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RAW MATERIALS PROCESS TESTING PROGRAM

SEMIANNUAL PROGRESS REPORT

JULY 1, 1954, TO DECEMBER 31, 1954

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RAW MATERIALS PROCESS TESTING PROGRAM

SEMIANNUAL PROGRESS REPORT

JULY 1, 1954, TO DECEMBER 31, 1954

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RAW MATERIALS PROCESS TESTING PROGRAM
SEMIANNUAL PROGRESS REPORT
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SUMMARY

The raw materials process testing program was started July 1, 1954, to supplement the work of the Uranium Chemistry of Raw Materials Section* in developing solvent extraction processes for the recovery of uranium from ores. During the first six months, two of these processes were studied, both of which were designed to extract uranium from liquors of the type derived by leaching ores with sulfuric acid. These are: the Amine Extraction Process and the Slurry Extraction Process.

The amine extraction process utilizes a 0.1 molar solution of a high molecular weight secondary amine dissolved in an organic solvent such as kerosene as the uranium extraction agent. The work on this process may be summarized as follows:

1. The technical feasibility of the process was demonstrated in a complete test array under continuous flow conditions.

2. The results of the extraction studies showed that, over the range of compositions that cover most domestic ores, a satisfactory uranium concentrate was produced with greater than 99.9% recovery of uranium in a small test array using only four mixer-settlers in the extraction section and two in the stripping section.

3. Rohm and Haas EB765-2 and Armeen 2-12 were the only amines tested as uranium extraction agents. Both are secondary amines and both were suitable agents for extraction of uranium from sulfuric acid leach liquors.

The results of preliminary studies on the slurry extraction process showed that an organic to aqueous phase ratio of 4:1 or greater was necessary to prevent the formation of a stable emulsion. About 97% of the uranium was extracted from the slurry with a 0.1 molar soln. of di(2-ethylhexyl)phosphoric acid in kerosene after 40 seconds of contacting in batch tests. The principal problem was found to be the relatively high entrainment of organic in the slurry raffinate.

---

*K. B. Brown, Supervisor.

INTRODUCTION

For several years Oak Ridge National Laboratory has maintained a research program on uranium raw material chemistry.* One portion of the program has been the investigation and evaluation of different reagents for the separation of uranium from various aqueous systems by solvent extraction. The results of this work indicated that specific types of amines[1] and organophosphorus compounds, dissolved in an organic carrier such as kerosene, were suitable for the extraction of uranium from sulfate liquors of the type derived by sulfuric acid leaching of uranium ores. Moreover, under proper conditions, the reagents** are selective and the uranium extraction coefficients are such that only 2 to 4 equilibrium contactings are needed to remove essentially all of the uranium from solution. Subsequently, chemical development studies were initiated for the purpose of demonstrating feasibility of each of the process steps involved in extracting uranium from the sulfate leach liquors that are produced in many of the raw materials processing operations. Although these development studies were not complete in detail, the results indicated that the process technology was feasible and that a concurrent engineering development effort was warranted.

On July 1, 1954, a Raw Materials Process Testing Program was initiated as a separate but closely integrated effort to supplement with engineering studies the work of the Uranium Chemistry of Raw Materials Section.*** The program has been planned to test both the technical and economic feasibility of various extraction processes, and to ultimately provide the design information needed to install extraction facilities in an existing process, or to build a new plant incorporating processes based on the solvent extraction technique.

---

*This program has been under the direction of K. B. Brown.

**It is expected that several amines and at least one dialkyl phosphoric acid of the desired types will become commercially available provided that a definite market can be established.

***The work of the chemistry group is continuing with the objective of providing more selective extraction agents, improved stripping processes, reagent stability data, etc. Much of the work has been successfully completed in the laboratory but, due to manpower limitations within the engineering group, not all of the new flow sheets have been included in the process test program.

SCOPE AND OBJECTIVES OF THE WORK

Two solvent extraction processes for the recovery of uranium from sulfuric acid leach liquors have been studied in the process testing work. These are: the Amine Extraction Process and the Slurry Extraction Process. Figure 1 depicts a generalized flow diagram showing the basic steps of both processes beginning with the leach operation. Not shown are the crushing, sampling, and grinding steps that precede the leach operation.

From the engineering viewpoint the unit operations that are employed in the extraction and stripping steps for both processes are essentially the same although the chemistry of these steps differs for the two processes. In both, the uranium bearing liquor is passed through three to four equilibrium contacting stages, countercurrent to the organic phase, which extracts essentially all of the uranium from the leach liquor and the raffinate is neutralized and pumped to the waste disposal pond. The organic extract is then contacted, under the proper conditions, with an aqueous solution of an acid, base, or a salt, to transfer or strip the uranium from the organic to the aqueous phase. The barren organic is pumped back to the extraction operation to start another cycle. Uranium is precipitated from the strip solution, filtered, washed, dried, and packaged for shipping.

The two processes differ in the following respects:

The Amine Extraction Process employs a clarified leach liquor which is produced by passing the leach slurry through a sands removal operation and a clarification step, both of which utilize gravitational settling in a battery of individual units that are arranged for countercurrent washing with water so that the loss of soluble uranium is minimized. The organic phase consists of an amine dissolved in kerosene. The active component of the strip solution may be either a salt or a base. Specific compositions of both the organic extract and the strip solution that have been used in the test work will be given in the presentation of the experimental work.

The Slurry Extraction Process is designed to eliminate either the cost of clarification by employing a slurry from which the heavy particles of sand have been removed, or the costs of both sands slime separation and clarification by employing the slurry direct from the leach tanks. The organic

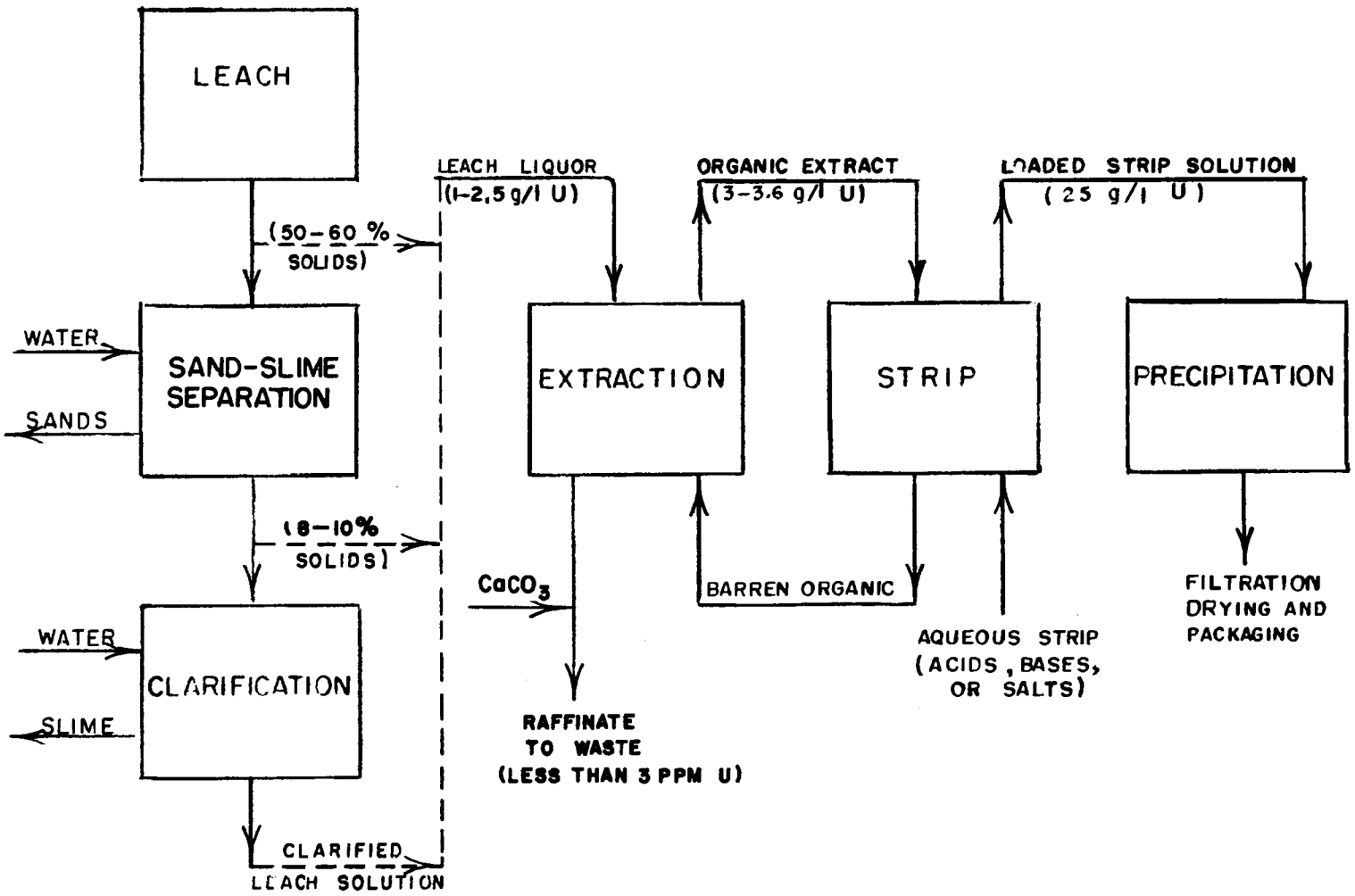


FIG. 1. GENERALIZED FLOW DIAGRAM FOR SOLVENT EXTRACTION PROCESSES

phase consists of an organophosphorus compound dissolved in kerosene. The active component of the strip solution may be either an acid, a base, or an acidic salt solution.

The objectives of the work on both processes are:

1. to prove process feasibility by carrying out the important steps of the process on a continuous basis.

2. to evaluate the effects of operating variables on the extraction efficiency, over-all recovery, and product quality.

3. to demonstrate the final operation in a complete pilot plant test array, employing a variety of domestic ores.

4. to make an economic comparison of the costs of the processes with the costs of existing and proposed processes.

The experimental work carried out during the first six months toward achieving these objectives is described in the following sections. The report of progress made on the cost evaluation studies is covered in a separate document which will have a more limited distribution than this report.

Since the work on the development of the amine extraction process was well advanced at the outset of the process test program, the major portion of the engineering effort (about 90%) was expended upon this process. In the future the slurry extraction process will receive a greater proportion of the effort than it did during the past period.

PART I: THE AMINE EXTRACTION PROCESS

An amine extraction process was recommended in some detail by the Uranium Chemistry Section as a basis for the start of the testing program.

The process employed a 0.1 molar solution of Armeen 2-12 dissolved in Amsco G containing 5 volume percent of capryl alcohol as the extraction agent. Armeen 2-12 (Armour Chemical Division, Chicago) is a mixture of secondary amines: R_2NH, in which the principal constituent is di-dodecyl (di-lauryl) amine, and R in the remaining amines varies from 8 to 16 carbon atoms. Amsco G (American Mineral Spirits Co.) is an aromatic petroleum fraction.

The strip solution was a 10 percent aqueous solution of sodium carbonate. The loaded strip solution was neutralized with sulfuric acid, heated to drive off carbon dioxide, and the uranium precipitated as sodium diuranate by the addition of sodium hydroxide.

The ratio of aqueous feed, organic, and strip were 20:8:1, respectively.

A scrubbing step was also proposed as a means for removing Fe^{+3} from the organic extract in the event its concentration was high enough to cause phase separation problems from ferric hydroxide precipitation in the stripping step. In this operation the extract is countercurrently contacted prior to the stripping step with dilute sulfuric acid at an aqueous to organic phase ratio of 1 to 5. The relatively small amount of scrub acid would be mixed with the acid used in the leaching step so that no over-all loss of uranium would result as a consequence of employing the scrubbing operation.

Later, an amine reagent (Rohm and Haas EB 765-2) that is readily soluble in kerosene and a direct stripping method was recommended for process testing by the chemistry section.

The engineering development of the process consisted of feasibility tests, extraction studies, stripping studies, mixing, and phase separation studies as described in the following sections.

PROCESS FEASIBILITY

The first objective of the test work was to demonstrate feasibility of the process recommended by the chemistry group in July, 1954, by carrying out the important operations in small-scale equipment on a continuous basis using a synthetic leach liquor. This was done by making a series of runs in a test array that included the extraction, scrubbing, stripping, and precipitation operations as shown in Figure 2. A secondary objective of the runs was to evaluate the efficiency of the 6-inch mixer-column extractor over a range of flow rates and impeller speeds. The scrubbing and stripping conditions were varied only when necessary to achieve adequate performance.

A description of the equipment and the results obtained from five test runs are given in the following paragraphs. More complete information on the design of the test array may be found in ORNL CF-54-11-185.[2]

Equipment Description

Extraction. The extraction of uranium from the synthetic leach liquor in all runs was accomplished by countercurrently contacting it with the organic phase in a vertical multistage mixer-column similar to that described by Oldshue and Rushton.[3] The column consisted of a section of a 6-inch diameter Pyrex glass pipe, compartmented into ten sections by horizontal plates spaced 3 inches apart. The plates contained openings, 3-1/4 inches in diameter, through which a drive shaft fitted with ten equally spaced turbine type impellers was placed. The impellers were 3 inches in diameter with 4 blades, and they were positioned at the center of the compartments. The horizontal plates were fastened to four equally spaced vertical baffles, so that the unit could be readily disassembled by removing the shaft impeller assembly and the baffle-horizontal-plate assembly. A variable speed drive provided the means for varying the impeller speed over the range: 0 to 900 rpm. In run 4 every other horizontal plate and impeller were removed to provide five 6-inch-deep compartments with the impellers located at the center of the compartments.

Scrubbing. Two types of contactors were tested in the scrubbing operation: a spray column and a multistage mixer column. The spray column was a vertical 7-foot section of 3-inch diameter Pyrex glass pipe containing a 6-inch long section of 316 S.S. Yorkmesh Demister in the bottom of the

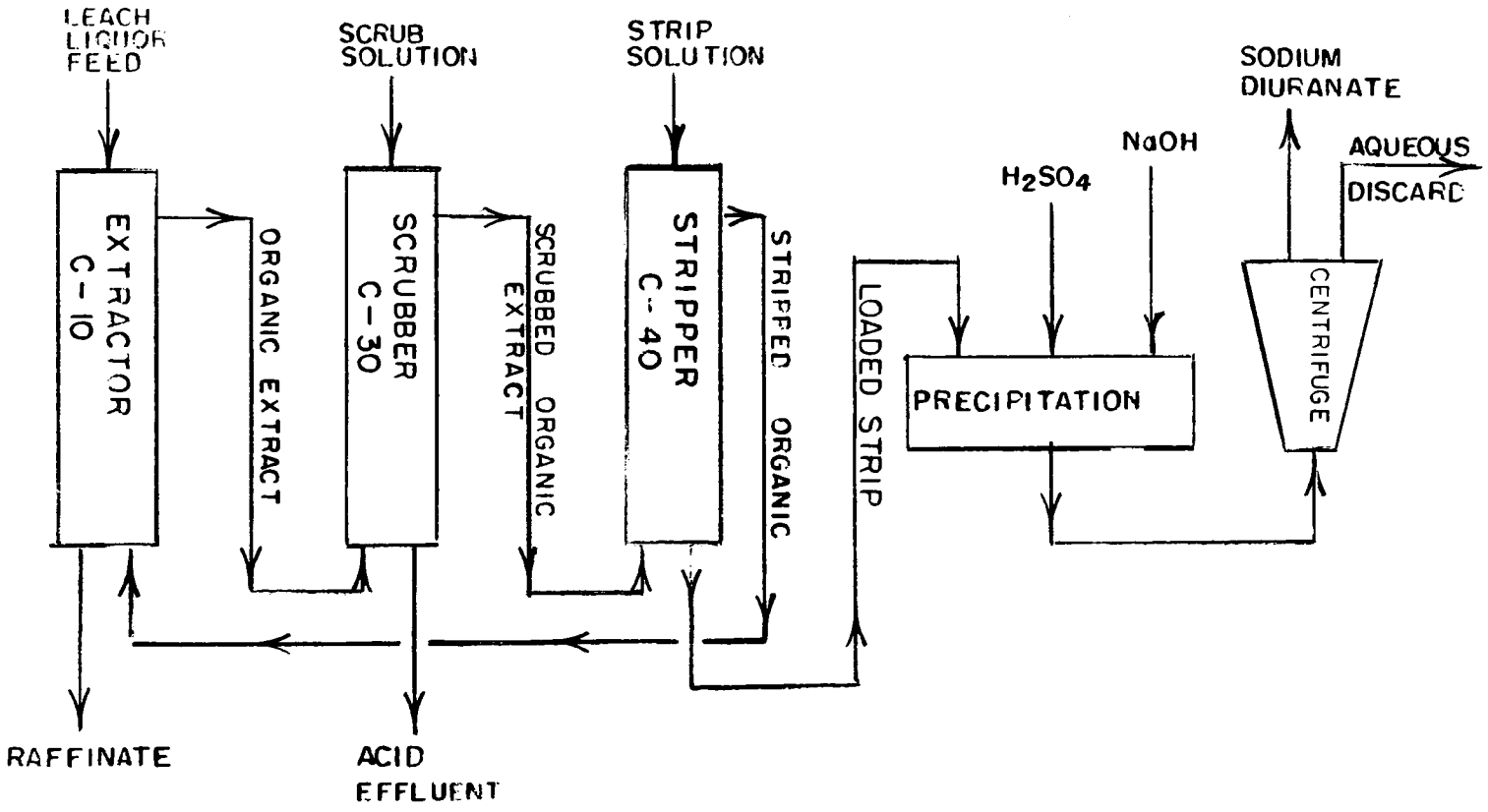


FIG. 2. FLOW DIAGRAM - AMINE EXTRACTION PROCESS FEASIBILITY TESTS

column to disperse the organic phase in the continuous aqueous phase. The mixer column was a 4-inch diameter, scaled-down replica of the 6-inch column described previously.

Stripping. Two types of contactors were also tested in the stripping operation: the 4-inch mixer column previously described and two baffled mixer tanks connected in series. Each of the tanks had an operating capacity of about 9 gallons. Agitation was provided by a 6-inch turbine type impeller rotating at a speed of about 300 rpm.

Operation of the Test Array

Prior to the start of a run the synthetic leach liquor, organic phase, scrub acid, and strip solution were made up to the desired composition in amounts sufficient to support one or more runs. Since the organic phase flow was cyclic, a total volume of only about 30 gallons was maintained in four feed tanks and two small head tanks. Usually only one of the organic feed tanks was used during a run and any additional amount of organic extractant that was needed to make up for withdrawals and accidental spills was added from one of the reserve tanks.

The composition of the aqueous feed solution simulated that of a typical clarified leach solution obtained by leaching Marysvale ore with sulfuric acid at the Vitro Uranium Company, Salt Lake City, Utah, in 1950. The organic phase consisted of a 0.1 molar solution of Armeen 2-12 dissolved in Amsco G containing 5 vol. % of capryl alcohol. The composition of the aqueous and organic phases employed in the five runs is shown in Table 1.

To start the run the extraction, scrubbing, and stripping units were filled with the corresponding aqueous phase and the phase flow rates were adjusted to the desired value. When countercurrent flows were employed the aqueous phase was continuous. The speed of the impellers in the extraction column was adjusted to 90 percent of the value at which flooding occurred. In run 3 tests were also made at 84 percent and 64 percent of flooding. Samples from the aqueous raffinate, organic extract, scrubbed organic and stripped organic were collected for analysis on an hourly basis. The results of earlier runs showed that steady state throughout the array was reached after about ten volume changes in the extractor (5 gallons holdup volume). In these runs the analysis of the last two samples that were collected during the run were averaged and these values are reported in the tabulated data.

TABLE 1. COMPOSITION OF THE LEACH LIQUOR

Run No.	pH	Analysis, g/l. U	Fe	Al	SO_4	F	PO_4
1	1.0	1.2	4.9	3.5	34.8	1.3	2.1
2	1.0	1.2	4.6	2.6	36.7	1.4	2.0
3	1.0	1.2	5.1	3.0	43.7	1.5	2.1
4	1.0	1.3	5.2	3.3	43.5	1.2	2.2
5	1.0	1.0	5.0	3.0	38.8	1.3	2.0

Composition of the Organic Phase

	Armeen 2-12 moles/l.	U, g/l. (average)
1	0.10	0.002
2	0.10	0.004
3	0.10	0.032
4	0.10	0.007
5	0.10	0.001

Composition of Scrub and Strip Solutions

	H_2SO_4 in Scrub soln.; g/l.	Na_2CO_3 in Strip soln.; g/l.
1	25.9	176.0
2	33.4	110.6
3	33.4	87.1
4	33.4	93.1
5	32.5	96.1

The important conditions and the data collected during the five runs are shown in Table 2.

Results

Extractor. The efficiency of the extraction unit was calculated with the aid of a McCabe-Theile type diagram.[4] The equilibrium curve was determined from the results of equilibrating various ratios of organic extractant and aqueous feed liquor and analyzing the separated phases for uranium. The operating line was established from the analysis of the organic extractant entering and the raffinate leaving the column with the slope equal to the aqueous to organic phase flow ratio. The number of stages required to effect the observed separation were then measured graphically and the results were expressed as the percent efficiency for each compartment. As an example, under the conditions of run 1, a total of 2.2 stages would be required to obtain the observed separation as shown in Figure 3. Since 10 compartments were employed, the compartment efficiency was 22 percent.

The results indicate that the extraction efficiency in the mixer column is proportional to the degree of agitation and that it is only slightly affected by the throughput rate. At 60 gph aqueous flow the efficiency increased from 7 to 16 percent as the agitator speed was increased from 80 to 112 rpm.

The effect of increasing the compartment height is shown by comparing the results of runs 3 and 4. In both of these runs the aqueous and organic flow rates were 60 and 24 gph, respectively, while the compartment height was 3 inches in run 3 and 6 inches in run 4.

Under the conditions of run 3, the compartment efficiency was 16 percent and the number of compartments needed to obtain the desired separation was 12.5. In comparison, the corresponding values for run 4 were: 20 percent and 10 compartments. The total compartment heights needed for runs 3 and 4 were 37.5 inches and 60 inches, respectively.

Extrapolating between the 20 gph aqueous feed rate and the 60 gph rate with the aid of the column flooding curves[5] indicates that the maximum total throughput that may be expected in a mixer column would be about 280 gallons per hour per square foot of cross sectional area (column) with 20 percent compartmental efficiency. This throughput is about 53 percent of that obtained by Oldshue and Rushton employing a similar mixer column for the extraction of acetic acid from water by methyl isobutyl ketone (compartment efficiency = 53%).[3]

TABLE 2. OPERATING DATA; RUNS 1 THROUGH 5

	Run Number						
	1	2	3a	3b	3c	4	5
Extraction							
Duration of runs, hours	7.8	6.5	-	6.5	-	3.3	5.3
Aqueous flow rate, gph	20	20	60	60	60	60	100
Organic flow rate, gph	8	8	24	24	24	24	40
No. complete cycles, organic phase	3.4	1.7	-	4.9	-	2.3	8.6
Agitator speed, rpm	133	133	112	105	80	130	86
Analysis,							
Aqueous feed; U, g/l.	1.2	1.2	1.2	1.2	1.2	1.3	1.0
Organic extractant; U, g/l.	0.002	0.004	0.04	0.029	0.028	0.007	0.001
Aqueous raffinate; U, g/l.	0.002	0.004	0.032	0.086	0.40	0.07	0.25
Organic extract; U, g/l.	2.4	2.8	2.5	2.4	1.1	2.8	1.8
Number of compartments	10	10	10	10	10	5	10
Compartment efficiency, %	22	20	16	10	7	20	8
Scrubbing[1/]							
Acid flow rate, gph	2.3[2/]	2.0	3.7[2/]	3.7[2/]	3.7[2/]	8[2/]	9.3
Organic flow rate, gph	8	8	24	24	24	24	40
Agitator speed, rpm	-	192	130	130	130	165	145
Analysis,							
Organic before scrub; Fe, g/l.	0.14	0.17	0.09	0.05	0.05	0.08	0.09
Organic after scrub; Fe, g/l.	0.16	0.02	0.06	0.02	0.02	0.04	0.04
Acid effluent; U, g/l.	0.17	0.18	-	0.14	-	0.18	0.04
U loss to scrub soln.; %	2.0	1.6	-	0.9	-	2.1	0.5
Stripping							
Aqueous flow rate, gph	2[3/]	2[4/]	-	6[4/]	-	3	10
Organic flow rate, gph	8	8	-	24	-	24	40
Residence time, minutes	8	53	-	18	-	42	23
Organic analysis							
Before strip; U, g/l.	2.3	2.7	-	2.4	-	2.8	1.8
After strip; U, g/l.	0.002	0.004	-	0.032	-	0.007	0.001

1/ Spray column in run 1, 4-inch mixer column in all others.
2/ Countercurrent phase flows.
3/ 4-inch mixer column.
4/ One mix-tank.

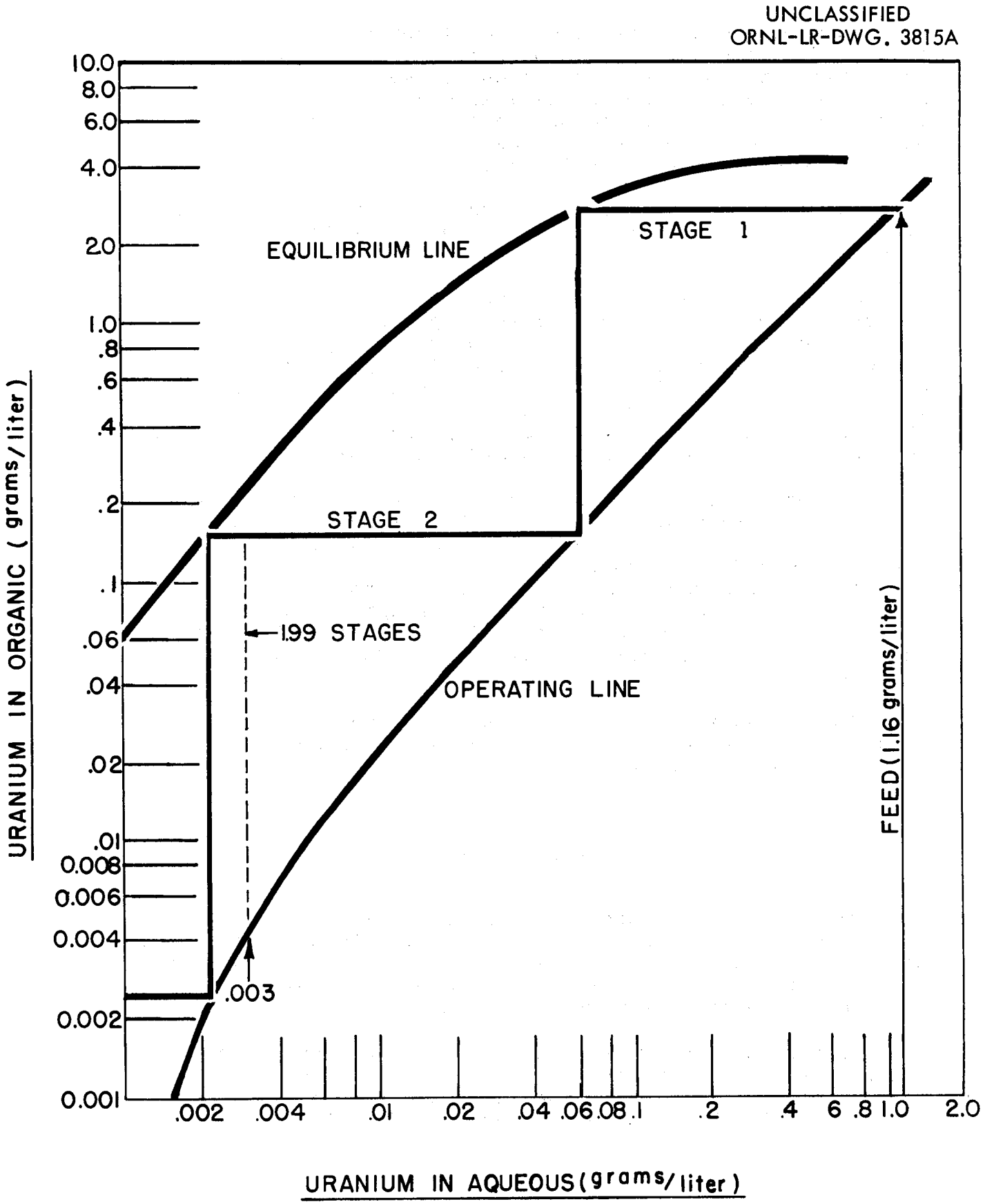


FIGURE 3. COMPUTATION OF STAGES FOR RUN I

In subsequent tests, the rate of separation of the organic and aqueous phases employed in the five runs was compared with that of the methyl isobutyl ketone, water, and acetic acid system under comparable conditions. In these tests the time required to obtain complete phase separation with the amine-aqueous system was 124 seconds as compared to about 30 seconds for the ketone-aqueous system.

In view of these results no further work with the multistage mixer column test array is planned for the immediate future.

Scrubber. The results of run 2 indicate that satisfactory scrubbing of iron from the organic extract was effected in the 4-inch diameter mixer column employing cocurrent phase flows and an impeller speed of 192 rpm. In comparison, only about 30 percent of the iron was removed from the organic phase in the spray column during run 1. The iron content of the organic extracts in the remaining runs was not high enough to warrant definite conclusions as to scrubbing efficiency.

Stripper. Satisfactory stripping was obtained in a cocurrent multistage mixer column with a residence time of 8 minutes in run 1. In run 5, the uranium content of the organic was reduced from 1.7 to 0.003 g/l. in a single mix tank with a residence time of 11 minutes and it was further reduced to 0.001 g/l. after passing through the second mix tank with a total residence time of 23 minutes. Stripping was incomplete in run 3, however, with a residence time of 18 minutes.

These results emphasize the need for the more fundamental studies of the effects of operating variables on the efficiency of the stripping operation.

LEACH LIQUOR VARIABLES

The treatment of uranium ores with sulfuric acid results in a leach liquor which contains several metals and anions in addition to uranium. The effect on the uranium extraction coefficient of a number of these possible contaminants was studied by the chemistry group in batch shakeout tests.[1]

Similar studies were needed on a larger scale and in a continuous, countercurrent system in order to more completely define the effect of variation in concentration of contaminants in the leach liquor on the number of contacting units

necessary to effect essentially complete extraction of uranium. Consequently, a series of sixteen runs were made employing countercurrent flow of the separated phases in a mixer-settler array. In these runs, the concentration of the ions: iron, vanadium, molybdenum, titanium, phosphate, fluoride, and sulfate were varied in the synthetic leach solutions and in two runs, the pH of the solution was adjusted to 0.5 instead of 1.0.

Equipment

The equipment employed in making the runs consisted of five mixer-settler units connected for countercurrent flow as shown in Figure 4. The aqueous feed was metered into unit 101 and it was pumped to succeeding units by means of airlifts located between the units. The organic phase was metered into unit 105 and flowed by gravity through the five mixer-settler units.

The mixers were 500 ml beakers (375 ml working volume) with four 1/4-inch baffles. Agitation was obtained with two, two-bladed turbines located on a common shaft and driven by a variable speed motor (0-600 rpm). The settlers were 500 ml beakers with adjustable gravity legs for level control. The units were small enough to permit attainment of steady state with less than 5 gallons of aqueous feed.

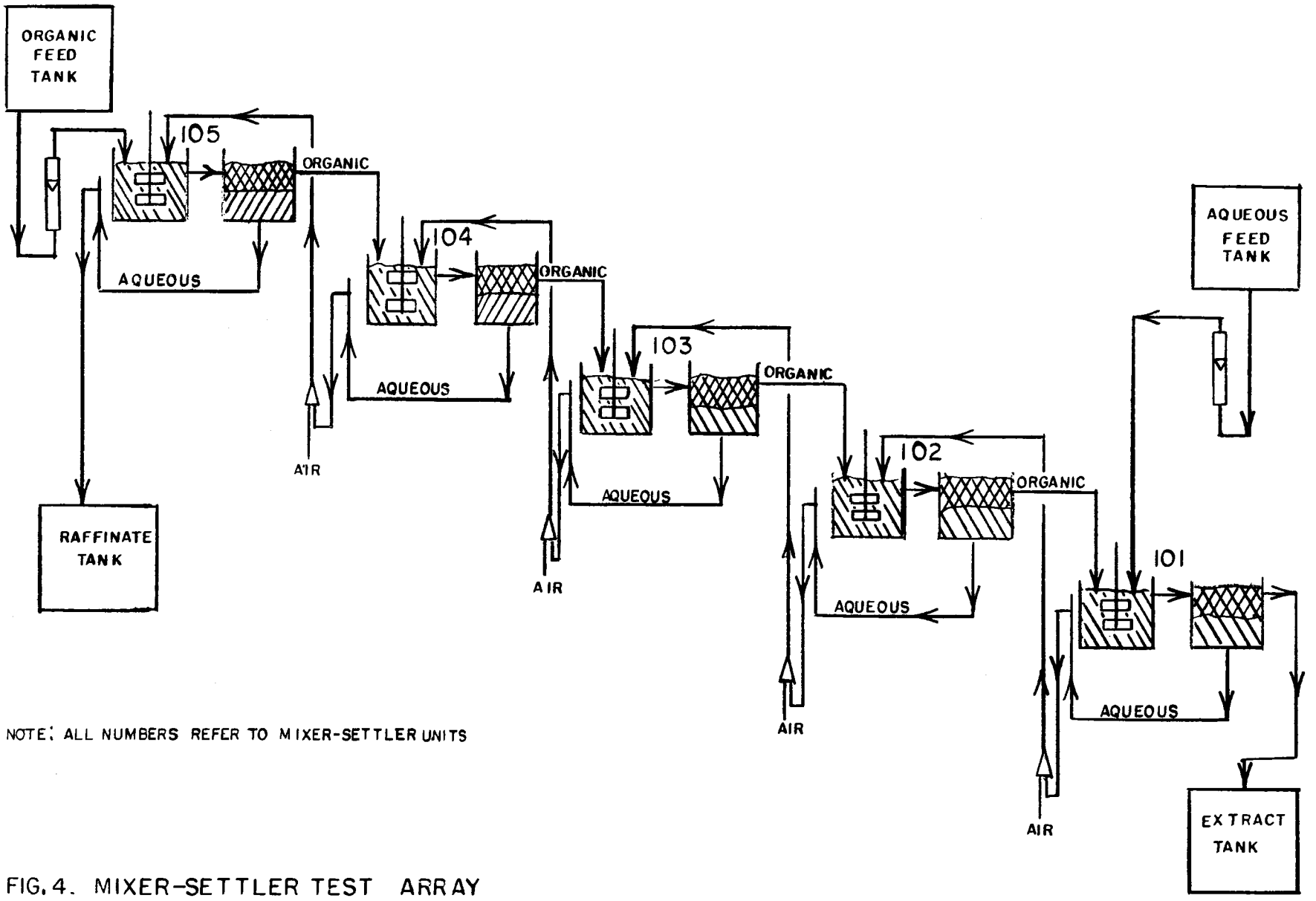
Operating Conditions

Batches of synthetic leach liquors were made using the composition of a typical Marysvale* liquor as a basis. To determine the effect of concentration of individual contaminants, the desired amount of contaminant was added to the standard liquor. The composition of the leach liquors and organic feed solutions used in the series is shown in Table 3.

It should be emphasized that the maximum concentration of the contaminants was higher in these tests than would be expected in actual leach liquors.

The organic phase was 0.1 molar Armeen 2-12 dissolved in Amsco G containing 5 volume percent capryl alcohol. After each run the organic phase was stripped batchwise with 10 percent Na_2CO_3 solution and analyzed before re-using.

*More properly a typical leach liquor composition at the Vitro plant in Salt Lake City in 1950 using Marysvale ore.



NOTE: ALL NUMBERS REFER TO MIXER-SETTLER UNITS

FIG. 4. MIXER-SETTLER TEST ARRAY

TABLE 3. AQUEOUS FEED AND ORGANIC PHASE COMPOSITIONS

Run No.	Aqueous Feed (g/l.)										Organic Phase		
	U	SO_4	pH	Al	Fe^{+3}	V^{+5}	PO_4	F	Mo	Ti	U (g/l.)	Fe (g/l.)	Amine M
1A	1.2	70	1.0	-	-	-	-	-	-	-	0.002	0.011	0.098
1B	1.2	69	1.0	-	-	-	-	-	-	-	0.002	0.043	0.098
2A	1.1	71	1.0	3.0	5.3	-	2.2	1.4	-	-	0.002	0.043	0.098
2B	1.2	66	1.0	3.1	5.0	-	2.0	1.4	-	-	<0.001	<0.001	0.102
3	1.1	72	1.0	3.1	15.0	-	2.4	1.6	-	-	0.001	0.027	0.099
4	1.1	71	1.0	2.8	15.0	-	-	-	-	-	<0.001	<0.001	0.102
5	1.2	69	1.0	3.1	5.3	-	21.0	1.3	-	-	0.002	0.008	0.098
6	1.2	68	1.0	3.1	5.2	-	2.3	4.9	-	-	0.002	0.008	0.098
7	1.2	118	1.0	3.1	5.1	-	2.2	1.5	-	-	0.001	0.003	0.098
8	1.2	69	0.5	3.0	4.9	-	2.1	1.3	-	-	0.001	0.049	0.096
9	1.2	75	1.0	3.0	4.9	-	2.0	1.2	1.1	-	<0.001	<0.001	0.099
10A	1.2	70	1.0	3.2	5.3	2.6	2.3	1.3	-	-	0.002	0.011	0.098
10B	1.2	67	1.0	3.0	5.4	2.5	2.2	1.3	-	-	0.014	0.018	0.104
11	1.2	65	1.0	3.1	5.4	-	2.4	1.4	-	0.5	0.005	0.007	0.098
12	1.2	115	1.0	3.2	16.0	2.6	5.2	4.3	0.92	0.5	0.001	0.003	0.098
13	1.2	114	0.5	3.2	16.0	2.1	5.4	5.1	0.91	0.5	0.005	0.007	0.098

In all runs the aqueous feed and organic phase flow rates were maintained constant at 3.0 liters per hour and 1.2 liters per hour, respectively. The agitator speed in the mixers was 450 rpm. In the first runs each mixer-settler was sampled hourly to determine the time required to reach steady state. It was found that 4 hours of uninterrupted operation was sufficient and, thereafter, each settler was sampled only after 4 hours to obtain the gradients throughout the five extraction units.

After the gradient samples were collected the contents of each mixer were agitated for an additional 30 minutes to obtain the equilibrium distribution of uranium and contaminates. Without exception, the analysis of the gradient samples checked those of the equilibrium samples showing that the efficiency of the mixer-settlers was very nearly 100 percent.

Results and Discussion

The uranium, iron, molybdenum, titanium and vanadium analyses of the samples that were collected after the system was at steady state are given in Tables 4, 5, and 6. A summary of the results from each run are reported in Table 7 which shows: (1) a description of the feed solution compared with a standard Marysvale leach liquor; (2) the number of mixer-settler units required to reduce the uranium content of the raffinate to 0.003 g/l.; (3) the organic extract analysis showing the concentration of uranium, iron, molybdenum, titanium, and vanadium in grams per liter.

Reproducibility. Runs 1, 2, and 10 were made in duplicate to test reproducibility of results by comparing the difference between the number of mixer-settler units (stages) needed to reduce the uranium content of the raffinate to 0.003 g/l. The maximum difference was 0.7 units (12 percent) which was observed in run 10.

Uranium Extraction. The number of mixer-settler units required to reduce the uranium content of the raffinate to 0.003 grams per liter was about 3 in all runs except 4, 12, and 13. In runs 4 and 12, about 4 units were needed while in run 13 about 5-1/2 units were estimated as being necessary. The conditions for runs 12 and 13 were essentially the same except that the pH of the leach liquor was 1.0 in run 12 and 0.5 in run 13. The results of laboratory studies of the effect of variation in pH of the leach liquor on the uranium

TABLE 4. URANIUM GRADIENTS (g/l.)

	Aqueous Phase					Organic Phase				
Run	101	102	103	104	105	101	102	103	104	105
1A	0.18	0.018	0.001	<0.001	<0.001	2.7	0.44	0.031	0.002	0.002
1B	0.30	0.021	0.001	<0.001	<0.001	2.6	0.66	0.056	0.004	0.001
2A	0.22	0.011	0.001	<0.001	<0.001	2.7	0.43	0.023	0.003	0.001
2B	0.14	0.010	0.003	0.001	0.001	3.0	0.40	0.023	0.005	0.003
3	0.23	0.031	0.002	0.001	0.001	2.9	0.69	0.080	0.017	0.014
4	0.41	0.081	0.012	0.002	0.001	2.5	1.2	0.26	0.036	0.011
5	0.35	0.033	0.004	<0.001	<0.001	3.1	0.92	0.14	0.016	0.003
6	0.32	0.027	0.002	<0.001	<0.001	3.1	0.79	0.070	0.005	0.002
7	0.28	0.024	0.003	<0.001	<0.001	3.0	0.91	0.071	0.007	0.002
8	0.28	0.020	0.002	<0.001	<0.001	2.7	0.59	0.044	0.005	0.001
9	0.64	0.098	0.006	0.001	0.001	2.5	1.6	0.12	0.013	0.002
10A	0.36	0.026	0.001	<0.001	<0.001	2.8	0.98	0.091	0.006	0.001
10B	0.66	0.058	0.005	<0.001	<0.001	3.0	1.8	0.28	0.024	0.006
11	0.24	0.015	0.001	0.001	<0.001	2.9	0.62	0.060	0.022	0.005
12	0.89*	0.15	0.019	0.003	<0.001	2.4*	2.2*	0.56*	0.078*	0.010
13	1.36*	0.65	0.27	0.052	0.008	2.2*	2.6*	1.6*	1.0*	0.15

*The presence of Mo interfered with the U analysis.

TABLE 5. IRON GRADIENTS

Run	Iron in Organic Phase (g/l.)				
	101	102	103	104	105
2A	0.030	0.15	0.16	0.16	0.19
2B	0.090	0.28	0.28	0.30	0.35
3	0.43	1.0	1.5	1.7	1.5
4	0.87	1.7	2.1	2.1	2.1
5	0.013	0.023	0.022	0.019	0.025
6	0.037	0.054	0.076	0.071	0.088
7	0.036	0.083	0.12	0.13	0.14
8	0.037	0.049	0.067	0.054	0.077
9	0.007	0.055	0.14	0.14	0.20
10A	0.079	0.11	0.17	0.17	0.27
10B	0.037	0.081	0.18	0.23	0.27
11	0.060	0.21	0.25	0.25	0.29
12	0.067	0.16	0.32	0.40	0.47
13	0.019	0.029	0.040	0.077	0.10

TABLE 6. MOLYBDENUM, TITANIUM, AND VANADIUM GRADIENTS

		Analysis (g/l.)									
		Aqueous Phase					Organic Phase				
Run	Ion	101	102	103	104	105	101	102	103	104	105
9	Mo	0.17	0.052	0.025	0.014	0.009	2.5	0.50	0.11	0.048	0.017
10A	V	2.9	2.9	2.8	2.9	2.4	1.3	0.91	0.96	0.65	0.56
10B	V	2.6	2.5	2.4	2.3	2.0	1.3	1.4	1.4	1.1	0.84
11	Ti	0.57	0.62	0.59	0.56	0.51	0.14	0.17	0.19	0.15	0.11
12	Mo	0.21	0.11	0.065	0.029	0.017	2.4	0.57	0.23	0.11	0.043
12	V	2.3	2.3	2.3	2.3	2.1	0.93	0.62	0.58	0.55	0.50
12	Ti	0.41	0.43	0.42	0.41	0.26	0.033	0.033	0.035	0.031	0.022
13	Mo	0.34	0.22	0.15	0.088	0.044	1.9	0.54	0.39	0.23	0.091
13	V	2.1	2.0	2.0	2.1	2.0	0.20	0.07	0.12	0.09	0.13
13	Ti	0.54	0.53	0.57	0.54	0.53	0.06	0.05	0.01	0.03	0.02

TABLE 7. SUMMARY OF EXTRACTION RESULTS

Phase ratio = 2.5 aq:1 org
Organic phase = 0.1 M Armeen 2-12 in Amsco G + capryl alcohol (5%)

Run No.	Description of Feed	Mixer-Settler Units Req'd*	Extract Analysis (g/l.) U	Fe	Mo	Ti	V
1A	1.2 g/l. U as uranium sulfate at a pH of 1	2.6	2.7	-	-	-	-
1B	Duplicate of 1A	2.6	2.6	-	-	-	-
2A	Standard (synthetic Marysvale leach liquor)**	2.4	2.7	0.030	-	-	-
2B	Duplicate of 2A	3.0	3.0	0.090	-	-	-
3	Standard except high in iron (15 g Fe/l.)	2.9	2.9	0.43	-	-	-
4	Standard except high in iron and no PO_4 or F	3.8	2.5	0.87	-	-	-
5	Standard except high in phosphate (20 g PO_4/l.)	3.1	3.1	0.013	-	-	-
6	Standard except high in fluoride (5 g F/l.)	2.8	3.1	0.037	-	-	-
7	Standard except high in sulfate (1.2 M or 115 g SO_4/l.)	2.9	3.0	0.036	-	-	-
8	Standard except pH was 0.5	2.7	2.7	0.037	-	-	-
9	Standard plus molybdenum (1 g Mo/l.)	3.3	2.5	0.007	2.5	-	-
10A	Standard plus vanadium (oxidized)(2.5 g V/l. or 4.5 g V_2O_5/l.)	2.6	2.8	0.079	-	-	1.3
10B	Duplicate of 10A	3.3	3.0	0.037	-	-	1.3
11	Standard plus titanium (0.5 g Ti/l.)	2.6	2.9	0.060	-	0.14	-
12	High Fe, F, SO_4, and PO_4 (5 g PO_4/l.) with V, Mo, Ti, pH = 1.0	3.9	2.4	0.067	2.4	0.03	0.93
13	Same as 12 except pH was 0.5	Approx. 5.5	2.2	0.019	1.9	0.06	0.20

*Number of actual units required to reduce the uranium content of the aqueous phase below 0.003 g/l.
**The standard solution contained 1.2 g U/l., 3 g Al/l., 5 g Fe/l., 1.5 g F/l., 2 g PO_4/l., 0.7 M SO_4 (67 g/l.), and the pH was 1.0.

extraction coefficient, with other conditions being unchanged, showed that there was a significant reduction in the uranium extraction coefficient as the pH was decreased.

Iron Extraction. As shown in Table 5, the iron in the organic extract was less than 3 percent of the extracted uranium in all runs except runs 3 and 4. The feed liquors for these two runs contained 15 g Fe/l. which is much more than that normally present in actual leach liquors. The feed for runs 12 and 13 also contained 15 g Fe/l.; however, the preferential loading of the amine with molybdenum and vanadium contributed to the significant reduction in the amount of iron that was extracted.

The iron gradients given in Table 5 show the effect of uranium loading in the organic phase upon the amount of iron extracted. In the raffinate end of the system an appreciable amount of iron was extracted, most of which was replaced by uranium at the extract end. Therefore, it is important to maintain a high loading of uranium in the organic phase by use of proper phase ratios of aqueous to organic.

Molybdenum Extraction. Molybdenum was extracted almost as readily as was uranium. In runs 9, 12, and 13 the feed liquor contained approximately 1 g Mo/l. The raffinate from the fifth mixer-settler unit contained 0.044 to 0.009 g Mo/l., indicating an over-all extraction of 95 to 99 percent of the molybdenum originally in the feed. It should be noted that molybdenum would not likely be a serious contaminant of the final uranium cake since it is not precipitated by ammonia or sodium hydroxide; therefore, it should be removed from the uranium precipitate in the washing operation.

Titanium Extraction. The extraction of titanium in run 11 amounted to about 11 percent of that originally in the feed. In runs 12 and 13, the presence of molybdenum and vanadium reduced the amount that was extracted to less than 5 percent of that originally present in the feed. These results indicate that titanium will not be a serious contaminant of the uranium recovered by the solvent extraction methods.

Vanadium Extraction. In runs 10, 12, and 13, the feed liquor contained 2.5 g V^{+5}/l. In run 13 where the pH was 0.5, less than 5 percent of the vanadium was extracted. In runs 10 and 12, which were at a pH of 1.0, about 20 percent of the vanadium was extracted yielding an extract in which the vanadium was about 40 percent of the uranium content.

Contamination of the uranium product by vanadium can be eliminated in several ways. For example, tetravalent vanadium is not extracted by Armeen 2-12; therefore by reducing the vanadium in the liquor before extraction, virtually no vanadium contamination of the uranium product would occur. If recovery of vanadium is desired, the loaded amine can be selectively stripped of uranium by chloride or nitrate solutions and the vanadium can be subsequently stripped by basic solutions. The details of preliminary studies of this process are given in ORNL-1734.[1]

Summary

The result of the runs may be summarized as follows:

(1) Less than 4 extraction stages are necessary to recover 99.8 percent of the uranium with the pH of the feed adjusted to 1.0; at a pH of 0.5, one or two additional stages may be required.

(2) Scrubbing to remove extracted iron appears to be unnecessary except when the iron content of the aqueous phase is very high and the vanadium and molybdenum are low.

(3) The small amount of titanium that was extracted indicates that it will not be a serious contaminant of the uranium product.

(4) The amounts of molybdenum and vanadium that were extracted indicates that, when ores are used that contain a significant amount of these metals, special processing will be necessary in order to separate them from the uranium. The procedures for accomplishing this separation have been studied by the laboratory group and their recommendations will be tested in subsequent work.

(5) The effects of high concentrations of sulfate, phosphate or fluoride upon the number of stages required to obtain good uranium extraction are negligible; other conditions being equal.

TESTING OF AMINE REAGENTS

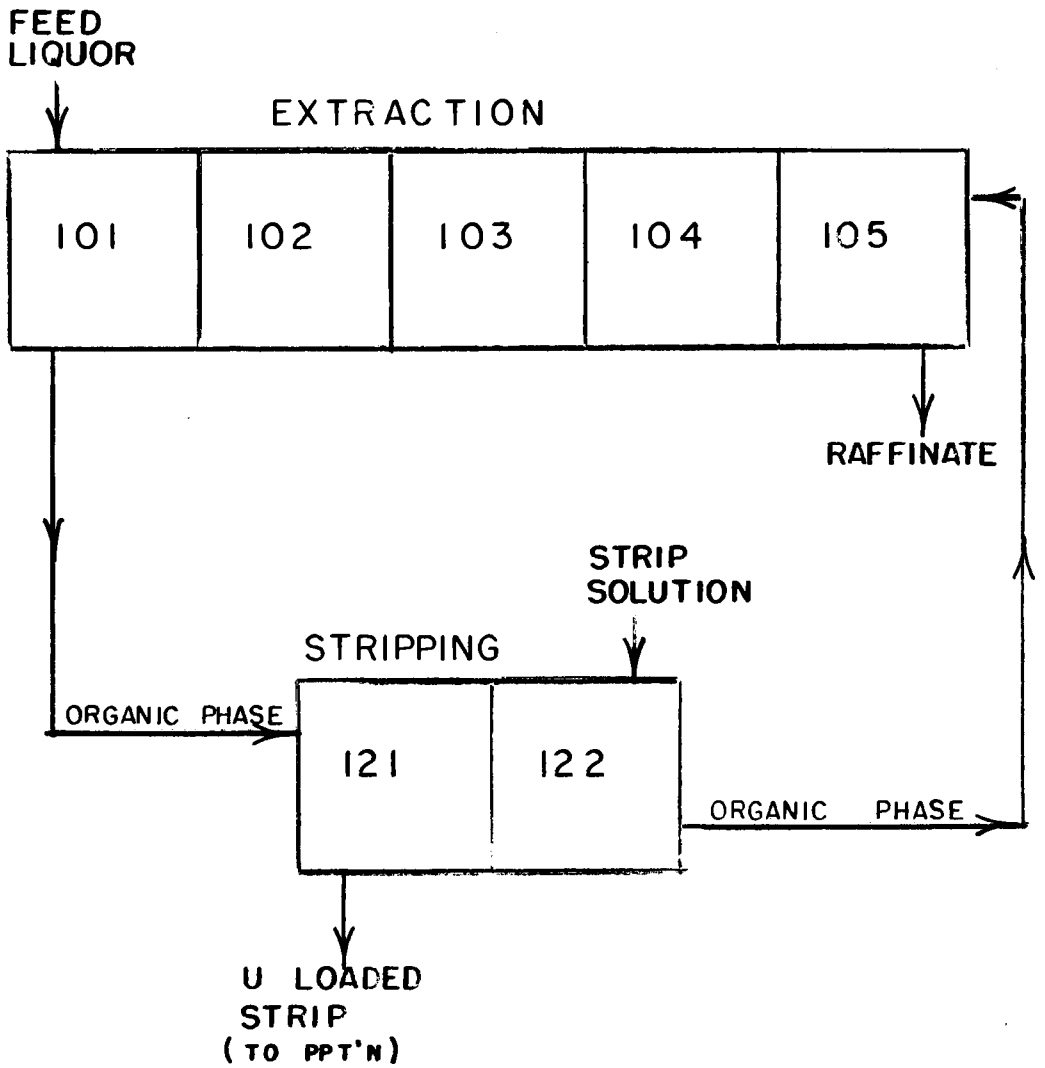
On December 1, 1954, the chemistry group recommended the testing of Rohm and Haas EB 765-2 (a secondary amine) as a suitable reagent for the extraction of uranium from clarified sulfate leach liquors. The Rohm and Haas amine is readily soluble in kerosene, its selectivity for uranium is high, it has presented no phase separation problems in laboratory tests, and it may become commercially available at a reasonable cost if the potential use warrants its production.

The initial testing of the Rohm and Haas amine and others that may be recommended subsequently, will be made in the mixer-settler test array with a stripping section added, using four of the thirteen different synthetic leach liquor compositions that were employed in previous extraction studies.[6] The equipment arrangement is shown in Figure 5. The compositions of the liquors are shown in Table 8. The results of these runs will provide a basis for comparing the performance of the various amines under similar operating conditions. One liquor is typical for Marysvale type ore, one contains high iron (15 g/l.) without fluoride and phosphate, and two contain high concentrations of Fe, V^{+5}, Mo, Ti, PO_4, SO_4, and F differing only in that the pH was 0.5 in one and 1.0 in the other. In previous tests the last three liquors provided the most severe conditions for Armeen 2-12.

TABLE 8. COMPOSITION OF SYNTHETIC LIQUORS

TO BE USED FOR COMPARISON OF AMINES

	Liquor Analysis (g/l.)									
Run	U	SO_4	Al	Fe^{+3}	F	PO_4	V^{+5}	Mo	Ti	pH
2	1.2	70	3.0	5.0	1.5	2.0	0	0	0	1.0
4	1.2	70	3.0	15.0	0	0	0	0	0	1.0
12	1.2	120	3.0	15.0	5.0	5.0	2.8	1.0	0.5	1.0
13	1.2	120	3.0	15.0	5.0	5.0	2.8	1.0	0.5	0.5



NOTE: ALL NUMBERS REFER TO MIXER-SETTLER UNITS

FIG. 5. FLOW DIAGRAM FOR RUNS 14–15

Operating Conditions

The first testing of Rohm and Haas amine (EB 765-2) consisted of two runs which were made with the amine dissolved in kerosene containing 5 vol. % capryl alcohol. Run 14 employed the typical leach liquor composition of Run 2 while Run 15 was made using the leach liquor composition of Run 4.

The feed rates were maintained at 3 liters per hour for the leach liquor and 1.2 liters per hour for the organic extractant. The ratio of the flow rates of feed, organic, and strip solution were: 12.5/5/1, respectively. The mixer-settler test array was composed of an extraction section and a stripping section both of which were operated under continuous countercurrent flow conditions. The extraction section consisted of four mixer-settler units and the stripping section two mixer-settler units, all of which were the same as those described previously except that the volume of the first mixer in the stripping section was 125 ml. The conditions employed in the runs are listed in Table 9.

Results

The results showing concentration gradients for each mixer-settler unit for extraction and stripping are given in Table 10 for Run 14 and in Table 11 for Run 15.

Extraction. In both runs, only three mixer-settler units were required to extract greater than 99 percent of the uranium in the feed. The feed contained 1.2 g U/l. and the aqueous raffinate from the third mixer-settler (103, Fig. 4) contained less than 0.003 g U/l. In the units containing low uranium concentration (103, 104, 105) the extraction coefficient for iron was found to be nearly the same (org/aq = 0.02) for both run 14 where the concentration in the feed was 5 g Fe/l. and for run 15 where the concentration was 15 g Fe/l. The loading of uranium in the unit 101 reduced the amount of iron that was extracted so that the concentration in the extract leaving unit 101 was about one-half of that in the other extraction stages.

Sodium Carbonate Strip. The results of the continuous countercurrent stripping of uranium using two mixer-settler units are also shown in Tables 10 and 11. In both runs, the results show that one mixer-settler (121) with a residence time of 5 minutes gave incomplete stripping; the uranium remaining in the organic phase was 0.29 g/l. for run 14 and

TABLE 9. SUMMARY OF OPERATING CONDITIONS FOR RUNS 14 AND 15

		Run 14	Run 15
Operating time	(hours)	4	4
Organic Phase: (Solvent: kerosene + 5% capryl alcohol)			
Rohm and Haas EB 765-2	(molarity)	0.099	0.099
Uranium	(g/l.)	0.008	0.008
Iron	(g/l.)	0.004	0.004
Aqueous Feed			
Uranium	(g/l.)	1.21	1.15
Iron	(g/l.)	5.59	15.6
Aluminum	(g/l.)	3.09	3.08
Fluoride	(g/l.)	1.14	0.00
Phosphate	(g/l.)	2.12	0.00
Sulfate	(g/l.)	62.7	70.1
pH		1.00	1.00
Acid Scrub			
H_2SO_4	(g/l.)	33	33
Basic Strip			
Na_2CO_3	(g/l.)	92	92
Flow Rates	(l./hr)		
Organic		1.2	1.2
Aqueous feed		3.0	3.0
Acid scrub		0.24	0.24
Basic strip		0.23	0.23

TABLE 10. SUMMARY OF RESULTS OF RUN 14

Mixer-Settler Unit	Aqueous Phase (g/l.)		Organic Phase (g/l.)		Distribution org/aq	
Extraction	U	Fe	U	Fe	U	Fe
101	0.29	-	2.67	0.080	9	0.015
102	0.019	-	0.73	0.089	38	0.016
103	0.001	-	0.053	0.13	53	0.023
104	<0.001	-	0.010	0.13	-	0.023
105	<0.001	-	0.007	0.16	-	0.030
Strip						
121	15.9	0.020	0.29	<0.005	-	-
122	1.30	0.015	0.001	<0.005	-	-

TABLE 11. SUMMARY OF RESULTS OF RUN 15

Mixer-Settler Unit	Aqueous Phase (g/l.)		Organic Phase (g/l.)		Distribution org/aq	
Extraction	U	Fe	U	Fe	U	Fe
101	0.22	-	2.4	0.15	11	0.010
102	0.010	-	0.54	0.36	54	0.024
103	0.001	-	0.030	0.29	30	0.020
104	<0.001	-	0.004	0.21	-	0.014
105	<0.001	-	0.004	0.30	-	0.020
Strip						
121	16.3	0.003	0.026	<0.001	-	-
122	0.29	0.003	0.001	<0.001	-	-

0.026 g/l. for run 15. However, the stripping was completed in the second unit (122) so that the concentration of uranium in the organic phase leaving the unit (122) was only 0.001 g/l.

The concentration of uranium in the loaded aqueous strip solution was 16 g/l. as compared to the feed liquor concentration of 1.2 g/l.

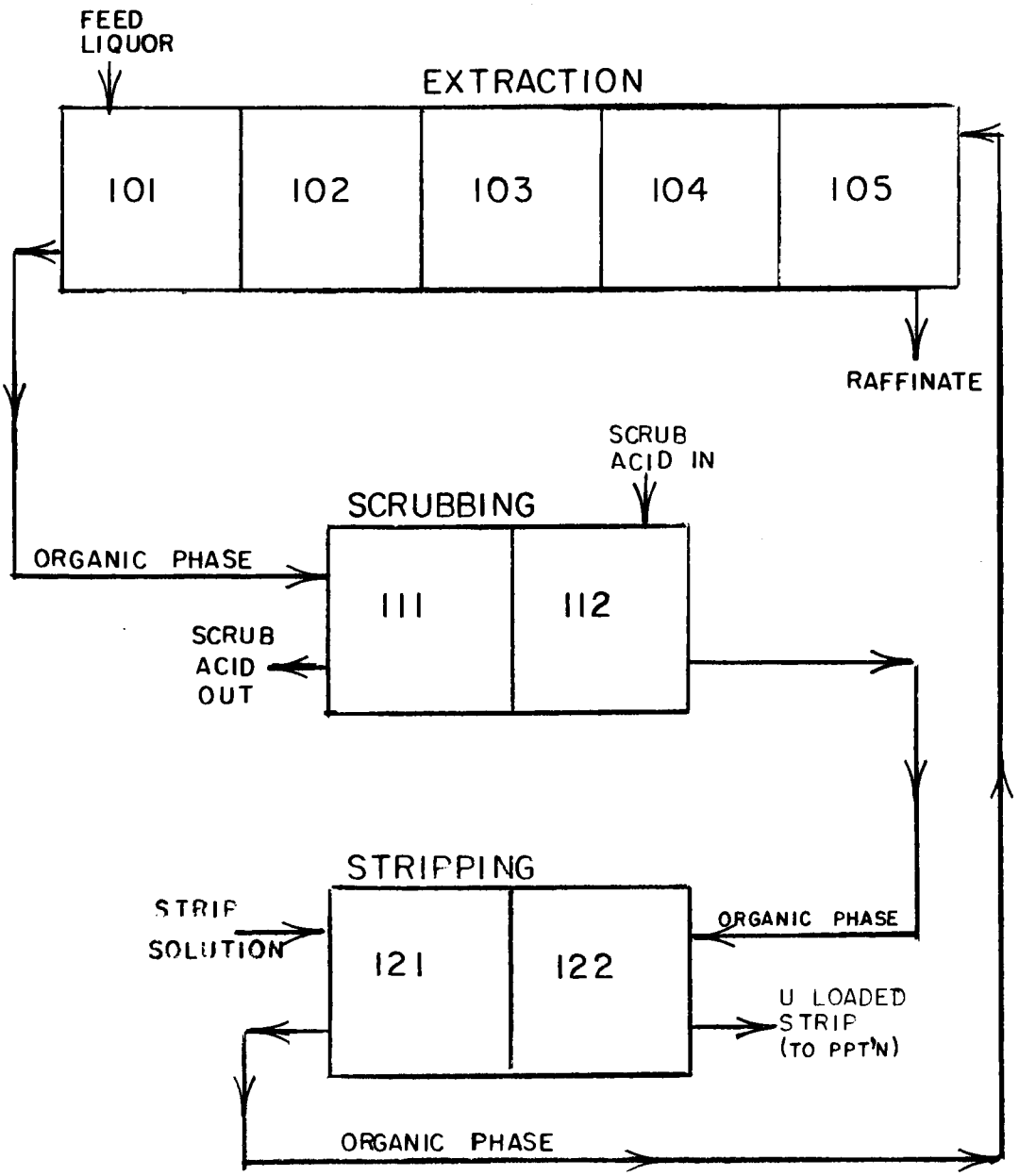
Comparison

A comparison of the results of runs 2 and 4 (Table 7, page 31) in which Armeen 2-12 was used as the extractant with the results of runs 14 and 15 shows that the principal difference between the two extractants was in the amount of iron extracted when the iron content of the leach liquor was high. With approximately the same uranium loading in the organic extract (2.4 - 2.5 g/l.) the Armeen 2-12 extract contained 0.87 g/l. of Fe (run 4) while the EB 765-2 extract contained only 0.15 g/l. (run 15).

EXTRACTION OF ACTUAL LEACH LIQUORS

As a part of the study of the effect of variation in leach liquor composition on the over-all extraction efficiency and the quality of the product, two additional runs (runs 16 and 17) were made employing a feed liquor that was obtained from Plant A. This liquor was produced by leaching a blend of Marysvale, Temple Mountain, and possibly small amounts of other uranium ores with sulfuric acid. The liquors were collected at Plant A in 13-gallon rubber drums about one month prior to the tests.

The extractant was EB 765-2 (Rohm and Haas amine) dissolved in kerosene containing 5 (vol.) percent capryl alcohol. In addition to the extraction and stripping operations, a scrubbing step was also used in which the equipment was the same as that employed in the stripping operation. The equipment arrangement is shown in Figure 6. The phase flow rates, operating conditions, and operation procedures were the same as those described previously with the ratio of the flow rates of feed, organic, scrub, and strip solution 12.5 : 5 : 1 : 1, respectively. The composition of the leach liquor and organic phase are shown in Table 12.



NOTE: ALL NUMBERS REFER TO MIXER-SETTLER UNITS

FIG.6. FLOW DIAGRAM FOR RUNS 16-17

TABLE 12. OPERATING CONDITIONS OF RUNS 16 AND 17

		Run 16	Run 17
Run time	(hours)	5	6
Organic Phase (recycled): kerosene + capryl alcohol			
Rohm and Haas EB 765-2	(molarity)	0.099	0.099
Uranium	(g/l.)	0.002	<0.001
Iron	(g/l.)	<0.001	<0.001
Aqueous Feed: Plant A leach liquor			
Uranium	(g/l.)	1.12	1.08
Iron (total)	(g/l.)	2.3	2.3
Iron ($^{+2}$)	(g/l.)	0.71	0.70
Aluminum	(g/l.)	2.3	2.6
Fluoride	(g/l.)	0.23	0.26
Phosphate	(g/l.)	0.78	0.76
Sulfate	(g/l.)	39.70	40.20
Titanium	(g/l.)	<0.005	<0.005
Vanadium (total)	(g/l.)	0.90	0.86
Vanadium ($^{+5}$)	(g/l.)	0.00	0.00
Molybdenum	(g/l.)	0.082	0.082
Chloride	(g/l.)	0.38	0.48
Calcium	(g/l.)	0.65	0.67
Nitrate	(g/l.)	0.15	0.36
Undissolved solids	(wt %)	0.0	0.064
Silicon (dissolved)	(g/l.)	0.12	0.14
pH		1.1	1.1
Acid Scrub Solution			
H_2SO_4	(g/l.)	33.4	33.4
Basic Strip Solution			
Na_2CO_3	(g/l.)	92.1	92.1
Flow Rates	(l./hr)		
Aqueous feed		3.0	3.0
Organic phase		1.2	1.2
Scrub solution		0.24	0.24
Strip solution		0.23	0.23

Extraction

The concentration gradients and extraction coefficients for runs 16 and 17 are shown in Tables 13 and 14, respectively. In both runs, greater than 99.5 percent of the uranium was extracted from the leach liquor after passing it through three mixer-settler units. After the fourth unit the concentration of uranium in the aqueous phase was less than 0.001 g/l. indicating greater than 99.9 percent recovery of uranium.

The gradients in the extraction section for molybdenum and iron, which were the only contaminating ions present in the Vitro leach liquor that are extracted to any degree, were obtained from the analysis of samples collected from both phases at the end of the runs (5 to 6 hours). The extraction coefficient of molybdenum (org/aq) ranged from 2.3 to 4.3 throughout the extractor units. The concentration of molybdenum in the aqueous phase decreased from 0.08 to 0.008 showing that 90 percent of the molybdenum was extracted.

The extraction of iron was very low, the organic extract leaving the extraction section (unit 101) contained only 0.006 g Fe/l. The uranium concentration in the organic extract was 3.0 g/l., so that the iron amounted to only 0.2 percent of the uranium.

Scrubbing

The purpose of the acid scrub was to remove iron from the uranium loaded extract. However, as shown in Tables 13 and 14, the iron contamination in the extract was so low in both runs that actually the scrub step was unnecessary.

Stripping

The results from both runs show that complete stripping of uranium, iron, and molybdenum from the organic phase was obtained in two stages using approximately 1.0 molar sodium carbonate solution. The concentration of uranium in the loaded aqueous phase was 15 g/l. which is about 12 times the concentration in the leach liquor. The analyses show that about 98 to 99 percent of the uranium was stripped from the organic phase in the first mixer-settler unit (121) and that remaining (0.03 to 0.06 g U/l.) was stripped in the second unit (122). These results indicate that a residence time greater than 5 minutes is needed to obtain complete stripping.

TABLE 13. MIXER-SETTLER GRADIENTS AND DISTRIBUTION COEFFICIENTS FOR RUN 16

Mixer-Settler Number	Aqueous Phase (g/l.)				Organic Phase (g/l.)				Distribution (org/aq)		
	U	Mo	Fe	V	U	Fe	Mo	V	U	Fe	Mo
Extraction											
101	0.67	0.040	-	-	3.00	0.006	0.17	-	4.5	0.003	4.3
102	0.092	0.025	-	-	1.85	0.013	0.092	-	20	0.006	3.7
103	0.005	0.016	-	-	0.31	0.046	0.071	-	>62	0.020	4.4
104	<0.001	0.012	-	-	0.022	0.037	0.037	-	>22	0.016	3.1
105	<0.001	0.008	-	-	0.004	0.067	0.018	-	4	0.029	2.3
Scrub											
111	1.22	-	-	-	-	0.003	-	-	2.4	-	-
112	0.88	-	-	-	-	0.004	-	-	3.1	-	-
Strip											
121	14.9	-	0.002	<0.05	0.060	<0.001	<0.002	0.05	-	-	-
122	0.25	-	0.002	<0.05	0.001	<0.001	<0.002	0.05	-	-	-

TABLE 14. MIXER-SETTLER GRADIENTS AND DISTRIBUTION COEFFICIENTS FOR RUN 17

Mixer-Settler Number	Aqueous Phase (g/l.)			Organic Phase (g/l.)				Distribution (org/aq)		
	U	Mo	Fe	U	Fe	Mo	V	U	Fe	Mo
Extraction										
101	0.39	0.027	-	2.80	0.006	0.24	-	7	0.003	8.9
102	0.034	0.021	-	1.17	0.011	0.016	-	34	0.005	7.6
103	0.002	0.014	-	0.13	0.025	0.057	-	65	0.011	4.1
104	<0.001	0.011	-	0.009	0.037	0.032	-	> 9	0.016	3.2
105	<0.001	0.007	-	0.003	0.054	0.017	<0.01	> 3	0.023	2.4
Scrub										
111	0.88	-	-	-	0.001	-	-	3.1	-	-
112	0.74	-	-	-	0.002	-	-	3.5	-	-
Strip										
121	13.0	-	0.001	0.032	<0.001	0.004	-	-	-	-
122	0.25	-	0.002	0.001	<0.001	0.003	-	-	-	-

Material Balance

For the last 2 hours of operation the material balance of uranium was calculated from concentrations and flow rates. The balances for runs 16 and 17 in Tables 15 and 16 show that the recovery of uranium was 110 and 98 percent, respectively.

Product Analysis

The loaded strip solutions from runs 16 and 17 were acidified to remove the CO_2 and the uranium was precipitated with sodium hydroxide. The precipitate was centrifuged and washed with water and dried at 110°C. The analyses of the products from runs 16 and 17 are shown in Table 17. The uranium concentration was 71.9 percent for run 16 and 68.7 percent for run 17 (84.8 and 81.0% U_3O_8, respectively). The concentration of iron, vanadium and molybdenum was 0.2, 0.1 and 0.1 percent, respectively. Spectrographic analysis of the product showed that the concentration of other metals (except sodium) was less than 0.1 percent.

STRIPPING STUDIES

In addition to the sodium carbonate strip method, the laboratory group developed stripping methods involving the use of aqueous solutions of sodium chloride, ammonium nitrate, and either sodium or ammonium hydroxide as stripping agents. The sodium chloride and ammonium nitrate methods are analogous to the sodium carbonate strip in that the uranium is transferred from the organic to the aqueous phase in solution. On the other hand, sodium or ammonium hydroxide simultaneously strip and precipitate the uranium as the diuranate salt (termed the "direct strip").

A comparison of the costs of chemicals consumed in the stripping operation indicates that the direct strip (hydroxide) is potentially the most economical followed by the sodium chloride, ammonium nitrate, and sodium carbonate in order of increasing costs. Consequently, the three methods were recommended for process testing.

Preliminary small-scale tests were made to study the effect of temperature, reagent concentration, and digestion time on the rate and degree of completeness of the stripping

TABLE 15. URANIUM MATERIAL BALANCE FOR RUN 16

	Flow Rate (l./hr)	U Conc. (g/l.)	Total U (gms/hr)
Input			
Aqueous feed	3.0	1.12	3.36
Organic extractant	1.2	0.00	0.00
			3.36
Output			
Aqueous raffinate	3.0	<0.001	0.00
Acid scrub	0.24	1.22	0.29
Basic strip	0.23	14.9	3.43
			3.72

Output/Input = 110%

TABLE 16. URANIUM MATERIAL BALANCE FOR RUN 17

	Flow Rate (l./hr)	U Conc. (g/l.)	Total U (gm/hr)
Input			
Aqueous feed	3.0	1.08	3.24
Organic extractant	1.2	0.00	0.00
			3.24
Output			
Aqueous raffinate	3.0	<0.001	0.00
Acid scrub	0.24	0.88	0.21
Basic strip	0.23	13.0	2.99
			3.20

Output/Input = 98%

TABLE 17. PRODUCT ($Na_2U_2O_7$) ANALYSIS

(dried at 110°C)

		Run 16	Run 17
Uranium	(as % U)	71.9	68.7
	(as % U_3O_8)	84.8	81.0
Iron	(%)	0.2	0.13
Vanadium	(%)	0.1	0.05
Molybdenum	(%)	0.13	0.02

NOTE: Spectrographic analysis of the product from run 16 showed that the concentration of trace elements was less than 0.1%.

reaction and on the filterability of the diuranate precipitate for both ammonium and sodium hydroxide stripping agents. The conditions that were shown to be satisfactory in the small-scale tests were then chosen to test both agents on a larger scale to measure organic entrainment in the precipitate.

The results of these tests showed that the amount of organic phase entrained in the precipitate under all conditions made the stripping costs higher than that for the carbonate strip. No further testing of direct stripping is planned for the near future.

MIXING AND PHASE SEPARATION STUDIES

In the feasibility tests, the capacity of the multistage mixer column was found to be low in comparison with other systems, largely due to the relatively slow rate of phase separation. Consequently, studies were initiated to more closely define the effect of the degree of dispersion in the extraction operation on the rate of uranium extraction, the rate of phase separation, and the amount of phase entrainment. The first study consisted of exploratory tests that were carried out with continuous phase flows in a small mixer tank which was a replica of those employed in the extraction section of the small mixer-settler test array.

In these tests, the extraction efficiency was evaluated at impeller speeds of 350, 450, and 550 rpm for each of the following total flow rates: 8.9, 16.7, 22.3, 27.7, and 33 gallons per hour. A constant aqueous to organic phase flow ratio of 2.5 to 1 was used in the tests. The separate phases entered the mixer at the desired flow rates near the bottom and the dispersed phases overflowed from a nozzle near the top. After about ten volume changes, samples of the effluent were collected in duplicate, the phases allowed to separate, and each phase was analyzed for its uranium content.

The extraction efficiencies, which represent the degree of attaining an equilibrium contacting stage, were used as a means for correlating the data. The uranium content of the aqueous phase after the leach liquor (1.18 g/l. U) had been equilibrated with the barren organic in a volume ratio of 2.5 aqueous to 1 organic was 0.069 g/l.

The analysis of the aqueous feed and the organic extract are shown in Table 18. The data collected during the runs and the calculated extraction efficiencies are reported in Table 19. Figure 5 shows a plot of the extraction efficiencies vs the aqueous flow rate for each of the impeller speeds.

The results show that: (a) there was a significant increase in the extraction efficiency for a given flow rate as the impeller speed was increased from 350 to 550 rpm; (b) the effect of increased flow rate on the extraction efficiency with a fixed impeller speed was not as pronounced, especially with the impeller speed at 550 rpm (the maximum speed that could be obtained).

STATUS AND FUTURE WORK

Technical Feasibility

The technical feasibility of the process was demonstrated in a complete test array under continuous flow conditions. No further work on this phase of the work is planned.

Extraction Studies

The results of the extraction studies showed that, over the range of compositions that cover most domestic ores, a satisfactory uranium concentrate was produced with greater than 99.9% recovery of uranium in a small test array using only four mixer-settlers in the extraction section and two in the stripping section.

Two secondary amines, Armeen 2-12 and Rohm and Haas EB 765-2, were shown to be satisfactory uranium extraction agents. EB 765-2 appeared to be the more desirable of the two because it is readily soluble in kerosene, and the loaded organic phase extracted less iron.

Future work will include tests to: (a) evaluate the effectiveness of other amine reagents that are recommended by the laboratory group for testing; (b) evaluate the stability of the Rohm and Haas amine in a test array that is operated through 200 extraction and stripping cycles of the organic phase (equivalent to about two weeks of large-scale plant operation); and (c) determine the optimum loading of uranium in the organic phase.

TABLE 18. COMPOSITION OF THE AQUEOUS AND ORGANIC PHASES

Aqueous Phase (pH = 1.0)	Analysis, g/l.
U	1.18
Fe	4.6
Al	2.6
PO_4	2.0
F	1.4
SO_4	37.0
Organic Phase	
Armeen 2-12*	0.1 molar in Amsco G containing 5 vol % capryl alcohol

*Eq wt = 378

TABLE 19. EXPERIMENTAL DATA

	Flow Rates* Aq. (gph)	Flow Rates* Org. (gph)	Res. Time (sec)	Raffinate U (g/l.)	Efficiency (%)
Impeller Speed 350 rpm	6.3	2.6	56	0.456	65
	11.9	4.8	30	0.428	68
	15.9	6.4	22	0.490	62
	19.8	7.9	18	0.459	65
	23.6	9.4	15	0.531	58
Impeller Speed 450 rpm	6.3	2.6	56	0.152	93
	11.9	4.8	30	0.163	92
	15.9	6.4	22	0.193	89
	19.8	7.9	18	0.262	83
	23.6	9.4	15	0.304	79
Impeller Speed 550 rpm	6.3	2.6	56	0.091	98
	11.9	4.8	30	0.117	96
	15.9	6.4	22	0.097	98
	19.8	7.9	18	0.120	95
	23.6	9.4	15	0.138	94

*Aqueous to organic phase ratio of 2.5:1.

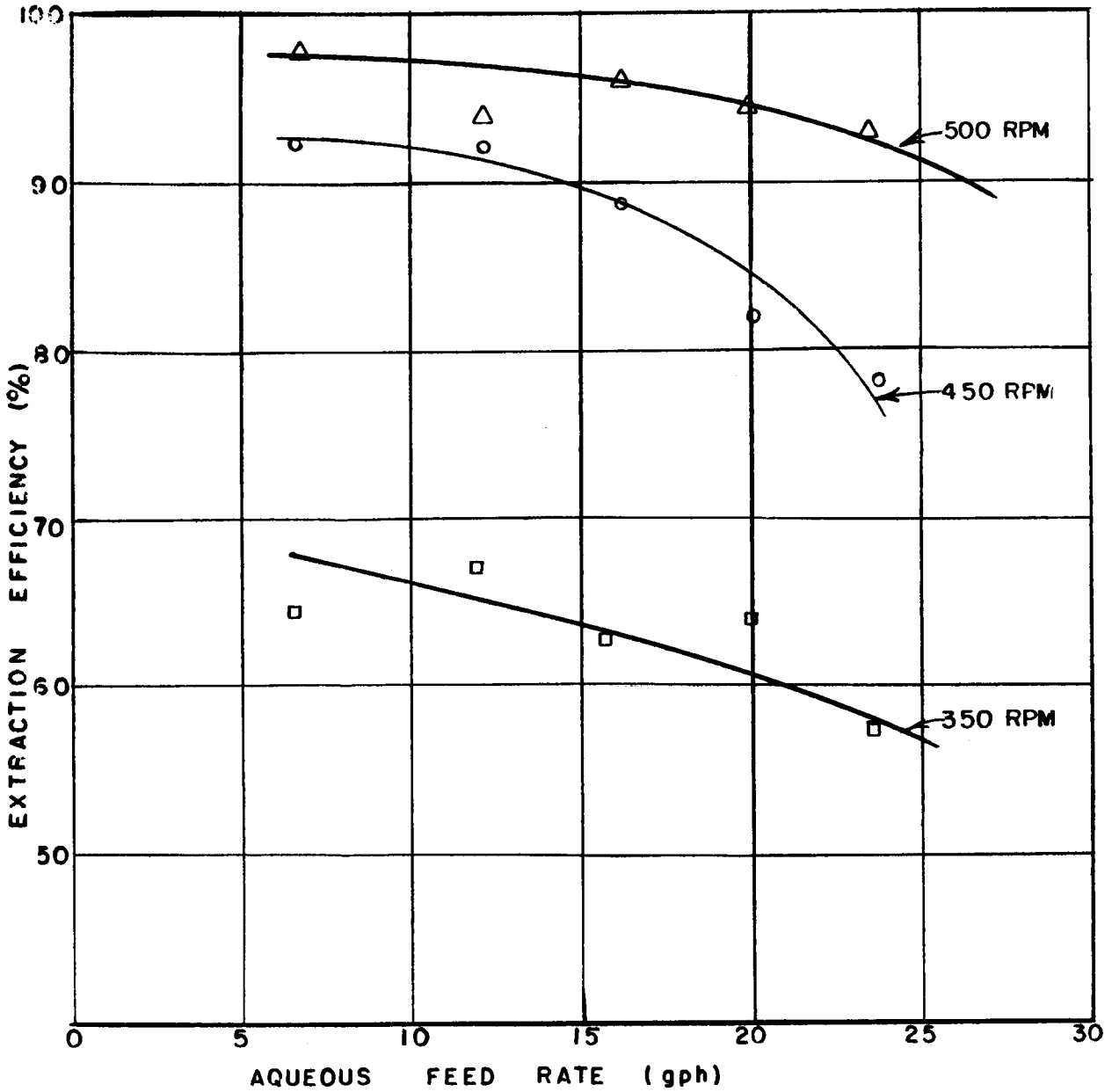


FIG. 7, EFFECT OF AGITATOR SPEED AND THROUGHPUT ON EXTRACTION EFFICIENCY

Stripping Studies

Future work will include a study of the sodium chloride stripping method, with and without free acid, and a more thorough study of the sodium carbonate strip.

Mixing and Phase Separation Studies

The results of preliminary tests showed that there was a significant increase in extraction efficiency at a fixed flow rate as the impeller speed was increased.

The studies will be continued in larger scale equipment with the objective of finding the conditions for obtaining essentially 100 percent extraction efficiencies in a mixer with a low holdup volume and with a minimum of phase entrainment.

Future work will include tests to evaluate the effect on the rate of extraction and the amount of phase entrainment of variation in: (a) impeller speed at different phase flow rates; and (b) impeller diameter with the power input held constant. A limited study of settler geometry will also be made with the objective of designing a settler to obtain a minimum of organic phase holdup in the raffinate.

Final Testing of the Process

The final testing of the process will be made in a complete test array using a clarified leach liquor made from a variety of domestic ores.* A design report will be prepared which will include the design and cost of a pilot plant to extract uranium from the clarified sulfate leach liquor produced by leaching 1,000 pounds of ore per hour.

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*A milling facility is now being installed which will produce either a clarified leach liquor or a leach slurry at a rate equivalent to about 20 pounds of ore per hour.

PART II: SLURRY EXTRACTION

The possibility of extracting uranium from acid leach slurries at some point in the process prior to the clarification step has been of increasing interest to the uranium producers in the Colorado Plateau region during the past few years. Potentially, the costs of the sands-slime separation and the clarification steps may be saved by processing the slurry direct from the leach tank, or the costs of clarification can be eliminated if it is economically desirable to process slimes. Currently, two processes for effecting such an extraction are undergoing development: the R.I.P. process (resin-in-pulp) which has been developed over a period of years by MIT and American Cyanamid at Boston and later by National Lead at Winchester, Mass., and Grand Junction, Colorado; and the Carnotite Solvent Extraction Process developed by Dow Chemical Company at Pittsburgh, California, and, in cooperation with the U. S. Bureau of Mines, at Salt Lake City, Utah, where the pilot plant work is being carried out.

The R.I.P. process is essentially an ion exchange process that is designed to extract uranium from acid leach slurries from which sands have been removed and which contain about 10 weight percent of solids. The equipment containing the ion exchange resin is arranged to simulate a continuous, countercurrent type operation.

The Dow process is designed to recover uranium from acid leach slurries by solvent extraction using dodecylphosphoric acid (mono-alkyl) as the extraction agent. The pilot plant extraction tests have employed leach slurries from which the sands have been removed (about 10 wt % solids) and slurries direct from the leach circuit which contain from 50 to 60 weight percent solids.

It is apparent that a significant reduction in costs may be achieved if a slurry extraction process can be developed which can be carried out in standard equipment, is operationally simple, does not involve appreciable loss of extraction agent, employs inexpensive chemicals, and introduces no corrosion problems in addition to those that exist in a normal sulfuric acid leaching process. Preliminary studies by the Uranium Chemistry Section on the use of amines for this extraction have not been encouraging due to high amine and diluent losses.

In the investigation and evaluation of different reagents for the separation of uranium from acid leach liquors, the Uranium Chemistry Section showed that specific organophosphorus compounds, dissolved in an organic carrier such as kerosene, were suitable extraction agents. In particular, di-2-ethylhexyl phosphoric acid was of interest in that it could be made commercially available (C and CC Co.), under proper conditions the uranium extraction coefficient was high, and the loaded organic phase could be stripped of its uranium content by either acidic or basic strip solutions of specific compositions.[7] However, it was also shown that it would be necessary to either partially or completely reduce the iron in the leach liquor since ferric iron would be extracted if present in significant amounts.

For preliminary process work it appeared desirable to investigate the feasibility of using the di-2-ethylhexyl phosphoric acid as the extraction agent. Consequently small-scale exploratory tests were carried out using this reagent dissolved in a kerosene carrier phase as an extractant for uranium from an actual process leach slurry containing about 10 weight percent solids.

PRELIMINARY TESTS[8]

Equipment

Preliminary batch tests were made in a small, turbine agitated vessel to show the effects of mixing variables and variation in phase ratios on the uranium extraction coefficient and the amount of phase entrainment. These effects were then studied in a mixer-settler which was operated under continuous flow conditions.

Composition of the Phases

Slurry. The slurry used in these tests was prepared by leaching -20 mesh Lukachukai ore with sulfuric acid and separating the heavy sand particles by gravitational settling.* It contained about 9 percent solids essentially all of which was -325 mesh particle size. After arrival, the pH was adjusted from 2.2 to the more typical value of 1.5. The composition of the slurry is shown in Table 20.

*The slurry was a portion of that obtained from the Grand Junction, Colorado, pilot plant facility by the ORNL Chemical Technology Division.

TABLE 20. COMPOSITION OF LUKACHUKAI SLURRY

EMF	+ 475 mv.	Fe^{+2}	0.59 g/l.
% solids	9%	Al	0.58 g/l.
pH	1.5	Mo	<0.001 g/l.
U	0.80 g/l.	Ca	0.48 g/l.
Total V	0.48 g/l.	SO_4	13.6 g/l.
V^{+5}	<0.05 g/l.	PO_4	0.119 g/l.
Total Fe	0.89 g/l.	Cl	<0.05 g/l.

Organic. The organic extractant was a 0.1 M solution of di-2-ethylhexyl phosphoric acid dissolved in kerosene which contained 2 vol. % capryl alcohol. Prior to its use the organic phase was pretreated by scrubbing it with several portions of both dilute sulfuric acid and sodium carbonate solution to remove water soluble components.

Equilibrium Data

Equilibrium data for the system were obtained by equilibrating various volume ratios of clarified leach liquor* and organic phase. Samples of the separated phases were analyzed for U, V, Fe, and Al and the results are reported in Table 21.

Batch Extraction Tests

The effect of variation in phase volume ratios on the formation of emulsions and of variation in impeller speed on the rate of extraction was studied in small scale tests on a batch basis. The equipment consisted of a 3-liter glass tank, 6 inches in diameter with four equally spaced 1/2-inch wide baffles. Agitation was provided by means of two, 3-inch diameter turbine type impellers (4-bladed) spaced 3 inches apart on a common shaft.

Phase Ratio. In the first series of tests, the volume ratio of organic to slurry phase was varied over the range 1:3 to 5:1 using an impeller speed of about 300 rpm. The results showed that stable emulsions formed with all ratios less than 4 organic to 1 slurry. With a 4:1 ratio or greater, the phases separated quickly although there was some entrainment of organic in the slurry phase. No measurements were made of the amount of organic entrained in the slurry phase.

*Filtrate from the Lukachukai slurry.

TABLE 21. EQUILIBRIUM DATA

Phase Ratio aq/org	U Extraction Coeff.	% U Extracted	Fe* Extraction Coeff.	V Extraction Coeff.	Al Extraction Coeff.
10:1	44	86	-	0.09	-
7:1	87	95	0.25	0.17	0.04
5:1	101	96	0.31	0.20	0.05
3:1	120	98	0.38	0.30	0.07
2:1	171	99	0.32	0.40	0.02
1:1	360	>99	0.28	0.39	0.04
1:2	420	>99	0.09	0.46	0.02
1:5	>420	>99	0.04	0.38	0.02

*Based on total iron.

Extraction Rate. The rate of uranium extraction was next determined using two types of mixing. Samples were collected at intervals and the separated phases analyzed for U, Fe, V, and Al. In run B1, each turbine was located at the mid-point of each phase and the impeller speed was maintained at 110 rpm which provided good internal mixing without dispersion of either phase into the other. In run B2 the impeller speed was about 300 rpm which was sufficient to disperse the slurry in the organic phase. The results are given in Table 22.

The results show that with an organic to aqueous phase ratio of 5:1 and an impeller speed of 300 rpm 97 percent of the uranium was extracted from the slurry after 40 seconds of contacting in the mixer. A small amount of organic phase was entrained in the slurry.

Continuous Extraction Tests

Exploratory tests also were carried out in a single mixer-settler unit on a continuous basis. In these tests several modifications of settler geometry and size were tried in an attempt to minimize the operating difficulties. The tests were of short duration; consequently, the experimental data are of questionable value for estimating maximum extraction efficiencies and in defining the effects of mixing variables on the amount of phase entrainment. However, the results showed that, with organic to aqueous phase ratios of 4 to 1 or greater, the phases separated quickly in the settler and uranium extraction efficiencies varied from 80 to 95 percent. The amount of organic phase entrained in the raffinate varied from about 3 to 48 ml per kilogram of slurry.

TABLE 22. BATCH SLURRY EXTRACTION TEST DATA

Test No.-	Turbine Speed	Phase Ratio Org:Slurry	Time (sec)	U Extrn. Coeff.	U Extr'd (%)	Fe Extr'd (%)	V Extr'd (%)	A Extr'd (%)
B1*	110 rpm	1:2	60	0.03	6	0	0	0
			120	0.04	6	0	0	0
			300	0.10	8	0	0	0
			600	0.13	-	0	0	0
			1200	0.26	9	0	0	0
			2400	0.39	10	0	0	0
B2	300 rpm	5:1	2	0.1	67	34	0	
			7	0.6	81	35	0	
			12	1.2	89	36	0	
			20	2.4	94	38	0	
			40	4.3	97	39	0	
			600	88	>99	56	0	

*Phases not dispersed.

FUTURE WORK

Batch tests will be made on a larger scale to study the effects of mixing variables on the rate of extraction and the amount of phase entrainment over a range of pulp densities. Emphasis will also be placed on studies directed toward recovering the organic phase that is entrained in the slurry raffinate.

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