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PROGRESS REPORT OF ENGINEERING SECTION
RAW MATERIALS PROCESS TESTING

May--June, 1955

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PROGRESS REPORT OF ENGINEERING SECTION

RAW MATERIALS PROCESS TESTING

May--June, 1955

AMINE EXTRACTION PROCESS TESTING

Countercurrent Stripping With Sodium Chloride

In laboratory studies of the effectiveness of chloride ion as an agent for stripping uranium from organic extract, both neutral and acid sodium chloride solutions were used. The results of these tests indicated that the equilibrium uranium concentration in the stripped organic decreased with decrease in pH. It was also shown that the equilibrium concentration decreased with increase in chloride excess in neutral salt solution. To study these effects in a continuous, countercurrent system, runs were made with 50 and 200% excess chloride with neutral salt solution, and with 50% chloride excess with the pH ranging from that of a neutral salt solution to the equivalent of a 0.18N acid solution.

The runs were made in a test array that contained three mixer-settlers in the extraction section and three in the stripping section, arranged as shown in Fig. 1.

The composition of the head liquor is given in Table 1. The organic phase was a 0.1M solution of amine 9D-178* dissolved in kerosene. The head liquor and organic flow rates were 150 and 50 ml/min, respectively, and the average loading of uranium in the organic phase was 3.6 g/l. A 1.0M sodium chloride stripping solution was used in all runs. The pH of the solution was adjusted with sulfuric acid in three runs and with hydrochloric acid in one run, in order to compare the effect of the two acids on the equilibrium uranium concentration in the stripped organic. The strip solution flow rates were 7.5 and 15.0 ml/min, respectively, for 50 and 200% chloride excess. The excess was calculated from the theoretical requirement of 1 mole of chloride per mole of amine. Operating time was sufficient to achieve 10 complete cycles of the organic phase in each run.

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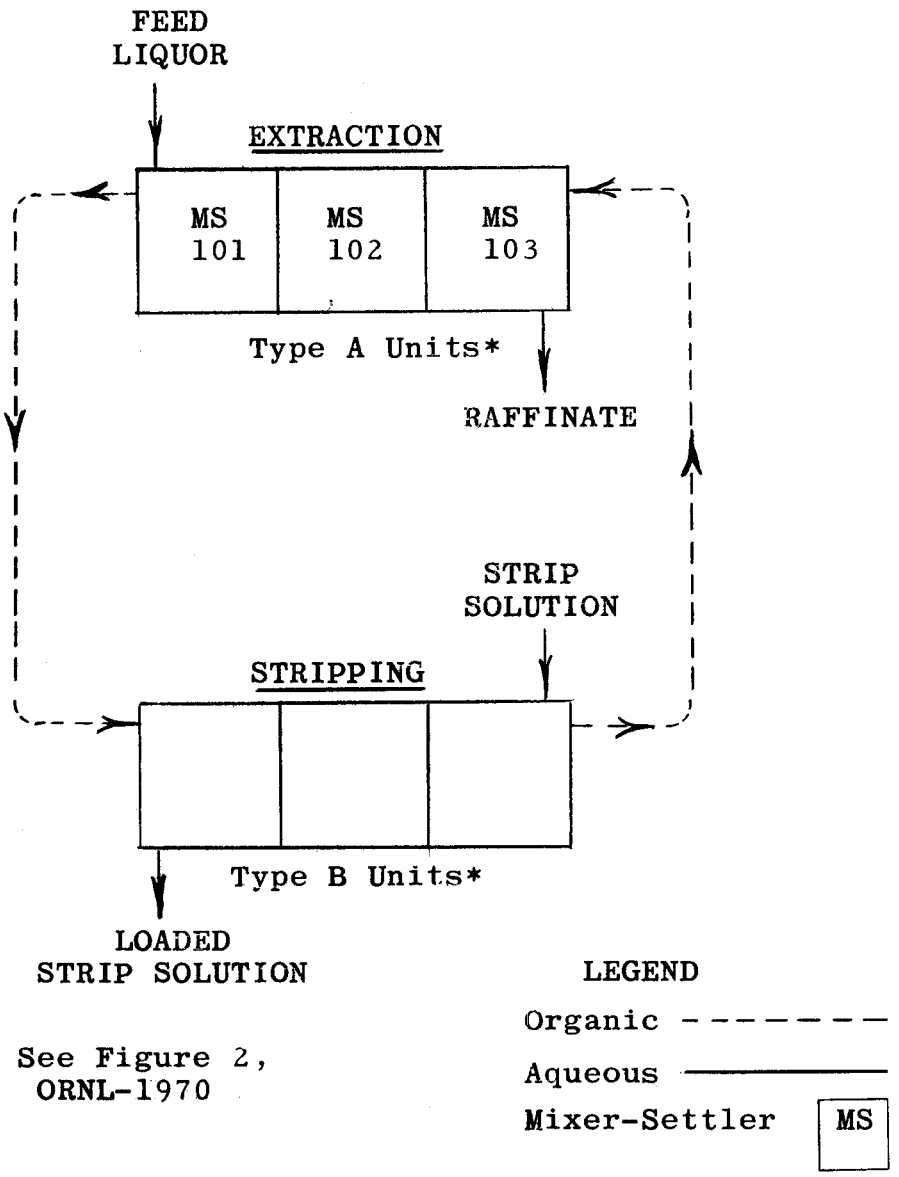
*Rohm and Haas Company, Philadelphia, Pa.



See Figure 2,
ORNL-1970

FIGURE 1. EXTRACTION-STRIPPING FLOW SHEET

TABLE 1. HEAD LIQUOR COMPOSITION

Component	Concentration, g/l[a]
Uranium	1.2
Iron	5.6
Aluminum	3.4
Phosphate	2.5
Sulfate	42
pH	1.1

(a) Concentrations in grams per liter except for pH.

The data showing the effects of pH and reagent excess on stripping efficiency are reported in Tables 2 and 3. An average of the product analyses for all runs is given in Table 4, and the extraction data for a typical run are shown in Table 5.

Effect of pH. The uranium concentration in the stripped organic decreased from 0.033 to 0.005 g/l when the pH was decreased from 6.5 to 0.9 (Table 2). A decrease in pH to 0.7 had no further effect.

Effect of Chloride Excess. As shown in Table 3, the uranium in the stripped organic decreased from 0.033 to 0.019 g/l as the chloride excess was increased from 50 to 200%, and although the uranium distribution coefficient nearly doubled in the first stage, it decreased by over three-fourths in the two following. The over-all result was a comparatively small increase in stripping efficiency in return for a large increase in reagent excess.

Uranium Product. The analyses of the products obtained from the runs by precipitation with sodium hydroxide were essentially the same. Therefore, an average of these analyses is shown in Table 4. The U_3O_8 content of the products was 84%, and no major impurity exceeded 0.5%. The chloride concentration was less than 0.05%.

TABLE 2. EFFECT OF pH ON STRIPPING

Run No.	Strip Solution[a] H_2SO_4 Conc.,N	pH	Mixer-Settler No.	Concentration, g/l Aqueous pH	U	Cl	Org U	Distribution, aq/org U
1[b]	0	6.5	121	1.9	23	15.	0.56	41
			122	2.3	3.4	35.	0.058	59
			123	2.5	0.30	35.	0.033	9
3	0.030	1.4	121	1.8	25	15.	0.62	40
			122	1.8	4.3	33.	0.044	98
			123	1.6	0.34	36.	0.013	26
4	0.088	1.0	121	1.6	24	15.	0.58	41
			122	1.4	3.7	33.	0.026	140
			123	1.2	0.26	36.	0.005	52
5	0.100[c]	0.9	121	1.4	24.	16.	0.44	55
			122	1.2	3.4	34.	0.023	150
			123	1.1	0.19	37.	0.006	32
6	0.182	0.7	121	1.1	22.	15.	0.35	63
			122	0.9	3.8	33.	0.025	150
			123	0.8	0.23	36.	0.005	46

(a) 1N chloride, 50% excess; phase ratio 6.67 org/aq.

(b) Data confirmed by a duplicate run.

(c) Acidified with HCl rather than H_2SO_4.

TABLE 3. EFFECT OF SODIUM CHLORIDE EXCESS ON STRIPPING

Run No.	Strip Solution Excess[a], %	Phase Ratio, org/aq	Mixer-Settler Number	Concentration, g/l Aqueous pH	Aqueous U	Aqueous Cl	Org U	Distribution, aq/org U
1[b]	50	6.67	121	1.9	23.	15	0.56	41
			122	2.3	3.4	35	0.058	59
			123	2.5	0.30	35	0.033	9
2	200	3.33	121	2.3	12.	27	0.15	80
			122	2.6	0.38	37	0.031	12
			123	2.8	0.042	37	0.019	2

(a) 1N chloride, pH 6.5.

(b) Data confirmed by a duplicate run.

TABLE 4. PRODUCT COMPOSITION

(Dried at 130°C)

Constituent	wt %*
U_3O_8	84.0
Fe	0.27
Al	0.25
PO_4	0.37
SO_4	0.26
Cl	0.05
Loss on ignition	4.3

*Average analysis from several runs.

Extraction. The variation in stripping conditions in these runs had no appreciable effect on the extraction over the 10 cycles of organic phase; therefore, the extraction data presented in Table 5, which are for the run made with 50% excess neutral sodium chloride solution are considered typical. Three stages were sufficient for satisfactory extraction (to 0.003 g U/l in the raffinate). Previous runs (Feb. '55) with carbonate stripping have also required about three stages, indicating that the recycling of chloride stripped organic has no appreciable effect on the extraction.

TABLE 5. EXTRACTION DATA*

Stage	Concentration, g/l			Uranium Distribution, org/aq
	Aqueous		Organic	
	U	Cl	U	
101	0.57	<0.1	3.2	6
102	0.036	0.3	1.6	46
103	0.003	1.0	0.16	53

*Run 1. Data from other runs was essentially the same.

Future Work. The study of chloride stripping in the countercurrent system will be continued using feed liquors containing molybdenum and vanadium. These metals are not stripped by chloride and would accumulate in the organic phase. The maximum concentrations of these metals in the head liquor at which no appreciable interference with uranium extraction occurs will be determined, and the use of a secondary strip with sodium carbonate will be studied for extracts from liquors exceeding the maximum concentrations.

Rate of Stripping from Armeen 2-12

Earlier in the raw materials process testing program, Armeen 2-12* dissolved in Amsco G containing 5 vol % capryl alcohol was shown to be a suitable agent for extracting uranium from sulfuric acid leach liquors. Although aqueous sodium carbonate solutions** were used to strip uranium from the organic extracts in the tests, the effects of the degree of dispersion (as measured by the power input to the impeller) on the stripping rate have not been studied.

To obtain the data needed for preliminary cost estimates, batch tests were made in the 6-in. dia. mixer tank with power inputs of 0.002 and 0.03 hp per gal to a 3-in. dia. turbine-type impeller. The equipment, test procedures, and methods for deriving the reaction rate constants are described in detail in ORNL-2026. The organic phase was 0.1 molar in amine and the extract contained 3.6 g/l uranium. Sodium carbonate (0.7 molar sol'n) was 35% in excess of the theoretical requirement based on 1/2 mole per mole of amine and 3 moles per mole of uranium. A summary of the test data is shown in Table 6.

The results show that the reaction rate constant, K, decreased from 27 to 7 seconds with increase in power from 0.002 to 0.03 hp/gal. These results were not significantly different from those obtained with other amines dissolved in kerosene.

No further tests with Armeen 2-12 are planned for the immediate future.

---

*A mixture of secondary amines of which di-dodecyl (di-lauryl) amine is the principal constituent.

**Aqueous sodium chloride solutions are not suitable for stripping Armeen 2-12 since the amine chloride salt is not readily soluble in the kerosene-capryl alcohol solvent at room temperature.

TABLE 6. RATES OF STRIPPING OF URANIUM FROM ARMEEN 2-12* BY Na_2CO_3

35% excess Na_2CO_3 (0.7M Na_2CO_3 sol'n)
Phase ratio: 5.2 organic to aqueous
Turbine dia.: 3-inch

Impeller Speed, rpm	Power Input, hp/gal	K,** sec	Uranium Concentration in Organic, g/l — Mixing Time, sec 0	10	30	60	120	240	480
278	0.002	27	3.6	1.20	0.89	0.39	0.046	0.008	0.003
700	0.03	7	3.6	0.64	0.022	0.006	0.003	0.003	0.003

*0.1 molar in Amsco G containing 5 vol % capryl alcohol.

**Reaction rate constant.

SLURRY EXTRACTION

Mixing Variables with 40 wt % Slurry

In continuation of the study of the effects of mixing variables on the rate of extraction of uranium from leach slurries and the amount of organic entrainment, batch extraction tests were made with 40 wt % slurry in which the impeller size and speed were varied over the same ranges as those employed with 50 wt % slurry (ORNL-2034).

The slurry was prepared by leaching -20 mesh Marysvale ore with dilute sulfuric acid* for 16 hours. The organic phase was a 0.1 molar solution of di(2-ethylhexyl) phosphoric acid dissolved in kerosene containing 2 vol % capryl alcohol.

The equipment and procedures employed in making the tests were the same as those described in ORNL-2034. The test data are shown in Table 7.

Effect on Extraction. As in the previous period (ORNL-2034) rates of extraction were evaluated by the use of rate constants (see ORNL-2026). The extraction data are summarized in Table 8.

The results show that with a D/T ratio of 0.5 there was a decrease in the rate constant from about 16 to 4 seconds as the power was increased from 0.03 to 0.12 hp/gal; there was no further change when the power was increased to 0.31 hp/gal. With a D/T ratio of 0.67 there was a consistent decrease in the rate constant from 17 to 2 seconds as the power was increased from 0.03 to 0.31 hp/gal. With the power constant at 0.03 hp/gal the rate constant was 8 seconds with a D/T ratio of 0.33 and about 16 with ratios of 0.5 and 0.67. These results show that a power input of 0.12 hp/gal and a D/T ratio of 0.5 are satisfactory from the standpoint of uranium extraction.

In the tests made with 50 wt % slurry (ORNL-2034) under essentially the same conditions there was no significant effect of either power input or D/T ratio on the reaction rate.

Effect on Entrainment. There was no marked effect of power input or D/T ratio on the amount of initial organic entrainment as shown in Table 9.

The lowest residual entrainment after dilution and slow agitation was 2 gal/ton of ore which was obtained with a D/T ratio of 0.67 at a power input of 0.03 hp/gal as shown in Table 10.

*Equivalent to 100 lbs of 98% H_2SO_4 per ton of ore.

TABLE 7. TEST DATA FOR 40 WT % SLURRY

Mixing Conditions			Uranium Concentration in Raffinate, g/l							Reaction Rate Constant, sec
Turbine Diameter, in.	Turbine Speed, rpm	Power Input, hp/gal	Mixing Time, sec							
			0	10	30	50	70	120	300	
2	1380	0.03	1.8	0.053	0.033	0.019	0.017	0.011	0.006	8
3	700	0.03	1.8	0.16	0.044	0.034	0.039	0.023	0.014	16
3	1100	0.12	1.8	0.043	0.018	0.012	0.012	0.011	-	4
3	1500	0.31	1.8	0.036	0.02	0.018	0.013	0.012	0.004	4
4	430	0.03	1.8	0.15	0.055	0.034	0.032	0.023	0.013	17
4	680	0.12	1.8	0.068	0.035	0.028	0.025	0.020	0.012	11
4	930	0.31	1.8	0.024	0.013	0.010	0.009	0.008	-	2

TABLE 7 (continued)

Mixing Conditions			Organic Entrainment			
			Before Dilution		After Dilution	
Turbine Diameter, in.	Turbine Speed, rpm	Power Input, hp/gal	ml / Kg slurry	gal / ton ore	ml / Kg slurry*	gal / ton ore
2	1380	0.03	170	100	25	15
3	700	0.03	150	90	8	5
3	1100	0.12	100	60	35	20
3	1500	0.31	120	70	15	9
4	430	0.03	150	90	3	2
4	680	0.12	110	70	5	3
4	930	0.31	150	90	8	5

*Based on original slurry.

TABLE 8. RATE OF EXTRACTION

Power Input, hp/gal	Rate Constants, sec		
	D/T,* 0.33	D/T,* 0.50	D/T,* 0.67
0.03	8	16	17
0.12	-	4	11
0.31	-	4	2

*Diameter of impeller/diameter of tank.

TABLE 9. ORGANIC ENTRAINMENT BEFORE DILUTION

Power Input, hp/gal	Entrainment, gal/ton ore		
	D/T ratio* 0.33	D/T ratio* 0.50	D/T ratio* 0.67
0.03	100	90	90
0.12	-	60	70
0.31	-	70	90

*Diameter of impeller/diameter of tank

TABLE 10. ORGANIC ENTRAINMENT AFTER DILUTION

Power Input, hp/gal	Entrainment, gal/ton of ore		
	D/T Ratio* 0.33	D/T Ratio* 0.50	D/T Ratio* 0.67
0.03	20	5	2
0.12	-	20	3
0.31	-	10	5

*Diameter of impeller/diameter of tank.

The initial entrainment in tests with 40 wt % slurry were about 50 percent higher than they were with 50% slurry under essentially the same test conditions. However, there was little difference in the amount of residual entrainment.

Effect of Pulp Density

To determine the effects of slurry density on extraction rate and phase entrainment, batch extraction tests were made using a leach slurry containing 30 wt % solids and slurries containing 15, 10, and 5 wt % solids from which +200 mesh sands had been removed. The slurries were prepared by leaching Marysvale ore with dilute sulfuric acid as described previously (ORNL-2034). Uranium concentration in the 10 and 5% slurries was increased to equal that in the 15%. The organic phase, equipment, and procedures were the same as those employed in the studies made with 40 and 50 wt % slurries. The tests were carried out with power input and D/T ratio fixed at 0.03 hp/gal and 0.5, respectively. All other conditions were the same as those used previously. The data are reported in Table 11.

The results show that (a) the extraction rate was 2 seconds with all four slurries showing that the extraction rate was very rapid; (b) the initial organic entrainment with 30, 15, and 10 wt % slurries ranged from 90 to 110 gal/ton of ore while with 5 wt % it was 30 gal/ton of ore; and (c) the residual organic entrainment (after dilution to 5 wt % solids and slow agitation) ranged from 1 to 2 gal/ton of ore with all four slurries.

Batch extraction tests are in progress using 50, 10, and 5 wt % Uravan slurries in order to provide a comparison of the extraction rate and organic entrainment between slurries made from leaching two different ores.

Extraction Rate and Phase Entrainment with Uravan Slurries

The effects of mixing variables on the rate of uranium extraction and amount of organic phase entrainment have been studied in batch tests using leach slurries prepared from Marysvale ore. To investigate the possible differences in results due to types of ore, batch tests were made with leach slurries prepared from Uravan ore* containing 50, 8, and 5 wt % solids.

---

*Uravan stock pile.

TABLE 11. TEST DATA FOR DILUTE MARYSVALE SLURRY

Slurry Density, % Solids	Reaction Rate Constant, sec	Uranium Concentration in Raffinate, g/l						
		Mixing Time, sec						
		0	10	30	50	70	120	300
30	2	0.89	0.002	0.002	0.001	0.001	0.002	0.002
15*	2	0.86	0.006	0.006	0.004	0.004	0.003	0.005
10*	2	0.86	0.006	0.002	0.002	0.001	0.001	0.001
5*	2	0.86	0.004	0.001	0.002	0.001	0.001	0.001

*Slime slurries free of +200 mesh sands.

TABLE 11 (continued)

Slurry Density, % Solids	Organic Entrainment	
	Before Dilution, gal/ton of ore	After Dilution,** gal/ton of ore
30	110	1
15*	90	2
10*	110	1
5*	30	2

*Slime slurries free of +200 mesh sands.

**Diluted to 5 wt % solids.

The 8 and 5 wt % slurries were prepared by diluting 50 wt % slurry with water and removing the +200 mesh sands. The organic phase was a 0.1 molar solution of di(2-ethylhexyl) phosphoric acid dissolved in kerosene containing 2 vol % capryl alcohol. The equipment and procedures employed in making the tests were the same as those described in ORNL-2034. The test data are summarized in Table 12.

The results show that the rate of uranium extraction was very rapid with all three slurries, initial organic entrainment decreased from 80 gal/ton of ore to 7 as the solids content of the slurry decreased from 50 to 5 wt %, and the residual organic entrainment ranged from 1 to 2 gal/ton of ore with all three slurries. These results were not appreciably different from those obtained with Marysvale slurries containing about the same amount of solids. No further work on this phase of the slurry extraction program is planned.

Recovery of Organic from Slurry Raffinate

Previously (ORNL-2026), scouting tests were started to determine methods for recovery of organic from slurry raffinate. The results of these tests showed that the organic could be recovered by alternate agitation and settling of diluted slurry raffinate (5% solids). The study of organic recovery was continued in a mechanically agitated tank to determine the effect of agitator speed and mixing time on the organic recovery.

The tests were made in a 6-in. diameter tank with a rake-type agitator as shown in Fig. 2. The agitator consisted of rakes and screens (10-mesh) designed to keep the slimes suspended so that small droplets of entrained organic would be freed and rise to the surface of the slurry.

The slurry raffinate for the tests was prepared by extracting a 5% Marysvale slurry (-200 mesh) in a 6-in. mix tank using a 3-in. turbine at 700 rpm. The organic phase was 0.1 molar di(2-ethylhexyl) phosphoric acid in kerosene (2% capryl alcohol). The phase ratio was 10 volumes of organic to 1 of slurry. After extraction the slurry raffinate was separated from the organic phase and charged into the organic recovery tank to a level even with the top of the agitator. To prevent re-entrainment of released organic a layer of water was maintained over the slurry. After the slurry was agitated for the desired time, all of the slurry phase was withdrawn and the residual organic was determined by steam distillation.

TABLE 12. TEST DATA FOR URAVAN SLURRY

Phase ratio: 10 org to 1 slurry
Power input: 0.03 hp/gal (700 rpm)
D/T ratio: 0.5 (3-in. turbine dia.)

Slurry* Density, wt % Solids	Uranium Concentration in Raffinate, g/l							Reaction Rate Constant, sec
	Mixing Time, sec							
	0	10	30	50	70	120	300	
50	2.9	0.031	0.028	0.021	0.020	0.015	0.005	2
8	1.4	0.043	0.007	0.006	0.003	0.001	0.001	4
5	0.69	0.003	0.001	0.003	0.001	0.001	0.001	2

TABLE 12 (continued)

Slurry* Density, wt % Solids	Before Dilution, gal/ton ore	After Dilution, gal/ton ore
50	80	2
8	30	1
5	7	1

*Leached ore contained about 30 wt % of -200 mesh solids.

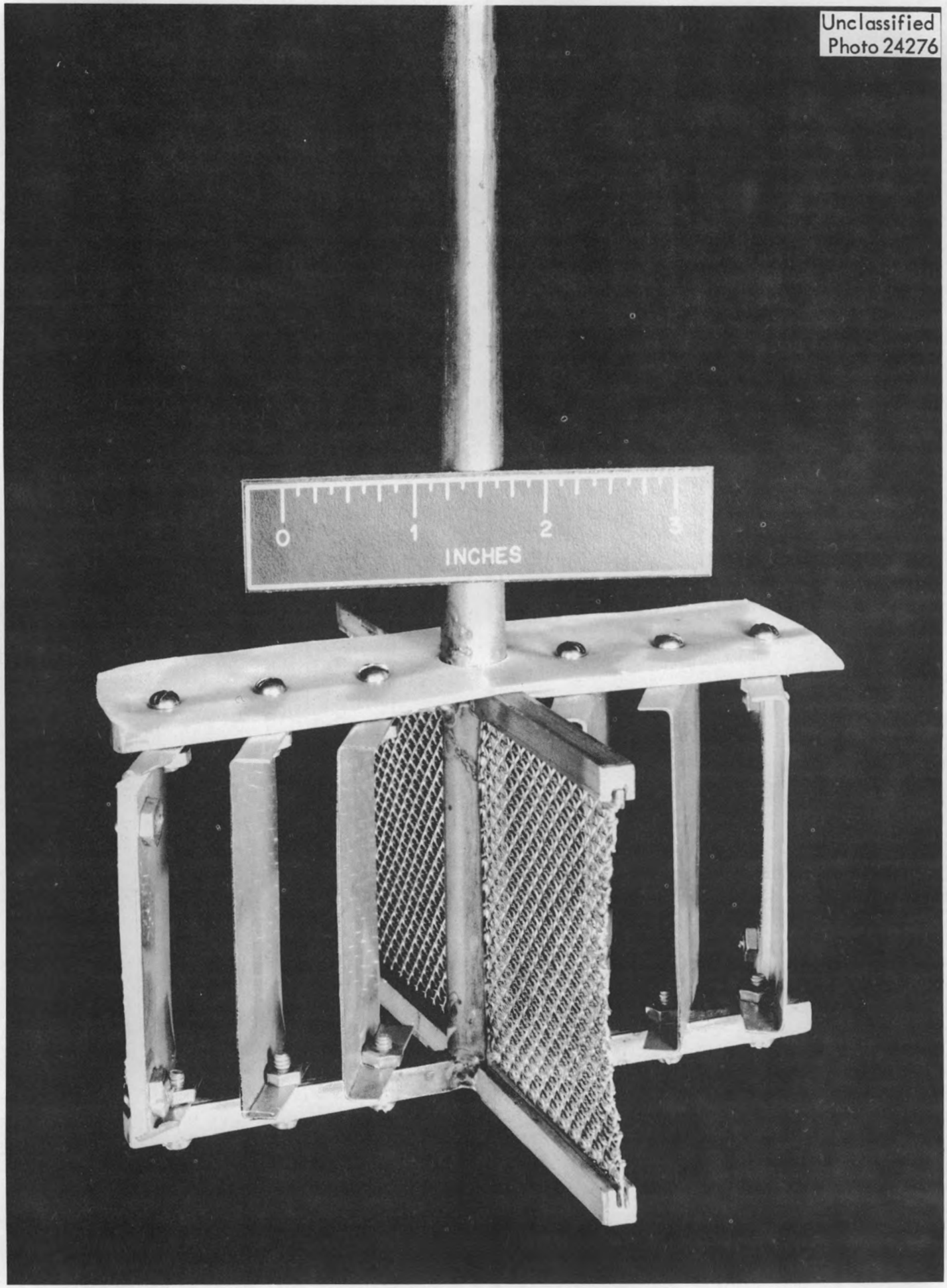


Figure 2. Rake Agitator Used in Organic Recovery Tests.

A plot of the residual organic entrainment and time of agitation is shown in Fig. 3. With an agitator speed of 1 rpm the organic entrainment decreased from the original 50 gal/ton of ore to about 0.6 gal/ton of ore after 3 hours' agitation. A loss of 1.2 gal of organic per ton of ore has been chosen for preliminary cost comparison of slurry extraction with clarified liquor extraction. As shown in Fig. 3 about 2 hrs were required to reduce the organic entrainment to 1.2 gal/ton of ore. The rate of recovery of organic was essentially the same with agitator speeds of 1, 2, 3, and 4 rpm. Higher agitator speeds were tried, but the slurry was mixed into the water layer giving a more dilute slurry. The rate of organic recovery was increased, but not enough to overcome the larger holdup required for the more dilute slurry.

A single mixer-settler unit will be fabricated and installed so that the effects of mixing variables on the amount of phase entrainment can be studied under continuous operating conditions. It is also planned to continue studies of the possible utility of slow agitation in settlers or hold tanks as a means for decreasing organic entrainment in raffinate.

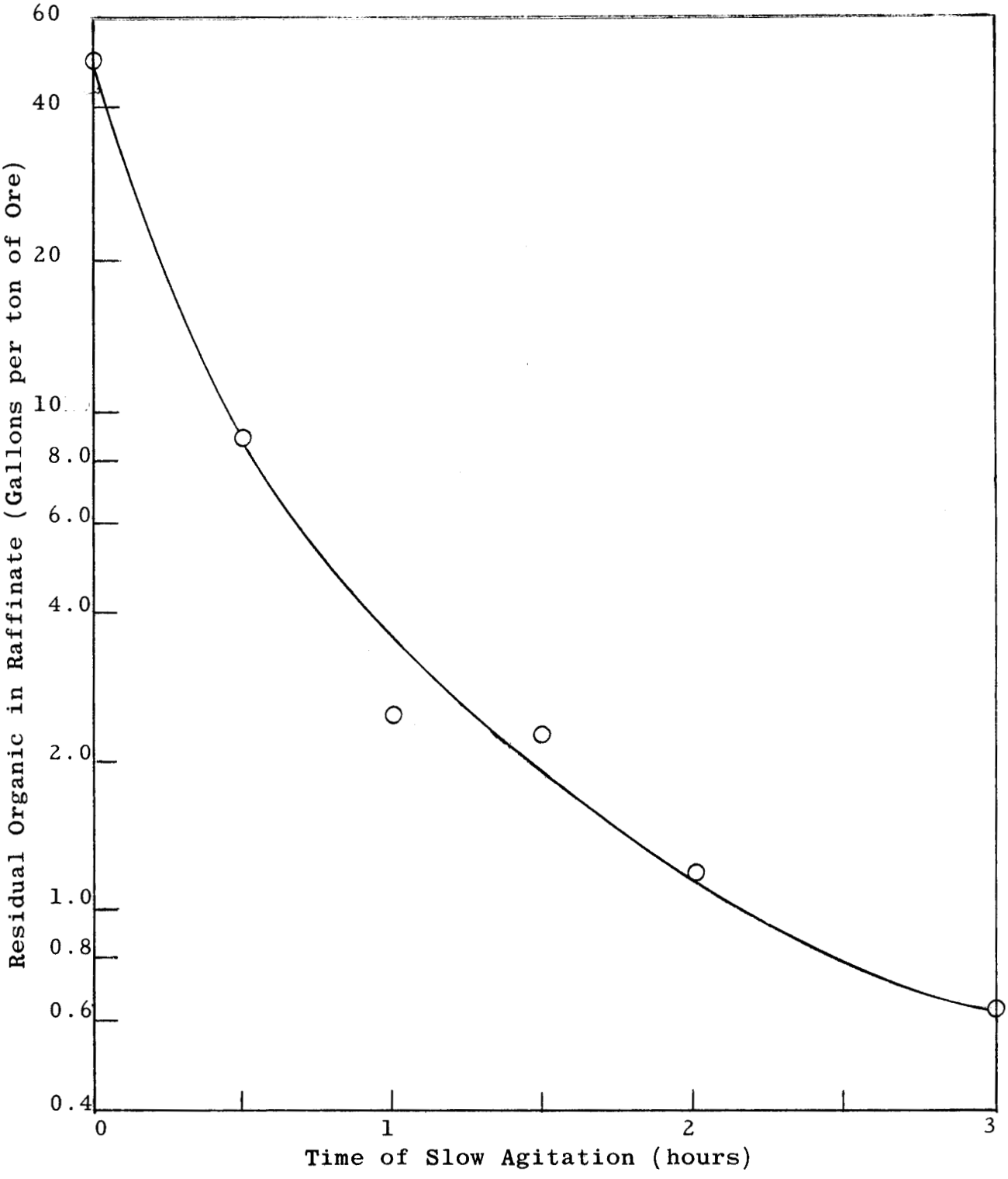


FIGURE 3. EFFECT OF SLOW AGITATION TIME ON RESIDUAL ORGANIC