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PROGRESS REPORT OF PILOT PLANT SECTION

RAW MATERIALS PROCESS TESTING

MARCH 1955

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PROGRESS REPORT OF PILOT PLANT SECTION RAW MATERIALS PROCESS TESTING

March, 1955

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AMINE EXTRACTION PROCESS TESTING

Stripping Studies

In the amine extraction process, uranium is stripped from the organic extract by use of a stripping agent for which the amine has a stronger affinity than it has for either sulfuric acid or the uranium sulfate complex. With sodium carbonate solution, for example, the amine associated with the uranyl sulfate complex and amine sulfate are converted to free amine while the uranyl sulfate reacts with sodium carbonate to form a carbonate complex which is soluble in the aqueous phase. In most of the work carried out to date, sodium carbonate in aqueous solution has been employed as the stripping agent. In addition to sodium carbonate, the laboratory group has recommended aqueous solutions of sodium chloride and of ammonium nitrate.

Batch stripping tests were made with each of these agents. The results of these tests will define the operating conditions for tests to be made on a continuous basis.

Sodium carbonate and sodium chloride were tested to determine the effects of reagent excess, power input and impeller size* on the rate and degree of completion of each stripping reaction, and to evaluate the amount of residual entrainment in each phase after the primary phase separation. Ammonium nitrate was also tested, but only the effect of reagent excess was investigated.

The organic extract used in the tests contained 3.37 g/l uranium. It was prepared by continuous countercurrent extraction of a standard synthetic liquor with a 0.1 M amine 9D-178** solution in kerosene using an aqueous to organic phase flow ratio of 3:1. The tests were carried out by mixing

---

*Rushton and coworkers have shown that, in a mixer at constant power, the ratio of internal flow to turbulence varies as the size of the impeller is varied. For example, a large-diameter low-speed impeller produces a large ratio of flow to turbulence while a small-diameter high-speed impeller with the same power input will give a small ratio[1].

**Rohm and Haas Company, Philadelphia, Pa.

measured volumes of organic extract and strip solution in a standard baffled mixer with turbine type impellers (Fig. 1). In all tests the aqueous phase was dispersed in the continuous organic phase.

Evaluation of Results

The results have been evaluated by computing a stripping rate constant, according to the method of Hixon and Smith.[2] This constant is directly proportional to holdup time and, since low holdup time means small working volume, the conditions that give low K values are the most desirable.

K is defined as:

$$K = -\frac{\theta}{\ln(1-E)}$$

where θ is the time in seconds and E is the batch stripping efficiency. In turn E is defined as:

$$E = \frac{C_o - C_t}{C_o - C_{eq}}$$

where C_o is the original uranium concentration in the organic, C_{eq} the equilibrium concentration, and C_t the concentration at time θ.

The residence time, θ_H, required in a continuous mixer can be predicted from K by use of the equation:[3,4]

$$\theta_H = \frac{KE_{av}}{1-E_{av}}$$

where E_{av} is the given stage efficiency for continuous stripping.

A plot of 1-E versus time for each run gave a curved line, indicating an increase in K with approach to equilibrium. For this reason all K's were calculated at 1-E = 0.01; therefore, they represent a rate constant for stripping to 99% of equilibrium.

As an example of the method, the calculation of K for the first test shown in Table 1 is given in the following.

DIMENSION RATIOS OF TURBINE

$D : D_p : L_b : W = 20 : 15 : 5 : 4$

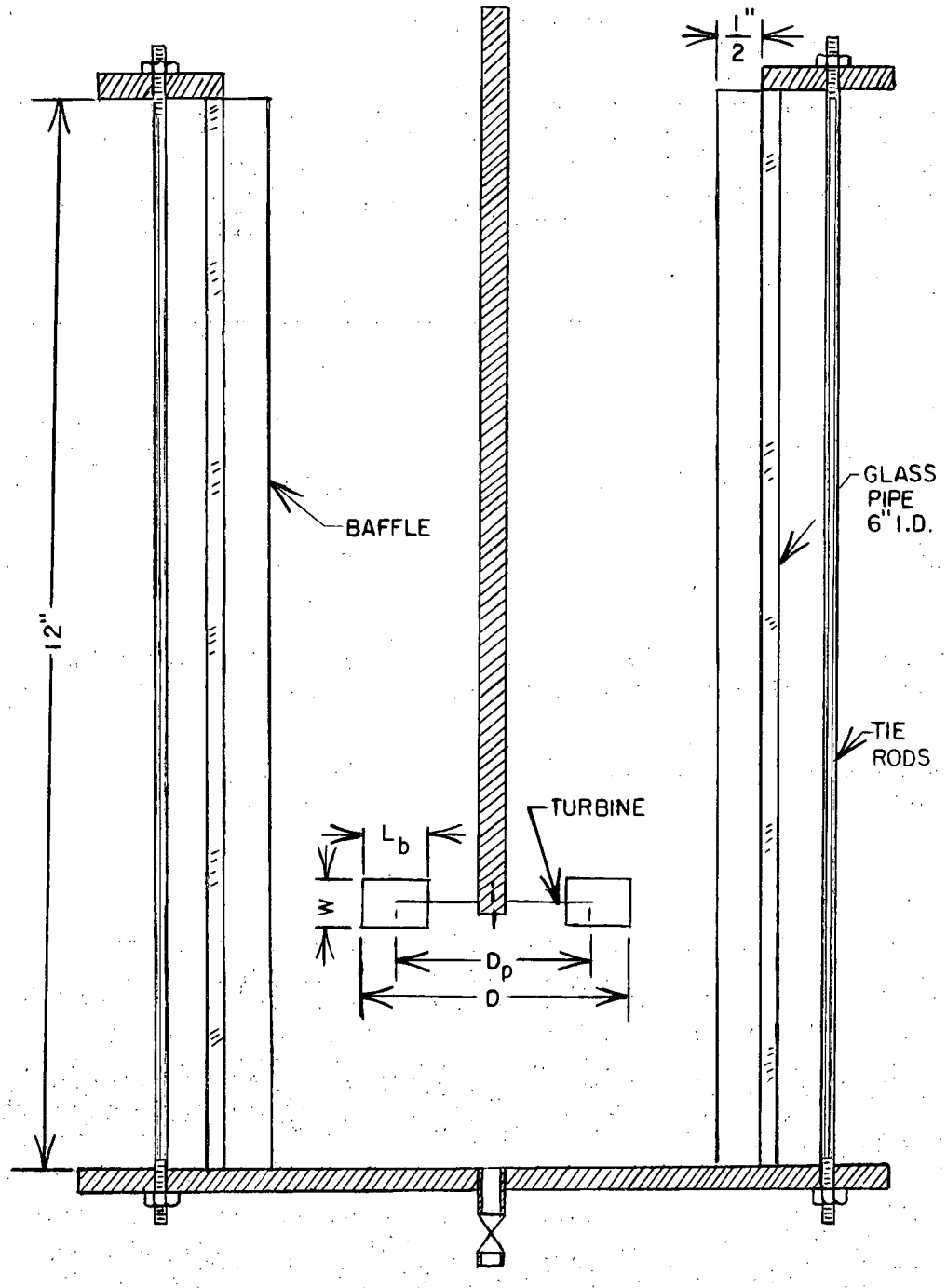

FIG. 1 — DETAILS OF BATCH MIXER

The data from the test were plotted in Fig. 2. The equilibrium concentration of uranium in the organic was assumed to be the average over the level portion of the curve, so that:

$$C_o = 3.37 \text{ g/l}$$

$$C_{eq} = 0.023 \text{ g/l}$$

$$C_o - C_{eq} = 3.35 \text{ g/l}$$

The 1-E values were calculated for each time:

	Time, sec		
	10	30	60
C_t	0.110	0.048	0.028
$C_t - C_{eq}$	0.087	0.025	0.005
$1 - E = \frac{C_t - C_{eq}}{C_o - C_{eq}}$	0.026	0.008	0.002

The value for θ, 26 seconds, at 1-E = 0.01, was read from the plot of 1-E versus time given in Fig. 3. Then, at 1-E = 0.01:

$$K = -\frac{\theta}{\ln(1-E)} = -\frac{26}{\ln(0.01)} = \frac{26}{4.6} = 5.7 \text{ sec}$$

Sodium Carbonate

The stripping of uranium by sodium carbonate is essentially a quantitative reaction. However, incomplete stripping was observed in the runs with less than 35% carbonate excess. In these runs, an apparent plateau in the concentration of uranium in the organic was reached which was assumed to be the equilibrium concentration. The theoretical carbonate requirement was assumed to be 1/2 mole per mole of amine and 3 moles per mole of uranium.

Reagent Excess. The effect of reagent excess upon the rate and completeness of stripping is shown in Table 1. As the carbonate excess was increased from 5% to 35%, K decreased

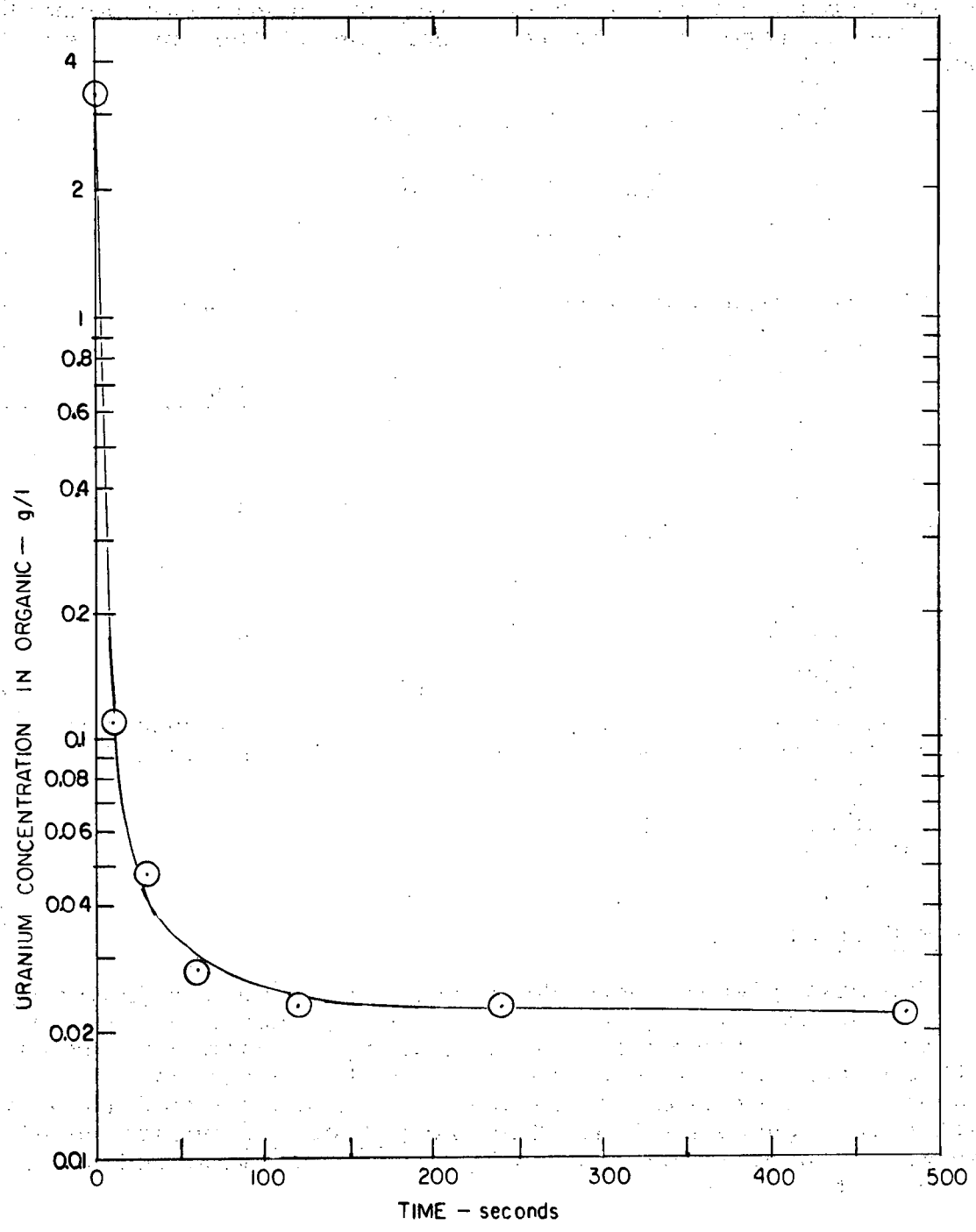

FIGURE 2 — BATCH STRIPPING DATA, RUN 1.

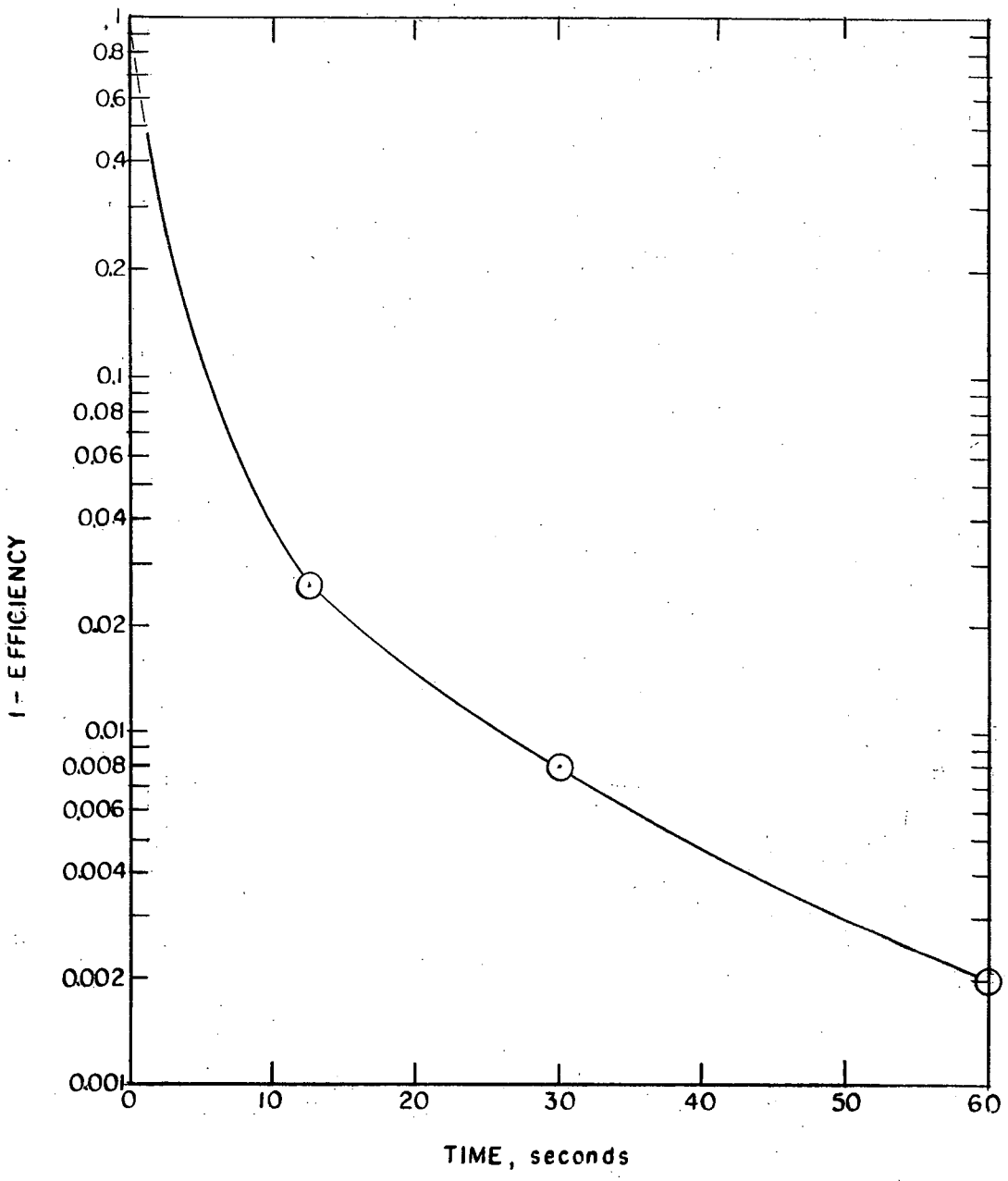

FIGURE 3 — STRIPPING EFFICIENCY, RUN 1.

TABLE 1. EFFECT OF CARBONATE EXCESS ON STRIPPING RATE

Stripping solution: 0.7M Na_2CO_3

Three-inch turbine at 700 rpm: 0.03 hp/gal

D/T ratio*: 0.5

Carbonate Excess, %	Phase Ratio, Org/Aq	K, sec	Uranium Concentration in Organic, g/l — Mixing Time, sec. 0	10	30	60	120	240	480	Entrainment, Org in Aq, Vol %
5	7.05	5.7	3.37	0.110	0.048	0.028	0.023	0.023	0.022	-
10	6.74	4.4	3.37	0.078	0.040	0.026	0.018	0.017	0.017	29
20	6.17	1.7	3.37	0.028	0.016	0.016	0.015	0.014	0.016	16
35	5.56	< 1.7	3.37	-	0.003	0.001	0.003	0.002	0.001	< 0.5

*Ratio: Turbine dia/tank dia.

from 5.7 to less than 1.7 sec, and the equilibrium concentration of uranium in the organic phase decreased from about 0.023 to 0.002 g/l.

A persistent emulsion was formed in the aqueous phase when the reagent excess was 20% or less. The organic entrainment in the aqueous phase after 10 minutes' settling was 16 to 29 volume percent. With 35% excess, the entrainment was less than 0.5%. The entrainment of aqueous in the organic phase was less than 0.4 volume percent in all of the tests.

D/T Ratio. The effect of D/T (turbine diameter/tank diameter) on the stripping rate at two levels of power and reagent excess is shown in Table 2. With a power input of 0.002 hp/gal and a 10% excess reagent, K was about 13 seconds and was independent of D/T. With an increase in power input to 0.03 hp/gal and an increase in excess reagent to 35%, K was 18 seconds for a D/T ratio of 0.67 and less than 2.2 seconds for D/T ratios of 0.50 and 0.33.

Power Input. The data in Table 3 show the effect of power input on the stripping rate with 10% carbonate excess. An increase in the power from 0.002 to 0.008 hp/gal resulted in a decrease in K, from 13.2 to 4.1 sec. A further increase to 0.03 hp/gal had no effect on K.

Sodium Chloride

The stripping of uranium by chloride ion is a reversible reaction requiring several stages to obtain complete stripping. In these tests, the concentrations of uranium in the organic extract and sodium chloride solution approximated the concentrations that would exist in the uranium rich stage of a countercurrent system (Unit 121, Fig. 1, ORNL-2025). The sodium carbonate tests indicated that D/T ratios of 0.5 and 0.33 were equally satisfactory; without further investigation, a D/T ratio of 0.5 was selected for the sodium chloride tests. The theoretical chloride requirement was assumed to be 1 mole per mole of amine.

Reagent Excess. The data in Table 4 show that there was a significant change in the uranium concentration at equilibrium with a change in chloride excess. With an increase in chloride excess from 10 to 50%, K increased from 4.4 to 6.1 seconds while the concentration of uranium in the organic phase at equilibrium decreased from about 1.24 g/l to 0.55 g/l.

TABLE 2. EFFECT OF D/T RATIO ON SODIUM CARBONATE STRIPPING RATE

Stripping solution: 0.7M Na_2CO_3

Power, hp/gal	Phase Ratio, Org/Aq	Reagent Excess, %	D/T* Ratio	Turbine Dia, in.	Turbine Speed, rpm	K, sec	Uranium Concentration in Organic, g/l — Mixing Time, sec 0	10	30	60	120	240	480
0.03	5.56	35	0.67	4	430	18.0	3.37	-	0.023	0.009	0.003	0.003	0.002
			0.50	3	700	< 2.2	3.37	-	0.003	0.001	0.003	0.002	0.001
			0.33	2	1380	< 2.2	3.37	-	0.003	0.001	0.002	0.001	0.001
0.002	6.74	10	0.67	4	172	13.5	3.37	0.29	0.14	0.063	0.036	0.026	0.023
			0.50	3	278	12.6	3.37	0.28	0.12	0.059	0.041	0.034	0.032
			0.33	2	548	13.5	3.37	0.28	0.16	0.069	0.049	0.029	0.030

*Diameter of turbine/tank diameter.

TABLE 3. EFFECT OF POWER INPUT ON SODIUM CARBONATE STRIPPING RATE

10% excess of 0.7M Na_2CO_3 solution

Phase ratio: 6.74 org/aq

Power, hp/gal	K, sec	Uranium Concentration in Organic, g/l — Mixing Time, sec: 0	10	30	60	120	240
0.002*	13.2	3.37	0.28	0.14	0.064	0.042	0.030
0.008	4.1	3.37	0.092	0.035	0.022	0.021	0.018
0.03	4.4	3.37	0.078	0.040	0.026	0.018	0.017

*Data at 0.002 hp/gal is the average of three tests.

TABLE 4. EFFECT OF CHLORIDE EXCESS ON STRIPPING RATE

Stripping solution: 1M NaCl
Three-inch turbine at 700 rpm: 0.031 hp/gal
D/T ratio: 0.5

Chloride Excess, %	Phase Ratio, org/aq	K, sec	Uranium Concentration in Organic, g/l — Mixing Time, sec: 0	10	30	60	120	240	480
10	9.11	4.4	3.37	1.27	1.24	1.23	1.23	1.26	1.22
50	6.68	6.1	3.37	0.70	0.56	0.51	0.55	0.56	0.56

Power Input. The effect of power input on K is shown in Table 5. An increase in power from 0.002 to 0.008 hp/gal resulted in a decrease in K from 12 to 6.5 seconds. With a further increase in power to 0.03 hp/gal, K decreased only to 5.2 seconds.

Phase Separation. Phase separation was rapid at all power levels and reagent excesses tested. The entrainment after two minutes' settling time was less than 0.5 vol % in either phase.

Comparison of Sodium Carbonate and Sodium Chloride Stripping

Stripping. The results of the carbonate and chloride tests may be compared as follows:

1. In the sodium carbonate system the rate of uranium stripping increased as the reagent excess was increased over the range of 5 to 35 percent, other conditions remaining unchanged. The degree of completion also increased with increase in reagent excess so that the reaction was virtually complete within 30 seconds with 35% excess.

2. With sodium chloride, there was no appreciable change in the stripping rate with 10 and 50% chloride excess; however, the equilibrium concentration of uranium in organic decreased from 1.2 to 0.6 g/l as the reagent excess was increased.

3. With both systems, the stripping rate increased as the power input increased over the range 0.002 to 0.008 hp per gal. There was no significant change in the rate when the power was increased to 0.03 hp per gal.

4. With the sodium carbonate system at 35% reagent excess, the stripping rate increased as the D/T ratio decreased from 0.67 to 0.5. There was no detectable change in the stripping rate with a further decrease in D/T ratio to 0.33, indicating that the proper balance between turbulence and pumping in the mixing operation is reached with D/T ratios of 0.5 to 0.33.

Ammonium Nitrate

The stripping of uranium by nitrate ion is a reversible reaction analogous to chloride stripping. Nitrate is a more effective stripping agent than is the chloride; however,

TABLE 5. EFFECT OF POWER INPUT ON CHLORIDE STRIPPING RATE

50% excess of 1.0M NaCl solution
Three-inch turbine; D/T ratio: 0.50
Phase ratio: 6.68 org/aq

Power, hp/gal	Turbine Speed, rpm	K, sec	Uranium Concentration in Organic (g/l) Mixing Time (sec) 0	10	30	60	120	240	480
0.002	278	12.0	3.37	0.84	0.82	0.75	0.75	0.72	0.71
0.008	440	6.5	3.37	0.86	0.67	0.67	0.67	0.63	0.65
0.03	700	5.2	3.37	0.70	0.56	0.51	0.55	0.56	0.56

because of the higher cost of the nitrate, in practical operation it would be necessary to contact the stripped amine with a hydroxide* (ammonium hydroxide) and to recycle the ammonium nitrate thus recovered to the uranium strip step. This treatment would require close control of the flows in order to maintain the chemical costs at a level comparable to that of the chloride strip. Consequently, the tests with this system were limited to a study of the effect of reagent excess on the rate and degree of completion of stripping, using mixing conditions (power input and D/T ratio) that were found suitable in the sodium carbonate and sodium chloride stripping tests.

In these tests the rate of the stripping reaction was measured with 5 and 16.7% excess of nitrate which was added in the form of nitric acid. The rate of reaction for the regeneration step was measured with ammonium hydroxide in 5% excess. The theoretical requirements were assumed to be 1 mole of nitrate per mole of amine for the stripping step and one mole of hydroxide per mole of nitrate for the regeneration step. The tests were carried out in the same manner as those described previously for sodium carbonate and sodium chloride.

As shown in Table 6, K was 3.9 sec with 5% excess nitrate and 8.7 sec with 16.7% excess. The data for the regeneration tests are not shown since the time required to reach equilibrium was 30 sec in both tests.

Phase separation was rapid in both the uranium stripping and regeneration steps. The entrainment after two minutes' settling time was less than 0.5 vol % in either phase.

Future Work

Tests are planned to study the stripping of uranium from organic extract by sodium chloride in continuously operated equipment to determine the effects of pH and reagent excess on the rate and degree of completion of the stripping reaction. No further testing of either sodium carbonate or ammonium nitrate will be made until the results of estimates comparing the costs of stripping methods are available.

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*Termed "regeneration."

TABLE 6. EFFECT OF EXCESS NITRATE ON STRIPPING RATE

Three-in. turbine at 700 rpm, 0.031 hp/gal
D/T ratio 0.5

Nitrate Excess, %	Phase Ratio, org/aq	K, sec	Uranium Concentration in Organic, g/l						
			Mixing Time, sec						
			0	10	30	60	120	240	480
5 *	7.52	3.9	3.37	0.54	0.36	0.34	0.35	0.35	0.34
16.7**	7.62	8.7	3.37	0.53	0.21	0.15	0.16	0.12	0.13

*Strip solution concentration 0.75M ammonium nitrate plus 0.0375M nitric acid.

**Strip solution concentration 0.75M ammonium nitrate plus 0.125M nitric acid.

Organic Entrainment in Raffinate

In the preceding month (ORNL-2025) the results of exploratory tests made in a mixer-settler under conditions simulating the raffinate end of an extraction section, showed that the primary break time for the emulsion entering the settler was virtually independent of the mixing conditions. Moreover, with linear velocity in the settler as high as 3.1 fpm, the primary break was contained in a small part of the settler. In contrast, the amount of residual entrainment after the primary break and the time required for its separation was dependent on the mixing conditions (impeller speed) as well as linear velocity in the settler. To more closely define the settler lengths associated with the primary break zone and the entrainment separation zone, tests were made with flow rates at 1, 2.3, and 4.7 gpm in which settler lengths of 22, 44, 66, and 88 inches were employed for each flow rate.

Except for the mixer, the equipment and its arrangement was the same as that described in ORNL-2025. A 6-in. dia. baffled mixer tank with a 3-in. dia. turbine impeller (4 blades), as shown in Fig. 4, was used in place of the mixer column. The impeller speed was 400 rpm and the aqueous to organic phase ratio was 2.5:1 in all tests. Only the raffinate was sampled; other conditions and procedures were the same as those described previously. The test data and results are reported in Table 7.

Primary Break. The results show that the 22-in. settler length contained the primary break at all flow rates. With a velocity in the settler of 3.1 fpm, entrainment was 7 ml/l with a holdup time of 0.6 min and 2 ml/l with a holdup time of 2.4 min.

Total Settler Length. A plot of entrainment, E, and holdup time, H, for settler velocities of 1.5 and 3.1 fpm, indicate a linear relation of the form: $\log y = n \log x + \log c$ as shown in Fig. 5. Extrapolation to E = 0.1 ml/l indicates that a holdup time of about 14 minutes would be required with V = 1.5 fpm, while about 60 minutes would be needed with V = 3.1 fpm. It is interesting to note that the entrainment data reported previously (ORNL-2025) for 400 rpm and V = 3.1 fpm are in close agreement with the above while those for V = 1.5 fpm show entrainment values that are approximately 100% greater.

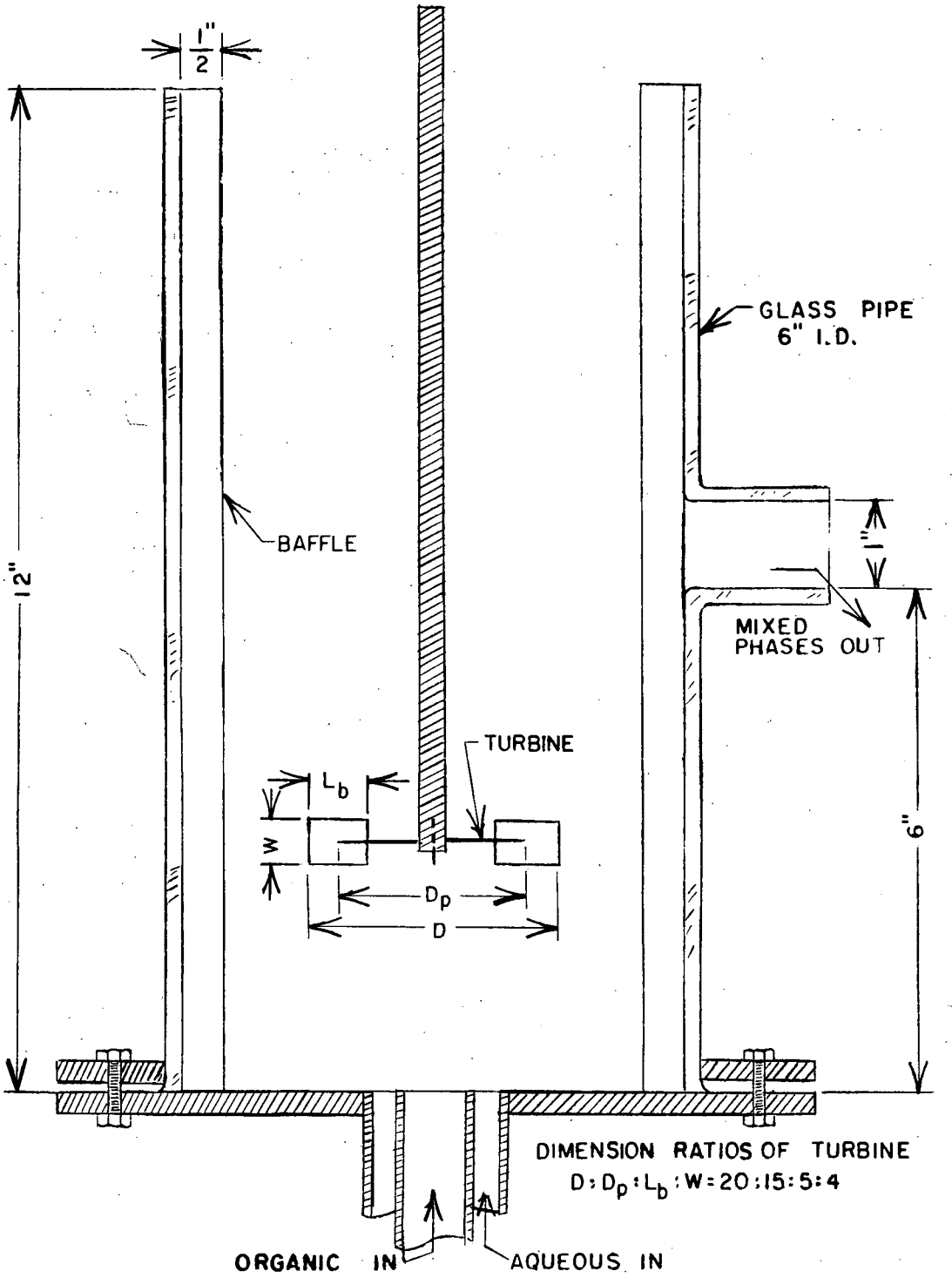

FIG. 4 – DETAILS OF CONTINUOUS MIXER

TABLE 7. ORGANIC ENTRAINMENT DATA

Mixer: 3 in. turbine at 400 rpm (0.005 hp/gal)
Phase ratio: 2.5 aq/org

Total Flow, gpm	Linear Velocity, ft/min	Length, in.	Holdup Time, min	Organic Entrainment in Raffinate, ml/l
1.0	0.66	22	2.8	<0.1
		44	5.5	<0.1
		66	8.3	<0.1
		88	11.	<0.1
2.3	1.5	22	1.2	1.
		44	2.4	0.5
		66	3.7	0.3
		88	4.9	0.3
4.7	3.1	22	0.6	7.
		44	1.2	4.0
		66	1.8	2.0
		88	2.4	2.

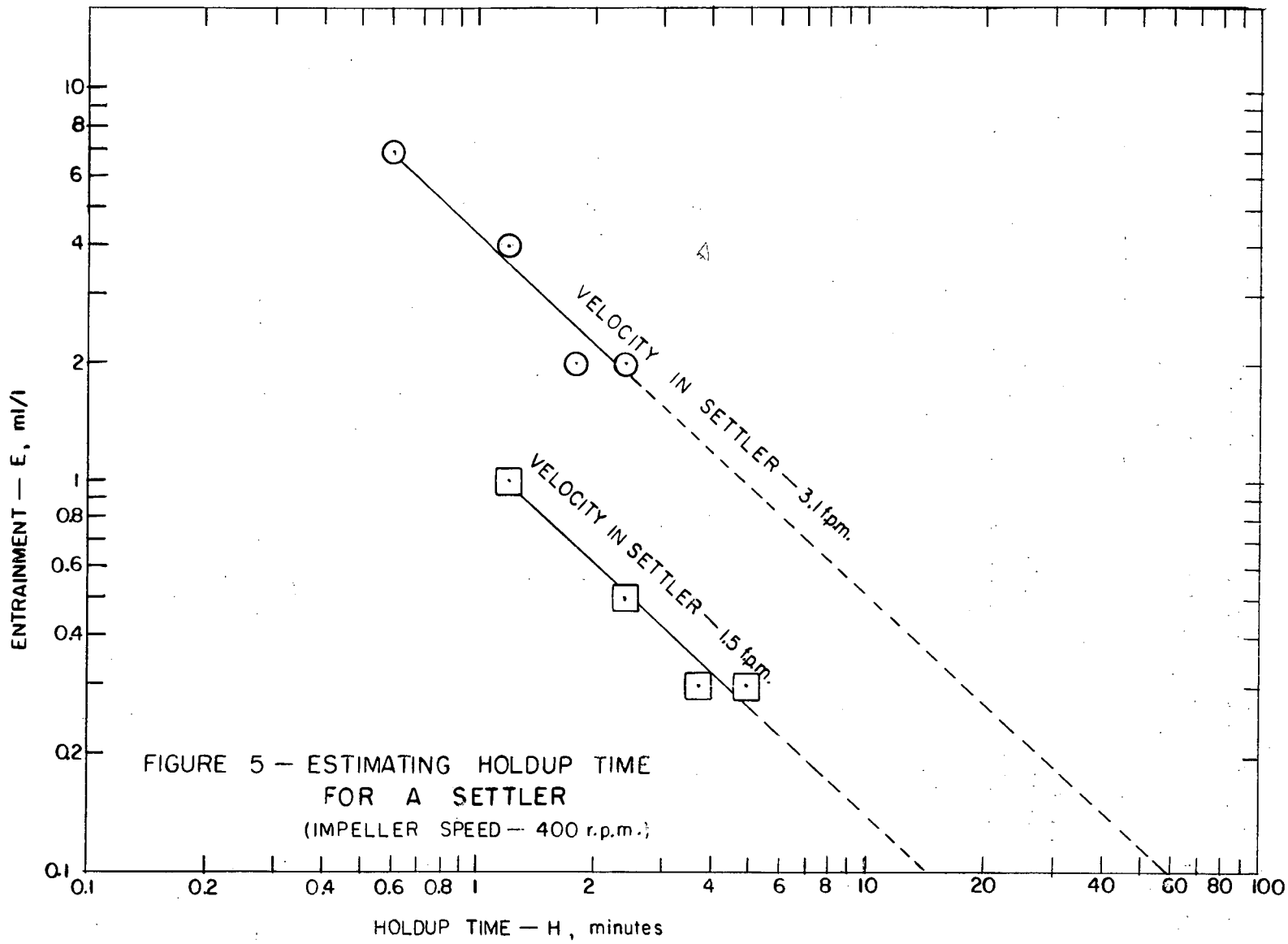

FIGURE 5 — ESTIMATING HOLDUP TIME FOR A SETTLER
(IMPELLER SPEED — 400 r.p.m.)

Future Work. The present settler is not suitable for studying the effect of phase depth on the amount of residual entrainment in either phase; therefore, work has been started on design of a rectangular settler, 12 inches wide, 14 inches deep, and about 66 inches in length. No further work on phase separation with continuous flow conditions is planned until the settler has been fabricated and tested.

Slurry Extraction

The slurry extraction tests to date have shown the entrainment of organic in the slurry raffinate ranged from 20 to 30 gal per ton of ore. A preliminary cost comparison of slurry extraction with extraction from clarified liquor shows that it is necessary to recover most of the organic in the slurry raffinate in order for the process to be competitive. Scouting tests have been started to determine whether the organic entrainment is a surface adsorptive phenomena or is mechanical and to find methods of recovering the organic.

Several different treatments of the diluted slurry have shown no improvement in recovery. These include raising the temperature to 70°C, neutralization with sodium hydroxide, addition of a wetting agent (Penetrant) and use of a flocculating agent (Jaguar gum).

Dilution of the slurry raffinate (50% solids) with sufficient water so that the solids content is about 5% produces a slurry of low viscosity and entrained droplets of organic rise to the surface. By repeated gentle agitation, settling and decantation of the organic, 98% of the entrained organic can be recovered indicating that the entrainment is mechanical in nature.

Mild agitation of the diluted slurry with a rake type mixer was found to be effective in keeping the slurry suspended to promote coalescence of small droplets of organic. Studies are in progress to determine the effects of rake speed and dilution on the amount of organic recovered.

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