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PROGRESS REPORT OF ENGINEERING SECTION

RAW MATERIALS PROCESS TESTING

JULY – DECEMBER, 1955

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ENGINEERING SECTION
H. M. McLeod, Jr., Supervisor

MATERIALS CHEMISTRY DIVISION
G. H. Clewett, Director

Edited by
K. O. Johnsson

PROGRESS REPORT OF ENGINEERING SECTION RAW MATERIALS PROCESS TESTING

July--December, 1955

Authors
Members of the Engineering Section

Work done by

H. F. Bauman
J. R. Buchanan
V. A. DeCarlo
R. H. Guymon
B. B. Klima
H. M. McLeod, Jr.
J. F. Manneschmidt
A. D. Ryon
R. R. Wiethaup

Date Issued
JUL 12 1956

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SUMMARY

Engineering studies on extraction processes for recovery of uranium from sulfate leach liquors were continued. Leaching and clarification equipment have been installed so that the extraction processes can be tested with actual leach liquors. The equipment is arranged to provide for make-up of either 50% slurry, dilute slime slurry, or clear liquor feed stocks.

Several tons each of six different Colorado Plateau ores have been received, ground, and blended to provide a supply of feed material for testing. Leaching tests have been made on samples of ground ore to determine acid requirements for uranium leaching and composition of leach liquor.

The Amex process testing work consisted of studying the chemical behavior in a countercurrent system using several types of clear leach liquors. An investigation has been started to evaluate the variables affecting the extraction efficiency of mixer-settler equipment to obtain design data.

In the slurry extraction program, the extraction efficiency and organic entrainment were studied in a single mixer-settler unit.

PROGRESS REPORT OF ENGINEERING SECTION

RAW MATERIALS PROCESS TESTING

July--December, 1955

ORE PROCESSING

Six types of ore from the Colorado Plateau have been obtained for testing the Amex and Dapex extraction processes. These are: Anaconda, Lukachukai, Marysvale, Slick Rock, Temple Mt. and Utex. Two lots of Utex ore were received and have been designated as Utex A and Utex B.

GRINDING

The ore was dry ground to -20 mesh and blended in 2500-pound batches to provide a uniform supply ready for acid leaching.

The grinding circuit was arranged as shown in Fig. 1. The ore was fed from the ore bin by a vibrating feeder to the hammer mill. The ore was discharged from the hammer mill directly to the roll crusher. The crushed ore dropped to the vibratory screen, where the +20 mesh material was separated for recycle and the -20 mesh ore was collected in the conical blender. The oversize was recycled until the amount of +20 mesh ore was less than 1% of each blender load.

ORE ANALYSIS

The screen analyses of each type of ore are shown in Table 1. The chemical analyses are shown in Table 2, and the qualitative spectrographic analyses are shown in Table 3.

LEACHING TESTS

Leaching tests were made with each type of ore to determine the amount of sulfuric acid required to dissolve the uranium and to determine the composition of the resultant leach liquor.

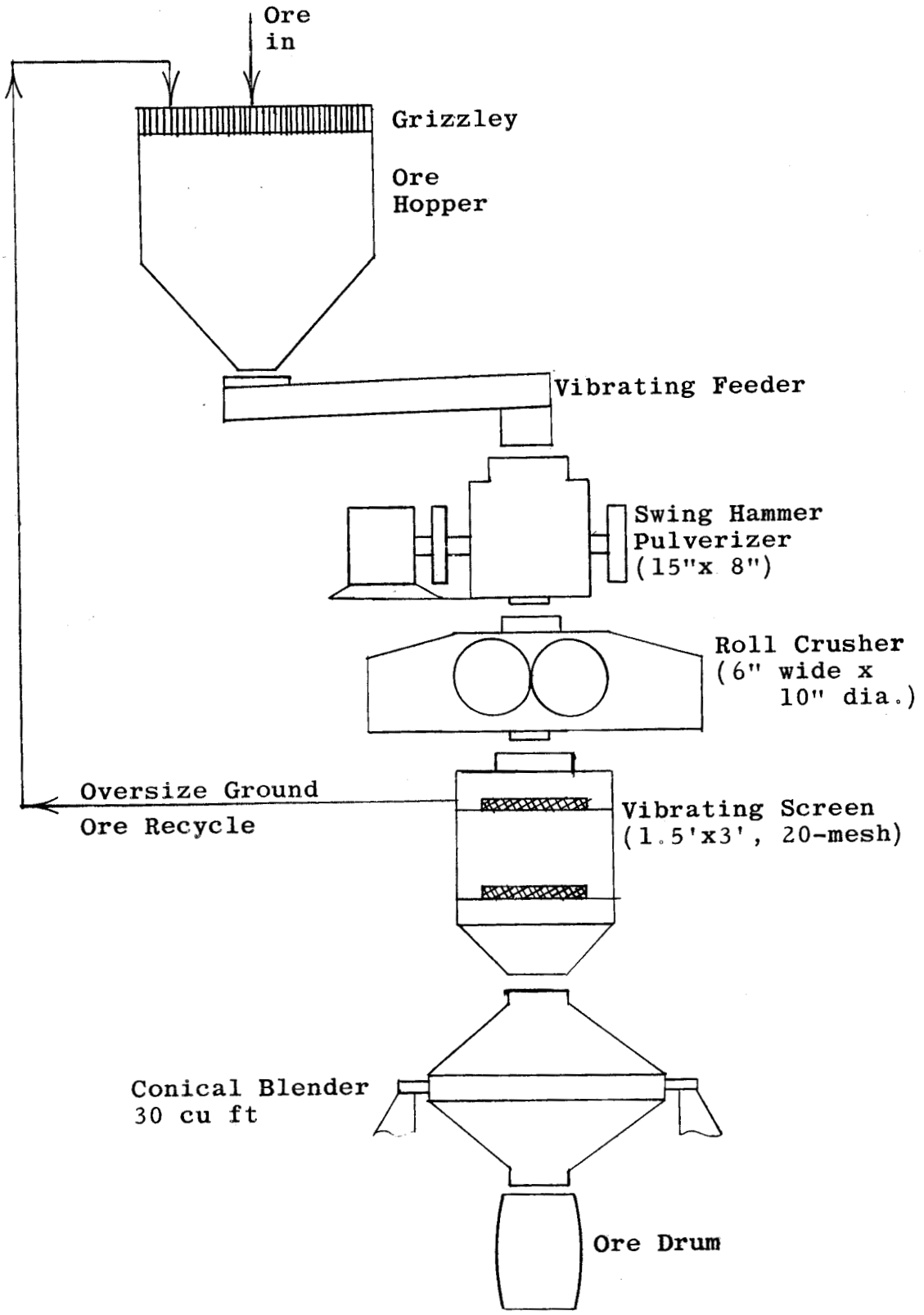

Fig. 1. ORE GRINDING FACILITY

TABLE 1. SCREEN ANALYSES OF GROUND ORES

Mesh Size (Tyler)	Weight Percent						
	Anaconda	Lukachukai	Marysvale	Slick Rock	Temple Mt.	Utex A	Utex B
+20	0	0	0	0	1	0	0
-20 + 48	36	9	34	17	30	21	13
-48 +100	44	31	33	46	38	34	37
-100 +200	9	40	15	25	14	22	24
-200	11	20	18	12	17	23	26

TABLE 2. CHEMICAL ANALYSES OF ORES

Constituent	Weight Percent						
	Anaconda	Lukachukai	Marysvale	Slick Rock	Temple Mt.	Utex A	Utex B
U_3O_8	0.41	0.33	0.14	0.17	0.28	0.22	0.30
V_2O_5	0.27	1.1	0.05	1.2	0.8	1.4	1.0
Fe_2O_3	3.0	1.6	6.3	0.84	1.1	1.6	1.2
CaO	2.0	5.5	2.8	1.7	2.2	5.3	6.4
CO_2	0.88	4.2	0.37	1.6	1.8	4.2	5.1
Mo	<0.01	0.02	0.12	<0.01	<0.01	0.03	0.01
C	<0.1	<0.1	0.1	<0.1	3.3	<0.1	<0.1

TABLE 3. QUALITATIVE SPECTROGRAPHIC ANALYSES OF TRACE ELEMENTS

	Weight Percent						
Constituent	Anaconda	Lukachukai	Marysvale	Slick Rock	Temple Mt.	Utex A	Utex B
Al	>5	3	5	3	3	3	3
Ba	0.1	0.1 - 1.0	0.1	0.1 - 1.0	0.1	0.1 - 1.0	0.1 - 1.0
Be	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Cb	0.1	-	<0.1	<0.1	<0.1	<0.1	<0.1
Co	0.01 - 0.1	0.01 - 0.1	0.01 - 0.1	0.01 - 0.1	<0.1	<0.05	<0.05
Cr	<0.05	<0.05	<0.05	<0.05	0.1	<0.05	<0.05
Cu	<0.1	<0.05	<0.05	<0.1	<0.01	<0.05	<0.05
K	0.1 - 1.0	-	1.0	0.1 - 1.0	0.1 - 1.0	0.1 - 1.0	0.1 - 1.0
Li	0.01 - 0.1	-	0.01 - 0.1	0.01- 0.1	0.01 - 0.1	0.01	0.01
Mg	1.0	1.0	1.0	1.0	0.1 - 1.0	1.0	1.0
Mn	0.01 - 0.1	0.01 - 0.1	0.01 - 0.1	0.01 - 0.1	0.01 - 0.1	0.1	0.01 - 0.1
Na	0.1 - 1.0	-	0.1 - 1.0	0.01 - 0.1	0.01 - 0.1	0.1 - 1.0	0.1 - 1.0
Ni	0.01 - 0.1	<0.05	0.01 - 0.1	<0.05	<0.05	<0.05	<0.05
Pb	<0.1	0.01 - 0.1	0.1 - 1.0	<0.1	<0.05	<0.1	<0.1
Rb	0.01 - 0.1	-	0.01- 0.1	0.01 - 0.1	-	0.01 - 0.1	0.01 - 0.1
Si	>10	>10	>10	>10	>10	>10	>10
Ti	0.1 - 1.0	0.1	0.1 - 1.0	0.1 - 1.0	0.1 - 1.0	0.1 - 1.0	0.1 - 1.0
Zn	<0.1	-	0.1 - 1.0	0.1 - 1.0	0.1 - 1.0	-	-
Zr	<0.1	<0.1	<0.1	-	<0.1	<0.1	<0.1

The tests were made using 200 gram portions of ground ore (-20 mesh). The ore was leached as a 50% solids slurry in a vigorously agitated vessel at 50 to 60°C for 16 hours. After the leaching, the slurry was centrifuged to provide a clear liquor for chemical analysis. The solids were slurried with five portions of 0.1 N sulfuric acid using centrifugation and decantation between each wash. The washed solids were dried, ground to -200 mesh and analyzed.

The data showing the effect of the amount of sulfuric acid used on the uranium and vanadium leaching are shown in Table 4. The leaching efficiency is based on the analyses of the ore samples and leached residues. In all tests the percent uranium leached leveled off at a constant value as a function of amount of acid added. With the exception of Marysvale and Temple Mt, 95% leaching of the uranium was obtained. Additional leaching tests with oxidants and roasting of the ore are planned for these two ores.

The vanadium leaching was of secondary interest and the data are shown only to give the order of magnitude of leaching vanadium with dilute sulfuric acid. Although the percent vanadium leached increased with amount of acid used the best leaching was 50 to 80% for most of the ores and was only about 20% for the Slick Rock ore.

In all cases the amount of impurities (iron, aluminum, etc.) dissolved increased with increased acid usage. Therefore, typical liquor compositions were obtained by selecting tests in which the acid added was slightly in excess of the minimum required where uranium leaching was independent of acid added. The composition of leach liquors, which are the clear liquors from the leach slurry (50% solids), are shown in Table 5.

TABLE 4. EFFECT OF AMOUNT OF ACID ON LEACHING OF URANIUM AND VANADIUM

Ore	H_2SO_4, * lb/ton	Leached Residue U_3O_8, %	Leached Residue V_2O_5, %	Percent Leached Uranium	Percent Leached Vanadium
Anaconda	100	0.019	0.20	95	26
	150	0.020	0.20	95	26
	200	0.020	0.14	95	48
	250	0.021	0.12	95	55
Lukachukai	200	0.080	0.74	76	33
	250	0.014	0.63	96	43
	300	0.019	0.41	94	63
	350	0.010	0.29	97	74
Marysvale	100	0.033	-	76	-
	150	0.031	0.025	78	50
	200	0.024	0.029	83	42
	250	0.027	0.025	81	50
Slick Rock	100	0.010	-	94	-
	150	0.010	1.04	94	13
	200	0.009	0.97	95	19
	250	0.009	0.93	95	22
Temple Mt.	100	0.055	0.54	80	32
	150	0.049	0.54	82	32
	200	0.045	0.48	84	40
	250	0.043	0.45	85	44
Utex A	200	0.060	0.36	73	74
	250	0.019	0.30	91	78
	300	0.014	0.20	94	86
	350	0.007	0.23	97	84
Utex B	250	0.045	0.29	85	71
	300	0.019	0.46	94	54
	350	0.018	0.36	94	64
	400	0.015	0.29	95	71

*Conditions: 16 hours at 50-60°C.

TABLE 5. COMPOSITION OF LEACH LIQUORS

Concentrations in g/l unless noted

Ore:	Anaconda	Lukachukai	Marysvale	Slick Rock	Temple Mt	Utex A	Utex B
H_2SO_4 Used, lb/ton	150	300	200	150	150	300	350
U	3.7	3.3	1.5	1.7	2.2	2.4	3.3
V	0.4	4.4	0.2	2.1	1.8	1.9	2.3
Fe (total)	8.9	4.9	9.9	3.7	2.5	5.2	5.7
Fe^{+2}	3.4	4.8	2.3	0.1	1.4	2.9	3.1
Al	2.5	3.4	5.0	2.1	1.1	2.5	3.5
Mo	0.001	0.004	0.15	0.002	0.001	0.05	0.04
SO_4	59	70	54	53	24	69	76
pH	1.4	1.2	1.3	0.8	1.2	1.0	1.1
Sp. Gr.	1.06	1.08	1.04	1.05	1.06	1.07	1.08

AMINE EXTRACTION PROCESS

Process testing of the amine extraction process (Amex) is divided into two general parts dependent on the objectives of the work. One objective is to test and demonstrate the chemical feasibility of the process for a variety of feed liquors and to investigate variations in the chemical flow sheet. This work is usually performed in small-scale equipment containing the essential extraction, stripping and recycle features of the process. The other main objective is to obtain engineering data required for design and scale-up of the equipment. For mixer-settlers the study of variables affecting efficiency of mixers and phase separation in settlers can be made by operating a single mixer-settler for relatively short periods of time.

ACTUAL PLANT LIQUORS

As a part of the study of the effect of leach liquor variations on over-all extraction efficiency and product quality, samples of actual plant liquors have been used to test the amine extraction process. In continuation of this study, a plant D* liquor was extracted with Rohm and Haas 9D-178 amine in Amsco G and stripped with an aqueous chloride solution. This liquor was characterized by a low pH (0.4), a high vanadium concentration, and appreciable titanium and molybdenum concentrations. The compositions of the head liquor, organic phase, and strip solution are shown in Table 6.

The run was carried out in a continuous countercurrent test array which contained four mixer-settlers in the extraction section and three in the stripping section, as shown in Fig. 2.

The run was continued for ten cycles of the organic phase, to observe the buildup of molybdenum in the organic (since molybdenum is known to be extracted by the amine, but not appreciably stripped from it by chloride reagent).

The flow rates of liquor, organic and strip were 150, 50, and 7.5 ml/min, respectively, and the organic cycle time was approximately 45 min.

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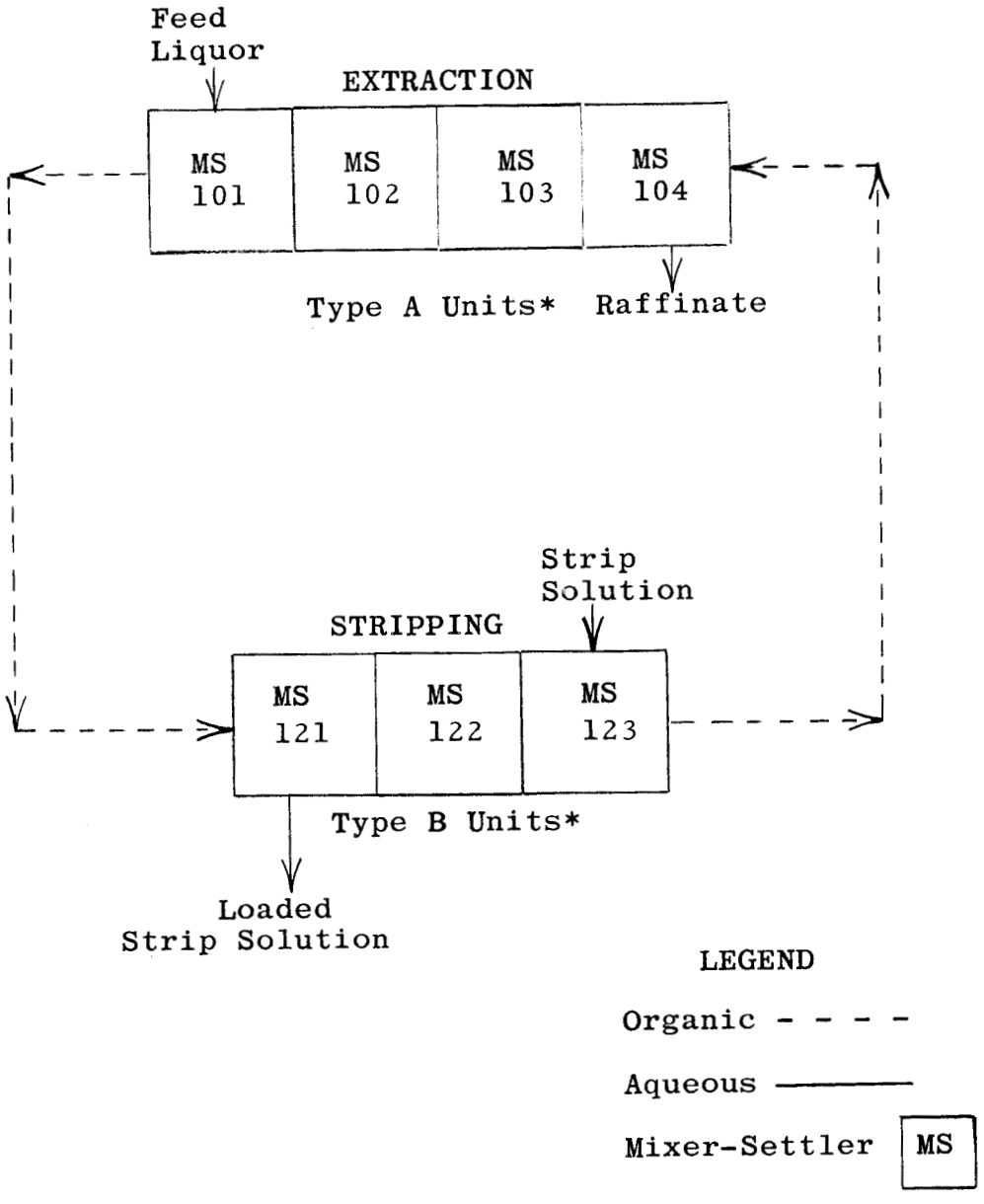
*Colorado Plateau ore processing plant.

TABLE 6. COMPOSITION OF ENTERING STREAMS

Concentrations in grams per liter except as noted

Head Liquor			
Uranium	1.05	Sulfate	110
Iron (total)	4.8	Phosphate	0.41
Iron (II)	1.3	Chloride	0.16
Aluminum	6.6	Fluoride	0.063
Molybdenum	0.012	Silicon	0.024
Titanium	0.24	Nitrate	<0.05
Vanadium (total)	4.1	pH	0.4
Vanadium(V)	<0.01		
Calcium	0.64		
Organic Phase			
Amine 9D-178, in Amsco G, M		0.13	
Strip Solution			
Sodium chloride, M		1.0	
Sulfuric acid, M		0.05	



*See Fig. 2, ORNL-1970

Fig. 2. EXTRACTION-STRIPPING FLOW DIAGRAM

The extraction and stripping data are given in Tables 7 and 8. Molybdenum concentrations in the organic phase are given in Table 9, and the compositions of the loaded strip solution and uranium product in Table 10.

Uranium Extraction and Stripping

In four stages, the steady state uranium concentration in the aqueous phase was reduced to 0.005 g/l. This compares with about three stages required for similar extraction of a standard synthetic liquor at pH 1.0 (ORNL-2035) under the same conditions. In practice, it would probably be desirable to increase the pH of a liquor of the plant D type to obtain greater extraction coefficients (since previous work has shown that the extraction coefficient increases with an increase in pH).

The uranium stripping was complete in three stages; this is the same as for a run with standard liquor under the same conditions (ORNL-2035). The uranium concentration in the loaded strip solution was 20 g/l, compared to 1.05 g/l in the head liquor.

Molybdenum Extraction and Stripping

Molybdenum was the only contaminating element of those present in the plant D liquor which was readily extracted by the organic, but not appreciably stripped from it by the chloride stripping solution.

As shown in Table 9, the molybdenum concentration in the organic at the end of ten cycles had built up to 0.10 g/l and was still rising slowly. A longer run would be needed to determine the final equilibrium concentration. The buildup of molybdenum in these tests did not interfere with uranium extraction. However, if molybdenum buildup should become great enough to interfere with uranium extraction, the molybdenum could be stripped from the organic as needed with sodium carbonate.

Product

The uranium in the loaded strip solution collected over the last four cycles of the run was precipitated with ammonia. As shown in Table 10, the product was mainly uranium as sodium diuranate; all other metals totaled less than one percent. The small amount of ammonia in the dried producd was removed by calcining.

TABLE 7. EXTRACTION DATA AFTER TEN CYCLES

Stage	Composition, g/l							Distribution, org/aq	
	Aqueous			Organic					
	U	Mo	pH	U	Mo	V	Fe	U	Mo
101	0.35	0.012	0.4	3.1	0.10	<0.01	0.016	9	7
102	0.048	0.010	0.4	1.2	0.10	0.02	0.022	24	8
103	0.014	0.010	0.4	0.19	0.09	0.02	0.019	14	8
104	0.005	0.009	0.4	0.038	0.10	0.02	0.012	8	9

TABLE 8. STRIPPING DATA AFTER TEN CYCLES

Stage	Composition, g/l								Distribution, aq/org	
	Aqueous				Organic					
	U	Mo	Fe	pH	U	Mo	Fe	V	U	Mo
121	20.	0.032	0.063	0.8	0.88	0.11	<0.01	<0.01	23	0.3
122	5.7	0.034	0.004	1.0	0.028	0.09	<0.01	<0.01	20	0.4
123	0.29	0.018	0.004	0.9	0.003	0.09	<0.01	<0.01	10	0.2

TABLE 9. MOLYBDENUM CONCENTRATION IN ORGANIC PHASE

Cycle	Mo Concentration, g/l[a]
2	0.02
4	0.03
6	0.07
8	0.06
10	0.10

(a) Average of concentrations in extract and stripped organic, which are essentially identical because of the small amount of molybdenum stripped by chloride solution.

TABLE 10. LOADED STRIP SOLUTION AND URANIUM PRODUCT COMPOSITIONS

	Loaded Strip Solution, g/l[a]	Product[b], %	
		Dried at 130°C	Calcined at 600°C
U	20.	70.1	77.2
U as U_3O_8	-	82.8	91.1
Fe	0.07	0.21	-
Ti	0.06	0.10	-
V	<0.1	0.11	-
Mo	0.032	0.14	-
Al	0.08	<0.1	-
Cl	9.4	0.04	<0.01
pH	0.8	-	-
SO_4	-	2.1	-
PO_4	-	0.14	-
NH_3	-	1.79	0.06
Loss on Ignition, 600°C	-	11.1	-

Note: Spectrographic analysis showed no additional element present as more than a trace, except zirconium, 0.4%.

(a) Composite, cycles 7 through 10.
(b) Precipitated with ammonia from strip solution collected over cycles 7 through 10.

EFFECT OF THE PRESENCE OF MOLYBDENUM AND VANADIUM

In continuation of the study of the effect of leach liquor variation on over-all extraction efficiency in the extraction of uranium with amine reagents, synthetic liquors containing molybdenum and vanadium were extracted with amine 9D-178 and stripped with a chloride solution. Laboratory tests have shown that molybdenum and vanadium (V) are extracted by amine, but not completely stripped from it by chloride reagent. Therefore, test runs were made to determine broadly the liquor compositions which would result in buildup of molybdenum or vanadium in the organic, and the effect of such buildup on the uranium extraction efficiency. Secondary stripping with sodium carbonate for removal of molybdenum and vanadium from the organic was demonstrated in one run.

The first series of runs was made with kerosene as the amine solvent, but the runs were unsuccessful because the complex which the amine forms with molybdenum and vanadium was only slightly soluble in kerosene. The first of these runs employed a feed containing 0.3 g/l molybdenum and 1.0 g/l vanadium (V). A precipitate, later identified as a molybdenum-vanadium-amine complex, began forming at a molybdenum concentration of less than 0.9 g/l in the organic phase. The second run was made with a feed containing 0.1 g/l molybdenum and 1.0 g/l vanadium (V). Precipitate began to form at a molybdenum concentration in the organic of about 0.6 g/l. The final run with kerosene solvent was made to determine whether the precipitate would form in the absence of vanadium (V). The feed was the same as that used in the first run, but was reduced with ferrous ammonium sulfate, so that it contained 0.3 g/l molybdenum and 1.0 g/l vanadium (IV), but no vanadium (V). Precipitate began to form at a molybdenum concentration in the organic of about 1 g/l.

Since the amine-molybdenum complex was so slightly soluble in kerosene, shakeout tests were made with Amsco G, an aromatic solvent. It was found that the molybdenum complex was soluble in an organic phase made with this solvent, and a series of four runs employing Amsco G was completed without precipitation difficulty.

The runs were made in a continuous countercurrent test array that contained four mixer-settlers in the extraction section and three in the primary stripping section. In addition, a secondary stripping section containing one mixer-settler was provided for optional use, as shown in the flow sheet, Fig. 3.

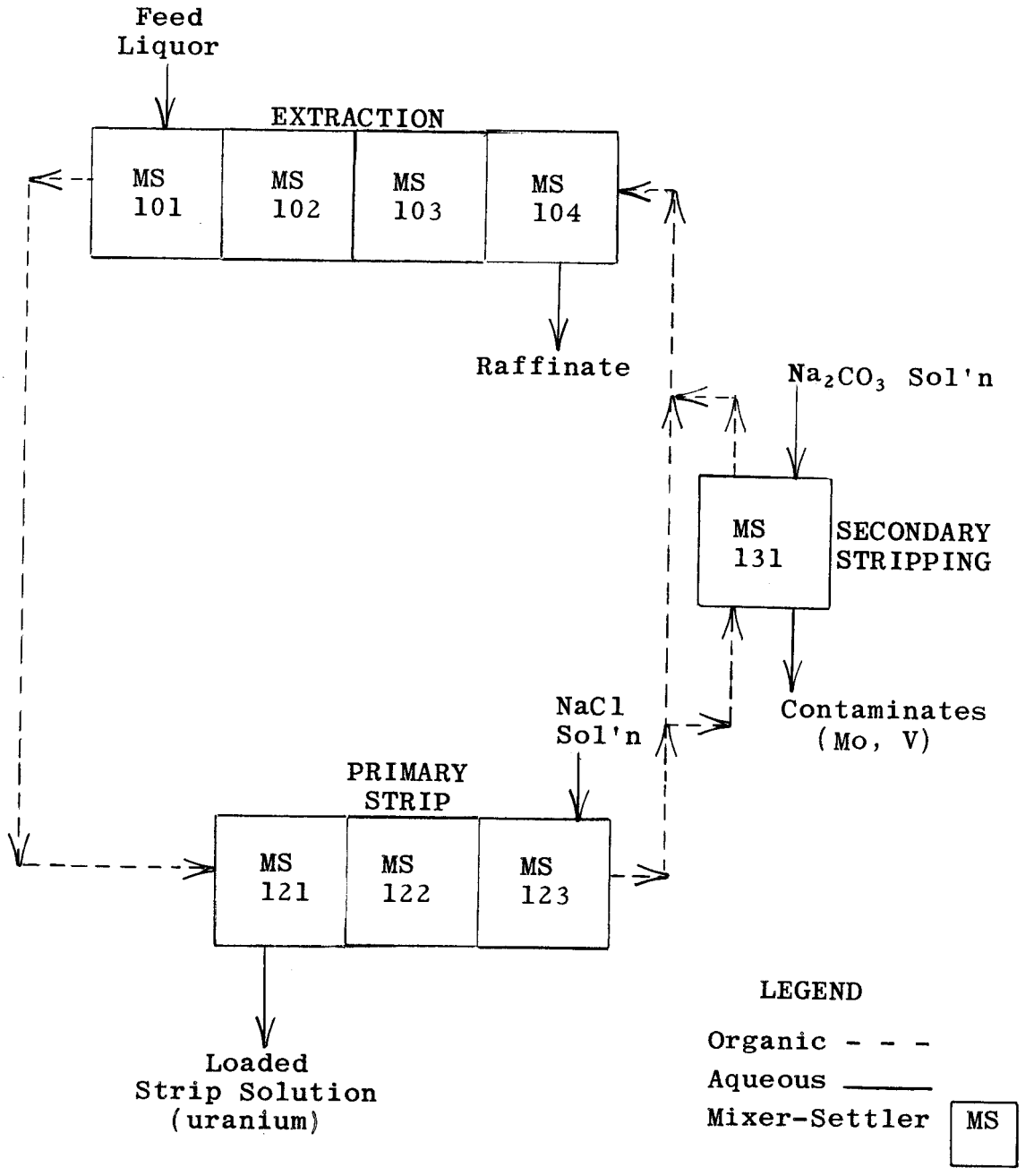


Fig. 3. EXTRACTION--STRIPPING FLOW DIAGRAM

The operating conditions for each run employing Amsco G solvent are given in Table 11, and the compositions of the head liquors and other entering streams in Table 12. The extraction and stripping data for these runs are shown in Tables 13 and 14, and the effect of molybdenum-vanadium buildup in the organic on extraction is shown graphically in Fig. 4. The composition of the uranium products are shown in Table 15.

In runs 1 and 2 of this series, molybdenum or molybdenum and vanadium built up in the organic throughout the run. To show the effect of this accumulation, the data are given, in Table 13, by cycles of the organic phase. However, in runs 3 and 4 the concentrations of these metals in organic were constant, and the data for the entire system at steady state is presented for each of these runs, in Table 14.

Extraction from Mo-V(V) Liquor

In run 1, with a liquor containing 0.3 g/l molybdenum and 0.9 g/l vanadium (V), both metals built up steadily in the organic to 6.0 g/l molybdenum and 1.7 g/l vanadium at 5.6 cycles. A significant loss of uranium in the raffinate started between 1.3 and 2.7 cycles, at an organic molybdenum concentration of about 3 g/l, as shown in Table 13. As shown also, the ratio of molybdenum to vanadium in the organic was essentially constant; the average molar ratio for the run was 1.93.

Extraction from Mo-V(IV) Liquor

Only molybdenum built up in run 2, with a liquor containing 0.3 g/l molybdenum and 0.9 g/l vanadium (IV), but no vanadium(V). The molybdenum concentration in the organic increased steadily to 8.3 g/l at 10 cycles. Loss of uranium to the raffinate began between 8 and 10 cycles, at an organic molybdenum concentration of about 7 g/l.

Extraction from V(V) Liquor

Vanadium did not build up in the organic from a liquor containing 0.7 g/l vanadium(V) and no molybdenum, run 3. The uranium extraction required about three stages, the same as for a run with a standard synthetic liquor under the same conditions.

TABLE 11. OPERATING CONDITIONS

Run number	1	2	3	4
Number of cycles of organic	5.6	10	10	5.6
Flow rates, ml/min:				
Head liquor	150	150	150	150
Organic	50	50	50	50
Chloride strip	7.5	7.5	7.5	7.5
Carbonate strip	-	-	-	3.2
Chloride excess, %	50	50	50	50
Carbonate excess, %	-	-	-	10

TABLE 12. COMPOSITION OF ENTERING STREAMS

Concentrations in grams per liter except as noted

Run	1	2	3	4
Head liquor				
U	1.2	1.2	1.2	1.2
Fe	4.5	2.1	2.0	2.0
Al	3.4	2.9	3.0	2.9
V^{+5}	0.9	0.0	0.7	0.9
Total V	1.2	0.9	1.1	1.1
Mo	0.3	0.3	0.0	0.3
pH	1.0	1.0	1.1	1.0
SO_4	28	39	39	42
PO_4	2.5	2.0	2.0	2.0
Organic				
Amine 9D-178 in Amsco G, M	0.11	0.12	0.11	0.11
Chloride strip				
NaCl, M	1.0	1.0	1.0	1.0
H_2SO_4, M	0.05	0.05	0.05	0.05
Carbonate strip				
Na_2CO_3, M	-	-	-	1.0

TABLE 13. MOLYBDENUM-VANADIUM BUILDUP IN ORGANIC WITH CHLORIDE STRIPPING

No. Number	Organic Cycles	Concentrations, g/l								
		Organic Extract		Stripped Organic		Raffinate		Loaded Strip Solution		
		U	Mo[a]	U	V	U	Mo	U	Mo	V
1[b]	0.7	3.2	1.2	0.001	0.3	0.011	0.02	19	0.05	0.3
	1.3	3.1	2.2	0.001	0.5	0.006	0.03	24	0.06	0.3
	2.7	3.0	3.6	0.001	1.0	0.13	0.04	21	0.06	0.3
	4.1	2.6	4.7	0.001	1.3	0.24	0.05	17	0.07	0.3
	5.6	2.3	6.0	0.002	1.7	0.39	0.05	16	0.08	0.3
2[c]	2	3.6	2.1	0.005	0.1	<0.001	0.02	21	0.09	0.07
	4	3.5	3.7	0.005	0.1	<0.001	0.02	22	0.11	0.06
	6	3.5	5.1	0.005	0.1	<0.001	0.02	22	0.13	0.08
	8	3.5	6.7	0.004	0.2	0.006	0.02	20	0.14	0.05
	10	3.2	8.3	0.004	0.1	0.15	0.03	19	0.14	0.05

(a) Average of extract and stripped organic analyses.

(b) 0.3 g/l Mo
0.9 g/l V(V)

(c) 0.3 g/l Mo
0.9 g/l V(IV)

TABLE 14. EXTRACTION-STRIPPING OF MOLYBDENUM AND VANADIUM LIQUORS AT STEADY STATE

Run Number	Mixer-Settler Number	Concentrations, g/l								Distribution, org/aq		
		Aqueous					Organic					
		U	Mo	V(V)	Cl	pH	U	Mo	V	U	Mo	V
3(a)	Extraction											
	101	0.28	-	0.7	0.3	1.1	3.6	-	0.2	13	-	0.3
	102	0.013	-	0.6	0.4	1.1	1.0	-	0.5	77	-	0.8
	103	0.003	-	0.6	0.4	1.1	0.091	-	0.5	30	-	0.8
	104	0.003	-	0.6	1.3	1.1	0.060	-	0.2	20	-	0.3
	Chloride Stripping											
	121	20.5	-	1.1	15	1.3	0.52	-	0.07	1/41	-	1/16
	122	2.6	-	0.3	35	1.1	0.098	-	0.05	1/27	-	1/6
	123	0.30	-	<0.1	38	0.9	0.064	-	0.03	1/5	-	-
4(b)	Extraction											
	101	0.24	0.03	0.9	<0.05	1.0	3.8	1.1	0.4	16	33	0.5
	102	0.006	<0.01	0.9	<0.05	1.0	0.74	0.23	0.6	120	-	0.6
	103	<0.001	<0.01	0.9	<0.05	1.0	0.023	0.02	0.7	-	-	0.8
	104	<0.001	<0.01	0.7	<0.05	1.1	0.004	0.02	0.7	-	-	1.0
	Chloride Stripping											
	121	21	0.07	1.0	12	1.3	0.87	1.1	0.4	1/24	16	1/2.5
	122	3.8	0.14	0.3	32	1.1	0.11	1.1	0.3	1/35	7.9	1.0
	123	0.56	0.14	<0.1	35	1.0	0.031	1.0	0.3	1/18	7.1	-
	Carbonate Stripping											
	131	0.42	12	2.6	52	6.3	0.004	0.03	<0.1			

(a) 0.0 g/l Mo
0.7 g/l V(V)

(b) 0.3 g/l Mo
0.9 g/l V(V)

TABLE 15. COMPOSITION OF URANIUM PRODUCT*

	Weight Percent			
	Run 3		Run 4	
	Dried at 130°C	Calcined at 600°C	Dried at 130°C	Calcined at 600°C
U	56.	62.	64.	68.
U as U_3O_8	67	73	75	81
Fe	0.28	-	0.35	-
Al	0.04	-	0.03	-
V	3.8	-	3.1	-
Mo	-	-	0.29	-
PO_4	0.46	-	0.62	-
Cl	1.9	<0.1	0.67	<0.1
NH_3	<0.1	0.01	1.8	0.04
L.O.I.(600°C)	7.7	-	11.8	-

*Uranium was precipitated with ammonia from the loaded strip solution.

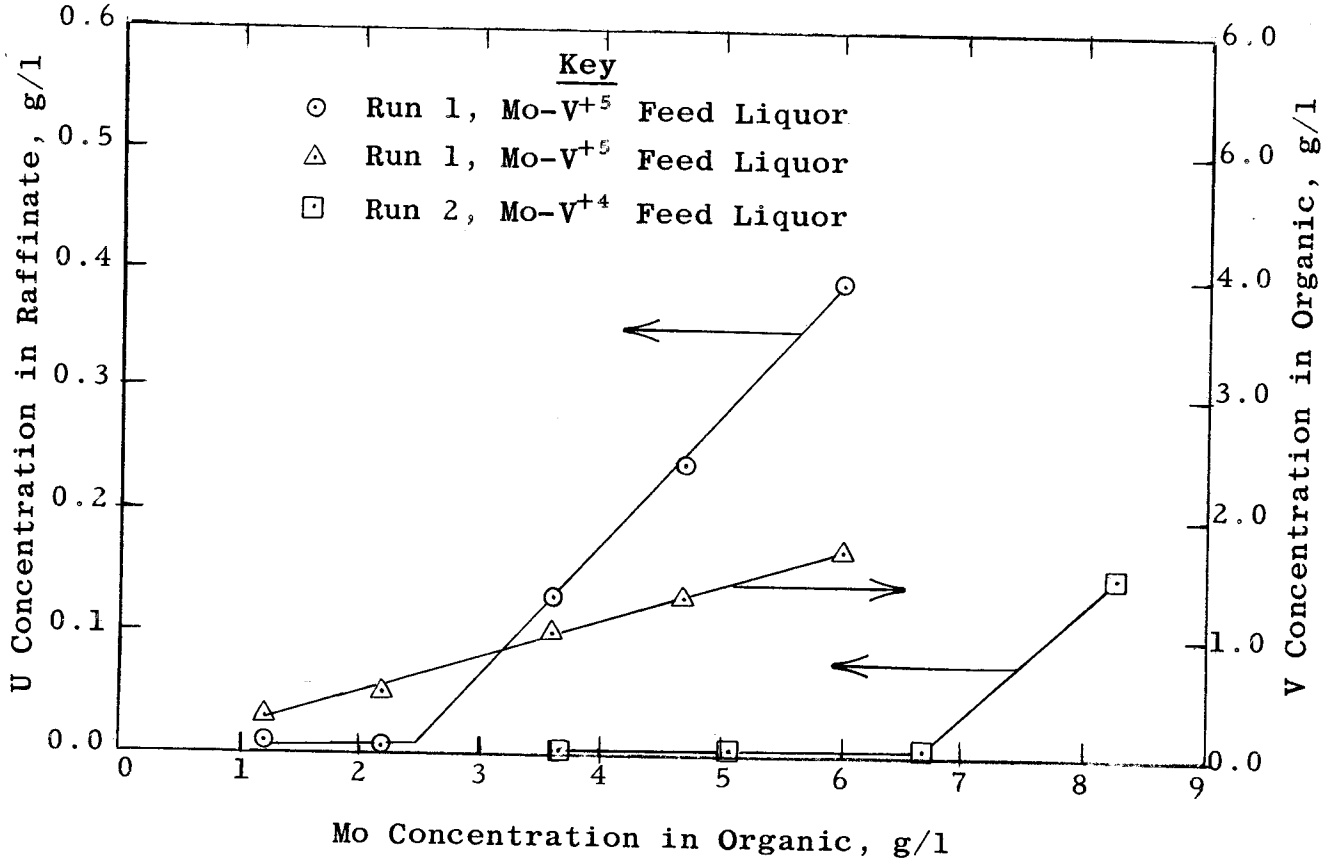


Fig. 4. EFFECT OF MO AND V ON U EXTRACTION

Extraction from Mo-V(V) Liquor with Secondary Stripping

Run 4 is a duplicate of run 1, except that a secondary stripping with sodium carbonate was employed. Since the secondary stripping removed essentially all the molybdenum and vanadium from the organic, there was no buildup in this run. As in run 3, the uranium extraction required about three stages.

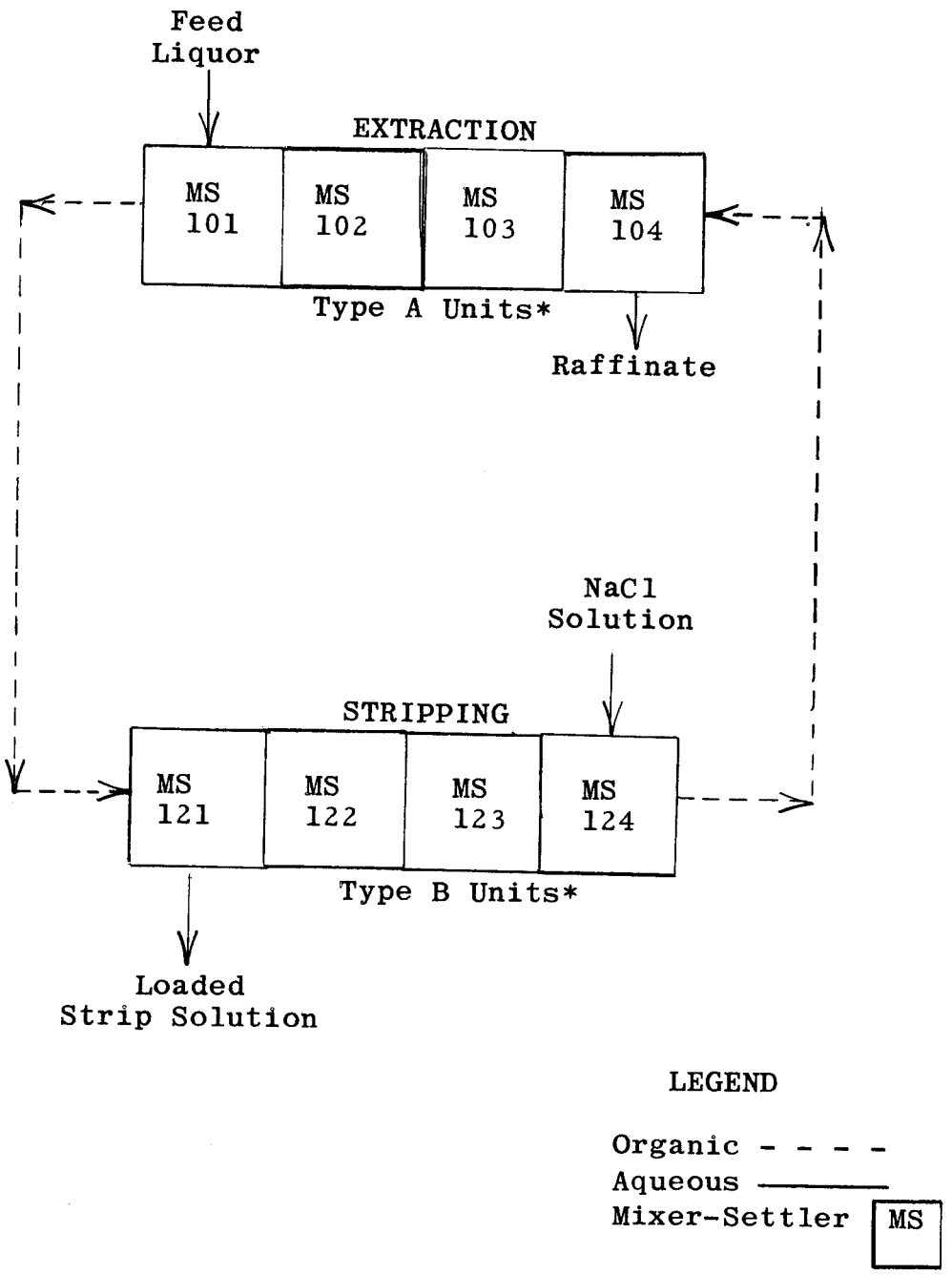
Stripping. The uranium concentration in the chloride stripped organic ranged from 0.001 g/l in run 1 to 0.064 g/l in run 3, compared with about 0.006 g/l in previous tests of chloride stripping under the same conditions (ORNL-2035). As yet, no satisfactory explanation for this variation has been found.

An alternative to secondary stripping for prevention of molybdenum-vanadium accumulation in the organic, is primary stripping with sodium carbonate. However, the consumption of carbonate is considerably greater for primary stripping, since, in this case, 3 moles of carbonate are required per mole of uranium, in addition to the 1/2 mole required per mole of amine in either case. Furthermore, in liquors containing lesser amounts of molybdenum, it would be necessary to secondary strip only part of the organic each cycle, thus further reducing the carbonate consumption. The choice between these two methods depends upon economic factors.

EXTRACTION WITH TRI-N-OCTYLAMINE

Laboratory tests have shown that tri-n-octylamine is an effective uranium extraction agent of high specific loading and selectivity. Three runs were made to determine the feasibility of using this reagent for uranium extraction of both standard and high molybdenum synthetic liquors, in a continuous countercurrent system with chloride stripping. The first two runs employed a standard liquor, and the third a similar liquor containing 1 g/l vanadium(V) and 0.3 g/l molybdenum.

The runs were made in a test array containing four mixer-settlers in the extraction section and four in the stripping section, as shown in Fig. 5. The operating conditions and entering stream compositions are given in Tables 16 and 17, and the extraction-stripping data in Tables 18 and 19. In order to utilize the high loading capacity of tri-n-octylamine, an aqueous to organic flow ratio of 3.9 was maintained in the extraction section, compared with a 3.0 ratio in similar runs with other amines.



*See Fig. 2, ORNL-1970

Fig. 5. EXTRACTION--STRIPPING FLOW DIAGRAM

TABLE 16. OPERATING CONDITIONS

Run number	1	2	3
Operating time, hours	6	6	4
Flow rates, ml/min:			
Head liquor	150	150	150
Organic	39	39	39
Strip solution	5.8	11.6	11.6
Strip solution excess, %	50	200	200

TABLE 17. COMPOSITION OF ENTERING STREAMS

Concentrations in grams per liter except as noted

Run number	1 and 2	3
Head liquor		
Uranium	1.2	1.2
Iron	2.0	2.0
Aluminum	3.0	2.9
Vanadium(V)	0.0	0.9
Molybdenum	0.0	0.3
Phosphate	2.1	2.0
Sulfate	38.	42.
pH	1.0	1.0
Organic		
Tri-n-octylamine, M (in kerosene containing 2 vol % tridecyl alcohol)	0.11	0.11
Chloride strip		
NaCl, M	1.0	1.0
H_2SO_4, M	0.05	0.05

TABLE 18. RUN 1 EXTRACTION-STRIPPING DATA, BY HOURS

Run Time, hrs	Uranium Concentration, g/l			
	Organic Extract	Stripped Organic	Raffinate	Loaded Strip Solution
1	5.0	0.38	<0.001	13
2	5.4	0.54	0.001	15
3	5.5	0.68	0.002	20
4	5.7	0.73	0.002	20
5	5.4	0.75	0.003	24
6	5.6	0.89	0.002	25

TABLE 19. EXTRACTION-STRIPPING DATA AT STEADY STATE

Run Number	Section	Mixer-Settler Number	Composition, g/l			Distribution org/aq
			Aqueous		Organic	
			U	Cl	U	U
1	Extraction	101	0.16	<0.05	5.6	35
		102	0.003	0.06	1.2	400
		103	0.002	0.12	0.83	420
		104	0.002	0.78	0.72	-
2	Extraction	101	0.043	<0.05	4.9	110
		102	0.001	<0.05	0.43	430
		103	<0.001	0.13	0.23	-
		104	<0.001	0.90	0.23	-
2	Stripping	121	13	24	2.0	1/6.5
		122	5.5	33	0.81	1/6.8
		123	1.8	36	0.47	1/3.8
		124	0.91	36	0.23	1/4.0

Presentation of Data. The uranium concentrations in the loaded strip and stripped organic in run 1 were still increasing after six hours, as shown in Table 18. However, over the last four hours of the run the extraction section was essentially at steady state, despite the slightly increasing uranium concentration in the entering stripped organic. Therefore, for this run, the extraction data only are given in the steady state data, Table 19. In run 2, the chloride excess was increased to 200% to increase the stripping efficiency. Since both the extraction and stripping reached steady state, the data for both are given.

Standard Liquor Extraction

The extraction required only two stages, and coefficients of over 400 were obtained in the raffinate stages. In run 1, with 50% chloride excess, the uranium concentration in the stripped organic recycled to the extraction section was 0.9 g/l. Recycling uranium in this manner will increase the loss of uranium to the raffinate, and will also increase the loading of the extract. However, with tri-n-octylamine, the loading capacity and extraction coefficients attained were such that, even at the high extract loading of 5.6 g/l, the uranium concentration in the raffinate was only 0.002 g/l.

In run 2 with 200% chloride excess, the uranium concentration in the stripped organic was 0.2 g/l, and the uranium in the raffinate was less than 0.001 g/l.

The uranium was precipitated with ammonia from the chloride strip solutions. The composition of the dried and calcined products for runs 1 and 2 are shown in Table 20. The grade of the products was high, 86% U_3O_8 after drying and 93% after calcining at 600°C. All impurities in dried product were very low and calcining at 600°C reduced the ammonia content from 1.2 to less than 0.1%.

Molybdenum-Vanadium(V) Liquor Extraction

In run 3 with molybdenum-vanadium(V) liquor, a precipitate, similar to the molybdenum-amine complex precipitate encountered in extraction with amine 9D-178 in kerosene was formed in the stripping section. The exact composition of the precipitate was not determined, but it was undoubtedly an amine complex, since the amine concentration in the organic phase dropped from 0.11 to 0.053M after only five cycles of the organic phase. It is apparent that chloride stripping

TABLE 20. COMPOSITION OF URANIUM PRODUCT*

	Weight Percent			
	Run 1		Run 2	
	Dried at 130°C	Calcined at 600°C	Dried at 130°C	Calcined at 600°C
U	73	80	73	79
U as U_3O_8	86	95	86	93
Fe	101	-	0.06	-
Al	0.05	-	0.10	-
PO_4	0.15	-	0.15	-
Cl	<0.1	<0.1	<0.1	<0.1
NH_3	1.2	<0.1	1.2	<0.1
L.O.I.(600°C)	8.0	-	9.4	-

*Uranium was precipitated with ammonia from the loaded strip solution.

cannot be used in the extraction of molybdenum liquors with tri-n-octyl amine. However, carbonate stripping can be used, since laboratory tests have shown that no amine precipitation is encountered with carbonate stripping under these conditions.'

MIXING AND PHASE SEPARATION

Previous extraction, stripping and entrainment studies using the 6-in. turbine agitated mixer were carried out in March, 1955 (ORNL-2026). Results from these tests indicated that data over a wider range of operating conditions were needed and also that operating techniques needed to be revised to give more consistent and reproducible data.

The fundamental aims of the present program are (1) to determine the extraction and stripping efficiencies of the 6-in. turbine agitator-mixer over an extended range of operating conditions, so that the data may be used for scale-up of the mixer, and (2) to investigate phase separation and entrainment of organic in the aqueous raffinate in mixer-settler equipment.

Extraction-Stripping Studies

Variables having the greatest effect on the extraction-stripping processes are turbine diameter and speed, throughput, phase ratio, and choice of dispersed phase. In the extraction studies to be carried out, tests will be made using the 2", 3", and 4" dia. turbine operating at 0, 100, 200, 300, and 400 rpm. Flow rates will range from 0.5 gpm to 7.0 gpm.

Phase Separation Studies

During the period of January to May, 1955, a limited investigation of phase separation was made using a horizontal settler constructed of 6-in. glass pipe (7 ft long). Data from these tests indicated that a larger settler would be required to obtain scale-up information. A new settler has been fabricated which is rectangular in cross section (1 sq ft) and 5 ft long. Tests are planned to determine the effect of linear flow velocity and settler length on the primary break of phases and also the final entrainment of organic in the aqueous raffinate.

Status

The equipment has been installed and shakedown runs have been made. The study of the efficiency of the mixer for extraction and stripping is now in progress.

SLURRY EXTRACTION

Previously (ORNL-2034 and 2035) batch tests were made in a small turbine agitated mix tank to determine the effect of turbine speed and diameter on the rate of uranium extraction and the amount of organic entrainment in the slurry raffinate. The tests included slurries prepared from two different ores and of varied solids content ranging from 50% to 5 wt % slime slurry. Based on the results of the batch tests a single mixer-settler was designed.

The mixer-settler was operated with continuous flow of phases to determine the extraction efficiency and amount of organic entrainment using three different slurries; Marysvale 5% slime, Lukachukai 9% slime, and Lukachukai 50% sand and slime.

The mixer-settler is shown in Fig. 6. The mixer tank was 6 inches in diameter and 7 inches high with a stand pipe around the shaft to permit operation with the mixer filled with liquid and free of air. The volume of the mixer was 3.5 liters. A standard 3-in. flat-bladed turbine was located in the center of the mixer tank. The settler was a cone-bottom tank 8 inches in diameter and 18 inches high. The nominal volume of slurry and organic in the settler was 2 liters and 10 liters, respectively.

The slurry feed and organic extractant were metered into the bottom of mixer along with recycled organic to maintain the desired phase ratio in the mixer. The mixed phases entered the settler 2 inches above the slurry-organic interface and the organic extract overflowed at the top of the settler. The interface level was controlled by discharging the slime slurries through an adjustable gravity leg and by pumping out the 50% slurry.

The organic phase was kerosene containing di(2-ethylhexyl)phosphoric acid (0.10M) and TBP (30 g/l). In previous slurry studies the organic phase was modified with capryl alcohol; however, recent laboratory tests (ORNL-2002) have shown that TBP is superior to capryl alcohol because in addition to preventing third phase formation in the carbonate strip step, TBP enhances the extraction coefficient for uranium.

The slurries used in the tests were prepared by leaching -20 mesh ore with dilute sulfuric acid (50% solids content) at 50 to 60°C for 16 hours. The slime slurries were prepared by dilution and desanding of the leach slurry in Atkins type classifiers. Final removal of sands was effected in a hydroclone so that less than 1% of the solids were +200 mesh. The composition of slurry feeds is shown in Table 21.

The extraction efficiency and the organic entrainment were determined by sampling the system at steady state, which was during the operating period after four volume changes of slurry in the system. A summary of the test data is given in Table 22.

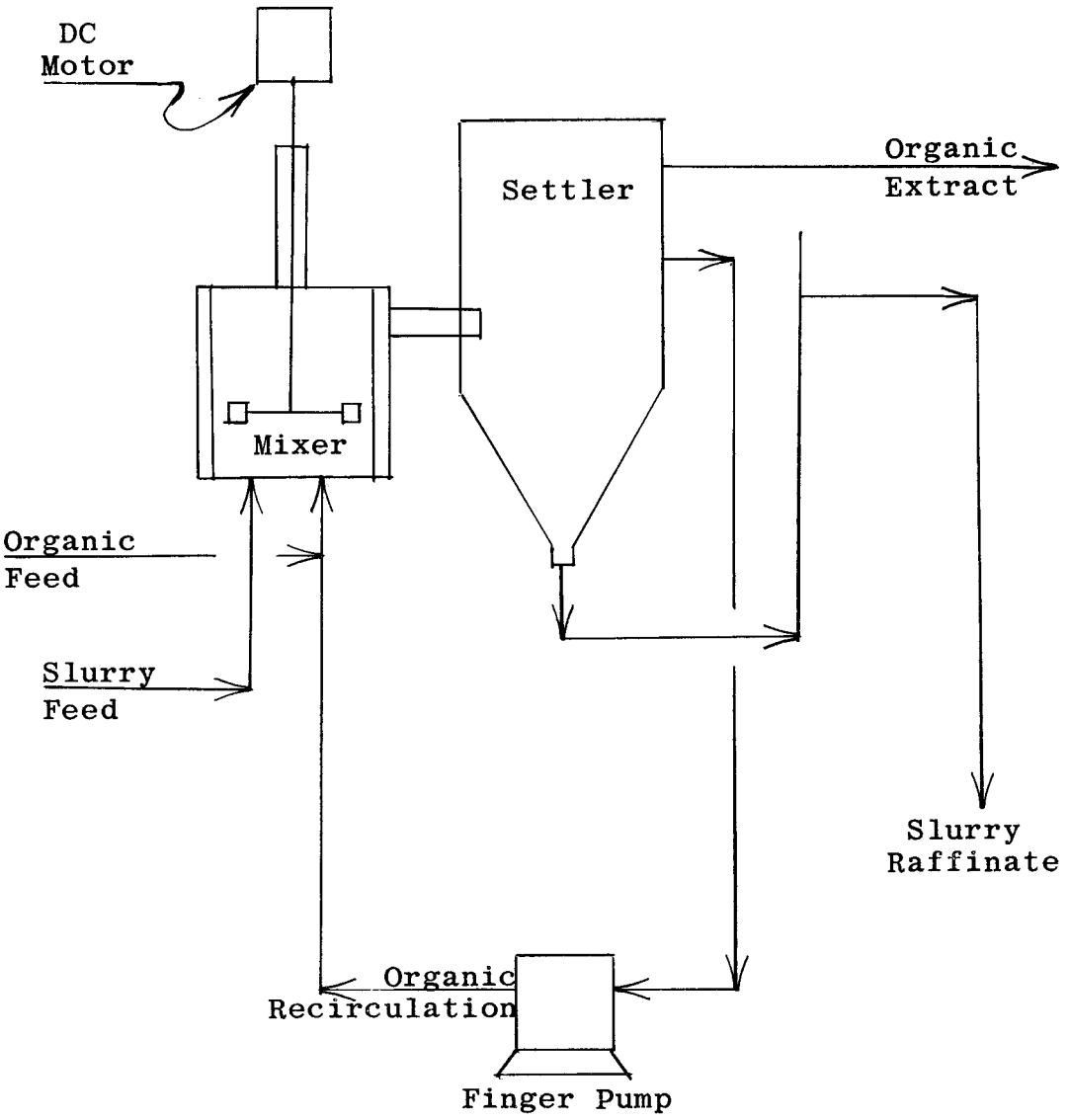


Fig. 6. CONTINUOUS MIXER-SETTLER UNIT

TABLE 21. COMPOSITION OF SLURRY FEEDS

Ore	Marysvale	Lukachukai	Lukachukai
Slurry type	slime	slime	leach
% solids	5	9	50
Liquor portion, g/l			
U	0.34	0.87	3.3
ΣFe	0.83	0.89	2.9
Fe^{+2}	0.23	0.59	2.2
V	-	0.48	3.2
SO_4	14.	15.	41.
PO_4	0.36	0.11	-
pH	1.3	1.3	1.3

The extraction efficiency was calculated from:

$$E = \frac{C_F - C_R}{C_F - C_R*}$$

C_F = Concentration of uranium in slurry feed

C_R = Concentration of uranium in slurry raffinate

C_R* = Concentration of uranium in slurry raffinate after equilibration with the organic extract

The extraction efficiency of the mixer-settler ranged from 83 to 96% depending on the operating conditions. The data shows that the efficiency is virtually independent of residence time in the mixer over the range of 1.6 to 5.8 minutes. The data also shows that efficiency increases with increasing turbine speed, i.e., at 700, 1100, and 1500 rpm the efficiency was 87, 92, and 96%, respectively. At constant turbine speed, the efficiency increased with increasing phase ratio of organic to slurry in the mixer.

TABLE 22. SUMMARY OF EXTRACTION AND ENTRAINMENT DATA

Slurry	Mixer Speed, rpm	Slurry Feed Rate, cc/min	Phase Ratio in Mixer, org/aq	Slurry Residence Time Mixer, min	Slurry Residence Time Settler, min	Agitator Speed in Settler, rpm	Organic* Entrainment gal/ton ore 95% C.I.	Extraction Efficiency, %
Marysvale	700	200	3/1	4.4	10	10	70±10	87
5% slime	1100			4.4	10	10	110±31	92
	1500			4.4	10	10	86±10	96
" "	700	200	2/1	5.8	10	2	110±24	83
			3/1	4.4	10	2	94± 5	85
			5/1	2.9	10	2	120±29	87
			10/1	1.6	10	2	86±24	90
" "	700	70	3/1	12	30	10	98±29	-
			10/1	4.5	30	10	65±24	95
			20/1	2.4	30	10	62±12	96
" "	700	200	3/1	4.4	10	2	94± 5	-
				4.4	10	4	84±10	-
				4.4	10	10	70±10	-
Lukachukai	700	200	5/1	2.9	10	0	64±19	-
9% slime	700	200	10/1	1.6	10	0	32± 9	-
Lukachukai	700	200	20/1	0.8	10	0	100±24	93
50% leach	1500	200	20/1	0.8	10	0	48±30	96

*Based on ore which was 50% slime.

The organic entrainment in the slurry raffinate was determined by extraction of the di(2-ethylhexyl)phosphoric acid with several portions of a benzene-ethyl alcohol mixture. The total alkyl phosphoric acid in the combined benzene phases was determined by titration and the entrainment was calculated therefrom. An over-all comparison of the entrainment data in Table 22 shows that the entrainment is of the same order of magnitude (30 to 120 gal/ton ore) for all three slurries tested, 5% Marysvale slime, 9% Lukachukai slime and 50% Lukachukai sand and slime. And in all cases the entrainment was considerably greater than the amount that can be discarded. Therefore, it would be necessary to provide an organic recovery step.

The operating conditions for extraction from 5% Marysvale slime were varied in an attempt to get low entrainment. Although minor effects of turbine speed, phase ratio, settler residence time and agitation in the settler were observed, no real progress was made toward attaining entrainment in the order of 2 or 3 gal per ton or less.

From the results of these preliminary tests it is apparent that the major problem of slurry extraction remains to be recovery of the entrained organic from the slurry raffinate. Furthermore there is no large difference of entrainment in dilute slime slurries and 50% leach slurries. Therefore, future studies are planned to investigate extraction from 50% leach slurry followed by dilution of the raffinate to recover the organic. The first phase of this study will be a comparison of slurries from different ores.