TDA diluent) for water showed that the water extracted per mole of quaternary decreased from ~8 to ~5.5 moles as the alcohol/quaternary mole ratio was increased from 2.5 to 8 (Fig. 4.5). Extractions of water were only slightly lower with 0.041 N compared to 0.083 N extractant.

f. Maximum Uranium Loading. In extractions from 0.35 M Na_2CO_3 solution containing 7.5 g of uranium per liter, maximum loading of Aliquat 336 was one mole of uranium per four moles of quaternary which is consistent with extraction of a tetravalent

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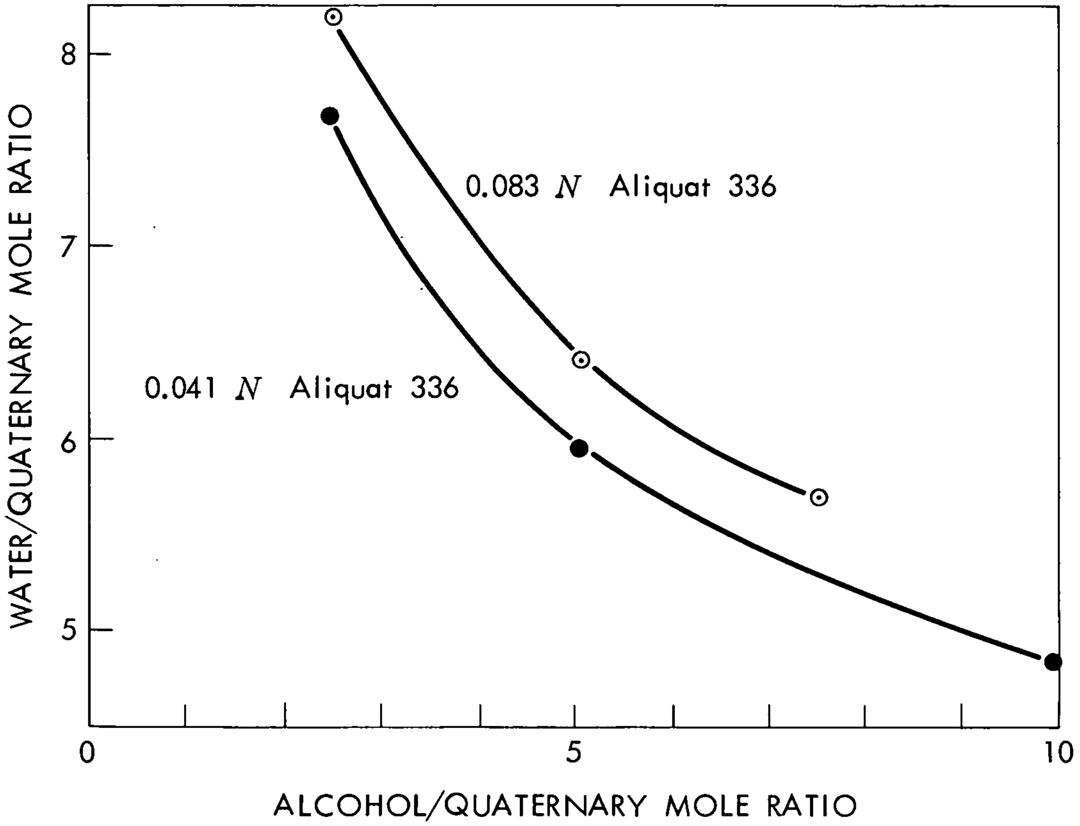

Fig. 4.5. Water content of the solvent phase after contact with 0.5 $\underline{M}$ Na_2CO_3 solution. Organic: 0.041 or 0.083 $\underline{N}$ Aliquat 336 carbonate in kerosene—TDA diluent. Water analyses by Karl Fischer and azeotropic distillation methods.

anion (eq. 1):

Contact	Uranium, g/liter Organic	 Aqueous	Quaternary/Uranium Mole Ratio in Organic
1	4.4	2.7	4.06
2	4.4	7.1	4.06
3	4.5	7.3	3.97
4	4.5	7.3	3.97
5	4.5	7.4	3.97

Conditions: 0.075 $\underline{N}$ Aliquat 336 in kerosene + 2.5 vol % TDA cascaded against successive volumes of 0.35 $\underline{M}$ Na_2CO_3 solution containing 7.5 g of uranium per liter, phase ratio 1/1, 10 min contact

g. Effect of Other Anions. Addition to the carbonate liquor of chloride and nitrate, particularly the latter, caused a serious loss in uranium extraction efficiency (Fig. 4.6). For example, adding 0.06 M nitrate decreased extraction coefficients by a factor >100. Chloride or nitrate can be introduced into the extraction circuit if chloride or nitrate salts are used for stripping (Sec. 5.1) and the extractant is recycled without regeneration to the carbonate form.

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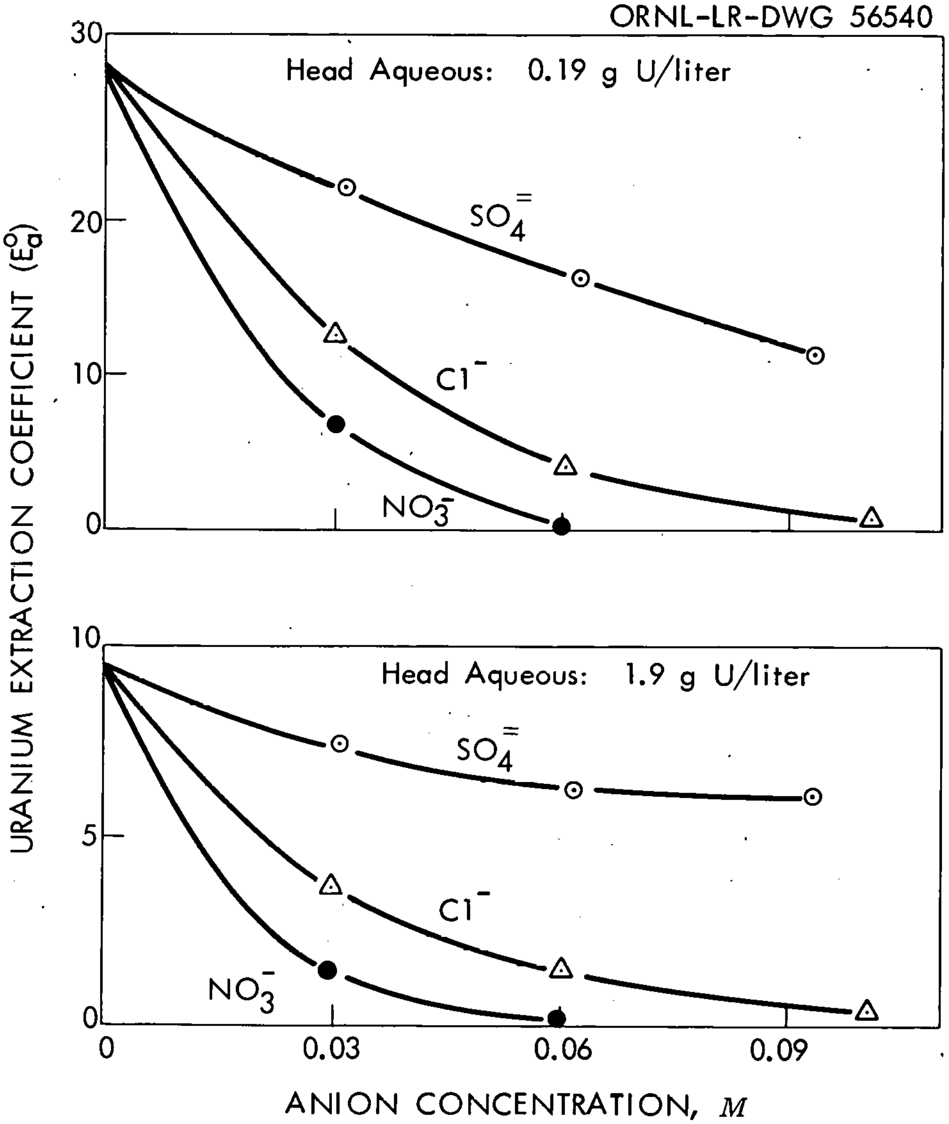

Fig. 4.6. Effect of sulfate, chloride, and nitrate on extraction of uranium from carbonate solutions with 0.095 N Aliquat 336 carbonate in kerosene + 9.5 vol % TDA. Aqueous: 0.4 M Na_2CO_3—0.1 M $NaHCO_3$ containing 1.9 or 0.19 g of uranium per liter; sulfate, chloride, and nitrate added as sodium salt; a/o phase ratio = 1.5/1.

Sulfate also interfered with extractions (Fig. 4.6) but, at low concentrations (<0.1 M), the effect was not prohibitive. However, additional tests (Table 4.3) at higher sulfate concentrations showed a decrease in the uranium extraction coefficient by a factor of ~5 as the sulfate was increased from 0 to 0.5 M. The head liquor in the latter tests also contained vanadium and molybdenum, extractions of these contaminants being virtually unaffected by variation in sulfate concentration. Vanadium coefficients were higher than those for uranium even when the liquor contained no sulfate. The serious interference from sulfate observed at the higher concentrations is an obstacle to commercial application, since buildup in sulfate concentration (due mainly to oxidation of sulfide minerals or metathesis of gypsum in the ore) to 0.5 M or higher in carbonate leach liquors is not uncommon (Sec. 8.0).

Table 4.3. Effect of Sulfate on Uranium Extraction

Organic: 0.075 N Aliquat 336 carbonate in kerosene + 7.5 vol % TDA
Aqueous: Synthetic liquors containing 0.4 M Na_2CO_3—0.1 M $NaHCO_3$ (pH 10.2), 2 g of uranium per liter and indicated concentrations of vanadium, molybdenum, and sulfate; sulfate added as sodium sulfate
Contact time: 5 min
Phase ratio, a/o: 1/1

Conc in Head Liquor, g/liter			Analyses, g/liter						Uranium Extraction Coefficient (E_a^o)
			Organic			Aqueous			
SO_4	V	Mo	U	V	Mo	U	V	Mo	
0	1	-	1.19	0.69	-	0.79	0.28	-	1.5
10	1	-	1.01	0.68	-	0.98	0.29	-	1.0
20	1	-	0.83	0.62	-	1.17	0.31	-	0.7
50	1	-	0.50	0.66	-	1.48	0.32	-	0.3
0	-	1	1.25	-	0.36	0.59	-	0.77	2.1
10	-	1	1.08	-	0.33	0.81	-	0.77	1.3
20	-	1	0.85	-	0.27	0.97	-	0.80	0.9
50	-	1	0.50	-	0.26	1.28	-	0.82	0.4

4.2 Vanadium and Molybdenum

Both vanadium and molybdenum, which are common contaminants of ore carbonate-leach liquors, were extracted fairly strongly by Aliquat 336 from carbonate solutions and were replaced by uranium only with difficulty. Raising the liquor pH improved separations from vanadium but not from molybdenum. Attempts to scrub these contaminants from the solvent were only partially successful.

a. Vanadium. An isotherm (Fig. 4.7) for extraction of vanadium with Aliquat 336 had the same unorthodox shape which is characteristic of vanadium extraction by amines in an acid system.[9]

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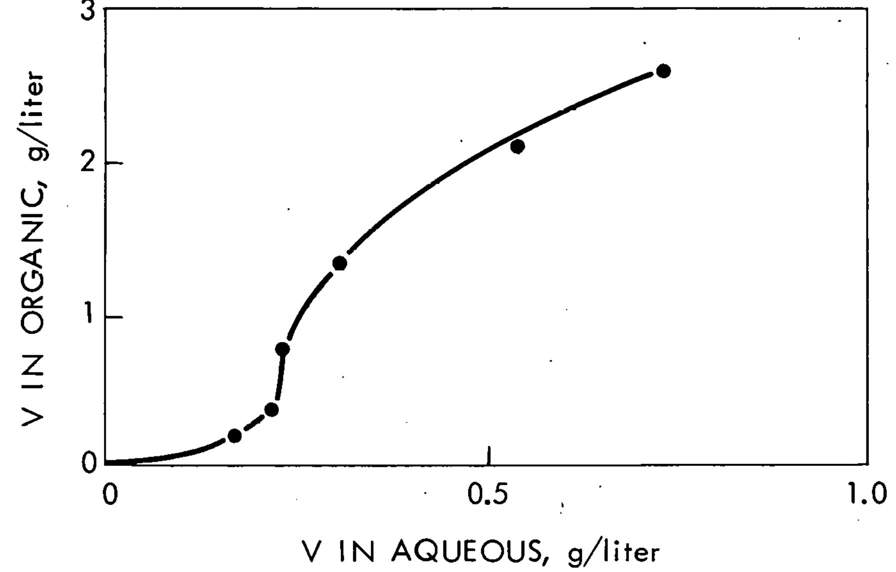

Fig. 4.7. Extraction of vanadium(V) from carbonate solution with 0.075 N Aliquat 336 carbonate in kerosene + 7.5 vol % TDA. Aqueous: 0.4 M Na_2CO_3—0.1 M $NaHCO_3$, 1 g V per liter. 5 min contact time.

Extractions with Aliquat 336 from 0.4 M Na_2CO_3—0.1 M $NaHCO_3$ solution (pH 10.2) containing 2 g of uranium and 1 g of vanadium per liter showed more effective extraction of vanadium than of uranium at high solvent loadings (Table 4.4). Control of vanadium contamination by saturating the solvent with uranium obviously is not feasible in treating a liquor of this composition. A repeat of the test, after adjustment of the aqueous solution to pH 11.1 with sodium hydroxide, showed displacement of the vanadium from the solvent with uranium under these conditions, but at the highest loading, the vanadium content of the extract (~5% V_2O_5 based on U_3O_8) was still above the specification limit (2% V_2O_5) for uranium concentrates.

Scrubbing Vanadium from the Solvent. Attempts to scrub vanadium from uranium-vanadium extracts with sodium carbonate, sodium hydroxide, and mixtures of sodium carbonate and sodium hydroxide were only partially successful (Table 4.5). Results were best with 1 M Na_2CO_3—0.2 M NaOH, which removed 70% of the vanadium (and 5% of the uranium) in a single contact at an organic/aqueous ratio of 4/1. However, the residual vanadium contamination of the extract was still high (~10% V_2O_5 based on U_3O_8).

Table 4.4. Effect of Uranium Loading and pH on Vanadium Extraction

Aqueous: 0.4 M Na_2CO_3—0.1 M $NaHCO_3$ solution (pH 10.2) containing 2 g of uranium and 1 g of vanadium per liter; or above solution adjusted to pH 11.1 with NaOH pellets

Organic: 0.075 N Aliquat 336 carbonate in kerosene + 7.5 vol % TDA

Contact time: 5 min

pH of Head Aqueous	Phase Ratio, a/o	Analysis, g/liter				Extraction Coefficient (E_a^o)	
		Organic		Aqueous			
		U	V	U	V	U	V
10.2	1/4	0.50	0.20	0.018	0.16	28	1.2
	1/2	0.81	0.32	0.054	0.19	15[a]	1.7
	1/1	1.50	0.70	0.46	0.30	3.3	2.3
	2/1	1.46	1.1	1.2	0.41	1.2	2.7
	5/1	0.84	1.9	1.8	0.59	0.5	3.2
	10/1	0.47	2.5	2.0	0.75	0.2	3.3
11.1	1/4	0.50	0.17	0.016	0.28	31	0.60
	1/2	0.95	0.28	0.032	0.41	30	0.68
	1/1	1.8	0.33	0.14	0.58	13	0.57
	2/1	2.8	0.22	0.57	0.70	4.9	0.32
	5/1	3.5	0.14	1.4	0.90	2.5	0.16
	10/1	3.4	0.11	1.6	0.93	2.1	0.12

[a] Poor material balance.

b. Molybdenum. Unlike vanadium, molybdenum showed normal-shaped extraction isotherms and more efficient extraction at pH 11.2 than at 10.2 (Fig. 4.8). Coefficients at low loadings for extraction from 0.5 M carbonate solution with 0.075 N Aliquat 336 were $\sim$1.2 at pH 10.2 and $\sim$1.8 at pH 11.2

In extractions with Aliquat 336 from 0.5 M carbonate solutions containing both molybdenum (1.1 g/liter) and uranium (1.9 g/liter), separations from molybdenum were only slightly better at pH 11.2 than at pH 10.2, since coefficients for both elements increased with increase in pH by approximately the same factor (Table 4.6). In each case there was some displacement of molybdenum with uranium, but molybdenum contamination of the extract was still excessive (10-11% molybdenum based on U_3O_8) even at the highest uranium loadings.

Scrubbing Molybdenum from the Solvent. Contact of Aliquat 336, loaded to 2 g of uranium and 0.16 g of molybdenum per liter, with 0.5 M Na_2CO_3—0.1 M NaOH solution for 5 min at an organic/aqueous ratio of 4/1 removed $\sim$20% of the molybdenum and 1.4% of the uranium from the solvent.

Table 4.5. Scrubbing Extracted Vanadium from Aliquat 336

Organic: 0.075 N Aliquat 336 in kerosene + 7.5 vol % TDA loaded from carbonate solution to (A) 1.95 g of uranium and 0.5 g of vanadium per liter, or (B) 2.5 g of uranium and 0.45 g of vanadium per liter
Phase ratio, o/a: 4/1
Contact time: 5 min

		Organic		Aqueous		Removed by Scrub, %	
Organic	Scrub	U	V	U	V	U	V
A	0.5 M Na_2CO_3	1.85	0.40	0.25	0.45	3.2	22
	0.5 M Na_2CO_3—0.1 M NaOH	1.91	0.30	0.17	0.81	2.1	40
	0.1 M NaOH	1.97	0.47	<0.001	0.09	<0.1	4
B	0.1 M NaOH	2.5	0.44	<0.001	0.13	<0.1	7
	0.3 M NaOH	2.4	0.45	0.06	0.10	0.6	5
	0.6 M NaOH	2.2	0.44	0.49[a]	0.16	~12	8
	1.0 M NaOH	2.4	0.34	0.18[a]	0.46	~5	25
	0.2 M Na_2CO_3—0.2 M NaOH	2.4	0.34	0.06	0.44	0.6	25
	1 M Na_2CO_3—0.2 M NaOH	2.2	0.15	0.46	1.3	5	70

[a] Some uranium precipitation; filtered before analysis.

5.0 URANIUM STRIPPING

Uranium was stripped very effectively from the solvent with nitrate or chloride salt solutions and with sodium carbonate—sodium hydroxide solution. Sodium sulfate, sodium bicarbonate, and sodium hydroxide solutions were considerably less efficient stripping agents.

5.1 With Salt Solutions

The uranium is present in the extract as a uranium-carbonate-quaternary complex along with excess quaternary carbonate and/or bicarbonate. Treatment of the extract with neutral nitrate or chloride salt solutions results in displacement of the uranium and carbonate with nitrate or chloride:

$$\underset{\cdots\cdots\cdots\cdots\cdots}{(R_4N)_4UO_2(CO_3)_3} + 4\ NO_3^- \rightleftharpoons 4\ \underset{\cdots\cdots}{R_4NNO_3} + UO_2(CO_3)_3^{4-} \qquad (2)$$

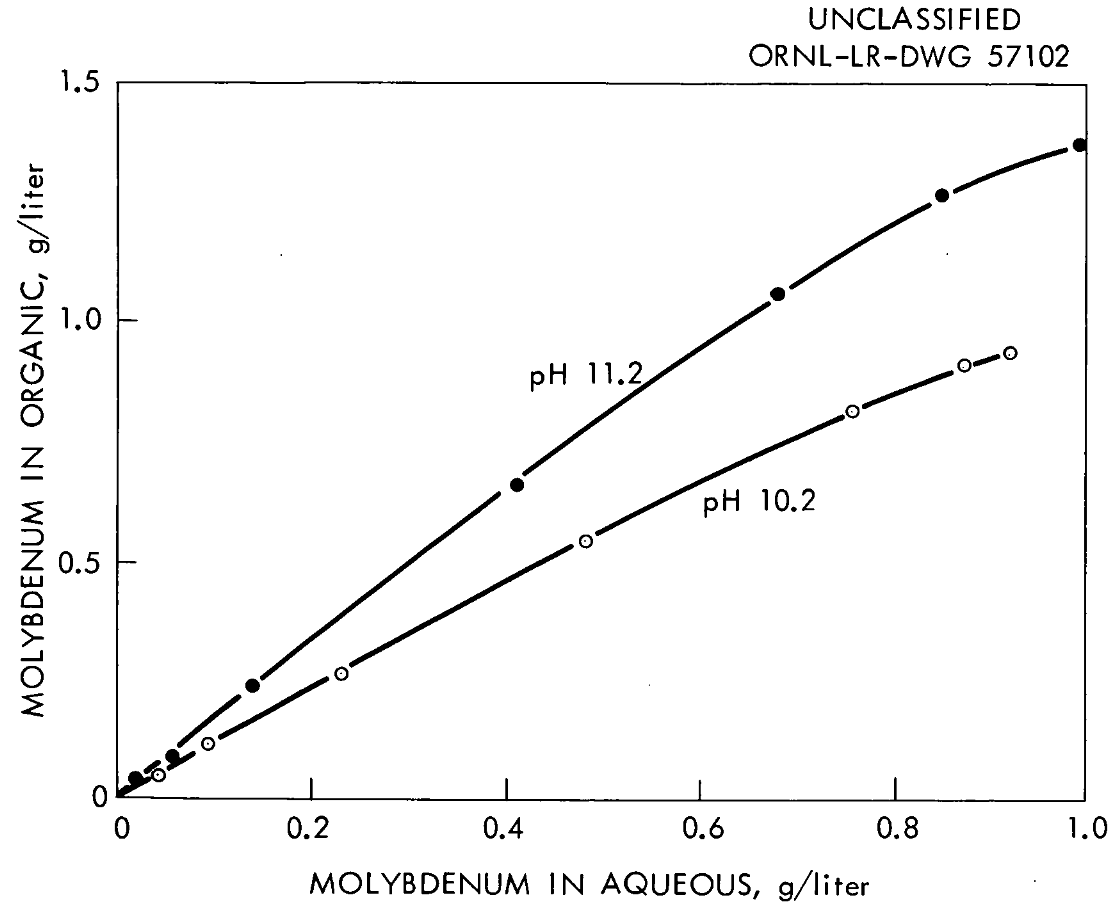

Fig. 4.8. Extraction of molybdenum from carbonate solution with 0.075 $\underline{N}$ Aliquat 336 carbonate in kerosene + 7.5 vol % TDA. Aqueous: 0.4 $\underline{M}$ Na_2CO_3—0.1 $\underline{M}$ $NaHCO_3$ solution (pH 10.2) containing 1 g of molybdenum per liter; or same solution adjusted to pH 11.2 with NaOH. Simulated countercurrent batch extractions, 5 min contact per stage.

and

$$\underset{\cdots\cdots\cdots}{(R_4N)_2CO_3} + 2\ NO_3^- \rightleftharpoons 2\ \underset{\cdots\cdots}{R_4NNO_3} + CO_3^= \qquad (3)$$

where dotted underlines mark species in the organic phase. Coefficients for stripping uranium from 0.075 $\underline{N}$ Aliquat 336 were $\sim$50,000 for 1 $\underline{M}$ $NaNO_3$ and $\sim$11,000 for 1 $\underline{M}$ NaCl (Table 5.1). Greater than 98% stripping could be obtained in a single ideal stage while loading 1 $\underline{M}$ $NaNO_3$ to 30 g of uranium per liter or 1 $\underline{M}$ NaCl to 20 g of uranium per liter. In contrast, stripping coefficients for 1 $\underline{M}$ Na_2SO_4 ranged only from 1 to 2.

In spite of the efficient stripping with nitrate and chloride solutions, process use of these reagents appears

Table 4.6. Effect of Uranium Loading and pH on Molybdenum Extraction

Aqueous: 0.4 M Na_2CO_3—0.1 M $NaHCO_3$ solution (pH 10.2) containing 1.9 g of U and 1.1 g of Mo per liter; or above solution adjusted to pH 11.2 with NaOH

Organic: 0.075 N Aliquat 336 carbonate in kerosene + 7.5 vol % TDA

Procedure: Simulated countercurrent batch extractions, 5 min contact per stage

pH of Head Aqueous	Stage	Analysis, g/liter				Extraction Coefficient (E_a^o)	
		Organic		Aqueous			
		U	Mo	U	Mo	U	Mo
10.2	1	0.003	0.07	0.0004	0.064	7.5	1.1
	2	0.038	0.16	0.005	0.15	7.6	1.1
	3	0.36	0.31	0.047	0.34	7.7	0.9
	4	1.47	0.36	0.41	0.67	3.6	0.5
	5	2.1	0.36	1.2	1.04	1.8	0.3
	6	2.3	0.34	1.5	1.06	1.5	0.3
	7	2.4	0.32	1.8	1.05	1.3	0.3
11.2	1	<0.001	0.05	<0.0001	0.028	-	1.8
	2	0.007	0.13	0.0005	0.078	14	1.7
	3	0.17	0.34	0.011	0.20	15	1.7
	4	1.7	0.48	0.19	0.54	9.0	0.9
	5	2.7	0.52	0.75	1.0	3.6	0.5
	6	3.0	0.43	1.4	1.1	2.1	0.4
	7	3.2	0.39	1.7	1.1	1.9	0.4

unattractive since the quaternary nitrate or chloride salt must be regenerated to the carbonate form prior to recycle in order to avoid serious interference from nitrate or chloride in the extraction step (Sec. 4.1g). Since displacement of the nitrate and chloride with carbonate is difficult (Sec. 3.0), basic stripping methods are more useful.

5.2 With Basic Solutions

With 1 M $NaHCO_3$. Stripping coefficients ranging only from 1 to 3 were obtained in stripping uranium from 0.1 N Quaternary B-104 (Amsco G + 3 vol % TDA diluent) with 1 M $NaHCO_3$:

Contact	Uranium Analysis, g/liter		Stripping Coefficient (S_o^a)
	Organic	Aqueous	
Head	2.3	-	-
1	1.0	1.3	1.3
2	0.31	0.69	2.2
3	0.09	0.22	2.4

Table 5.1. Stripping of Uranium with Nitrate, Chloride, and Sulfate Salt Solutions

Organic: 0.075 N Aliquat 336 in kerosene + 7.5 vol % TDA loaded to 2.5 g of uranium per liter
Contact time: 5 min

Stripping Agent	Phase Ratio, o/a	Uranium Analysis, g/liter		Stripping Coefficient (S_a^o)
		Aqueous	Organic	
1 M $NaNO_3$	0.5	1.3	<0.0002	>6,500
	1	2.5	<0.0002	>12,000
	2	4.9	<0.0002	>24,000
	4	9.9	<0.0002	>49,000
	8	19	0.0013	15,000
	16	34	0.25	140
1 M NaCl	0.5	1.2	0.0002	6,000
	1	2.3	0.0002	11,000
	2	4.3	0.0004	11,000
	4	9.7	0.0017	5,700
	8	20	0.020	1,000
	16	29	0.66	44
1 M Na_2SO_4	0.5	0.86	0.76	1.1
	1	1.5	1.1	1.4
	2	2.3	1.4	1.6
	4	3.3	1.7	1.9
	8	4.6	1.9	2.4

These tests were made by cascading the extract against three successive volumes of 1 M $NaHCO_3$ solution at a phase ratio of 1/1.

With NaOH. Uranium was stripped from Quaternary B-104 and simultaneously precipitated as sodium polyuranate by contact with caustic solutions (Table 5.2). With 1 M NaOH, stripping was not complete even after several successive contacts with fresh strip solution, and most of the uranium did not precipitate but remained in solution. Two contacts (phase ratio of 1/1) with 2 or 3 M NaOH, however, stripped >99% of the uranium. The precipitate showed little tendency to collect at the organic-aqueous interface or to cause emulsions but settled fairly rapidly in the aqueous phase.

With Sodium Carbonate—Sodium Hydroxide Solutions. Uranium was >95% stripped by a 20-min contact of Aliquat 336 uranium extract with 1 M Na_2CO_3—0.6 M NaOH or 0.5 M Na_2CO_3—1 M NaOH at an organic/aqueous phase ratio of 4/1 (Table 5.3). Stripping with these solutions in a 5-min contact was only slightly less efficient. Sodium carbonate solutions (0.5-1 M) containing 0.3 M NaOH stripped only 15-30% of the uranium, and only 70-90% of the stripped uranium precipitated. With solutions containing

Table 5.2. Stripping of Uranium with Caustic

Organic: 0.1 N Quaternary B-104 in (A) Amsco G + 3 vol % TDA, loaded to 2.3 g U per liter, or (B) Amsco G + 25 vol % TDA, loaded to 3.5 g of uranium per liter

Procedure: organic cascaded against fresh volumes of strip solution, 5 min contacts

Strip Solution	Extract	Contact	Uranium, g/liter Organic	Uranium, g/liter Aqueous[a]	Total Uranium Stripped, %
1 M NaOH	A	1	0.70	1.6	69
		2	0.47	0.23	79
		3	0.35	0.12	85
		4	0.21	0.14	91
2 M NaOH	B	1	0.55	2.95	84
		2	0.009	0.54	>99
3 M NaOH	B	1	0.59	2.91	83
		2	0.02	0.57	>99

[a] Filtered to remove uranium precipitate before analysis.

Table 5.3. Stripping Uranium from Aliquat 336 with Na_2CO_3-NaOH Solutions

Organic: 0.075 M Aliquat 336 in kerosene + 7.5 vol % TDA loaded to 2.5 g U/liter

Phase ratio, o/a: 4/1

Strip Solution	Contact Time, min	Uranium in Stripped Organic, g/liter	Uranium Stripped, %
0.5 M Na_2CO_3—0.3 M NaOH	5	2.1	16
	20	2.0	20
0.5 M Na_2CO_3—0.6 M NaOH	5	0.56	78
	20	0.58	77
0.5 M Na_2CO_3—1 M NaOH	5	0.23[a]	91
	20	0.08	97
1 M Na_2CO_3—0.3 M NaOH	5	1.9	24
	20	1.8	28
1 M Na_2CO_3—0.6 M NaOH	5	0.14	94
	20	0.11	96

[a] A second 5-min contact with fresh 0.5 M Na_2CO_3—1 M NaOH at an organic/aqueous phase ratio of 2/1 decreased the uranium concentration in the organic to 0.05 g/liter.

0.6-1 M NaOH, however, precipitation of the stripped uranium was >99% complete. In all tests the phases separated in <1 min, with the precipitate settling fairly rapidly in the aqueous phase. The stripping and precipitation reactions can be expressed as

$$\underset{\cdots\cdots\cdots\cdots\cdots}{2(R_4N)_4UO_2(CO_3)_3} + 6NaOH \longrightarrow 4\underset{\cdots\cdots\cdot}{(R_4N)_2CO_3}^{*} + \underline{Na_2U_2O_7} + 2Na_2CO_3 + 3H_2O \qquad (4)$$

Separations of Uranium from Vanadium and Molybdenum. To determine whether the alkaline stripping cycle would separate uranium from vanadium and molybdenum, two extracts (0.075 N Aliquat 336 in kerosene + 7.5 vol % TDA) were prepared, the first containing 2.0 g of uranium and 0.5 g of vanadium per liter and the second 2.0 g of uranium and 0.16 g of molybdenum per liter. Each was scrubbed 5 min with 0.5 M Na_2CO_3—0.1 M NaOH at an organic/aqueous phase ratio of 4/1 and then stripped by two 5-min contacts with 0.5 M Na_2CO_3—1 M NaOH solution, the first contact at 4/1 and the second at 2/1 organic/aqueous phase ratio. In the uranium-vanadium test, 38% of the vanadium and 2% of the uranium were removed from the solvent by the scrub. The first strip contact increased uranium removal to 85% and vanadium removal to 88%. After the second strip contact, the organic still contained 8% of the uranium and 3% of the vanadium. Uranium stripping was much less complete than in earlier tests (Table 5.3), suggesting an adverse effect from the presence of vanadium. The washed uranium precipitate contained 5% V_2O_5 based on U_3O_8, indicating appreciable but still inadequate separation from vanadium in precipitation. A duplicate test with 20-min contacts in scrubbing and stripping gave approximately the same results.

In treatment of the uranium-molybdenum extract, 20% of the molybdenum and only 1.4% of the uranium were removed in the scrub step. Uranium stripping was only ~50% complete after the first strip and 70% after the second strip, indicating a strong adverse effect from the presence of molybdenum. Approximately 40% of the molybdenum originally present in the extract was removed in the first strip contact and an additional 13% in the second. Separation from molybdenum was favorable in uranium precipitation since the washed uranium precipitate contained <0.4% molybdenum based on U_3O_8. In a duplicate test with 20-min contacts in scrubbing and stripping, uranium removal from the solvent in two contacts increased to 83% whereas the amount of molybdenum stripped was about the same.

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*Some of the reagent is converted to the hydroxide form, i.e., R_4NOH, but the amount is relatively small since its affinity for carbonate ion is much greater than for the hydroxide ion.

6.0 LOSS OF EXTRACTANT TO AQUEOUS LIQUORS

Both Quaternary B-104 and Aliquat 336 showed a relatively low (<20 ppm) steady-state solubility loss to aqueous solutions of appreciable solute content (Table 6.1). Measured losses to 0.5 M Na_2CO_3 solutions were 8 and 18 ppm, respectively, while losses of Quaternary B-104 to 1 M HNO_3 or HCl were <5 ppm. The high loss rate (1 g/liter) of Quaternary B-104 to water indicates that contact of the organic phase with water or very dilute aqueous solutions should be avoided in process use.

Table 6.1. Loss of Extractant to Aqueous Liquors

Quaternary[a]	Aqueous Solution	Loss of Quaternary[b] Fraction Readily Lost, % of initial	Steady-state Loss, mg per liter of aqueous
B-104	water	-	~1000
	1 M HCl	0.6	3
	1 M HNO_3	5	4
	0.5 M Na_2CO_3	4	8
Aliquat 336	0.5 M Na_2CO_3	<2	18

[a] Quaternary initially in chloride form, 0.1-0.15 N in kerosene + 5 vol % TDA.

[b] Method of determining extractant loss was described previously.[1]

7.0 CONTINUOUS TESTS

A flowsheet for recovering uranium from carbonate liquors by extraction with Aliquat 336 in kerosene-alcohol diluent and precipitation of uranium directly from the solvent with 0.5 M Na_2CO_3--1 M NaOH solution was tested in continuous equipment with synthetic liquors. These liquors were, of course, much more amenable to processing than the highly contaminated plant liquor described in Sec. 8.0. Physical performance in both the extraction and stripping circuits was satisfactory in all runs but separations from vanadium were not adequate.

The total circuit (Fig. 7.1) included four extraction stages, two stripping stages, and a product settling tank. (Description of equipment design and size is given in Appendix.) Mixer-settlers were used for contacting the phases. The product settling tank and the settlers in the stripping system had conical bottoms to allow effective discharge of solids and were originally filled with 0.5 M Na_2CO_3--1 M NaOH solution. The precipitate slurry was pumped from the first stage

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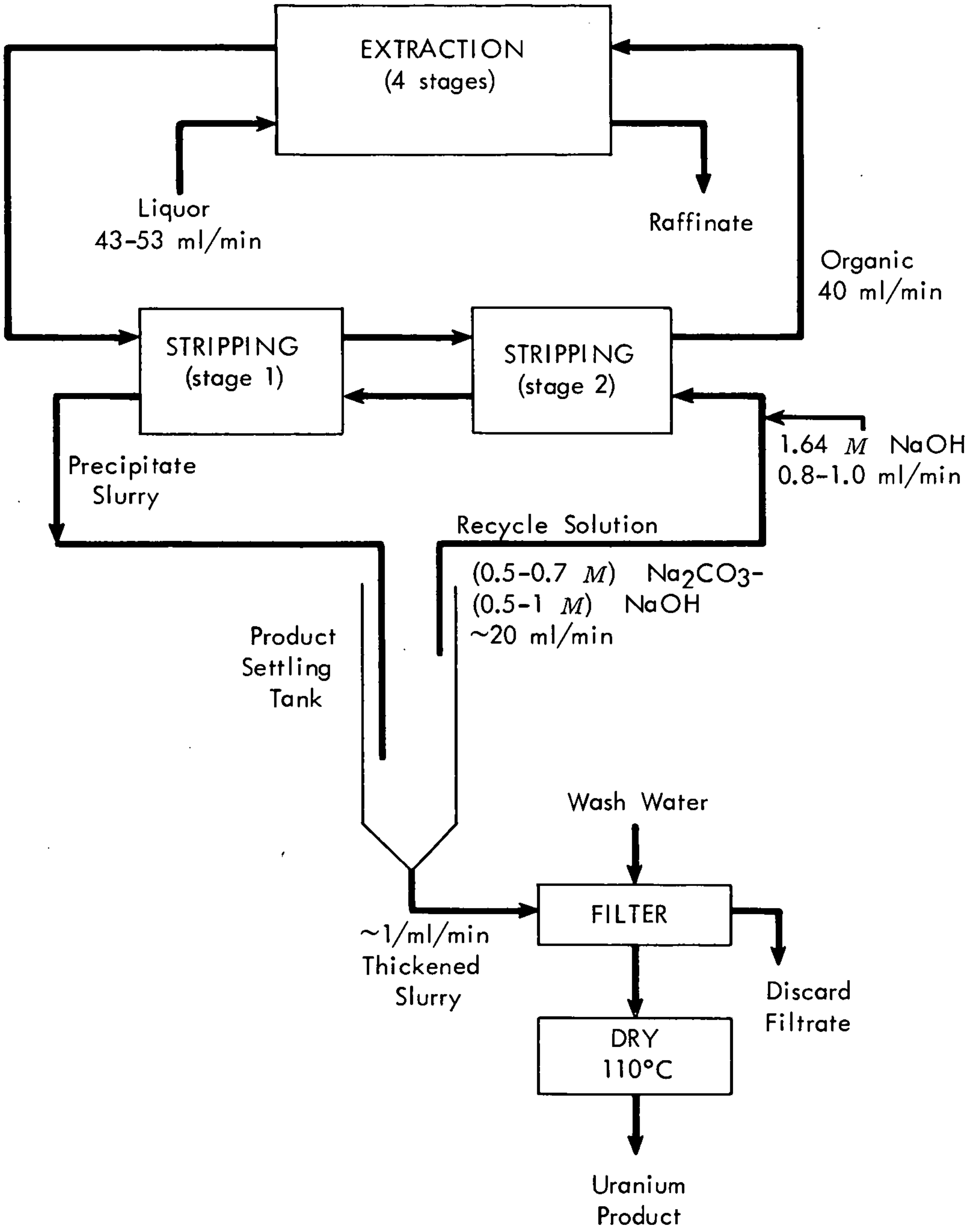

Fig. 7.1. Flowsheet for uranium extraction from carbonate liquors. Organic: 0.075 N Aliquat 336 carbonate in kerosene + 7.5 vol % TDA.

stripping settler to the product settling tank where solution was decanted and, after fortification with sodium hydroxide, was recycled to the stripping system. The only aqueous bleed from the stripping system was in the thickened slurry removed from the product settling tank.

In the shakedown run, the solvent in the stripping circuit turned brown in color and, on recycle to the extraction system, had a considerably decreased capacity for uranium. Batch tests demonstrated that this was caused by reaction of the quaternary carbonate and hydroxide (a small fraction of the quaternary is converted to the hydroxide form in the stripping step) with the Tygon tubing used for piping. The contaminated solvent was discarded and the Tygon tubing in the extraction and stripping system was replaced with neoprene tubing which showed no reaction with the solvent.

Continuous Run 1 (Table 7.1). A 12.5-hr run (five complete cycles of the organic) was made with 0.075 N Aliquat 336 carbonate (kerosene + 7.5 vol % TDA) and "pure" carbonate solution containing 2 g of uranium per liter. Four raffinate samples taken during the run analyzed 0.01-0.1 g of uranium per liter, averaging 0.04 which is equivalent to 98% recovery. Solvent profiles showed pinching in the top stages (particularly at 7.5 hr run time) owing to inadequate solvent flow, which accounts for the relatively poor recovery. Stripping was >98% complete, the recycle solvent containing 0.03-0.05 g of uranium per liter.

Addition of makeup sodium hydroxide to the stripping system was insufficient since the hydroxide concentration in the recycle solution dropped* during the run from its original value of 1 M to ~0.7 M. Mixing was maintained organic-continuous in the stripping system. Under these conditions the uranium precipitate settled rapidly in the aqueous phase and there was no emulsion formation. The thickened precipitate slurry filtered rapidly, yielding a uranium product, which, after washing and drying at 110°C, contained 80.2% U_3O_8. The uranium concentration in the filtrate (which is discarded) was ~0.01 g/liter, equivalent to a loss of <0.05% of the uranium. This concentration was much lower than that in aqueous samples from the product settling tank, presumably because the thickened slurry was allowed to stand about 24 hr prior to filtering which increased the completeness of precipitation.

Continuous Run 2 (Table 7.2). A 12.5-hr run was made with a synthetic liquor containing 2 g of uranium and 0.8 g of vanadium per liter. To repress vanadium extraction, the liquor (originally 0.4 M Na_2CO_3—0.1 M $NaHCO_3$) was adjusted to pH 11.1

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*Hydroxide is consumed, not only in precipitating uranium (eq. 4), but also by reaction with small amounts of quaternary bicarbonate present in the extract and by conversion of a small fraction of the quaternary to the hydroxide form.

Table 7.1. Continuous Run 1: Recovery of Uranium from "Pure" Carbonate Solution

Feed liquor: 0.4 M Na_2CO_3—0.1 M $NaHCO_3$, 2.0 g of uranium per liter, pH 10.2; flow rate 53 ml/min for first 7.5 hr, 48 ml/min for last 5 hr

Organic: 0.075 N Aliquat 336 in kerosene + 7.5 vol % TDA, flow rate 40 ml/min

Strip solution: 0.5 M Na_2CO_3—1 M NaOH at startup; flow rate of makeup NaOH (1.64 M) 0.8 ml/min for first 7.5 hr, 0.9 ml/min for last 5 hr

Run Time, hr	Stage	Uranium, g/liter Organic	Uranium, g/liter Aqueous	pH	Hydroxide Concentration in Aqueous, M
		Extraction System			
5	1	2.6	-	-	-
	4	-	0.01	-	-
7.5	1	2.6	1.9	-	-
	2	2.3	1.7	-	-
	3	2.0	0.8	-	-
	4	0.95	0.1	10.3	-
10	1	2.5	-	-	-
	4	-	0.03	10.3	-
12.5	1	2.5	1.8	-	-
	2	2.2	1.3	-	-
	3	1.5	0.3	-	-
	4	0.4	0.02	10.3	-
		Stripping System			
5	2	0.03	-	-	-
7.5	1	0.04	0.29[a]	-	-
	2	0.03	0.29[a]	-	-
	PT[b]	-	0.21[a]	-	0.81
12.5	1	0.08	0.29[a]	-	0.67
	2	0.05	0.38[a]	-	0.74
	PT[b]	-	0.34[a]	-	0.72

[a] Filtered when sampled to remove uranium precipitate prior to analysis.

[b] PT = product settling tank.

Table 7.2. Continuous Run 2: Recovery of Uranium from Carbonate Liquor Containing Vanadium

Feed liquor: synthetic liquor containing 0.4 M Na_2CO_3—0.1 M $NaHCO_3$, 2.1 g of uranium and 0.8 g of vanadium per liter adjusted to pH 11.2 with NaOH prior to extraction; flow rate 51 ml/min for first 6 hr, 54 ml/min for last 6.5 hr
Organic: 0.075 N Aliquat 336 in kerosene + 7.5 vol % TDA; flow rate 40 ml/min
Strip solution: solution remaining in stripping system from run 1; flow rate of makeup NaOH (1.64 M) 0.9 ml/min

Run Time, hr	Stage	Analysis, g/liter: Organic U	Organic V	Aqueous U	Aqueous V
		Extraction System			
2.5	1	2.7	0.04	-	-
	4	-	-	0.012	-
5	1	2.8	0.05	1.14	0.80
	2	1.7	0.17	0.22	0.86
	3	0.4	0.23	0.033	0.81
	4	0.1	0.21	0.014	0.68
7.5	1	2.9	0.08	-	-
	4	-	-	0.013	0.74
10	1	2.9	0.08	-	-
	4	-	-	0.014	0.76
12.5	1	2.9	0.07	1.75	0.86
	2	2.5	0.16	0.92	0.97
	3	1.3	0.38	0.16	1.0
	4	0.3	0.35	0.014	0.75
		Scrub Stage			
2.5	1	1.77	<0.01	-	-
5	1	2.5	<0.01	0.92[a]	0.147
		Stripping System			
2.5	2	0.071	<0.002	-	-
5	1	0.056	<0.002	0.13[a]	0.008
	2	0.062	<0.002	0.21[a]	0.008
	PT[b]	-	-	0.23[a]	0.008
7.5	2	0.050	0.004	-	-
10	2	0.055	0.004	-	-
12.5	1	0.14	0.007	0.38[a]	0.09
	2	0.055	0.004	0.28[a]	0.07
	PT[b]	-	-	0.27[a]	0.08

[a] Filtered when sampled to remove uranium precipitate prior to analysis.

[b] PT = product settling tank; this solution at 12.5 hr contained 0.51 M OH^-.

with caustic prior to extraction, the required amount of caustic to reach this pH being approximately equivalent to the original bicarbonate. In the first 5 hr of the run, a scrub stage was included in the circuit to scrub extracted vanadium from the solvent prior to stripping. The organic/scrub flow ratio was 8/1 and the spent scrub solution was sent downstream to the first extraction stage. Some uranium precipitated when 1 M Na_2CO_3—0.2 M NaOH (first 2.5 hr) or 1.0 M Na_2CO_3—0.1 M NaOH (next 2.5 hr) was used for scrubbing. Since this precipitate caused physical troubles, the scrub stage was eliminated for the rest of the run.

The uranium concentration in raffinate samples averaged 0.013 g/liter, equivalent to 99.3% recovery. Most of the vanadium extracted in the lower stages was rejected from the solvent as it became loaded with uranium, but vanadium contamination of the extract was still relatively high. The scrub stage (when in operation) removed >75% of the extracted vanadium.

Approximately 98% of the extracted uranium and 90-95% of the extracted vanadium were removed from the solvent in stripping. The vanadium content of the washed and dried (110°C) product, which was collected in increments, increased as the run progressed, finally stabilizing at about 2.2% V_2O_5 (based on U_3O_8), which is slightly above vanadium specifications (2% V_2O_5) for uranium concentrates:

	Product Analyses, %	
Run Time, hr	U_3O_8	V_2O_5/U_3O_8
2	79.7	0.2
4	79.6	0.3
6	80.2	1.0
8	78.7	2.4
10	81.3	2.2
12	78.2	2.2

Loss of uranium to the filtrate was <0.05%.

Continuous Run 3 (Table 7.3). From a synthetic liquor containing 2 g of uranium, 0.74 g of vanadium, and 1.1 g of molybdenum per liter, recovery of uranium in the extraction circuit was only 97-98%. The liquor had been adjusted to pH 11.1 with caustic prior to extraction to repress extraction of vanadium. Both vanadium and molybdenum, but particularly the latter, competed for the extractant, lowering the uranium extraction efficiency.

The pregnant organic contained ~2.5 g of uranium, 0.1 g of vanadium, and 0.4 g of molybdenum per liter. About 94% of the uranium, 80-90% of the vanadium, and only 25% of the molybdenum were stripped from the solvent. The molybdenum concentration in

Table 7.3. Continuous Run 3: Recovery of Uranium from Carbonate Liquor Containing Vanadium and Molybdenum

Feed liquor: synthetic liquor containing 0.4 M Na_2CO_3 — 0.1 M $NaHCO_3$, 2.0 g of uranium, 0.74 g of vanadium and 1.1 g of molybdenum per liter, adjusted to pH 11.2 with NaOH prior to extraction; flow rate 48 ml/min for first 2 hr and 43 ml/min for last 13 hr

Organic: 0.075 N Aliquat 336 in kerosene + 7.5 vol % TDA; flow rate 40 ml/min

Strip solution: solution remaining in the stripping system from run 2; flow rate of makeup NaOH (1.64 M) 1.0 ml/min

Run Time, hr	Stage	Analysis, g/liter					
		Organic			Aqueous		
		U	V	Mo	U	V	Mo
		Extraction System					
2.5	1	2.4	0.09	0.40	-	-	-
	4	-	-	-	0.08	0.69	0.79
5	1	2.4	0.09	0.42	1.72	0.75	1.26
	2	2.0	0.12	0.58	1.18	0.81	1.48
	3	1.3	0.17	0.83	0.53	0.81	1.58
	4	0.6	0.18	0.85	0.07	0.70	0.99
7.5	1	2.4	0.10	0.44	-	-	-
	4	-	-	-	0.06	0.67	0.98
10	1	2.4	0.10	0.44	-	-	-
	4	-	-	-	0.06	0.67	0.98
12.5	1	2.5	0.09	0.39	-	-	-
	4	-	-	-	0.10	0.64	1.05
15	1	2.5	0.09	0.43	1.72	0.77	1.19
	2	2.0	0.13	0.58	1.13	0.82	1.47
	3	1.3	0.18	0.87	0.48	0.81	1.51
	4	0.6	0.19	1.02	0.06	0.67	1.05
		Stripping System					
2.5	2	0.08	0.007	0.14	-	-	-
5	1	0.16	0.018	0.34	0.42[a]	0.13	0.27
	2	0.07	0.013	0.31	0.36[a]	0.12	0.21
	PT[b]	-	-	-	0.41[a]	0.12	0.21
7.5	2	0.17	0.011	0.30	-	-	-
10	2	0.16	0.014	0.35	-	-	-
12.5	2	0.15	0.022	0.28	0.31[a]	0.15	0.29
15	1	0.42	0.026	0.40	0.31[a]	0.17	0.34
	2	0.15	0.022	0.28	0.32[a]	0.17	0.32
	PT[b]	-	-	-	0.26[a]	0.17	0.33

[a] Filtered when sampled to remove uranium precipitate prior to analysis.

[b] PT = product settling tank. The sample at 5 hr analyzed 0.71 M $CO_3^=$ and 0.54 M OH^-; at 15 hr, 0.72 M $CO_3^=$ and 0.45 M OH^-.

the solvent did not build up, however, over the period of the run. The relatively poor uranium stripping efficiency in this run compared to that in runs 2 and 3 can probably be attributed for the most part to the presence of molybdenum, which, in batch tests (Sec. 5.2) interfered severely with uranium stripping. The rate of caustic addition was adequate to maintain the sodium hydroxide concentration in the recycle solution at ~0.5 M. Consumption of sodium hydroxide was ~0.7 lb per pound of U_3O_8 recovered.

The uranium products, after being washed and dried at 110°C, contained 75-79% U_3O_8 and only 0.001% molybdenum but exceeded specifications for vanadium by a factor of about 2:

Run Time, hr	Product Analyses, % U_3O_8	V_2O_5/U_3O_8	Mo
2	78.5	3.1	<0.001
4	77.8	2.7	0.001
6	79.4	3.4	0.001
8	77.9	3.0	0.001
10	75.6	4.5	0.001
12	77.0	3.9	0.001
14	75.9	4.0	0.001

Uranium loss in the filtrate was <0.05%.

8.0 EXTRACTION OF URANIUM FROM A MILL LIQUOR

Attempts to extract uranium from a carbonate liquor received from a western mill (designated as "Plant E") were relatively unsuccessful owing to interference from sulfate, chloride, thiocyanate, molybdenum, vanadium, and organic matter present in the liquor. Because of the difficulties in the batch extraction tests, the "Plant E" liquor was not processed in continuous equipment.

The liquor was dark brown in color owing to dissolved organic matter (probably sodium humates). Analysis showed:

	Analysis, g/liter		Analysis, g/liter
U	3.6	SO_4	50
CO_3	20	Cl	1.4
HCO_3	13	NO_3	<0.04
V	0.21	PO_4	0.11
Mo	1.8	SCN	0.8
Si	0.07		

pH 10

Determination of organic material[10] by oxidation with NaOCl showed organic equivalent to NaOCl at 0.24 equivalent per liter of liquor.

In initial extraction tests (Table 8.1) with Aliquat 336, the organic matter in the liquor was transferred almost quantitatively to the solvent phase and uranium extraction was ineffective. The organic material was not extracted by the diluent alone, indicating that extraction occurred as a result of reaction with the quaternary extractant. Since, in some cases, large amounts of the quaternary-organic complex precipitated from the diluent, it is evident that the organic material should be removed from the liquor prior to extraction.

Table 8.1. Extraction of Uranium from Unadjusted Mill Liquor

Organic: 0.075 N Aliquat 336 carbonate in kerosene + 7.5 vol % TDA
Aqueous: "Plant E" liquor (analysis on p. 34)
Contact time: 5 min

Phase Ratio, a/o	Solvent Color	Uranium, g/liter Organic	Uranium, g/liter Aqueous	Uranium Extraction Coefficient (E_a^o)
0.25/1	brown	0.56	1.4	0.4
0.5/1	brown	0.46	2.6	0.2
1/1	brown	0.23	3.4	0.07
2/1	brown	0.038	3.6	0.01
5/1	colorless[a]	<0.001	3.6	<0.001
10/1	colorless[a]	<0.001	3.7	<0.001

[a] Brown solids at interface, presumably quaternary-organic complex.

8.1 Removal of Organic Matter from the Liquor

Several materials which previous studies[10] had shown to be useful for adsorbing organic material from ore carbonate liquors were examined briefly. Of the materials tested, activated carbon and magnesium oxide were the most effective, the former also being useful in removing thiocyanate (results not listed) which was shown (Sec. 8.2) to be detrimental to uranium extraction.

In a column sorption test with 20-50 mesh Type OL activated carbon (Pittsburgh Coke and Chemical Co.), breakthrough of organic material was rapid (Table 8.2). There was no apparent correlation between the organic content of the effluent, as determined by titration with NaOCl, and its color, since the former test showed breakthrough at only 2-4 column volumes whereas the color of the effluent did not approach that of the feed liquor until ~12 column volumes of liquor had passed the column.

Table 8.2. Adsorption of Organic Material on Activated Carbon

Carbon column: 19 in. bed of 20-50 mesh Type OL activated carbon in 1 in-dia column
Liquor: "Plant E" liquor (analysis on p. 34)
Liquor flow rate: ~7.5 ml/min (22 gal/ft^2/hr); effluent collected in 250-ml increments (~1 column volume)

		Effluent Analysis	
Effluent Increment	Total Effluent, column vol	Uranium, g/liter	Organic NaOCl Equivalent, equiv/liter
Head Liquor	-	3.5	0.24
1	1	-	-
2	2	3.5	0.046
3	3	-	-
4	4	3.6	0.24
5	5	-	-
6	6	3.6	0.22
7	7	-	-
8	8	3.6	0.23
9	9	-	-
10	10	3.5	0.25
11	11	-	-
12[a]	12	3.6	0.24
13	13	-	-
14	14	3.5	0.24
15	15	-	-
16	16	3.6	0.24

[a] At this point the color of the effluent, which had been gradually increasing in color but was still relatively light, changed rather suddenly to the very dark brown color of the feed liquor.

Attempts to regenerate the column with dilute caustic solution and with NaOCl solution (~2.5% available Cl_2) were unsuccessful, both solutions tending to cause disintegration of the carbon.

8.2 Effect of Thiocyanate on Uranium Extraction

In extractions with 0.075 N Aliquat 336 carbonate in kerosene + 7.5 vol % TDA from a carbonate solution containing thiocyanate, extraction of the thiocyanate was almost quantitative and interference with uranium extraction was severe:

Phase Ratio, a/o	Analysis, g/liter Organic U	Aqueous U	Aqueous SCN	Uranium Extraction Coefficient (E_a^o)
0.25/1	0.42	0.02	<0.001	21
1/1	1.6	0.43	<0.001	4
4/1	0.002	2.0	0.05	0.001

The aqueous solution used in this test was 0.4 M Na_2CO_3 — 0.1 M $NaHCO_3$ containing 2 g of uranium, and 1.1 g of SCN^- per liter.

8.3 Extraction Isotherms

Isotherms (Fig. 8.1) for the extraction of uranium from Plant E liquor were determined by cascading the solvent against fresh volumes of liquor. With liquor (pH 10) as received, uranium loading of the solvent reached a maximum of ~0.5 g/liter and then decreased to <0.1 g/liter as the quaternary became loaded with organic material, chloride, and thiocyanate. Results were appreciably better with liquor (pH 10) that had been treated with a large excess of activated carbon to remove organic material (and thiocyanate), but the maximum uranium loading (~0.7 g/liter) was still a factor of 3-4 lower than is obtained with "pure" carbonate solutions. Increasing the carbon-treated liquor pH to 11 with caustic to minimize vanadium competition increased the maximum uranium loading to ~1 g/liter.

Owing to the complications encountered in the batch extraction tests, plans for a continuous test with the Plant E liquor were abandoned.

9.0 PROCESS EVALUATION

The buildup in carbonate ore leach liquors of contaminants which interfere with solvent extraction is subject to some control. As mentioned before (Sec. 8.1), accumulation of dissolved organic material can be minimized by treating the liquor with an adsorbent. The concentration of sulfate, chloride, and molybdenum can be decreased by increasing the amount of barren liquor bled from the system above the ~5% bleed* used in "Plant E". Interference from vanadium can be decreased by increasing the pH of the liquor prior to extraction, although thus far, separations from vanadium have not been satisfactory. All these complications, however, detract from the potential usefulness of the process and it appears that solvent extraction with quaternary extractants has little chance of becoming competitive with the caustic precipitation process now used in western carbonate leach mills.

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*The loss of carbonate liquor to the ore tailings in the third stage filtration (Fig. 2.1) is estimated to be equivalent to an ~5% bleed.

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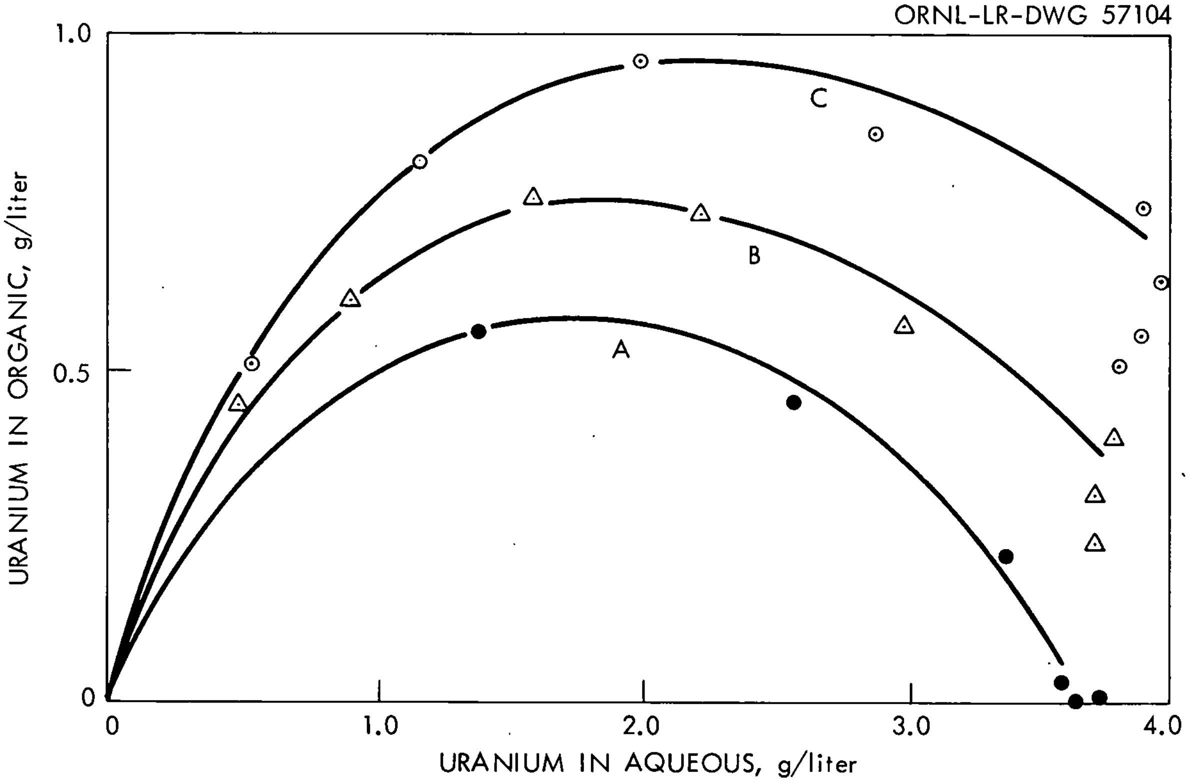

Fig. 8.1. Uranium extraction from mill carbonate liquor. Organic: 0.075 N Aliquat 336 carbonate in kerosene + 7.5 vol % TDA. Aqueous: Plant E liquor; A, as received, pH 10; B, organic material removed by contact with activated carbon, pH 10; C, organic material removed by contact with activated carbon, pH adjusted to 11 with caustic.

10.0 REFERENCES

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3. D. J. Crouse, K. B. Brown, W. D. Arnold, J. G. Moore, and R. S. Lowrie, "Progress Report on Uranium Extraction with Organonitrogen Compounds," ORNL-2099 (June 15, 1956).

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7. D. J. Crouse and K. B. Brown, "Amine Extraction Processes for Uranium Recovery from Sulfate Liquors," ORNL-1959 (Nov. 18, 1955).

8. C. F. Coleman, K. B. Brown, J. G. Moore, and D. J. Crouse, "Solvent Extraction with Alkyl Amines," Ind. Eng. Chem., 50: 1756 (1958).

9. K. B. Brown, C. F. Coleman, D. J. Crouse, and A. D. Ryon, "Progress Report on Raw Materials for September 1957," ORNL-2443.

10. D. R. George and J. T. Lynch, "Control of Organics in Carbonate Leaching Circuits," WIN-103 (July 25, 1958).

11. B. S. Weaver and D. E. Horner, "Distribution Behavior of Neptunium and Plutonium between Acid Solutions and Some Organic Extractants," J. Chem. Eng. Data, 5: 260 (1960).

11.0 APPENDIX

11.1 Description of Compounds

The structure, source of supply, and other pertinent descriptive material for the quaternary ammonium compounds used in these studies are given in Table 11.1.

11.2 Description of Equipment Used in Continuous Tests

The mixer-settlers used in the extraction system were of the type described in ORNL-2720, p. 57. In the stripping system the line connecting the mixer and settler of a given stage entered the mixer near the bottom and was inclined downward toward the settler to ensure more effective discharge from the mixer of the precipitate slurry solids.

Information on the size of the mixers and settlers used in the continuous runs is given in Table 11.2. It should be noted that the solution contacting times and settling areas used in these tests are not necessarily optimum for the process but were dictated to a great extent by the size of contacting equipment and pumps available.

Solution flows were controlled with flowrators or micro-bellows pumps, and slurry streams were transferred with finger pumps.

Table 11.2. Size of Equipment Used in Continuous Runs

System	Working Volume, ml Mixer	Working Volume, ml Settler	Settler Settling Area, in.^{2}
Extraction	250	450	5.9
Stripping	1120	2120	12.5
Product settling tank	-	~2000	10.2

11.3 Other Potential Applications for Quaternary Extractants

The quaternary extractants offer opportunity for extending solvent extraction metal recovery techniques to treatment of basic* solutions, an area where the organophosphorus acids and primary, secondary, and tertiary amines are ineffective. For example, in addition to uranium, the data on molybdenum and vanadium extraction (Sec. 4.2) suggest that these extractants should be useful for scavenging these elements from basic process

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*The quaternaries are also, of course, effective extractants for certain metals from acid solutions, particular attention thus far having been given to extraction of certain metal nitrates.[11]

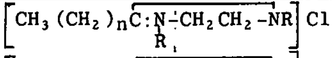
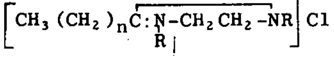
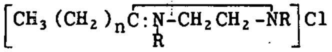
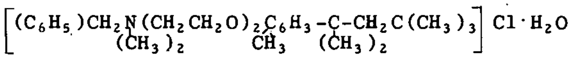
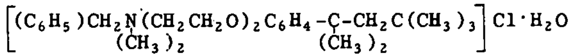
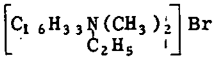
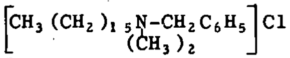
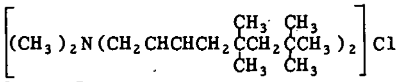
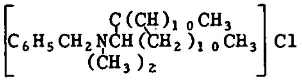
liquors. With respect to vanadium, other workers have recently studied (General Mills Technical Bulletin CDS3-60) more intensively the use of Aliquat 336 for recovering vanadium from various solutions. The strong affinity of the quaternaries for nitrate (and chloride) suggest the possibility of their use for removing this anion from waste basic liquors. In addition, of course, the quaternaries might also be useful for the recovery of certain other alkali-soluble metals. Thus far, only tungsten has been examined and only briefly. In a test with 0.1 N Quaternary B-104 carbonate, significant extraction of tungsten from 0.5 M Na_2CO_3 solution (phase ratio 1/1) was obtained although the extraction coefficient was relatively low:

Tungsten Analysis, g/liter			
Head Solution	Organic	Aqueous	Extraction Coefficient (E_a^o)
1.0	0.44	0.54	0.8

In a second test with the same solvent and 0.5 M $NaHCO_3$ solution containing ~0.5 g per liter each of tungsten and molybdenum, molybdenum was extracted preferentially, the separation factor (ratio of the extraction coefficients) being 1.5 under these conditions:

Final pH	Analysis, g/liter				Extraction Coefficient (E_a^o)	
	Organic		Aqueous			
	W	Mo	W	Mo	W	Mo
8.7	0.17	0.21	0.34	0.28	0.50	0.75

Table 11.1. Description of Compounds

Quaternary	Source[a]	Formula	Description by Vendor	Theoret Equiv Wt
Quaternary S	A	 $\left[CH_3(CH_2)_nC{:}N(R)-CH_2CH_2-NR\right]Cl$	-	455
Quaternary Q	A	 $\left[CH_3(CH_2)_nC{:}N(R)-CH_2CH_2-NR\right]Cl$	-	-
Quaternary C	A	 $\left[CH_3(CH_2)_nC{:}N(R)-CH_2CH_2-NR\right]Cl$	-	370
Hyamine 10X	RH	 $\left[(C_6H_5)CH_2N(CH_3)_2(CH_2CH_2O)_2C_6H_3(CH_3)-C(CH_3)_2-CH_2C(CH_3)_3\right]Cl\cdot H_2O$	Pure monohydrate salt	480
Hyamine 1622	RH	 $\left[(C_6H_5)CH_2N(CH_3)_2(CH_2CH_2O)_2C_6H_4-C(CH_3)_2-CH_2C(CH_3)_3\right]Cl\cdot H_2O$	Pure monohydrate salt	466
Trimethylphenylammonium chloride	EK	$\left[C_6H_5N(CH_3)_3\right]Cl$	-	172
Cetyldimethylethyl-ammonium bromide (Ammonyx DME)	Q	 $\left[C_{16}H_{33}N(C_2H_5)(CH_3)_2\right]Br$	75% solution	378
Cetyltrimethyl-ammonium bromide	M	$\left[(CH_3)_3N(CH_2)_{15}CH_3\right]Br$	-	364
Cetyldimethylbenzyl-ammonium chloride	M	 $\left[CH_3(CH_2)_{15}N(CH_3)_2-CH_2C_6H_5\right]Cl$	-	396
Cetylpyridinium chloride	M	$\left[CH{:}CHCH{:}CHCH{:}N(CH_2)_{15}CH_3\right]Cl$	-	339
Laurylpyridinium chloride	M	$\left[CH{:}CHCH{:}CHCH{:}N(CH_2)_{11}CH_3\right]Cl$	85-90% solution	283
Tributyllauryl-ammonium bromide	OR	$\left[(C_4H_9)_3N(CH_2)_{11}CH_3\right]Br$	-	435
Quaternary B-104	RH	 $\left[(CH_3)_2N(CH_2CHCHCH_2C(CH_3)_2CH_2C(CH_3)_2CH_3)_2\right]Cl$	65% solution in isopropyl alcohol	414
Aliquat 336	GM	$\left[R_3NCH_3\right]Cl$, alkyl groups are mixed n-octyl and n-decyl	75% solution	-
N-Benzyl-N-N-dimethyl-1-undecyldodecyl ammonium chloride	GM	 $\left[C_6H_5CH_2N(CH_3)_2CH(C(CH)_{10}CH_3)(CH_2)_{10}CH_3\right]Cl$		

[a] Source of compounds:

A	Alrose Chemical Co., Providence, R. I.	O	Onyx Oil and Chemical Co., Jersey City, N. J.
EK	Eastman Kodak Co., Rochester, N. Y.	RH	Rohm and Haas Co., Philadelphia, Pa.
GM	General Mills, Inc., Kankakee, Illinois	OR	Oak Ridge National Laboratory

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