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EXPERIMENTAL BASIS FOR THE DESIGN OF MIXER SETTLERS FOR THE AMEX SOLVENT EXTRACTION PROCESS

A. D. Ryon
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OAK RIDGE NATIONAL LABORATORY
operated by
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Unit Operations Section

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A. D. Ryon and R. S. Lowrie

ABSTRACT

The basis for design of mixer-settlers for the Amex solvent extraction process, which uses long-chain amines dissolved in a hydrocarbon diluent for the recovery of uranium from acid sulfate solutions typical of those obtained in uranium ore processing, was determined by a unit-operations study in scale-model units.

Long-term recycle tests in countercurrent equipment demonstrated the stability of amines and the general feasibility of the Amex process.

Mass transfer rates of uranium for both extraction and stripping are large, and greater than 90% stage efficiency was readily obtained.

The flow capacity of gravity settlers is generally limited by a dispersion band, which increases exponentially with flow rate.

The scaleup of settlers is based on the constant flow rate of dispersed phase per unit settler area and constant band thickness. The nominal flow capacity (50% of flooding) ranged from 0.4 to 0.8 gpm/ft^2, depending on the type of dispersion and amine used. The capacity can be increased (fourfold) by using packing wetted by the dispersed phase. Emulsion stabilized by silica (the worst offender) can be minimized by controlling the mixing in order to form solvent-continuous dispersions, which also minimizes entrainment of solvent in the aqueous waste.

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1. SUMMARY

The Amex process for extraction of uranium from acid sulfate solutions typical of those obtained from the acid leaching of uranium ores was successfully demonstrated in small-scale continuous countercurrent equipment showing (1) that repeated recycle of solvent (100 to 200 cycles) caused no degradation of amine and that the loss agreed with solubility data; (2) the comparative chemical usage for different stripping methods to separate uranium from molybdenum, the only impurity readily extracted; (3) steady-state stagewise profiles for uranium and molybdenum; and (4) that the uranium product purity is generally within feed-material specifications.

The basis for the design of mixer-settlers was obtained by a unit-operations study of mixing and phase separation in batch and continuous flow tests with single-stage units. Limited scale-up data were obtained to demonstrate that the same scale-up methods developed for the Dapex process could be applied to the Amex process.

The rate of uranium transfer for extraction of uranium from sulfate solutions and stripping from solvent by sodium chloride, ammonium nitrate, or sodium carbonate was large. Greater than 90% stage efficiency was obtained in a 6-in. mixer at a power input of 6 hp per 1000 gal or greater and at a residence time of 0.1 min for extraction, and at 50 hp per 1000 gal and 0.25 min for stripping with sodium chloride.

Phase Separation in Batch Tests

The rate of coalescence was demonstrated to be directly dependent on the cross sectional area of the settler and virtually independent of the volume of the dispersion. A survey of six commercial amines showed that the break time varied considerably for different amines and that the addition of a modifier such as tridecyl alcohol greatly improved the rate of phase separation in some cases, thereby making the use of most amines feasible. Variations of petroleum-type diluents had only minor effects on phase separation. Increased temperature decreased break time, which was directly proportional to the viscosity of the solvent.

Phase-separation tests with 14 leach-liquor samples received from uranium mills showed with one exception that organic-continuous dispersions separated in less than 300 sec. However, with aqueous-continuous dispersions, slow phase separation and stable emulsions were formed in many cases. The difficulty appeared to be dependent on silica content of the liquor, phase separation being satisfactory at less than 0.7 g of SiO_2 per liter and increasing emulsion at greater than 1.0 g of SiO_2 per liter. Two amines, Di(tridecyl) and S-24 were consistently better than the others for separation from silica-bearing liquors.

Continuous Settler Tests

The basis for the design of settlers was based on flow rate per unit cross sectional area of the settler. At a flow ratio of 1/4 or greater, a uniform-band dispersion existed at the interface, the thickness of which increased exponentially with flow rate. Nominal flow capacity was arbitrarily defined as the flow rate causing a 5-in. dispersion band. For more dilute dispersions (flow ratios of 1/6 or less, which are typical of the stripping circuit) the dispersion band did not change much with flow rate, but entrainment of the dispersed phase was much more sensitive to flow rate, increasing until flooding occurred because all of the dispersed phase was entrained in the continuous phase. For entrainment-type flooding, the nominal flow was arbitrarily chosen to be one half of flooding.

Settler scale-up tests in 6-in.- and 48-in.-diam settlers demonstrated that flow capacity is directly dependent on cross sectional area. Typical flow capacity of the dispersed phase for extraction was 0.7 gpm/ft^2 for aqueous-continuous dispersion at an A/O ratio of 4/1 and 1/1 and 0.4 gpm/ft^2 for organic-continuous dispersions. For stripping with sodium chloride, the nominal solvent flow capacity was 0.8 gpm/ft^2 for aqueous-continuous dispersion at an A/O ratio of 2/1 and 1/1 and ranged from 0.8 to 3.0 gpm/ft^2 for organic-continuous dispersion at an A/O ratio of 1/1 to 1/6.

The flow capacity of a settler can be increased about fourfold by the use of packing wetted by the dispersed phase. The additional flow is nearly proportional to the surface area of the packing.

Emulsion formation caused by silica in the feed liquor was minimized or eliminated entirely by controlling the mixing in order to maintain organic-continuous dispersions. The addition of decolorizing carbon, which remained suspended in the solvent, was also an effective method of eliminating silica-stabilized emulsion, but it caused slow phase separation in the sodium carbonate stripping circuit.

Entrainment was not great enough to be economically significant except for solvent losses in the waste aqueous raffinate. The entrainment for organic-continuous mixing was consistently less than 0.15 gal per 1000, but it ranged up to 6 gal per 1000 for aqueous-continuous mixing. The use of a secondary settler reduced entrainment to less than 0.2 gal per 1000 at a residence time of 2 hr; the addition of packing increased the efficiency so that only 15 min of residence time was required.

2. INTRODUCTION

Important variables affecting stage efficiency, primary phase separation and entrainment in mixer-settlers for the Amex solvent extraction process have been studied to provide a basis for design of plant equipment. The main emphasis was placed on flowsheets applicable to the recovery of uranium from sulfuric acid leach solutions produced in some uranium ore mills. Most of the results have been published in monthly progress reports.[1-4]

The approach to the problem consisted in a unit operations study of mixing and phase separation in a scale-model single-stage mixer-settler similar to that used for the engineering study of the Dapex process.[5] Scale-up relations for mixer-settlers were developed for the Dapex process and successfully demonstrated in plant equipment. Consequently only a few scale-up tests were made with the Amex process to verify their applicability.

Because of the number of amines that can be used in the process, it was not possible to obtain complete design data for each. Consequently, detailed studies of mixing and phase separation were made by using a secondary amine (Amberlite LA-1), supported by spot tests for the comparison of different amines. The reagents tested to some extent were the following secondary amines: Amberlite LA-2, Di(tridecyl) and S-24, and the following tertiary amines: triisooctyl, Alamine 336, and trilauryl amine (see Appendix, Table A.1).

Acknowledgments. This report is a summary of work done by a number of people: H. F. Bauman, F. L. Daley, R. H. Guymon, J. F. Manneschmidt, F. G. Kilpatrick, C. H. Tipton, and K. Ladd.

The analytical services were performed by the Y-12 section of ORNL Analytical Chemistry Division under direction of C. D. Susano.

3. TYPICAL FLOWSHEET OF THE AMEX PROCESS

The Amex process[6-9] for uranium utilizes long chain amines dissolved in kerosene (usually modified with a long-chain alcohol) to extract uranium from acid sulfate solutions. The uranium can be stripped from the solvent by aqueous solutions of salts such as chlorides or nitrates and bases, i.e., sodium carbonate, ammonium carbonate or magnesium oxide. A number of amines have been tested and shown to be applicable to processing uranium ore leach liquors. Typical equilibrium distribution curves for uranium are shown in Fig. 1.

A typical flowsheet of the Amex process is shown in Fig. 2. By the use of proper flow ratios of feed liquor and solvent, essentially complete extraction of the uranium is obtained in 3 to 5 countercurrent stages. Uranium loading in the solvent is usually set at 80 to 90% of maximum loading which, for 0.1 M amine, is 3.5 to 5.5 g of U_3O_8 per liter, depending on the particular amine used.

The uranium is stripped from the loaded solvent by aqueous solutions of salts or bases, usually in 1 to 4 countercurrent stages. The solvent is recycled to the extraction circuit either in the free base form or a salt form, depending on the stripping agent. When salt stripping is used, provision for regeneration of part or all of the solvent to the free-base form is installed in order to remove impurities such as molybdenum, which would not be stripped by the salt solution. The uranium product is recovered from the loaded strip solution by one of several precipitation methods.

4. LONG-TERM CONTINUOUS COUNTERCURRENT TESTS

Continuous runs of 100 to 200 cycles of the organic phase demonstrated (1) the steady-state loss of amine agreed with batch solubility data (20 to 30 ppm of raffinate); (2) the comparative chemical consumption

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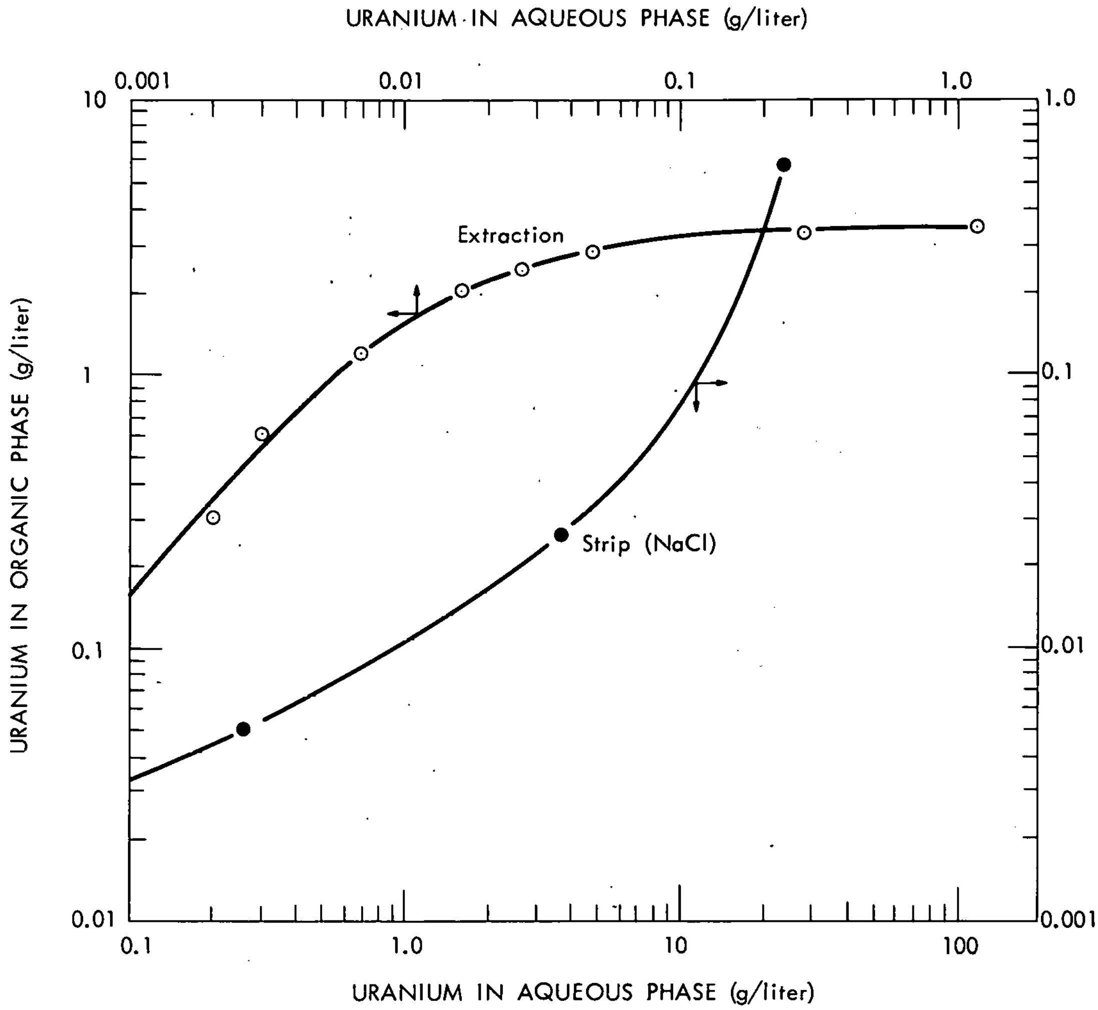

Fig. 1. Typical Equilibrium Distribution of Uranium for 0.1 M Amberlite LA-1 Solvent.

for flowsheets for liquors that contain molybdenum, for flowsheets that involve sodium chloride stripping with partial and complete regeneration, and for flowsheets that employ sodium carbonate stripping; (3) the steady-state stagewise profiles for uranium and molybdenum; and (4) that the uranium-product analyses are generally within specifications.

In most of the studies for process flowsheet development, countercurrent tests of 4 to 6 hr duration are sufficient to reach steady state in laboratory-scale mixer-settlers. However, because of the short duration of the runs, it was not possible to evaluate the effect of time and repeated recycle of the organic phase on organic losses, uranium recovery, and product purity. Consequently, three runs were made, one with 200 cycles of the organic phase and two runs with 100 cycles; each cycle is equivalent to about one hour of operation in a typical extraction plant.

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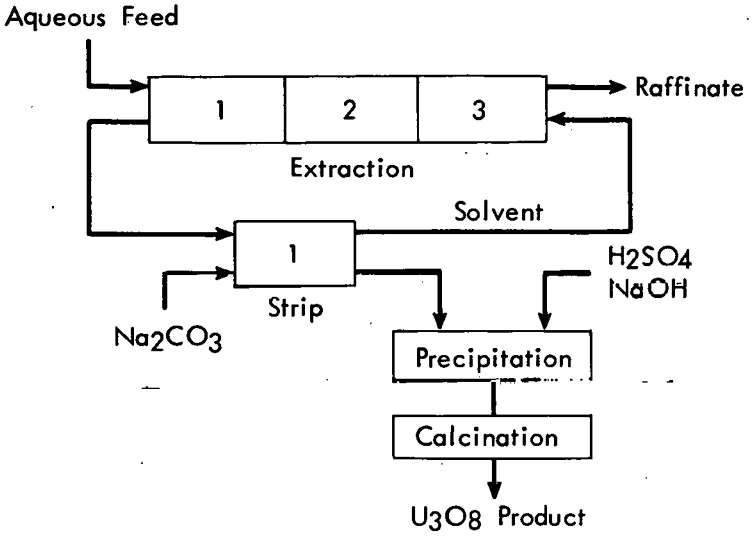
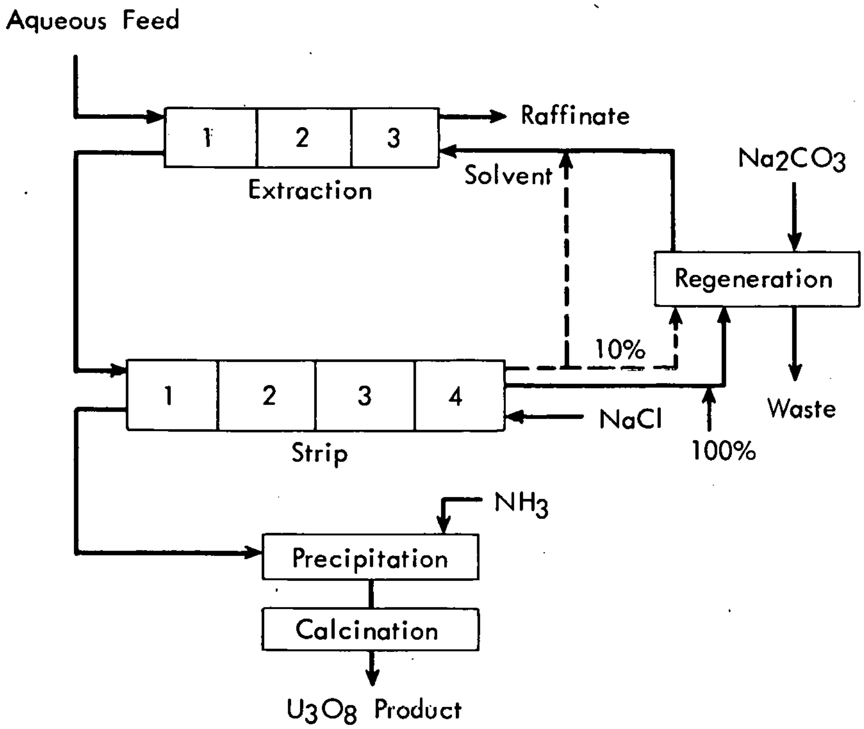


Sodium Carbonate Stripping Flowsheet (Run 1)



Sodium Chloride Stripping Flowsheet with 10% Regeneration (Run 2) and 100% (Run 3)

Fig. 2. Flowsheets for Long-Term Runs.

Three flowsheets (Fig. 2) involving different uranium-stripping circuits were tested. In each, three stages were used for uranium extraction. In run 1 the uranium was stripped with sodium carbonate (one stage), and the uranium was precipitated with sodium hydroxide after the carbonate was destroyed with sulfuric acid. In runs 2 and 3, the uranium was stripped with sodium chloride (four stages), and the amine was regenerated with sodium carbonate (one stage), 10% of the organic in run 2 and 100% in run 3. The aqueous feed was synthetic leach liquor, typical of that resulting from the sulfuric acid leaching of uranium ore. The feeds for runs 1 and 2 contained low-concentration molybdenum (0.02 to 0.05 g of molybdenum per liter), and that for run 3 contained 0.2 g per liter. The organic was 0.1 M Amberlite LA-1 in kerosene diluent (compositions shown in Table 1). The flow ratio of feed to organic was set to give uranium loading in the organic of about 80% of maximum (operating conditions, Table 2).

Table 1. Composition of Entering Streams

(g/liter except as noted)

Constituents of the Streams	Run 1	Run 2	Run 3
Feed liquor			
U(VI)	1.2	1.2	1.1
Fe(III)	2.2	2.1	2.0
Al(III)	2.8	2.9	3.2
V(IV)	0.4	1.0	1.0
V(V)	1.0	0.0	0.0
Mo(VI)	0.05	0.02	0.21
SO_4^{2-}	36.	42.	38.
PO_4^{3-}	2.1	2.2	2.2
pH	1.0	1.0	1.0
Organic			
Amine	Amberlite LA-1	Amberlite LA-1	Amberlite LA-1
Conc., M	0.094	0.108	0.105
Diluent	Kerosene	Kerosene	Kerosene
Modifier	None	None	None
Chloride Strip			
NaCl, M		1.0	1.0
H_2SO_4, M		0.05	0.05
Carbonate Strip			
Na_2CO_3, M	0.72	1.0	1.0

4.1 Loss of Organic Phase

The total loss of amine and kerosene was determined by inventories at the beginning and end of each run. In addition, the concentration

Table 2. Operating Conditions

	Run 1	Run 2	Run 3
Run time, hr	100	44	45
No. of cycles of organic	200	100	100
Flow rates, ml/min			
Feed	135	316	316
Total organic	50	105	105
Chloride stripped organic	0.0	105	105
Carbonate stripped organic	50	10	105
Chloride strip	0.0	16	16
Carbonate strip	9.0	0.64	6.4
Excess stripping agent			
Chloride, % excess		50	50
Carbonate, % excess	50	10	10

of amine in the organic phase was measured periodically (about 20 cycles) during the run to show the rate of loss and to provide a basis for amine additions in order to restore its concentration to 0.1 M. The results (Fig. 3 and Table 3) show that the volumetric inventory loss of organic was 0.14 to 0.47 gal per 1000 gal of aqueous phase processed. Only a small part of the loss was by entrainment (0.07 gal per 1000 gal); the remainder was by spillage, spray, evaporation, etc. The total inventory loss of amine reagent was 31 to 54 ppm of aqueous phase processed. The loss was consistently higher during the initial period of operation (Fig. 3), probably because of low-molecular-weight amines, which had higher solubility in the aqueous phase than the major component had. By using the steady-state loss of amine and correcting for the fraction lost with volumetric loss of organic phase, the loss of amine was equivalent to 20 to 26 ppm of aqueous phase processed. This agrees very closely to the solubility[9] of the amine in the aqueous phase, demonstrating that virtually no degradation occurred upon repeated recycle of the organic phase (100 to 200 cycles) in the three different flowsheets.

4.2 Uranium Extraction and Stripping

Stagewise profiles at steady state (Table 4) show that essentially complete extraction (0.1% loss) was effected with three countercurrent stages. In run 1, some difficulty was encountered with the sodium carbonate stripping of uranium due to a gradual accumulation of solids (iron and aluminum hydroxide) in the strip settler. The solids interfered with phase separation, and periodically a sufficient quantity of loaded strip solution was recycled with the stripped solvent, thereby interfering with uranium extraction. In runs 2 and 3, where sodium chloride stripping was used, phase separation was good and there were no

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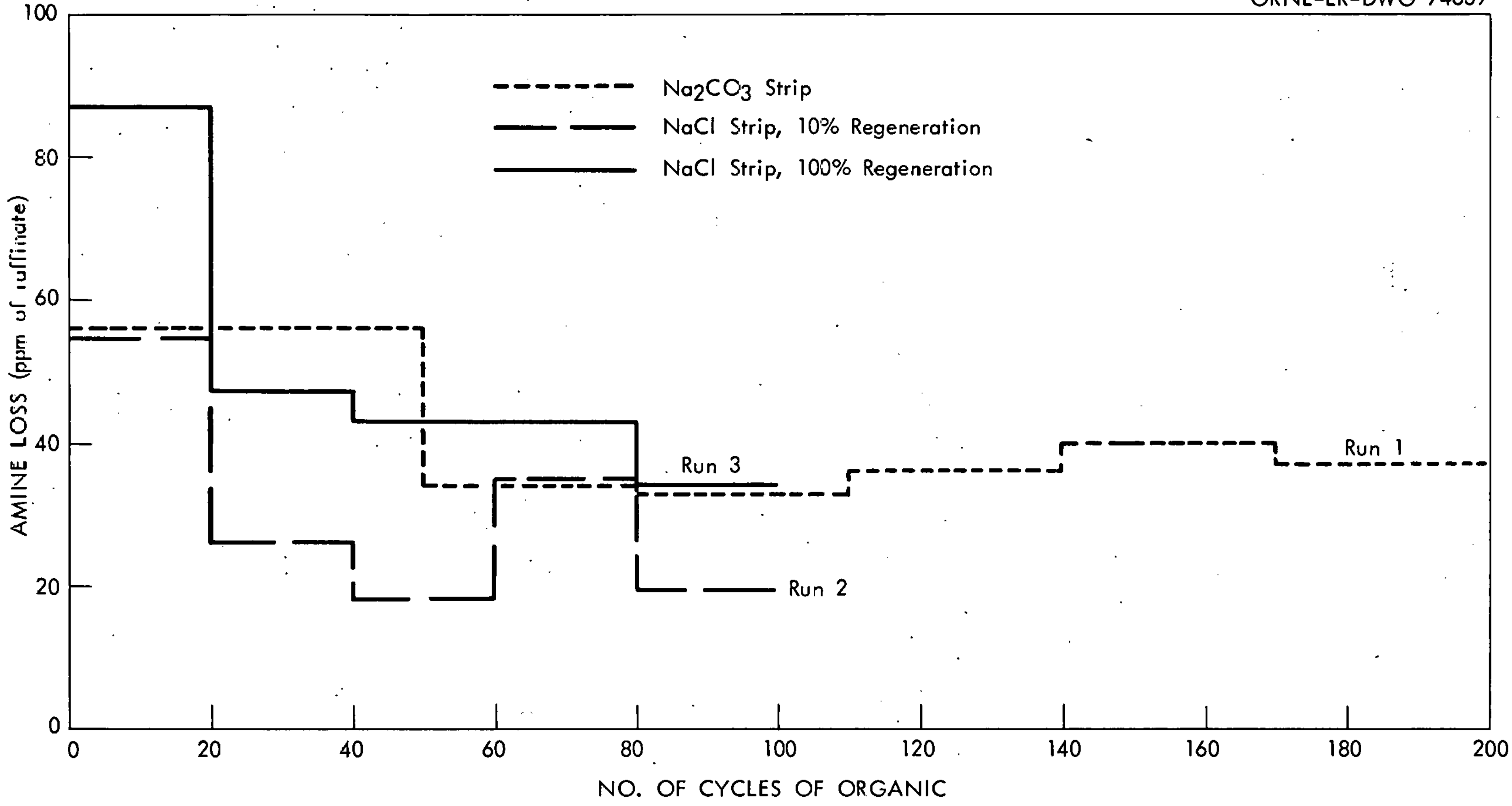

Fig. 3. Loss of Amine during Long-Term Runs.

difficulties. The loss of uranium to the carbonate regeneration stage was only 0.03% in run 2, where 10% regeneration was used, and 0.3% in run 3, where 100% regeneration was used.

Table 3. Organic Loss

	Run 1	Run 2	Run 3
Volumetric, gal solvent per 1000 gal raffinate			
Total by inventory	0.25	0.14	0.47
By entrainment	0.07	0.07	0.07
Spray, spillage, etc., by difference	0.18	0.07	0.40
Amine, ppm of raffinate			
Total by inventory	46	31	54
By volumetric loss	10	5	18
Solubility losses, etc., by difference	36	26	36
Steady-state soluble and degradation loss (corrected for volumetric loss)	29	20	24

Table 4. Composition (g/liter) at Steady State

	Run 1		Run 2				Run 3			
	Aq.	Org.	Aqueous		Organic		Aqueous		Organic	
	U	U	U	Mo	U	Mo	U	Mo	U	Mo
Extraction										
Feed	1.2		1.2	0.020			1.1	0.21		
Stage 1	0.22		0.18	0.022	3.4	0.29	0.17	0.05	3.4	0.94
Stage 2	0.004		0.005	0.014	0.48		0.003	0.02	0.51	0.47
Stage 3	0.001		< 0.001	0.013	0.037	0.26	< 0.001	0.01	0.01	0.37
Chloride Strip										
Stage 1			23.	0.061	0.78		21.	0.08	1.1	
Stage 2			6.9	0.044	0.12		7.6	0.09	0.21	
Stage 3			0.93	0.042	0.042		1.3	0.12	0.063	
Stage 4			0.19	0.039	0.013	0.28	0.32	0.11	0.013	0.93
Carbonate Strip										
Stage 1	20.	0.13	0.14	2.3	0.002	0.15	0.14	10.	0.005	0.34

4.3 Molybdenum Extraction and Stripping

The concentration of molybdenum in the raffinate was nearly the same (0.01 g of molybdenum per liter) in both runs 2 and 3, even though the concentration in the aqueous feed was 0.02 and 0.2 g of molybdenum per liter, respectively. As a result, in run 2, about 65% of the molybdenum in the feed went out in the raffinate, another 15% went out with the uranium in the chloride strip, leaving only 20% in the solvent, which was removed by the 10% regeneration with sodium carbonate. The steady-state concentration in the organic was only 0.3 g of molybdenum per liter which did not interfere with uranium recovery. In run 3, more than 90% of the molybdenum was recovered in the sodium carbonate regeneration step, and only 2% was stripped with the uranium in the chloride strip stages.

4.4 Uranium Product

The composition of uranium products obtained from each run are shown in Table 5. The grade was well above the 75% U_3O_8 minimum specification. The product from carbonate stripping (run 1) met impurity specifications, with the exception of vanadium (2.1% V). The products from chloride stripping (runs 2 and 3) contained less than 1% impurity, except for sulfate. Calcination tests[10] showed that sulfate can be reduced to less than 1% by calcining at 800°C instead of at 600°C, which was used in these tests.

4.5 Chemical Consumption and Costs

The chemical consumption for each run is shown in Table 6. The cost of chemicals, including solvent loss, stripping, and precipitation range from 6 to 16.5¢ per pound of U_3O_8 for the three flowsheets. Most of the difference in cost was due to the different uranium stripping methods used. The lowest cost was obtained with sodium chloride stripping followed by 10% regeneration with sodium carbonate (run 2). The cost was higher with 100% regeneration (run 3) because of the greater consumption of sodium carbonate involved with complete regeneration but also because of the lower uranium concentration in the feed and the higher organic losses. The highest costs (run 1) were due not only to

Table 5. Composition of Uranium Product (%)

Calcined at 600°C

Constitutent	Run 1	Run 2	Run 3
U_3O_8	90.8	82.0	87.6
Fe	0.39	0.30	0.38
Mo	0.47	0.14	0.26
V	2.1	< 0.4	0.04
Al	0.24		0.07
PO_4	1.0	0.76	0.85
SO_4		12.7	6.2
NH_3		< 0.05	< 0.05
Cl		< 0.05	< 0.05

Table 6. Chemical Consumption and Cost per Pound of U_3O_8

	Run 1		Run 2		Run 3	
	(lb)	(cents)	(lb)	(cents)	(lb)	(cents)
Extraction						
Amine	0.030	2.6	0.023	1.9	0.043	3.7
Kerosene	0.14	0.3	0.084	0.2	0.31	0.6
Stripping						
Sodium chloride			2.1	1.6	2.4	1.8
Sulfuric acid			0.17	0.3	0.20	0.3
Sodium carbonate	3.6	8.1	0.15	0.3	1.7	3.8
Precipitation						
Ammonia			0.29	1.7	0.34	1.9
Sulfuric acid	2.6	3.8				
Sodium hydroxide	0.37	1.7				
Total Cost		16.5		6.0		12.1

sodium carbonate consumption for uranium stripping and the sulfuric acid required to destroy the carbonate, but also because the amount of excess sodium carbonate used was somewhat greater than required. Although each flowsheet was not optimized with respect to chemical consumption, the results do demonstrate the relative costs of each flowsheet.

5. MIXING REQUIREMENTS FOR GOOD STAGE EFFICIENCY

The mixing requirements for good stage efficiency were measured in standard baffled-tank mixers (6 in. in diameter, agitated with a flat-bladed turbine (Fig. 4). Power input was calculated by the method of Rushton[11] and Laity,[12] $P = (k/g)\,\rho\, N^3 D^5$, in which power is proportional to turbine speed and diameter. Batch tests were used to obtain an order of magnitude for the rate of uranium transfer in the extracting and stripping steps for several amines. Continuous-flow tests for one flowsheet were made over a range of mixing power and flow rates to obtain stage efficiency for uranium extraction and stripping.

5.1 Batch Mixing

The rate of uranium transfer for both extraction and stripping was very rapid; less than 30 sec of mixing time was required to reach 97% of equilibrium at the lowest mixing power tested (2.5 hp per 1000 gal). There was no significant difference in the rate of extraction for different amines, two representative of secondary and one of a tertiary amine (Table 7). The rate of uranium stripping from loaded solvent was rapid when using typical solutions of sodium chloride, sodium carbonate or

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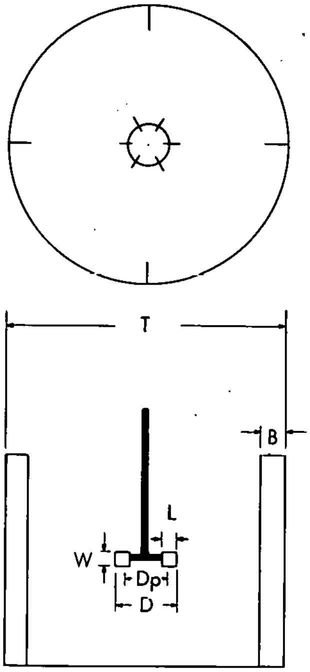


T	D	B	V
Inches			Gallons
6	2	0.6	0.74
12	4	1.2	5.9
20	6	2.0	27.0

DIMENSION RATIOS OF TURBINE
D:Dp:L:W = 24:16:6:5

Fig. 4. Baffled-Tank Mixers.

ammonium nitrate (Table 8). The rates were unaffected by excess stripping agents in the range 10 to 50% excess sodium chloride or 5 to 10% excess sodium carbonate. The percentage excess of stripping agents was based on the stoichiometric requirements, which for sodium carbonate stripping is 0.5 mole per mole of amine, plus 3 moles per mole of uranium; for sodium chloride or ammonium nitrate stripping, it is independent of uranium concentration, being 1 mole per mole of amine.

Table 7. Batch Extraction with Different Amines

Aqueous Feed: 1.2 g U per liter, 40 g SO_4 per liter, pH 1.0
Phase Ratio: A/O = 4/1
Power: 2.5 hp per 1000 gal

Solvent	Percent of Equilibrium Mixing Time (10 sec)	Percent of Equilibrium Mixing Time (30 sec)
0.1 M Amberlite LA-1	96	99
0.1 M Amberlite LA-1, 3% TDA[a]	93	98
0.1 M Di(tridecyl), 5% TDA	88	97
0.1 M triisooctyl, 5% TDA	92	98

[a] Mixed tridecyl alcohols.

Table 8. Batch Stripping from 0.1 M Amberlite LA-1

Stripping Agent	% Excess Agent	Power Input (hp/1000 gal)	Percentage of Equilibrium Concentration after Mixing (10 sec)	(30 sec)
1.0 M NaCl	10	30	99	99
	50	2	96	97
	50	8	95	99
	50	30	95	99
1.0 M Na_2CO_3	5	30	97	99
	10	2	92	97
	10	8	98	99
	10	30	98	99
0.8 M NH_4NO_3	5	30	94	99

The procedure for batch measurement consisted of mixing the phases at constant power and sampling the mixture at selected time intervals. Samples were dipped out of the mixer without stopping the agitator. The percentage transferred at each mixing time was calculated from analysis of the phases compared to equilibrium values obtained by mixing for an extended time, usually 8 min.

5.2 Continuous-Flow Mixing—Extraction

The stage efficiency of the 6-in.-diam mixer was greater than 90% at a power input of 6 hp per 1000 gal or greater and at residence times ranging from 0.1 to 1.5 min (Tables 9 and 10). Extraction rate increased with both power input and residence time to give nearly 100%

Table 9. Summary of Continuous Flow Mixing-Extraction Data

Solvent: 0.1 M Amberlite LA-1
Aqueous Feed: 1.1 g U per liter
Phase Ratio: A/O = 3/1

Total Flow Rate (gpm)	Residence Time (min)	Stage Efficiency (%) 0.0	0.8	2.6	6.2	12.	21 hp/1000 gal
0.5	1.5	42	90	99	> 99	> 99	> 99
2.0	0.37	43	74	93	98	> 99	> 99
3.0	0.25	40	71	92	98	99	99
5.0	0.15	50	70	90	94	97	98
7.0	0.09	50	66	85	94	98	99

Table 10. Data for Continuous-Flow Mixing Tests - Extraction

Solvent: 0.1 M Amberlite LA-1 in kerosene
Aqueous: Synthetic leach liquor, 1.1 g U per liter
Phase Ratio: A/O = 3/1

Turbine Speed (rpm)	Power Input (hp/1000 gal)	Uranium Conc. in Aqueous (g/liter)	Murphree Stage Efficiency (%)
Total Flow Rate, 0.5 gpm; Residence Time, 1.5 min			
0	0	0.69	42
200	0.77	0.17	90
300	2.6	0.077	99
400	6.2	0.065	99
500	12	0.066	99
600	21	0.056	99
Total Flow Rate, 2 gpm; Residence Time, 0.37 min			
0	0	0.67	43
200	0.77	0.34	74
300	2.6	0.14	93
400	6.2	0.087	98
500	12	0.067	99
600	21	0.066	99
Total Flow Rate, 3 gpm; Residence Time, 0.25 min			
0	0	0.70	40
200	0.77	0.38	71
300	2.6	0.15	92
400	6.2	0.077	98
500	12	0.066	99
600	21	0.058	99
Total Flow Rate, 5 gpm; Residence Time, 0.15 min			
0	0	0.61	50
200	0.77	0.39	70
300	2.6	0.17	90
400	6.2	0.13	94
500	12	0.10	97
600	21	0.083	98
Total Flow Rate, 7 gpm; Residence Time, 0.09 min			
0	0	0.62	50
200	0.77	0.42	66
300	2.6	0.22	85
400	6.2	0.11	94
500	12	0.080	98
600	21	0.066	99

stage efficiency. Further evidence of rapid uranium extraction is shown by the greater-than-40% efficiency obtained with no power input to the mixer, the energy of the incoming streams being sufficient to cause significant dispersion and extraction.

Continuous-flow tests were made in a 6-in.-diam mixer with a 3-in. flat-bladed turbine of the same configuration as that used in batch tests (Fig. 4). The aqueous feed and solvent were metered into the bottom of the mixer through concentric pipes to eliminate premixing of the phases. The mixed phases flowed out of the mixer at a point 6 in. above the bottom, giving an effective liquid volume of 0.75 gal.

Stage efficiency was calculated from analysis of samples of the mixed effluent taken at steady-state conditions of mixing power and flow rates. Efficiency was calculated as Murphree[13] efficiency, based on uranium concentrations in the aqueous phase from the effluent sample and the equilibrium curve (Fig. 1). The aqueous feed (Table 11) was a synthetic solution typical of leach liquor produced by sulfuric acid leaching of uranium ore. The solvent was 0.1 M Amberlite LA-1 in kerosene, which was scrubbed with a 10% sodium carbonate solution and dilute sulfuric acid to remove readily soluble fractions before use. The extraction tests were made at aqueous-to-solvent flow ratios of 3/1, giving a uranium loading in the solvent of 3 g of U per liter, which is about 80% of maximum loading for this particular solvent and aqueous feed.

Table 11. Composition (g/liter) of Aqueous Feed Solution

U(VI)	1.1	SO_4^{2-}	50
Fe(III)	5.0	F^-	1.3
Al(III)	2.6	PO_4^{3-}	2.1
		H^+ (pH)	1.0

5.3 Continuous-Flow Mixing-Stripping

The stage efficiency of the 6-in.-diam mixer for the stripping of uranium with sodium chloride solution is lower than that for extraction at the same mixing power and residence time. The data in Table 12 and Fig. 5 show that 90% stage efficiency was obtained at a power input of 50 hp per 1000 gal and a residence time of 0.25 min or more. Extrapolation of the curves to 100% efficiency at zero flow rate shows that 90% stage efficiency could be attained at 20 hp per 1000 gal and 2 min residence time. Slightly less than four stages at 90% efficiency are required for 99% uranium stripping in the typical flow sheet.

The stage efficiency of the sodium chloride stripping system was determined in the same manner as that described for extraction, except that Murphree efficiency was based on uranium concentration in the solvent-phase effluent and the stripping equilibrium data. The solvent feed was 0.1 M Amberlite LA-1 in kerosene, loaded with 3.3 g of uranium per liter. The stripping agent was a 1.0 M sodium chloride solution. The ratio of aqueous to solvent flow rate was 1/6, which provided about a 50% excess of the stoichiometric quantity of sodium chloride required for stripping.

Table 12. Continuous Flow - Stripping

Solvent: 0.1 M Amberlite LA-1 in kerosene, 3.3 g U per liter
Aqueous: 1.0 M NaCl
Phase Ratio: A/O = 1/6

Turbine Speed (rpm)	Power (hp/1000 gal)	Uranium, Conc. in Solvent (g/liter)	Murphree Stage Efficiency (%)
Total Flow Rate, 1 gpm; Residence Time, 0.75 min			
0	0	2.7	15
200	0.77	1.7	47
400	6.2	0.80	81
600	21	0.75	84
800	50	0.63	88
Total Flow Rate, 3 gpm; Residence Time, 0.25 min			
0	0	2.6	24
200	0.77	2.2	36
400	6.2	0.90	79
600	21	0.78	84
800	50	0.54	92
Total Flow Rate, 5 gpm; Residence Time, 0.15 min			
0	0	2.1	36
200	0.77	1.7	45
400	6.2	1.1	68
600	21	0.89	80

6. BATCH-PHASE SEPARATION

Phase separation is generally considered to be a two-step process, consisting of a primary break in which the bulk of the dispersion separates by both sedimentation and coalescence into its component phases, followed by a secondary break in which droplets of one phase entrained in the other settle out, leaving both phases clear. The rate of the primary break is the controlling factor for the design and operation of gravity-type settlers and may be studied in either batch or continuous-flow equipment. Batch testing was used to screen the effect of variables such as type of dispersion (aqueous continuous or solvent continuous), phase ratio, mixing time, mixing power, temperature, chemical composition of the phases, etc., on the rate of primary break. Flow capacity of settlers (discussed in Sec 7) was then determined as a function of the more important variables.

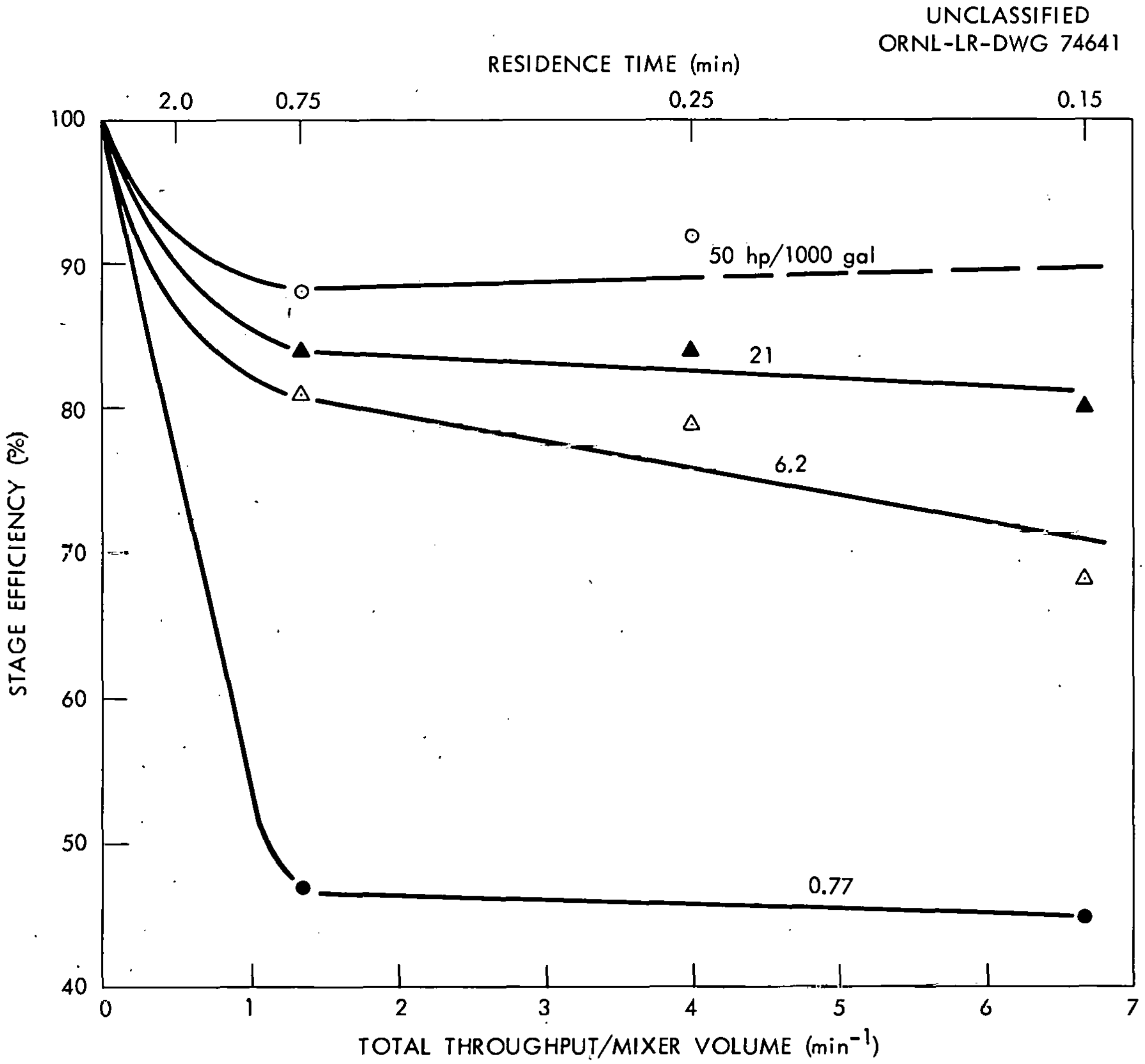


Fig. 5. Stage Efficiency for Stripping Uranium with 1 M Sodium Chloride.

The equipment for batch studies consisted of baffled-tank mixers (either 3 in. in diameter x 3-5/8 in. in depth or 12 in. in diameter x 12 in. in depth) as shown in Fig. 4. To determine the primary break time, a dispersion was formed by agitation at a power level sufficient to yield a uniform dispersion. The break time was the time required after the agitator was stopped until a sharp interface formed between the bulk phases.

Composition and physical properties of the solvents and synthetic aqueous feeds used in the testing program are shown in Table 13. The solvents were scrubbed with 10 volumes of sodium carbonate solution (5 wt-vol %) followed by 50 volumes of dilute sulfuric acid (5 vol %) to remove readily soluble components, thereby making them similar to recycled plant solvent and permitting reproducible results. The composition and important physical properties of a number of actual plant liquors are shown in Table 14.

Table 13. Physical Properties of Amex Test Solutions

Solution	Viscosity (centistokes) 25°C	Viscosity (centistokes) 50°C	Density (g/cc) 25°C	Density (g/cc) 50°C
0.12 M Amberlite LA-1 in kerosene	3.00	1.79	0.82	0.81
0.12 M Amberlite LA-1 in kerosene, modified with 3 wt-vol % TDA	3.07	1.91	0.82	0.80
0.10 M Di(tridecyl) amine in kerosene, modified with 3 wt-vol % TDA	3.14	1.96	0.82	0.80
0.10 M Alamine 336 in kerosene, modified with 3 wt-vol % TDA	2.80	1.79	0.81	0.80
Sulfate feed: 70 g/liter SO_4, pH 1.0	1.11	0.71	1.08	1.07
Chloride strip: 35 g/liter Cl, 9.6 g/liter SO_4, pH 1.0	0.97	0.63	1.04	1.03
Carbonate strip: 10% (wt-vol) Na_2CO_3	1.32	0.83	1.09	1.08

6.1 Batch Phase-Separation Tests with Synthetic Feed

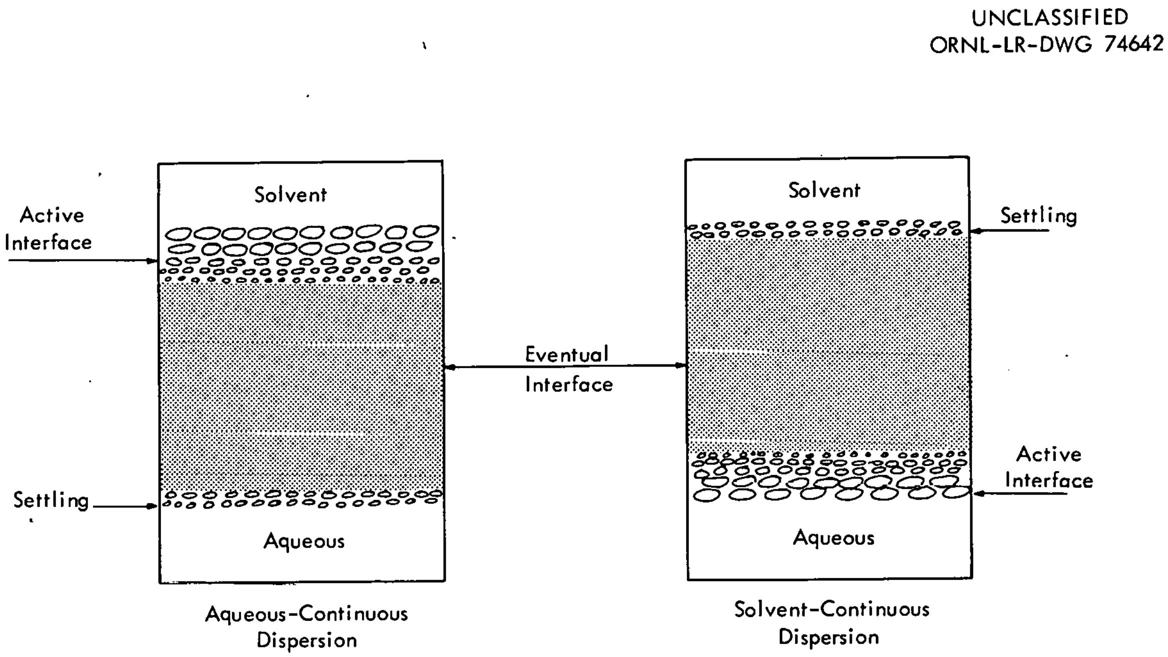
The general appearance of a dispersion during the primary break resembles a three-phase system consisting of a rather sharply defined dispersion band sandwiched between relatively clear layers of solvent and aqueous.[14,15] At one of the boundaries the rate of travel toward the final interface is dependent on sedimentation of the dispersed drops and shows little activity. The other boundary is characterized by the active coalescence of drops with neighboring drops and with the bulk phase which they contact. The active or coalescing interface for an aqueous-continuous dispersion is at the solvent-dispersion boundary, while, for a solvent-continuous dispersion, the coalescing interface is at the aqueous-dispersion boundary, as illustrated in Fig. 6.

The settler profile curves of both boundaries for several different amine dispersions are shown for the 12-in.-diam settler (Fig. 7). Note that the curve for the active interface is linear over most of the break, showing that the rate of coalescence is virtually independent of the dispersion volume. This independence of the rate of coalescence on dispersion volume is further demonstrated by the profile obtained by

Table 14. Composition of Typical Plant Liquors

Liquor	U (g/liter)	V (g/liter)	Mo (g/liter)	SiO_2 (g/liter)	SO_4 (g/liter)	Viscosity (centistokes at 25°C)	Density (g/cc at 25°C)	pH
K-M 11[a]	1.05	4.1	0.012	< 0.1	110			0.5
Slime Liquor[b]	5.1	3.8	0.007	< 0.1	78	1.14	1.08	1.0
Ship Rock[a]	0.70	0.7	0.003	0.3	23	1.02	1.02	1.4
Vitro No. 6[c]	1.1	0.76	0.084	0.6	40			1.1
Section No. 10[d]	0.88	0.1	0.004	0.7	20	0.94	1.02	1.4
Holly[d]	1.33	0.1	0.04	2.0	31	1.07	1.05	1.6
Sand Liquor No. 17[b]	1.9	2.2		$\cong 1.0$	108			0.4
Sand Liquor No. 18[b]	1.9	2.6		$\cong 1.0$	105			0.3
Sand Liquor No. 19[b]	1.83	2.3	0.013	$\cong 1.0$	109	1.25	1.10	0.4
Old Rifle Plant[e]	2.1	2.9	0.004	1.6	31	1.08	1.05	1.4
Recycle[d]	0.88	0.1	0.03	1.0	48	1.03	1.04	0.6
St. Anthony[d]	1.11	0.1	< 0.001	2.2	30	0.97	1.03	0.8
New Rifle Plant[e]	4.0	3.1	0.04	2.5	55	1.10	1.06	0.9
New Rifle Plant Plus 300 ppm gelatin[e]	4.0	3.1	0.04	0.4	55			0.9
VCA No. 12[f]	0.73	2.2	0.005	4.9	70			0.8

[a] Kerr-McGee Oil Industries, Shiprock, New Mexico.
[b] Climax Uranium Company, Grand Junction, Colorado.
[c] Vitro Uranium Company, Salt Lake City, Utah.
[d] Kermac Nuclear Company, Golden, Colorado.
[e] Union Carbide Nuclear Company, Rifle, Colorado.
[f] Vanadium Corporation of America, Durango, Colorado.



Aqueous-Continuous Dispersion

Solvent-Continuous Dispersion

Fig. 6. Illustration of the Types of Coalescence.

allowing equal volumes of dispersion to separate in 2-in.- and 5-1/2-in.-diam settlers (Fig. 8). The curves of the active interface not only are linear over most of the break but are nearly parallel, indicating that the rates of coalescence are almost the same. Doubling the volume of dispersion in the 5-1/2-in.-diam settler only increased the total break time, and the rate of coalescence remained constant (Table 15).

Table 15. Rate of Coalescence

Settler Diameter (in.)	Dispersion Volume (ml)	Rate of Coalescence (in./min) Solvent Continuous	Rate of Coalescence (in./min) Aqueous Continuous
2	1300	1.4	2.5
5-1/2	1300	1.2	2.2
5-1/2	2600	1.2	2.3

These data indicate that most of the coalescence occurs at the active interface, with little if any coalescence occurring within the dispersion or on the settler walls. Therefore, the flow capacity of a gravity-type settler is mainly dependent on the rate of primary break as a function of the area of the active interface; dispersion volume or residence time are of secondary importance.

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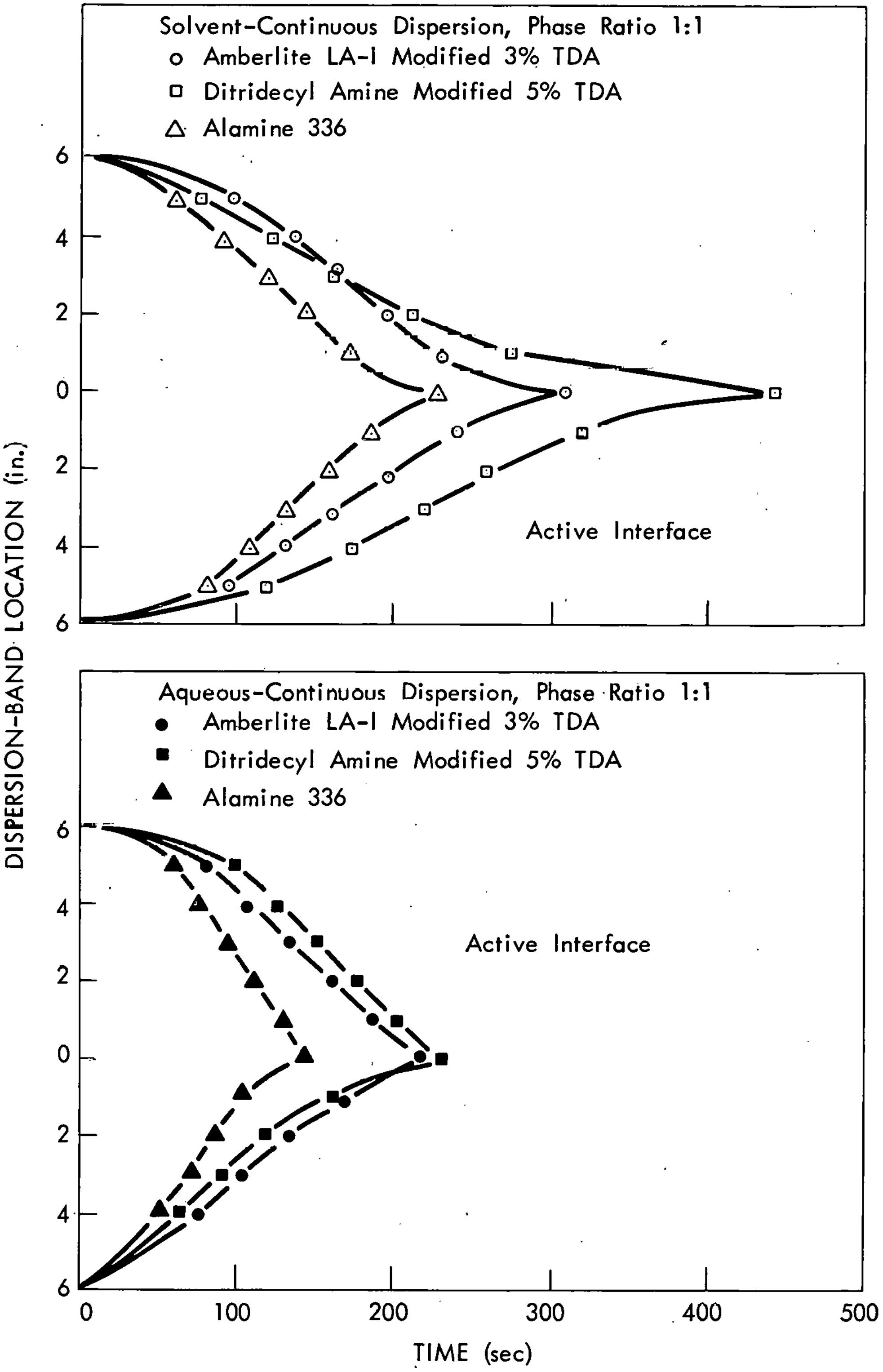

Fig. 7. Batch-Settling Profiles.

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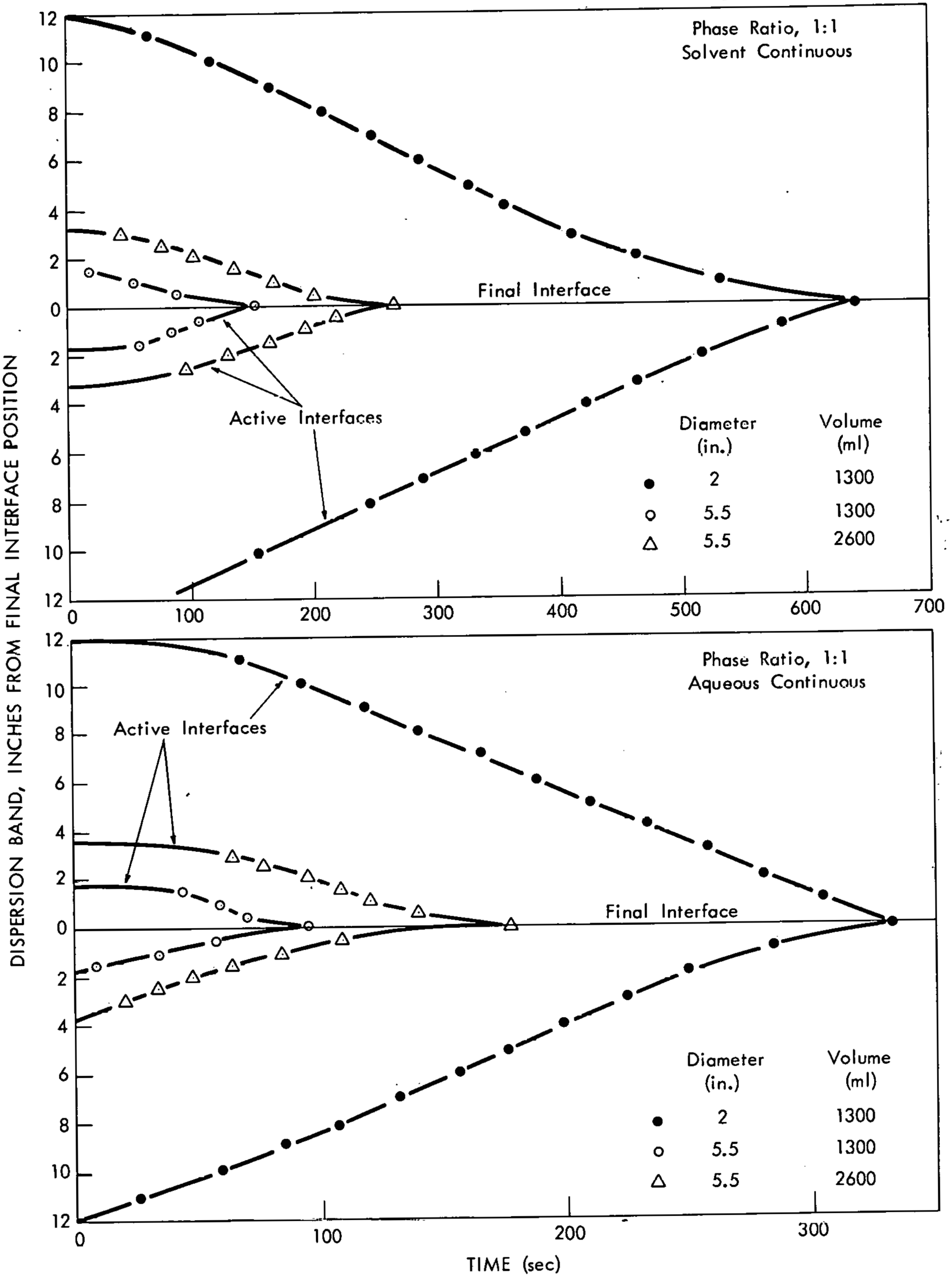

Fig. 8. Batch Settling in Different-Size Settlers, Using Amberlite LA-1 Modified vs Sulfate Feed.

Typical Primary Break Times. Although settling profiles have been useful for demonstrating coalescing and sedimentation rates, etc., the total time for the primary break is sufficient to evaluate the gross effect of the many variables tested. Typical primary-break times for three amine solvents with sulfate, chloride, and carbonate feeds are shown in Table 16. Certain general trends are apparent: First, a solvent-continuous dispersion breaks slower than a comparable aqueous-continuous dispersion; second, a low interfacial tension between the solvent-feed pair means a longer primary-break time; third, dilute dispersions break faster than dispersions having a 1/1 phase ratio.

Primary Break Times with Different Amines. Table 17 shows the primary-break times obtained with 0.1 M unmodified kerosene solutions of secondary and tertiary amines suggested for use as reagents in the Amex process. Aqueous-continuous dispersions generally separated quite fast; but several of the solvent-continuous tests produced semipermanent dispersions (dispersions which took longer than 5 min to break) indicating that the solvent would have to be modified to increase the rate of primary break if they were to be useful in actual processes.

The Effect of Solvent Modifiers on Primary Break. Several potentially useful reagents formed semipermanent emulsions when mixed solvent-continuous, prompting a search for a cheap solvent modifier to increase the rate of primary break.[9] A mixed tridecyl alcohol was used for most tests, although almost any relatively long-chain aliphatic alcohol could be used.

As shown in Table 18, the addition of 2 to 5% alcohol greatly decreases the time required for primary break, in some cases 90%. The addition of alcohol increased the interfacial tension, although not to the same extent with different amines.

The Effect of Reagent Concentration on the Primary Break. The particular requirements of each Amex flowsheet determine the concentration of amine to be used in the solvent. The effect of amine concentration on the primary break is shown in Table 19 for two amines. In general increasing the amine concentration had little effect on the primary break time of aqueous-continuous dispersion but markedly increased the primary break time of organic-continuous dispersion. The maximum break time for both amines occurred at concentrations (less than highest tested) where the interfacial tension was lowest. Addition of either more tridecanol or a surfactant such as Victowet-12 (Victor Chemical Company) reduced the break time considerably, indicating that solvents containing high concentrations of amines probably can be used in practical systems.

Diluent Effect on Primary Break. The data presented in Table 20 show the effect of several kerosene-type diluents on primary-break times. The diluent effect was quite small, and the cost of any particular kerosene delivered at the site would be the deciding factor in the choice of a diluent.

Table 16. Typical Primary-Break Times at 25°C

Solvent-Aqueous System	Interfacial Tension (dynes/cm)	Settler Diam (in.)	Settler Depth (in.)	Primary-Break Time (sec) Aqueous Continuous $4_{aq}:1_{org}$	Aqueous Continuous $1_{aq}:1_{org}$	Solvent Continuous $1_{aq}:1_{org}$	Solvent Continuous $1_{aq}:2_{org}$	Solvent Continuous $1_{aq}:6_{org}$
0.1 M Amberlite LA-1 in Kerosene Mod. with 3% TDA								
Sulfate feed	7.4	3	3-5/8	57	84	138	120	
		12	12	117	220	313		
Chloride feed	9.8	3	3-5/8	64	77	88	71	
		12	12		184	201		
Carbonate feed	< 1.0	3	3-5/8		313	541		376
		12	12		560	1558		
0.1 M Di(tridecyl) amine in Kerosene Mod. with 5% TDA								
Sulfate feed	10.6	3	3-5/8	65	95	134	127	
		12	12	116	224	443		
Chloride feed	11.8	3	3-5/8		100	130		121
		12	12		169	321		138
Carbonate feed	< 1.0	3	3-5/8		90	308		198
		12	12		246	1067		608
0.1 M Alamine 336 in Kerosene Mod. with 5% TDA								
Sulfate feed	11.2	3	3-5/8	45	64	126	95	
		12	12	90	144	239		
Chloride feed	14.5	3	3-5/8		44	83		74
		12	12		83	130		104
Carbonate feed	6.4	3	3-5/8		76	60		113
		12	12		185	202		167

Table 17. Primary-Break Time for Different Amines

3-in.-diam settler; 25°C; sulfate feed

Amine	Primary-Break Time (sec)			
	Aqueous Continuous		Solvent Continuous	
	$4_{aq}:1_{org}$	$1_{aq}:1_{org}$	$1_{aq}:1_{org}$	$1_{aq}:2_{org}$
Amberlite LA-1	60	94	190	166
Amberlite LA-2	65	106	> 300	> 300
Di(tridecyl)	59	97	> 300	> 300
S-24	52	70	105	97
Trilauryl	156	230	> 300	> 300
Triisooctyl	35	48	72	65

Table 18. Effect of Tridecyl Alcohol Modifier on Primary-Break Times

Synthetic sulfate feed; 3-in.-diam settlers; 25°C

Tridecanol (vol %)	Interfacial Tension (dynes/cm)	Primary-Break Time (sec)			
		Aqueous Continuous		Solvent Continuous	
		$4_{aq}:1_{org}$	$1_{aq}:1_{org}$	$1_{aq}:1_{org}$	$1_{aq}:2_{org}$
0.1 M Amberlite LA-1 in Kerosene					
0	6.0	60	94	190	166
1	6.0	59	93	175	147
2	6.4	58	93	160	137
3	6.6	57	84	138	120
5	7.2	56	83	132	115
0.1 M Amberlite LA-2 in Kerosene					
0	2.0	65	106	1880	2800
2	3.4	60	97	154	118
3	4.5	46	65	118	105
5	6.8	50	80	108	97
10	9.1	41	64	90	78
0.1 M Trilauryl Amine in Kerosene					
0	7.0	156	230	2840	2380
2	8.3	55	115	1520	1280
3	9.0	76	129	1460	1200
5	9.8	55	94	215	215
7	10.6	53	85	146	137

Table 19. Effect of Amine Concentration on Primary-Break

Measured in 3-in.-diam settler; 25°C,
phase ratio $1_{aq}:1_{org}$; sulfate system

Amine Concentration (M)	Solvent Properties			Break Time (sec)	
	Viscosity (centistokes)	Density (g/cc)	Interfacial Tension (dynes/cm)	Aq-Cont. Dispersion	Sol.-Cont. Dispersion
	Alamine 336 in 3% Tridecanol, Kerosene				
0.54	15.6	0.843	7.0	88	206
0.28	4.7	0.822	4.8	59	> 1800
0.14	2.8	0.813	5.7	64	209
0.07	2.4	0.808	10.8	71	100
0.04	2.3	0.806	12.4	72	79
	Amberlite LA-1 in 6% Tridecanol, Kerosene				
0.98[a]	82.9	0.885	< 1.0	200	> 3000
0.47	8.2	0.843	< 1.0	111	> 4500
0.23	3.6	0.825	3.0	97	330
0.11	2.8	0.816	3.8	95	117
0.05	2.5	0.812	4.6	95	94
0.03	2.4	0.809	5.6	105	94

[a] In 3% tridecanol, not in 6%.

Table 20. The Effect of Diluents on Primary-Break Time

All solvents were 0.1 M in Amberlite LA-1 amine;
run in 3-in.-diam settlers at 25°C

Diluent	Primary-Break Time (sec)			
	Aqueous Continuous		Solvent Continuous	
	$4_{aq}:1_{org}$	$1_{aq}:1_{org}$	$1_{aq}:1_{org}$	$1_{aq}:2_{org}$
Gulf kerosene	60	94	190	166
Sinclair (light)	44	64	85	108
Sinclair (heavy)	52	93	104	94
Shell 140	50	68	188	182
Napoleum 470	61	92	191	184
Jet fuel T-2	50	67	141	141
Amsco 123-15	62	82	155	146
Uinta kerosene	59	95	189	180
Xylene	60	83	73	62

The Effect of Mixing Power and Time on Primary Break. Data shown in Table 21 show that neither mixing power (15 to 75 hp per 1000 gal) nor mixing time (10 to 30 min) has any significant effect on the primary break. This simplifies the design of mixer-settler units because the mixing criteria can be selected to optimize stage efficiency without changing settler capacity.

Table 21. The Effect of Mixing and Power Time on Primary Break

0.1 M Amberlite LA-1 amine (modified) vs sulfate feed;
12-in.-diam mixer; A/O ratio = 1

Mixing Power (hp/1000 gal)	Mixing Time (min)	Batch Break Time (sec)	
		Aqueous-Continuous	Solvent-Continuous
15	10	210	290
40	10	220	310
40	30	220	300
75	10	210	300

Temperature Effect on Primary Break. Temperature has a marked effect on primary break (Fig. 9). Raising the temperature 30°C (from 15°C to 45°C) approximately halves the primary-break time for both types of dispersion. The break time was directly proportional to the viscosity of the continuous phase, which decreased with increased temperature (Table 13).

6.2 Batch Phase-Separation Tests with Plant Leach Liquor

Primary-break times for 14 leach liquors (received from uranium mills on the Colorado Plateau) vs several amine solvents were determined as a survey of phase-separation troubles that might be encountered with actual plant leach liquors. The data (Table 22) show the marked effect of type of dispersion and difference in amines on break time. With one exception, phase separation was good with organic-continuous dispersions at phase ratios, A/O, of 1/1 and 1/2; however, with aqueous-continuous dispersions, slow phase separation (break time greater than 300 sec) and stable emulsions were formed when many of the liquor samples were mixed with Amberlite LA-1 amine. Emulsion formation appeared to be a function of the concentration of soluble silica (not removable by filtration or centrifugation) in the leach liquor. No difficulty was encountered at silica concentrations less than 0.7 g of SiO_2 per liter. At concentrations greater than 1.0 g/liter, the break time was greater than 300 sec, and some stable emulsion (stable for longer than 24 hr) was formed; the volume of emulsion generally increased with increased silica concentration. The addition of silicic acid to synthetic leach solutions (Table 23) caused similar emulsification, demonstrating that silica is probably the main cause of difficulty with plant liquors.

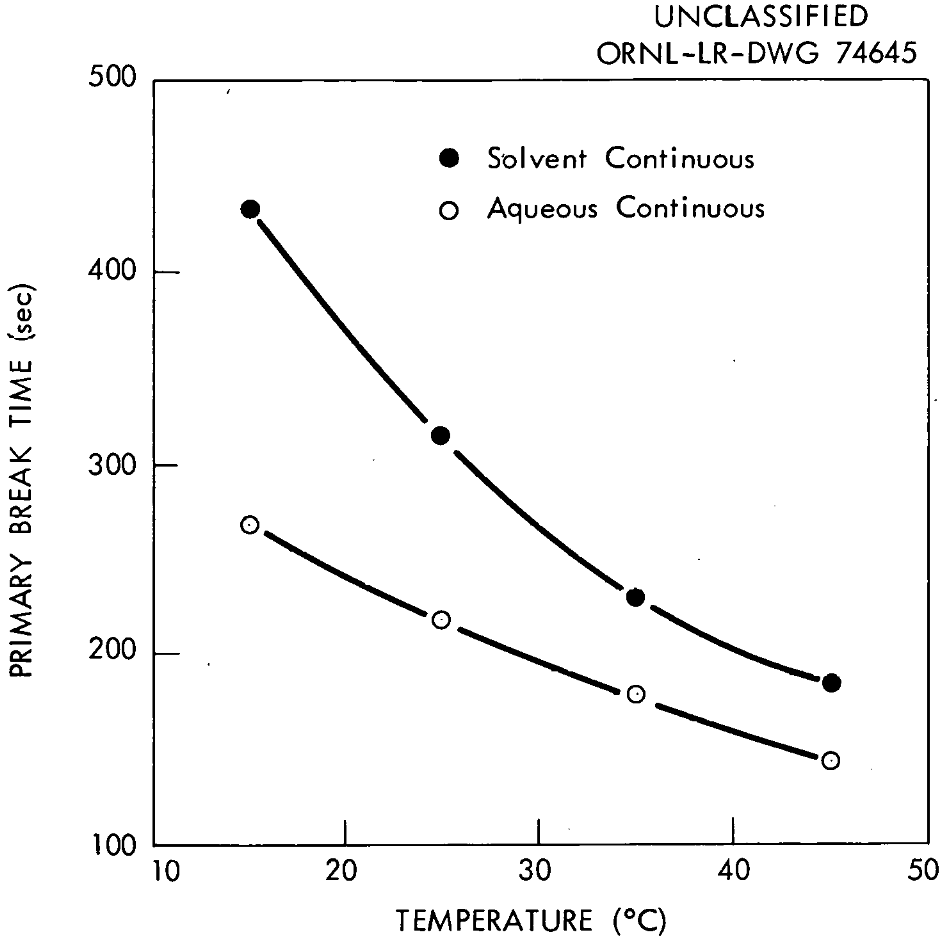

Fig. 9. Effect of Temperature on Primary-Break Time in 12-in.-diam Settler at a Phase Ratio of 1/1, 0.1 M Amberlite LA-1 in Kerosene (3% TDA) vs Sulfate Feed.

The comparative break times for different amines with both plant and synthetic liquors containing silica show that two amines, Di(tridecyl) and S-24, are consistently better than the others (Tables 22 and 23). No emulsions were formed with organic-continuous mixing of these two amines with any of the liquors tested, and the amount of emulsion with aqueous-continuous mixing was considerably reduced or prevented altogether.

6.3 Emulsion Prevention

The screening of plant leach liquors showed that the majority of the liquors tested contain emulsifying agents that stabilize aqueous-continuous dispersions. Control of mixing to produce a solvent-continuous dispersion is a simple method of preventing emulsions. Usually, solvent-continuous mixing can be maintained by starting the mixer with only solvent present, then adding the aqueous phase. Care should be taken to maintain at least 50% solvent in the mixer, either by establishing flowsheet conditions or by

Table 22. Primary-Break Times of Plant Liquors vs 0.1 M Solvents in 3-in.-diam Mixer at 25°C

Plant Liquor	SiO_2 Conc. (g/liter)	Amberlite LA-1 in Kerosene				Amberlite LA-1 in Kerosene + 3% TDA				Di(tridecyl) in Kerosene + 5% TDA			
		Aqueous-Cont.		Solvent-Cont.		Aqueous-Cont.		Solvent-Cont.		Aqueous-Cont.		Solvent-Cont.	
		4/1	1/1	1/1	1/2	4/1	1/1	1/1	1/2	4/1	1/1	1/1	1/2
K.M. 11[a]	< 0.1	76	103	153	158	80	124	162	150	90	110	126	115
Slime liquor[b]	< 0.1	90	127	110	110	73	120	110	99	71	118	100	100
Shiprock[a]	0.3	118	74	129	111	130	112	125	120	97	96	128	120
Vitro No. 6[c]	0.6									95	126	104	105
Section 10[d]	0.7	174	141	181	153	> 300	150	130	130	> 300	117	80	54
Recycle[d]	1.0	> 300	> 300	245	145	> 300	> 300	175	102	135	180	153	150
Sand liquor 17[b]	1.0	> 300								315	250	126	107
Sand liquor 18[b]	1.0	> 300								285	> 300	190	134
Sand liquor 19[b]	1.0	> 300	> 300	> 300	> 300	> 300	> 300	> 300	> 300	> 300	> 300	122	145
Old Rifle plant[e]	1.6					> 300	> 300	122	87	69	149	51	47
Holly[d]	2.0	> 300		184	150	> 300	> 300	172	158	110	127	107	100
St. Anthony[d]	2.2	> 300	244	140	106	> 300	> 300	127	106	208	212	127	99
New Rifle plant[e]	2.5						> 300	163			> 300	77	
New Rifle + gelatin	0.4		115	107			152	216					
VCA No. 12[f]	4.9	> 300								208	293	152	121

[a] Kerr-McGee Oil Industries, Shiprock, New Mexico.
[b] Climax Uranium Company, Grand Junction, Colorado.
[c] Vitro Uranium Company, Salt Lake City, Utah.
[d] Kermac Nuclear Company, Golden, Colorado.
[e] Union Carbide Nuclear Company, Rifle, Colorado.
[f] Vanadium Corporation of America, Durango, Colorado.

Table 23. Effect of Silica on Phase Separation

Settler: 3- x 3-5/8 in.
Organic: 0.1 M amine in kerosene
Aqueous: Synthetic leach liquor containing 0.5 g U, 0.5 g V^{4+} 2 g Fe^{3+}, 2 g Al, 75 g SO_4^{2-} and silica added as a solution of sodium silicate
Phase ratio: 1/1

		Break Time (sec)					
		Aqueous-Continuous			Solvent-Continuous		
Amine	Tridecanol (%)	0.0 g SiO_2/ℓ	0.4 g SiO_2/ℓ	1.6 g SiO_2/ℓ	0.0 g SiO_2/ℓ	0.4 g SiO_2/ℓ	1.6 g SiO_2/ℓ
S-24	0	60	70	180	90	90	100
S-24	2	60	70	130	80	80	80
Amberlite LA-1	0	90	70	> 300	150	180	170
Amberlite LA-1	2	70	70	> 300	100	110	120
Di(tridecyl)	0	80	70	100	> 300	250	290
Di(tridecyl)	5	90	70	150	110	80	110
Alamine 336	3	50	80	> 300	120	120	120
Trilauryl	3	120	90	> 300	> 300	300	270

recycle of organic from the settler back to the mixer, to prevent the localized formation of aqueous-continuous dispersion.

In cases where silica alone is the cause of emulsion, the silica can be flocculated by the addition of gelatin.[16] After filtration or settling out of the silica, the aqueous phase can be contacted with solvent without difficulty (Table 22). Flocculating agents that are normally used to aid in settling ore slimes are not very effective for flocculating silica.

During the testing of plant liquors it was noted that samples that contained a small amount of insoluble solids separated faster than filtered samples after mixing with organic. Therefore, a number of finely-divided-solid additions were tested for their possible effect in preventing the formation of silica emulsions. Solids such as Celite, kaolin, ore slimes, or decolorizing carbon had a spectacular effect on break time of silica-bearing liquor, resulting in nearly complete phase separation in less than 60 sec. All the solids except carbon collected at the interface and in themselves caused some emulsion; however, only a low concentration, 0.1 g/liter, was necessary to prevent silica emulsion (Fig. 10).

Decolorizing carbon differed from the other solid additions in that it remained suspended in the organic phase. Although a concentration of 5 to 10 g/liter was sufficient to prevent silica emulsion, it was observed that the addition of a larger amount of carbon (100 g/liter) made it impossible to maintain the aqueous phase continuous even at an A/O

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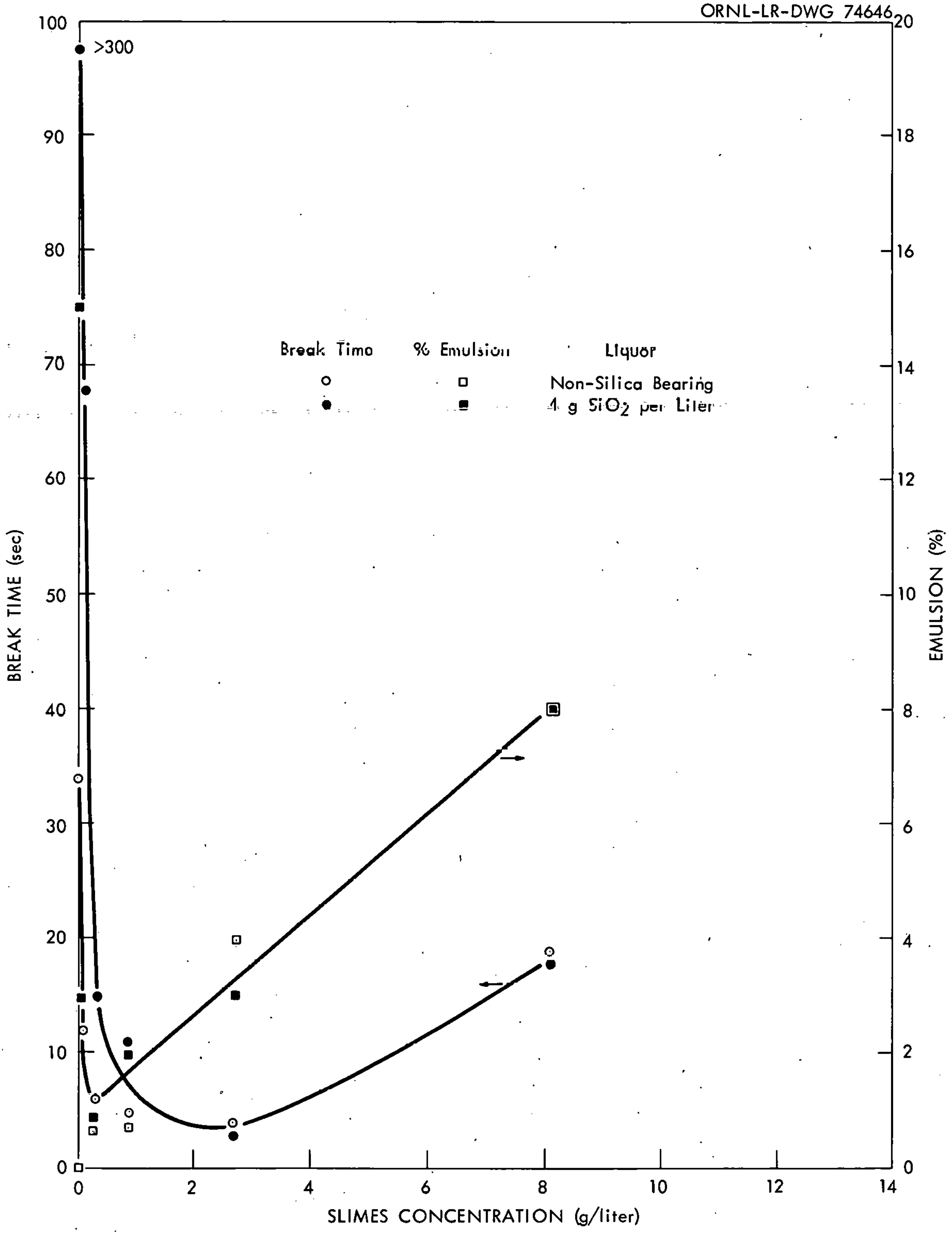

Fig. 10. Effect of Ore Slimes on Break Time and Emulsion Formation.

ratio of 3. This is in agreement with the generalization that solids tend to stabilize the type of emulsion in which they are wetted by the continuous phase.

7. CONTINUOUS-FLOW SETTLER TESTS

The capacity of continuous-flow settlers as well as the entrainment in the solvent and aqueous streams were determined for typical extraction and stripping circuits. A single mixer-settler unit (Fig. 11) was used in which solvent and aqueous phases of constant composition were recycled. The mixer was a baffled tank agitated with a flat-blade turbine. The settler was a cylindrical tank in which the total liquid depth was about 30 in. The interface was controlled near the midpoint of the settler by a simple gravity leg on the aqueous discharge. The temperature was maintained at 25°C unless noted otherwise. Physical properties of solvent and aqueous solutions tested are shown in Table 13.

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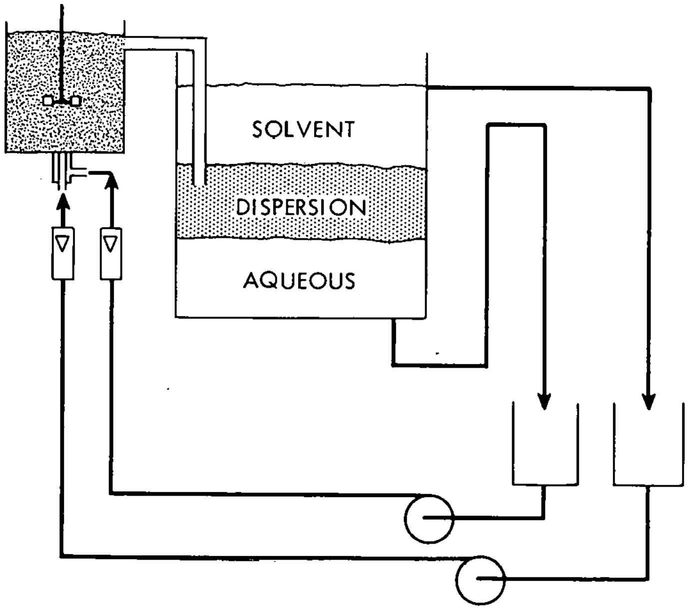

Fig. 11. Single Mixer-Settler Unit for Phase Separation Tests.

Flow ratios were varied from 4/1 to 1/1 (A/O) for aqueous continuous operation and from 1/1 to 1/6 (A/O) for solvent-continuous operation in both the extraction and stripping circuit tests. Under most of these conditions a distinct dispersion band existed at the interface which, at steady state, was of uniform thickness over the entire area of the settler. Steady state was usually reached within 20 min, and the band width was observed for 1 hr. The dispersion band was very stable with respect to operating time, 5 hr being the longest period observed. The dispersion-band thickness increased exponentially with increased flow, without showing a sharp flooding point. The best correlation of data was obtained by plotting dispersion-band thickness against the flow rate of the dispersed phase per unit settler area. This method of correlation could not be used for tests made with solvent-continuous dispersion at a phase ratio (A/O) of 1/6 since the dispersion band, if any, was not flow dependent, and settler capacity was limited by the entrainment of aqueous phase in the solvent leaving the settler. The best correlation was obtained by plotting entrainment values as a function of solvent flow rate.

The data can be summarized in terms of "nominal settler flow capacity." This was defined for cases when the dispersion-band thickness was flow dependent by first arbitrarily selecting a dispersion-band thickness of 2 ft as the flooding point. This is somewhat justified because a total liquid depth of 2 ft is usually sufficient for simple gravity-leg control of the interface. The nominal flow capacity was then chosen to be the flow rate at a band width of 5 in., which was about half the flow rate at flooding and allows a safety factor of 2 for design purposes. For cases where settler capacity was determined by entrainment values, the nominal flow capacity was then taken as half the flooding flow rate, where the entrainment was equivalent to the phase ratio of the dispersion entering the settler.

7.1 Settler Tests—Extraction Circuit

The sodium sulfate feed had previously been shown to have physical properties quite similar to typical sulfate mill liquors and could be expected to behave the same way in the settler tests (Tables 13 and 14). Accordingly, a series of continuous flow tests were made at phase ratios typical of those encountered in mill practice. The correlated data (Figs. 12 and 13, and Table 24) shows a family of nearly parallel lines. Nominal flow capacities, as determined from these plots for a 5-in. dispersion-band width, are summarized in Table 25.

Effect of Solvent. Changing the composition of the solvent either by the addition of a modifier or by the use of a different amine (of same class) had no apparent effect on the nominal flow capacity of settlers operating with an aqueous-continuous dispersion. Modifying the solvent with tridecyl alcohol (TDA) increased the nominal aqueous flow for a settler operating with the solvent phase continuous from 0.37 to 0.68 gal ft^{-2} min^{-1} for all A/O ratios tested.

Effect of Dispersion Type and Phase Ratio. The nominal solvent flow capacity for aqueous-continuous tests increased from 0.7 to 0.88 gal ft^{-2} min^{-1} as the A/O ratio decreased from 4/1 to 1/1, but the nominal aqueous flow remained constant for solvent-continuous tests as A/O ratio decreased from 1/1 to 1/2.

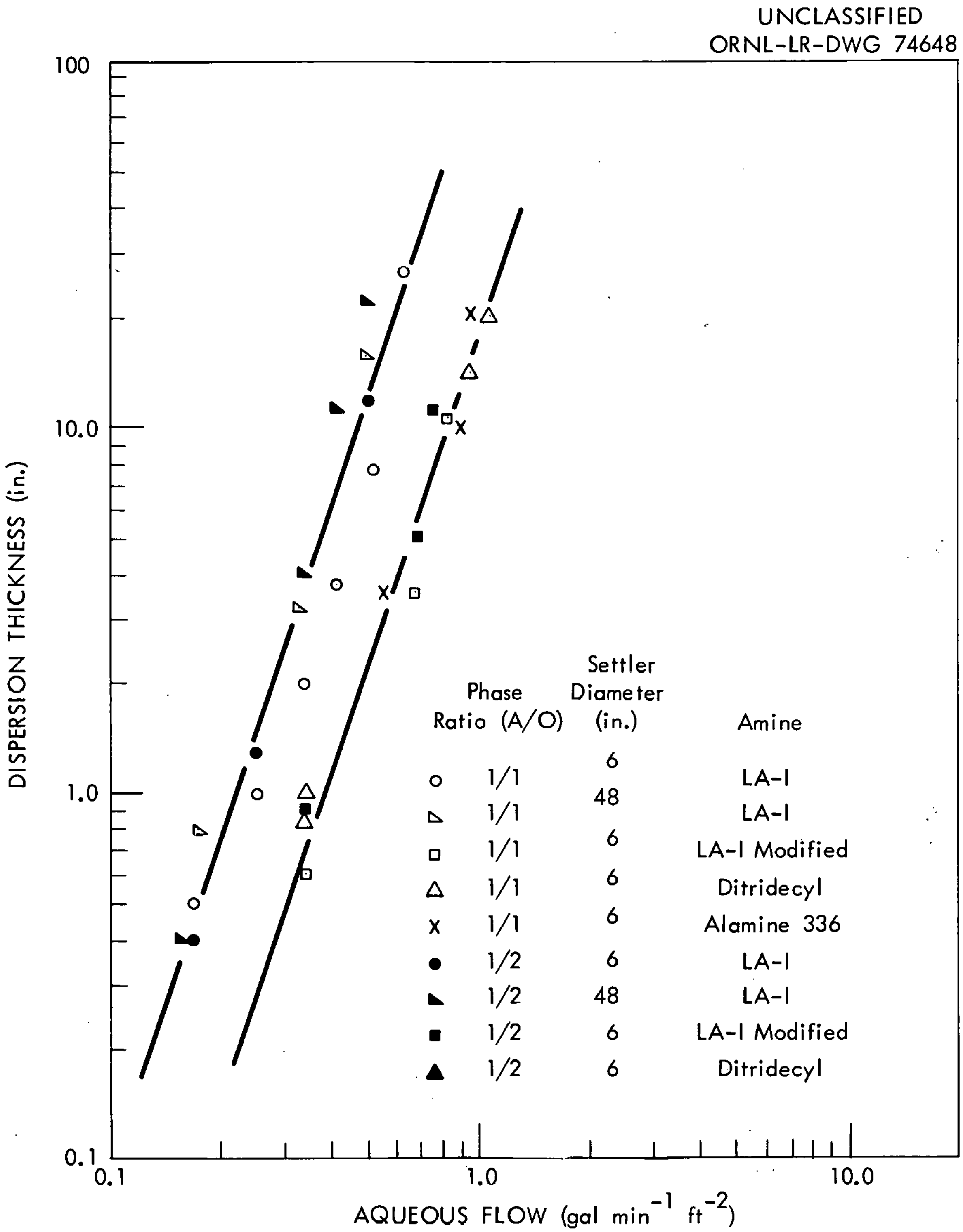

Fig. 12. Correlation of Data for Solvent-Continuous Operation of Continuous-Flow Settlers—Extraction Circuit.

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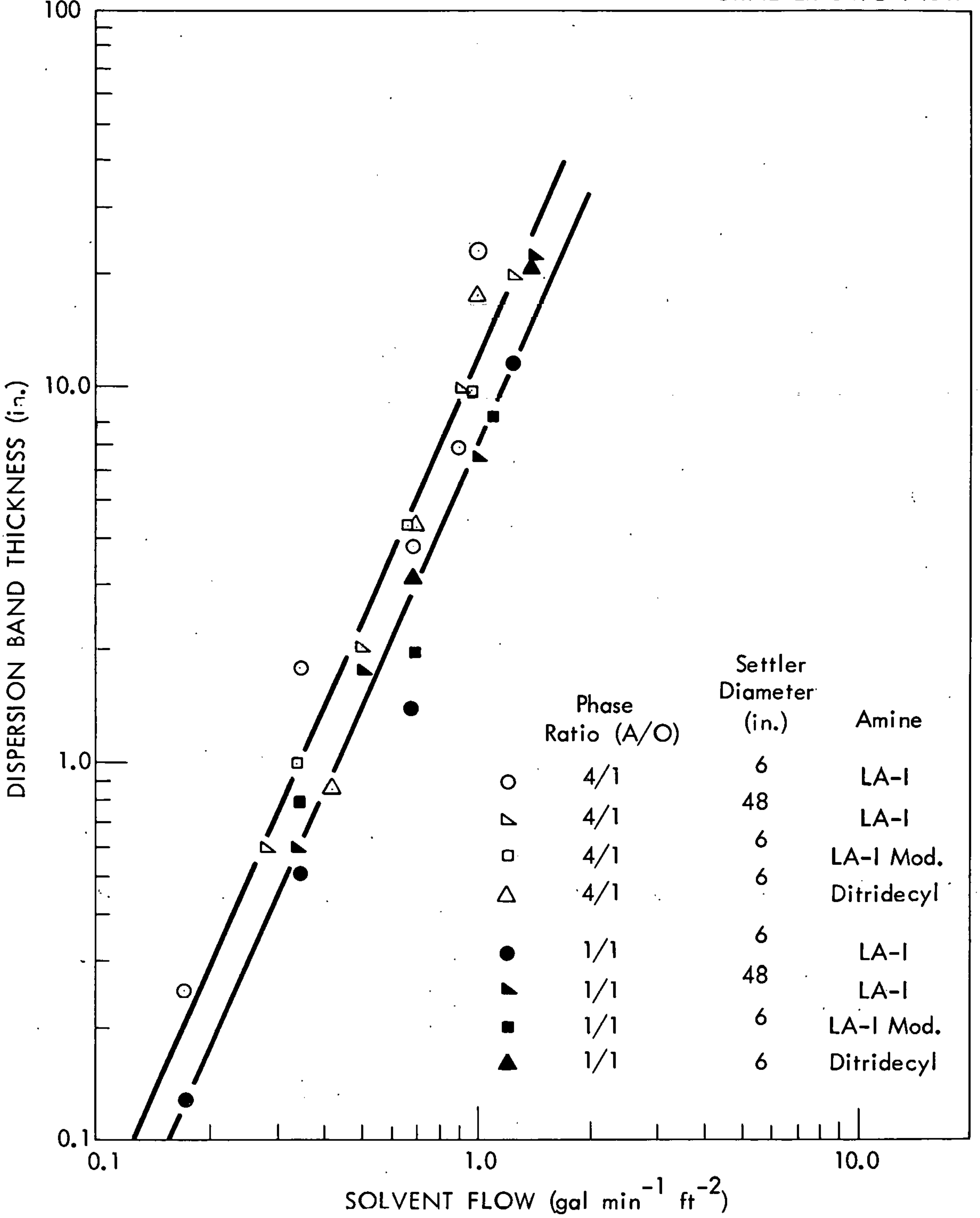

Fig. 13. Correlation of Data for Aqueous-Continuous Operation of Continuous-Flow Settlers—Extraction Circuit.

Effect of Temperature. Nominal flow capacity increased from 0.37 gal ft^{-2} min^{-1} at 25°C to 0.92 gal ft^{-2} min^{-1} at 50°C for solvent-continuous dispersion using unmodified Amberlite LA-1 solvent. Increased temperature would have a similar effect on flow capacity with other solvents. This agrees with the temperature effect observed in the batch break tests, where it was shown that the decrease of primary-break time with increased temperature corresponds roughly with the change of viscosity, which changes with temperature.

Table 24. Continuous-Flow Settler Data—Extraction Circuit

Phase Ratio (A/O)	Flow Rates (gal ft^{-2} min^{-1})		Dispersion Thickness (in.)			
	Aqueous	Solvent	Amberlite LA-1	Amberlite LA-1 + 3% TDA	Di(tridecyl) + 5% TDA	Alamine 336 + 3% TDA
6-in.-diam Settler; Aqueous-Continuous Dispersions						
4/1	0.68	0.17	0.25			
	1.35	0.34	1.8	1.0		
	1.62	0.41			0.88	
	2.70	0.68	3.8	4.3	4.25	
	3.50	0.88	7.0			
	3.78	0.95		10.3		
	4.00	1.00	23.0		17.75	
1/1	0.17	0.17	0.13			
	0.34	0.34	0.5	0.8		
	0.68	0.68	1.4	2.0	3.13	
	1.08	1.08		8.3		
	1.22	1.22	11.8			
	1.35	1.35			20.88	
6-in.-diam Settler; Solvent-Continuous Dispersion						
1/1	0.17	0.17	0.5			
	0.25	0.25	1.0			
	0.34	0.34		0.6	0.88	
	0.41	0.41	3.8			
	0.51	0.51	6.8			
	0.63	0.63	27.0			
	0.68	0.68	2.0[a]	3.6		3.5
	0.81	0.81		10.8		10.0
	1.08	1.08	6.6[a]		20.13	21.0
1/2	0.17	0.34	0.4			
	0.25	0.50	1.3			
	0.34	0.68	2.0	0.9	1.0	
	0.51	1.02	12.0			
	0.68	1.36		5.0		
	0.74	1.48		11.8		
	0.95	1.90			14.88	

[a] Temperature at 50°C; all others, 25°C.

Table 24 (Continued)

Phase Ratio (A/O)	Flow Rates (gal ft^{-2} min^{-1})		Dispersion Thickness (in.)			
	Aqueous	Solvent	Amberlite LA-1	Amberlite LA-1 + 3% TDA	Di(tridecyl) + 5% TDA	Alamine 336 + 3% TDA
	48-in.-diam Settler; Aqueous-Continuous Dispersions					
4/1	1.15	0.29	0.6			
	2.00	0.5	1.5			
	3.75	0.94	10.0			
	5.0	1.25	20.5			
1/1	0.34	0.34	0.6			
	0.50	0.50	1.8			
	1.00	1.00	6.5			
	1.40	1.40	22.8			
	48-in.-diam Settler; Solvent-Continuous Dispersions					
1/1	0.17	0.17	0.8			
	0.33	0.33	3.3			
	0.50	0.50	16.5			
1/2	0.17	0.34	0.4			
	0.33	0.66	4.0			
	0.42	0.84	11.5			
	0.50	1.00	22.5			

Table 25. Nominal Flow for Continuous-Flow Settlers—Extraction Circuit

Continuous Phase	Phase Ratio, A/O	Dispersed Phase Nominal Flow (gpm/ft^2)		
		Amberlite LA-1	Amberlite LA-1 + 3% TDA	Di(tridecyl) + 5% TD
		6-in.-diam Settler		
Aqueous	4/1	0.70	0.70	0.70
	1/1	0.88	0.88	0.88
Solvent	1/1	0.37	0.68	0.68
	1/1	0.92[a]		
	1/2	0.37	0.68	0.68
		48-in.-diam Settler		
Aqueous	4/1	0.70		
	1/1	0.88		
Solvent	1/1	0.37		
	1/2	0.37		

[a] Temperature = 50°C.

The temperature in most uranium-mill solvent extraction circuits depends on ambient conditions and is usually in the range 15 to 50°C. Because of the relatively large temperature effect on settler flow capacity, settler size should be designed for the minimum temperature expected, or facilities for heating to the design temperature should be provided.

Settler Scaleup. Dispersion thickness as a function of flow rate per unit cross sectional area was virtually independent of settler diameter for aqueous-continuous dispersion at A/O ratios of 1/1 and 1/2. Therefore, scaleup can be based on constant flow rate per square foot and constant dispersion thickness. (This is the same basis for scaleup as determined for the Dapex flowsheet.)[5] The nominal flow capacities (Table 25) were the same for 6-in. and 48-in. settlers for all variations of phase ratio and both types of dispersions tested. Overall, this represents an area scaleup of 64-fold.

For actual mill design data, flow capacity tests should be made with representative samples of plant solutions because of unknown factors that could affect phase separation. The scaleup data indicate that reliable design criteria could be obtained in settlers as small as 6 in. in diameter, with a concomitant saving in time and effort.

Entrainment. Solvent entrainment in the aqueous phase after primary phase separation was consistently lower when the mixer was operated with the solvent phase continuous (Tables 26 and 27). Solvent entrainment was less than 0.15 gal per 1000 gal in both 6-in. and 48-in.-diam settler tests with solvent-continuous dispersions at flow rates up to flooding and at A/O ratios of 1/1 and 1/2. For a typical application of the Amex process to uranium milling plants, the cost of solvent lost by entrainment at this level is less than 1¢ per pound of U_3O_8 recovered.[6]

In general, solvent entrainment for aqueous-continuous dispersions increased with increasing flow rates and A/O ratios; there was some evidence, particularly in the 48-in.-diam settler, that entrainment was lowest with the thickest dispersion bands. Entrainment was about 3 gal per 1000 gal for both 6-in.- and 48-in.-diam settlers at the nominal flow capacity (0.7 gal ft^{-2} min^{-1}). This would add about 15¢ per pound to the cost of U_3O_8 product, justifying the investigation of methods for recovering solvent.

The entrainment of aqueous phase in the solvent phase is not an important economic factor but is of interest because it can cause contamination of the product. The highest entrainment of aqueous phase in solvent, obtained with solvent-continuous type dispersions at an A/O ratio of 1/2 in the 48-in.-diam settler was about 30 gal/1000 gal. For a typical installation where the feed/solvent ratio is 3.5 to 1.0, entrainment at this level would result in a ratio of each contaminant to uranium in the product of 1/120. For average mill liquors, this amount of contamination would be less than that specified in the present product specifications although sufficiently high to warrant consideration of a scrub stage or holdup tank to lower the entrainment.

Table 26. Summary of Entrainment Data from Extraction Circuit Tests in 6-in.-diam Settler

Phase Ratio A/O	Dispersed-Phase Flow (gpm/ft^2)	Entrainment (gal/1000 gal)					
		Solvent in Aqueous Phase			Aqueous in Solvent Phase		
		LA-1[a]	LA-1[a] Mod.	Di(tridecyl)	LA-1[a]	LA-1[a] Mod.	Di(tridecyl)
		Aqueous-Continuous Dispersion					
4/1	0.17	0.9			1.4		
	0.34	1.3	1.6		3.3	2.1	
	0.41			0.8			1.3
	0.68	2.1	2.0	1.6	6.7	1.6	0.6
	0.88	3.4			6.7		
	0.95		1.6			0.9	
	1.00	1.2		1.2			0.7
1/1	0.17	< 0.04			2.1		
	0.34	< 0.04	< 0.04		2.8	1.6	
	0.68	< 0.04	< 0.04	< 0.04	4.2	1.4	0.5
	1.08		< 0.04			1.9	
	1.22	< 0.04			3.5	—	
	1.35			< 0.04			0.5
		Solvent-Continuous Dispersion					
1/1	0.17	< 0.04			0.4		
	0.25	< 0.04			0.7		
	0.34		< 0.04	< 0.04		0.4	< 0.04
	0.41	< 0.04			4.9		
	0.51	< 0.04			3.9		
	0.63	< 0.04					
	0.68		< 0.04			4.2	
	0.81		< 0.04			1.0	
	1.08			< 0.04			0.01
1/2	0.17	< 0.04			2.1		
	0.25	< 0.04			5.0		
	0.34	< 0.04	< 0.04	< 0.04	14.0	0.9	1.1
	0.51	< 0.04			11.2		
	0.68		< 0.04			1.4	
	0.74		< 0.04			2.0	
	0.95			< 0.04			5.6

[a] Amberlite LA-1.

Table 27. Summary of Entrainment Data from Extraction Circuit Tests in 48-in.-diam Settler

Phase Ratio A/O	Dispersed Phase Flow Rate (gpm/ft^2)	Entrainment (gal/1000 gal) Solvent in Aqueous	Entrainment (gal/1000 gal) Aqueous in Solvent
		Aqueous-Continuous Dispersion	
4/1	0.29	2.2	9.8
	0.5	3.2	13.3
	0.94	3.2	15.0
	1.25		17.0
1/1	0.34	0.19	12.3
	0.50	0.16	14.0
	1.00	0.28	15.4
	1.40	< 0.04	15.4
		Solvent-Continuous Dispersion	
1/1	0.17	0.10	1.4
	0.33	0.13	5.3
	0.50	< 0.04	5.3
1/2	0.17	0.08	11.2
	0.33	0.13	22.4
	0.42	0.08	24.5
	0.50	< 0.04	28.0

7.2 Settler Tests—Sodium Chloride Stripping Circuit

Flow capacity of the settlers were measured for aqueous-continuous dispersions at phase ratios (A/O) of 2/1 and 1/1 and for solvent-continuous dispersion at A/O ratios of 1/1, 1/2, and 1/6. The phase ratio of 1/6 is typical for most flowsheets; the other conditions provide a broader base for design, showing the effect of aqueous recycle on flow capacity and entrainment. The data (Table 28) are correlated in Figs. 14—16. The nominal flow capacities determined from these plots are summarized in Table 29.

Effect of Solvent. Changing the composition of the solvent either by addition of a modifier (tridecyl alcohol) or by use of a different amine had no apparent effect on the nominal flow capacity of settlers with either aqueous-continuous dispersion at phase ratios of 2/1 and 1/1 or solvent-continuous dispersions at phase ratios (A/O) of 1/1 and 1/2. The nominal flow capacity with Di(tridecyl) amine was about 1.5 times greater than either Amberlite LA-1 or LA-1 modified for solvent-continuous dispersions at 1/6 phase ratio.

Table 28. Summary of Continuous-Flow Test Data—Sodium Chloride Stripping Circuit

Phase Ratio A/O	Flow Rates (gal min^{-1} ft^{-2}) Solvent	Flow Rates (gal min^{-1} ft^{-2}) Aqueous	Dispersion Band Width (in.) LA-1[a] Unmod.	Dispersion Band Width (in.) LA-1[a] Mod.	Dispersion Band Width (in.) Di(tridecyl) Amine
		Aqueous-Continuous Dispersions			
2/1	0.33	0.66	0.8	0.4	
	0.68	1.36			3.1
	0.87	1.74		5.3	
	0.93	1.86	9.5	8.0	
	1.34	2.68			16.9
1/1	0.33	0.33	0.9	0.6	0.63
	0.60	0.68			2.5
	0.80	0.80		4.8	
	1.03	1.03	10.8	11.0	
	1.35	1.35			13.3
		Solvent-Continuous Dispersions			
1/1	0.27	0.27	0.8	0.8	
	0.34	0.34			0.9
	0.68	0.68	5.8	4.9	4.5
	0.87	0.87	13.3	10.3	
	1.35	1.35			23.0
1/2	0.68	0.34			1.3
	2.02	1.01			13.5
1/6	0.80	0.13	0.3	0.5	0.1
	1.60	0.27		0.5	0.5
	2.42	0.41	1.0	1.5	0.6
	3.24	0.54			0.8
	3.50	0.59	0.8		
	4.00	0.66	1.0	1.0	1.0
	4.86	0.81			1.0
	5.70	0.95			1.0

[a] Amberlite LA-1

Effect of Dispersion Type and Phase Ratio. The nominal solvent-flow capacity remained unchanged at 0.8 gpm/ft^2 for aqueous-continuous dispersions at phase ratios of 2/1 and 1/1, and for solvent-continuous dispersion it was 0.7 at 1/1, 1.4 at 1/2, and 3 gpm/ft^2 at 1/6, using Di(tridecyl) amine. Because the solvent flow capacity is reduced by aqueous recycle, the main advantage of recycle is reduced entrainment.

Effect of Temperature. A series of tests were carried out at a 1/1 phase ratio to determine the effect of temperature on flow capacity. The data (Table 30) were correlated in the usual manner (Figs. 17 and 18) and the nominal flow for a 5-in. dispersion band read from the plots.

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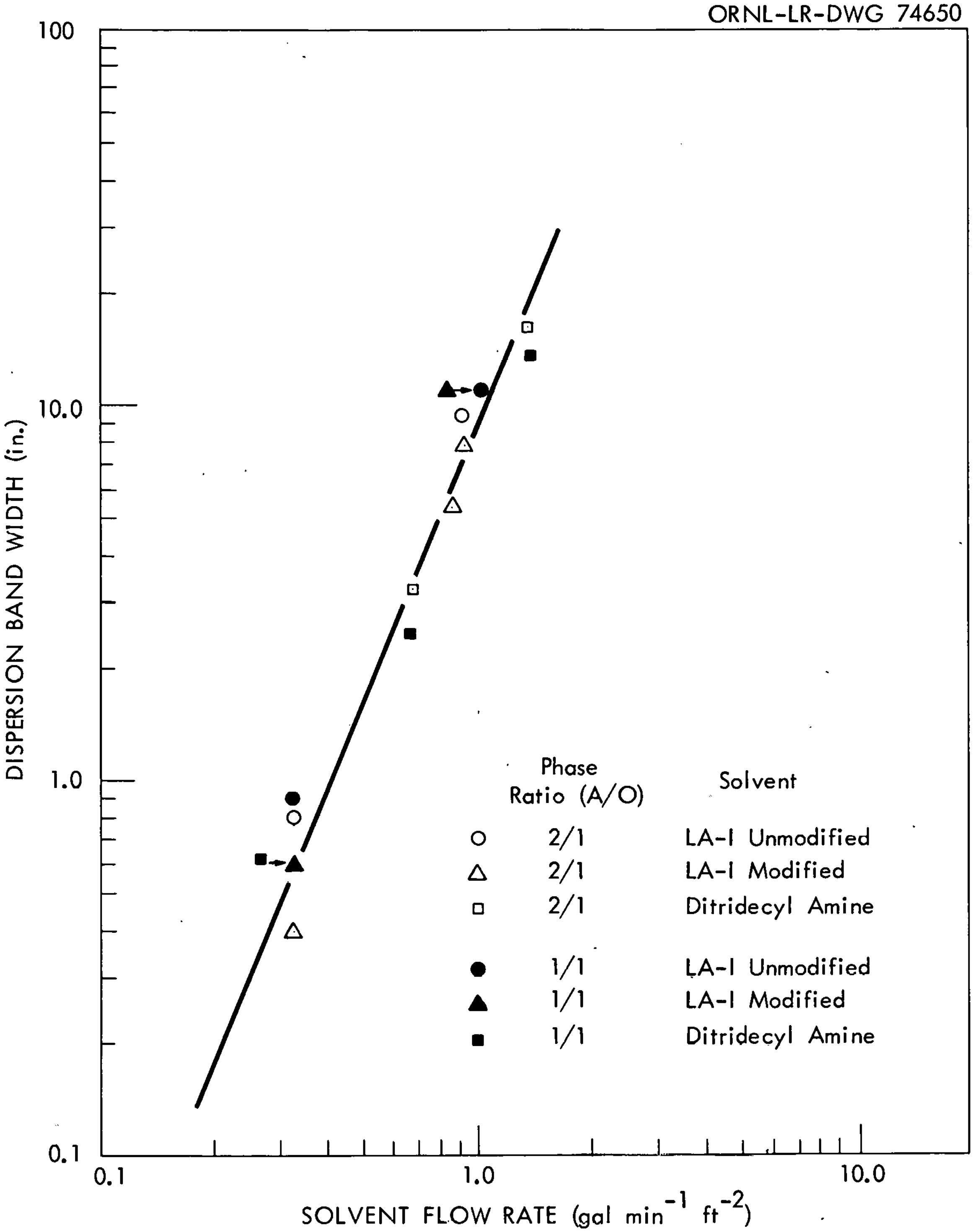

Fig. 14. Correlation of Data for Aqueous-Continuous Operation of Continuous-Flow Settlers—Sodium Chloride Stripping Circuit.

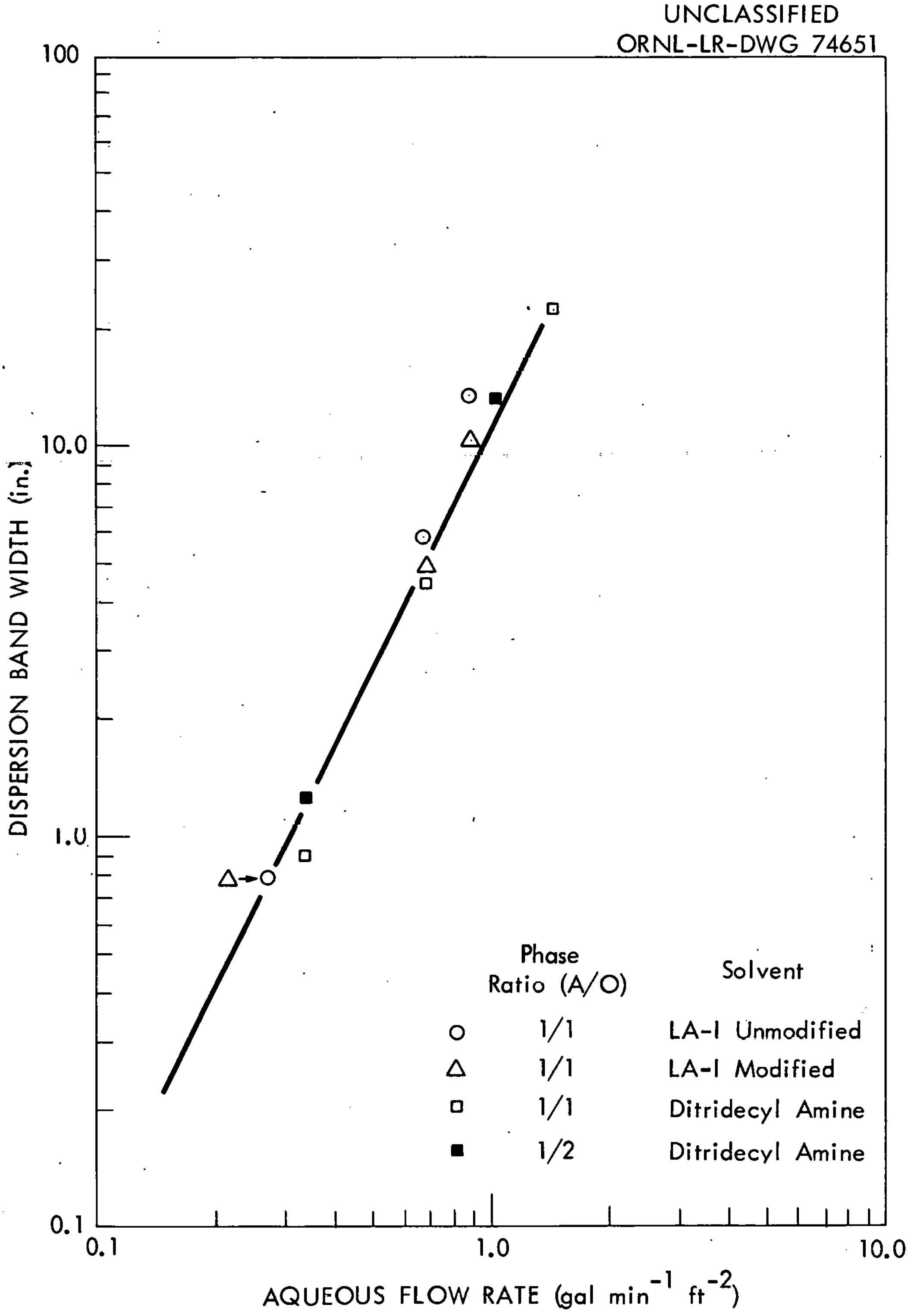

Fig. 15. Correlation of Data for Solvent-Continuous Operation of Continuous-Flow Settlers—Sodium Chloride Stripping Circuit.

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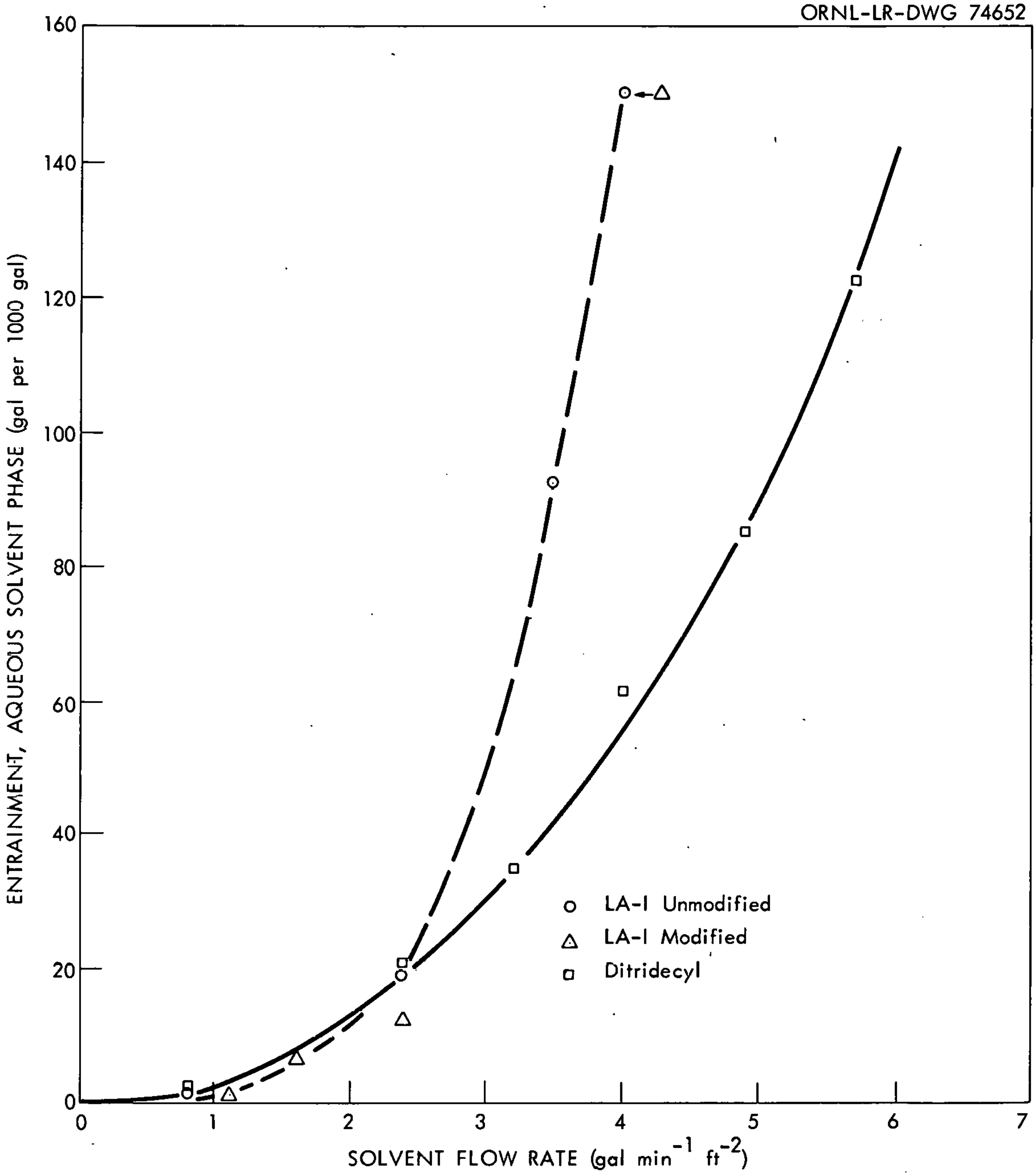

Fig. 16. Aqueous Entrainment at A/O Phase Ratio of 1/6—Sodium Chloride Stripping Circuit.

Table 29. Nominal Solvent Flow for Continuous-Flow Settler—Sodium Chloride Stripping Circuit

Continuous Phase	Phase Ratio A/O	Nominal Flow (gal min^{-1} ft^{-2})		
		LA-1	LA-1 Mod.	Di(tridecyl)
Aqueous	2/1	0.8	0.8	0.8
	1/1	0.8	0.8	0.8
Solvent	1/1	0.7	0.7	0.7
	1/2			1.4
	1/6	2.0	2.0	3.0

Increasing the temperature from 15 to 50°C approximately doubled the capacity of the settler for both aqueous- or solvent-continuous operation (Fig. 19).

Entrainment. The type of dispersion formed during mixing had a significant effect on the amount of solvent entrained in the aqueous phase after the primary phase separation (Table 31). The entrainment was consistently < 0.04 gal per 1000 gal for solvent-continuous mixing at flow rates up to flooding and at phase ratios from 1/1 to 1/6 (A/O). Entrainment was also low (< 0.04 gal per 1000 gal) for aqueous-continuous mixing at a 1/1 phase ratio but increased to 0.6 gal per 1000 gal at flooding for a 2/1 phase-ratio test with Di(tridecyl) amine. Assuming that the entrainment at the nominal flow would be approximately half that value, the cost of solvent lost in the aqueous would be about 1¢ per pound of U_3O_8 product.

Entrainment of the aqueous phase in the solvent depends more on the phase ratio and the flow rate. The higher the flow rate and the more dilute the dispersion (i.e., the smaller the ratio of dispersed phase to continuous phase), the higher the amount of dispersed phase entrained in the continuous phase. This is especially noticeable in the solvent-continuous 1/6 (A/O) phase-ratio test where the dispersion band is essentially unchanged by increasing the flow rate and flooding is specified as that flow rate where the entrainment value equals the phase ratio (about 140 gal per 1000 gal). Entrainment at the nominal flow capacity of the settler was about 10 gal per 1000 gal for Amberlite LA-1 and LA-1 modified solvent, and about 30 gal per 1000 gal for Di(tridecyl) solvent, which was low enough to avoid loss of stage efficiency due to back mixing of aqueous. Further, the loss of sodium chloride entrained in the solvent was not significant.

Entrainment can be reduced significantly by intrastage recycle of the aqueous phase so as to operate at a phase ratio of 1/1 or 1/2 (A/O) (Table 31). Higher operating temperature of the settler will also lower the entrainment. Increasing the temperature from 25 to 50°C while holding flow rate constant reduced the entrainment of aqueous in solvent $\sim 40\%$ at 1.6 gpm/ft^2 and 75% at 5.7 gpm/ft^2 (Table 32).

Table 30. Summary of Continuous-Flow Test Data, Showing the Effect of Temperature

Sodium Chloride Stripping Circuit—Di(tridecyl) Amine
Phase ratio = 1/1

Temperature (°C)	Solvent Flow Rate (gpm/ft^2)	Band Width (in.)	
		Aqueous Continuous	Organic Continuous
15	0.34	1.0	1.3
	0.68	4.0	
	0.95		18.1
	1.02	11.5	
25	0.34	0.6	0.9
	0.68	2.5	4.5
	1.35	13.3	23.0
35	0.34	0.6	0.3
	1.02	4.4	4.5
	1.48		12.5
	1.64	14.8	
50	0.34	0.4	
	0.68		0.6
	1.02	2.8	2.0
	1.35		4.8
	2.04	13.0	18.5

7.3 Settler Tests—Sodium Carbonate Stripping Circuit

Flow capacity of the 6-in.-diam settler was measured for solvent-continuous dispersions at A/O ratios of 1/1 and 1/6, the latter phase ratio being typical for most flowsheets. The data are summarized in Tables 33 and 34 and in Fig. 20.

Effect of Amine. Changing the composition of the solvent by using a different amine had a profound effect on the flow capacity of settlers operated with solvent-continuous dispersion. The nominal flow capacity of the 6-in.-diam settler at an A/O ratio of 1/1 and 1/6 using Alamine 336 was about twice that obtained with either modified or unmodified Amberlite LA-1 amine. This is probably due to the fact that the interfacial tension is about one order of magnitude higher for Alamine than for LA-1 (Table 16), and, the higher the interfacial tension value, the faster the dispersion breaks.

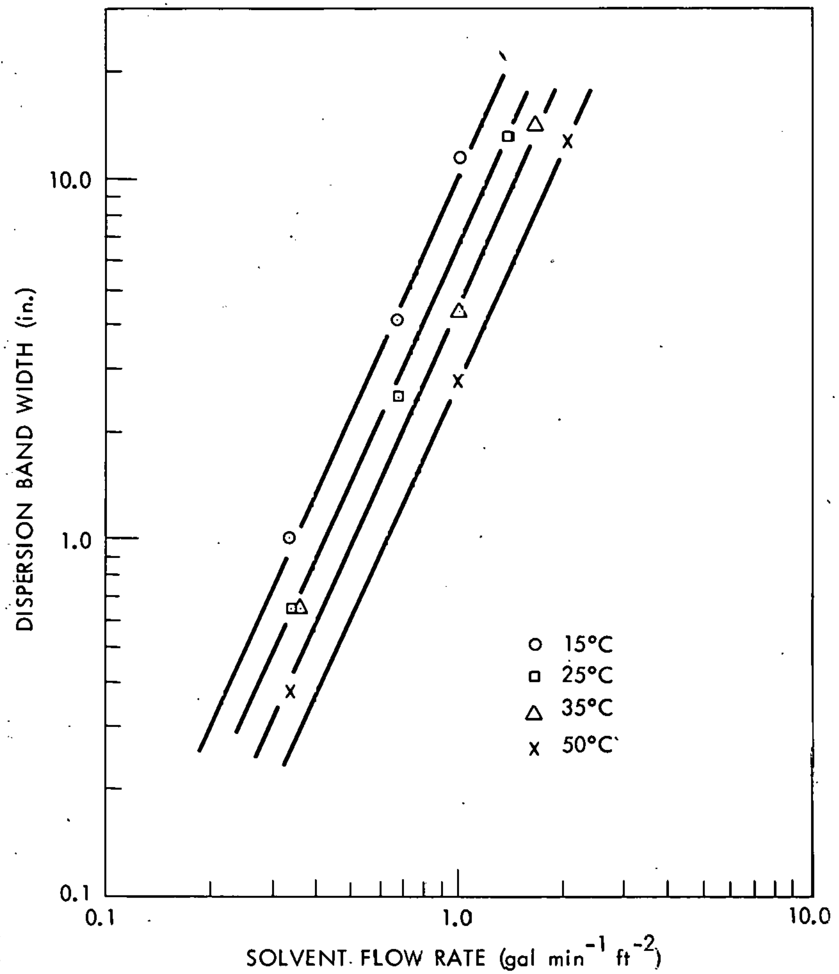

Fig. 17. Effect of Temperature on Band Width of Aqueous-Continuous Dispersion of Di(tridecyl) Amine vs Sodium Chloride Solution.

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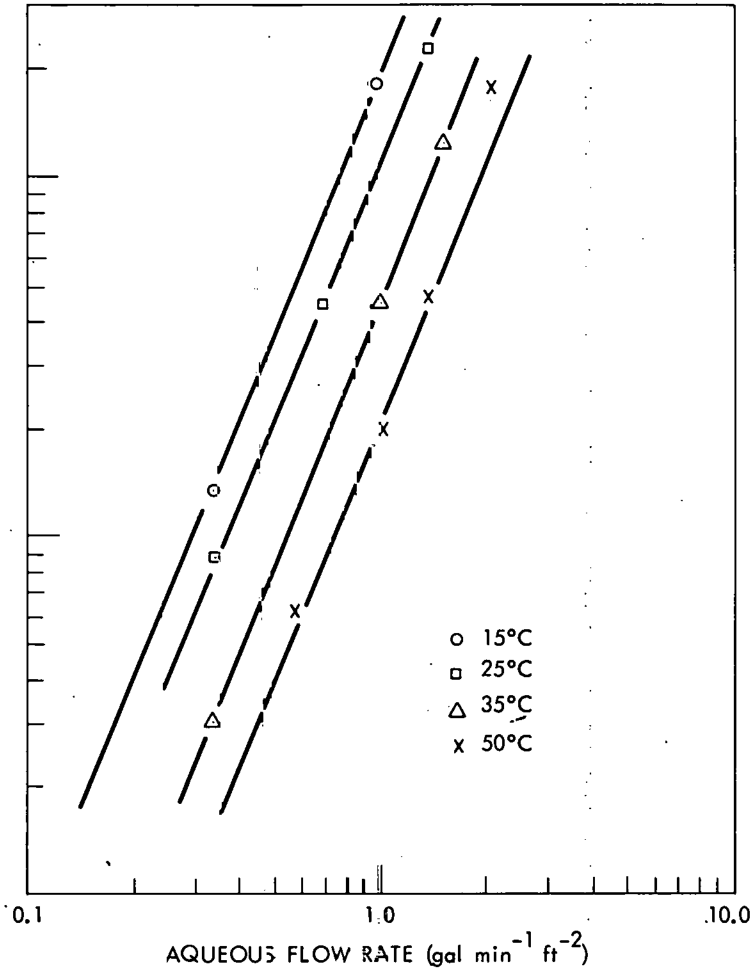

Fig. 18. Effect of Temperature on Band Width of Solvent-Continuous Dispersion of Di(tridecyl) Amine vs Sodium Chloride Solution.

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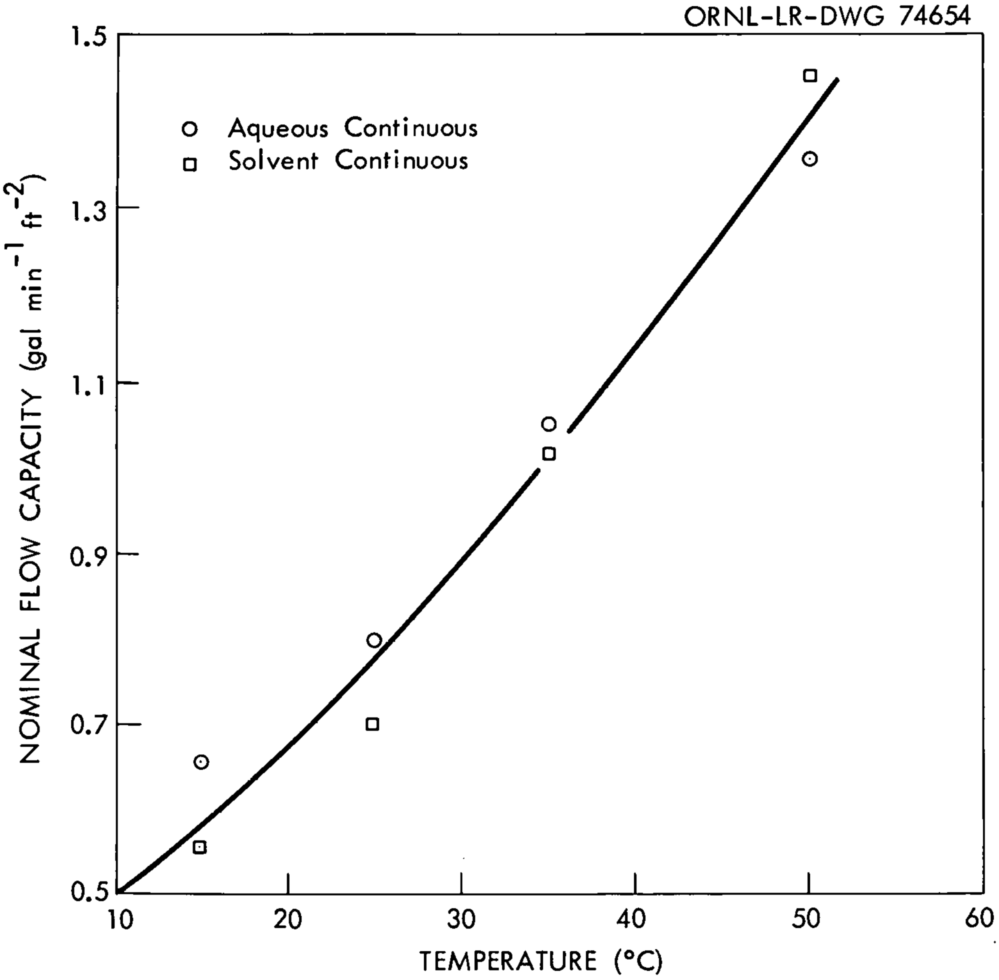

Fig. 19. Effect of Temperature on Nominal Flow Capacity of Continuous-Flow Settler—Sodium Chloride Stripping Circuit at Phase Ratio of 1/1 Di(tridecyl) Amine.

Effect of Phase Ratio. The nominal solvent flow capacity of settlers operated with solvent-continuous dispersion is approximately doubled as the A/O ratio is decreased from 1/1 to 1/6.

Effect of Temperature. Increasing the temperature from 25 to 45°C increased the nominal flow capacity of the settler operating with solvent-continuous dispersion at an A/O ratio of 1/6 from 1.7 to 2.2 gpm/ft^2.

Entrainment. In all tests, the amount of solvent lost in the aqueous phase at the nominal flow capacity of the settler was less than 0.3 gal per 1000 gal and would have an insignificant effect on the cost per pound of uranium product.

Table 31. Summary of Entrainment Data—Sodium Chloride Stripping Circuit

Phase Ratio A/O	Flow Rate (gal min^{-1} ft^{-2}) Org.	Flow Rate (gal min^{-1} ft^{-2}) Aq.	Entrainment (gal per 1000 gal) Solvent in Aqueous LA-1	Solvent in Aqueous LA-1 Mod.	Solvent in Aqueous Di-(tridecyl)	Aqueous in Solvent LA-1	Aqueous in Solvent LA-1 Mod.	Aqueous in Solvent Di-(tridecyl)
			Aqueous-Continuous Dispersion					
2/1	0.34	0.68	0.08	0.12		<0.07	<0.07	
	0.68	1.36			0.08			0.35
	0.87	1.74		0.16			<0.07	
	0.93	1.86	0.08	0.10		0.35	<0.07	
	1.34	2.68			0.60			11.2
1/1	0.34	0.34	<0.04	<0.04	<0.04	<0.07	<0.07	0.14
	0.68	0.68			<0.04			0.07
	0.80	0.80		<0.04			<0.07	
	1.03	1.03	<0.04	<0.04		<0.07	<0.07	
	1.35	1.35			<0.04			0.07
			Solvent-Continuous Dispersion					
1/1	0.27	0.27	<0.04	<0.04		<0.07	0.2	
	0.34	0.34			<0.04			0.07
	0.68	0.68	<0.04	<0.04	<0.04	0.14	1.1	<0.07
	0.87	0.87	<0.04	<0.04		0.07	1.1	
	1.35	1.35			<0.04			<0.07
1/2	0.68	0.34			<0.04			1.05
	2.02	1.01			<0.04			2.08
1/6	0.8	0.13	<0.04	<0.04	<0.04	1.2	1.3	1.9
	1.6	0.27		<0.04	<0.04		6.3	
	1.6[a]	0.27			<0.07			12.6
	2.4	0.41	<0.04	<0.04	<0.04	19.0	12.0	20.0
	3.2	0.54			<0.04			35.0
	3.5	0.59	<0.04			92.0		
	4.0	0.66	<0.04	<0.04	<0.04	150	150	61.0
	4.8	0.81			<0.04			85
	5.7	0.95			<0.04			122.0
	5.7[a]	0.95			<0.04			30.0

[a] 50°C.

Entrainment of aqueous phase in solvent phase depends on phase ratio, flow rate, and in some measure on the amine. In general, the higher the flow rate and the more dilute the dispersion (that is to say, the smaller the ratio of dispersed to continuous phase), the higher the entrainment level. Entrainment at the nominal flow of the settler at an A/O ratio of 1/6 was about 30 gal per 1000 gal for Amberlite LA-1 modified and unmodified solvents and less than 10 gal per 1000 gal for the Alamine 336

Table 32. Effect of Temperature on Entrainment of Aqueous in Solvent at 1/6 A/O Phase Ratio—Sodium Chloride Stripping Circuit

Solvent Flow Rate (gal min^{-1} ft^{-2})	Temp. (°C)	Entrainment, Aqueous in Solvent (gal per 1000 gal)
1.6	25	20.0
	50	12.6
5.7	25	122.0
	50	30.0

solvent. These levels are not sufficiently high to lower the efficiency by backmixing, and the loss of sodium carbonate would not be excessive. Recycling the aqueous to operate at a 1/1 phase ratio reduced the amount of entrainment but also reduced the settler capacity. Increasing the temperature increased the flow capacity of the settler but also increased the amount of aqueous phase in the solvent phase about 25%.

7.4 Packed Settler

One method of increasing the flow capacity of a gravity settler is to fill it with packing that is wetted by the dispersed phase, thereby increasing the area available for coalescence. The flow capacity of a 6-in.-diam x 48-in.-high settler was increased approximately fourfold when packed with 1/2-in. ceramic Berl saddles for organic-continuous dispersions but was virtually unchanged for aqueous-continuous (Table 35). The depth of dispersion increased exponentially with flow rate, with a lower slope in the packed settler than in the unpacked (Fig. 21).

The additional aqueous flow capacity due to the packing was calculated by subtracting the flow capacity of the settler without packing from the total at the same dispersion-band thickness. The net increase in aqueous flow varied from 0.006 to 0.014 gal min^{-1} ft^{-2} of surface area of packing in the dispersion band over the whole range of flow rate (0.1 to 1.0 gpm) and dispersion-band thickness (2 to 37 in.).

7.5 Emulsion Formation by Silica in Continuous Countercurrent Tests

Batch phase-separation tests with silica liquors showed that organic-continuous mixing, addition of ore slimes, or addition of decolorizing carbon significantly reduced the break time and the amount of stable emulsion. Each method was evaluated by continuous countercurrent tests in bench-scale mixer-settler equipment similar to that used in the long-term runs (Sec 4). (The uranium was extracted with 0.1 $\underline{M}$ Amberlite LA-1 in kerosene and stripped with 1 $\underline{M}$ NaCl, using three stages in each circuit.) The feed liquor contained 4 g of SiO_2 per liter, in addition to the usual ionic constituents. Aqueous-continuous mixing of this feed with the solvent resulted in complete emulsification, with very little separation in 24 hr.

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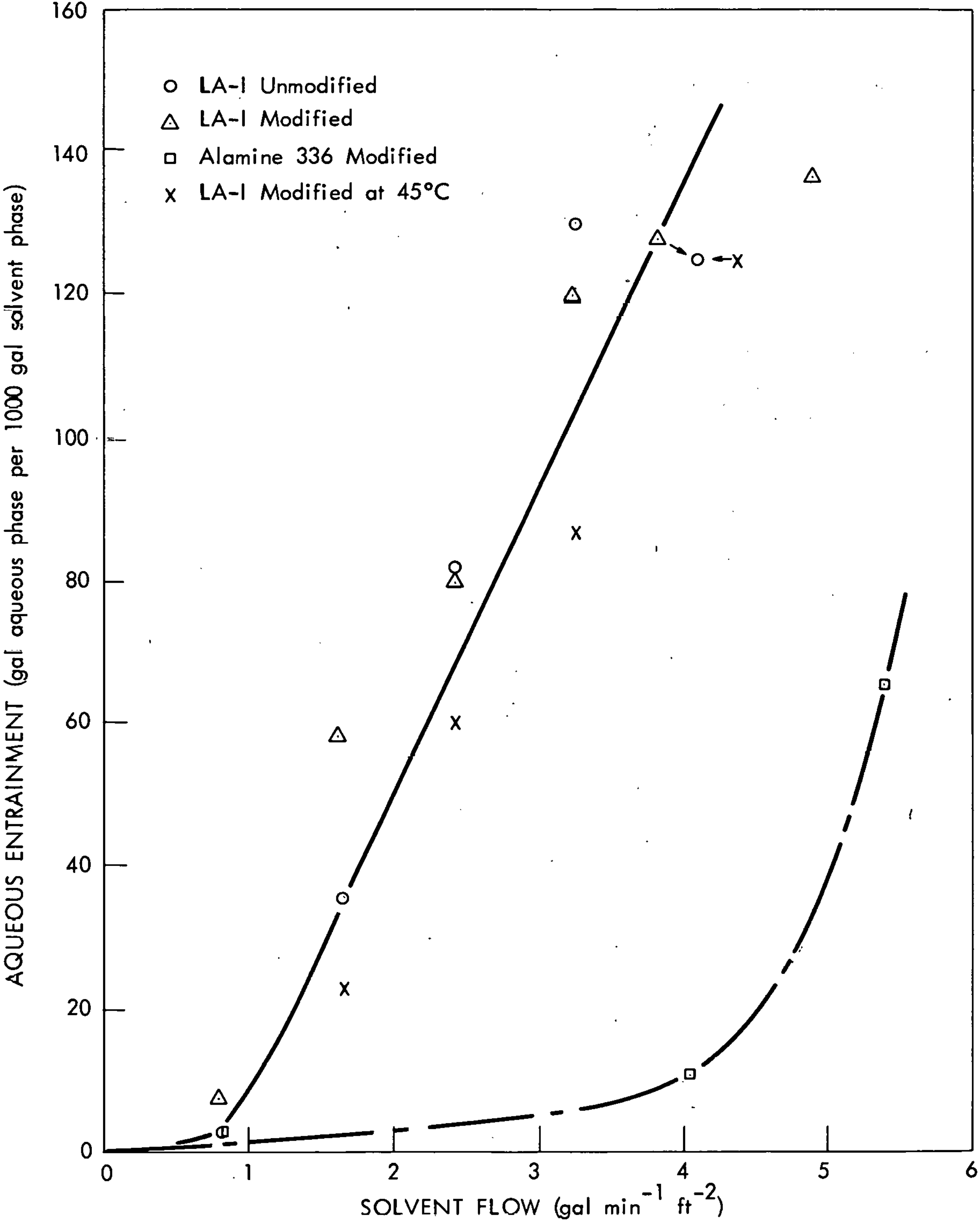

Fig. 20. Aqueous Entrainment at A/O Phase Ratio of 1/6—Sodium Carbonate Stripping Circuit.

Table 33. Summary of Continuous-Flow Settler Test Data—Sodium Carbonate Stripping Circuit

Phase Ratio A/O	Flow Rate (gal min^{-1} ft^{-2})		Band Width (in.)			Entrainment (gal per 1000 gal) Solvent in Aqueous			Entrainment (gal per 1000 gal) Aqueous in Solvent		
	Solvent	Aqueous	LA-1	LA-1 Mod.	Alamine 336	LA-1	LA-1 Mod.	Alamine 336	LA-1	LA-1 Mod.	Alamine 336
1/1[a]	0.68	0.68		15.8			< 0.04			< 0.07	
	1.35	1.35			3.0			< 0.04			3.2
	1.62	1.62			17.0			< 0.04			2.8
1/6[a]	0.81	0.14	0.1	0.3	0.1	0.20	0.06	0.12	3.8	8.0	3.7
	1.62	0.27	1.0	0.8		< 0.04	0.06		36.0	58.0	
	2.43	0.41	0.6	0.9		0.20			82.0	80.0	
	3.24	0.54	0.8	0.8					130.0	120.0	
	4.05	0.68	0.8	0.9	4.6	0.12	0.08	0.04	125.0	126.0	11.0
	4.86	0.82		0.9			0.10			137.0	
	5.40	0.92			3.5			0.20			72.0
1/6[b]	1.62	0.27		1.1			0.06			23.5	
	2.43	0.41		0.6			0.40			60.0	
	3.24	0.54		2.0			0.30			87.0	
	4.05	0.68		1.0			0.16			125.	

[a] Temperature = 25°C.

[b] Temperature = 45°C.

Table 34. Nominal Flow Rates for Continuous-Flow Settler—Sodium Carbonate Stripping

Phase Ratio A/O	Temp. (°C)	Solvent Flow Rate (gal min^{-1} ft^{-2})		
		LA-1	LA-1 Mod.	Alamine 336
1/1	25		0.6	1.5
1/6	25	1.7	1.7	3.0
1/6	45		2.2	

Table 35. Flow Capacity of 6-in.-diam Settler Packed with Berl Saddles

Organic Phase: 0.1 M Amberlite LA-1 in kerosene
Aqueous Phase: Sodium sulfate solution: 70 g SO_4/liter, pH 1.0

Phase Ratio A/O	Aqueous Flow Rate (gpm)	Dispersion-Band Thickness (in.)	Surface Area[a] of Saddles in Band (ft^2)	Additional Aqueous[b] Flow Rate due to Packing (gal min^{-1} ft^{-2} of packing)
			Organic-Continuous	
1/2	0.10	2	5	0.007
	0.25	8	20	0.009
	0.50	24	59	0.006
1/1	0.25	5	12	0.014
	0.50	12	29	0.013
	0.75	27	66	0.009
	1.00	37	92	0.009
			Aqueous-Continuous	
1/1	0.25	12	29	< 0.001
	0.50	28	69	0.002
4/1	0.50	4	10	< 0.001
	1.0	14	34	0.003
	1.5	27	66	0.005

[a] Surface area of 1/2-in. Berl saddles estimated to be 150 ft^2/ft^3.

[b] See Figs. 12 and 13 for flow rate in unpacked settler.

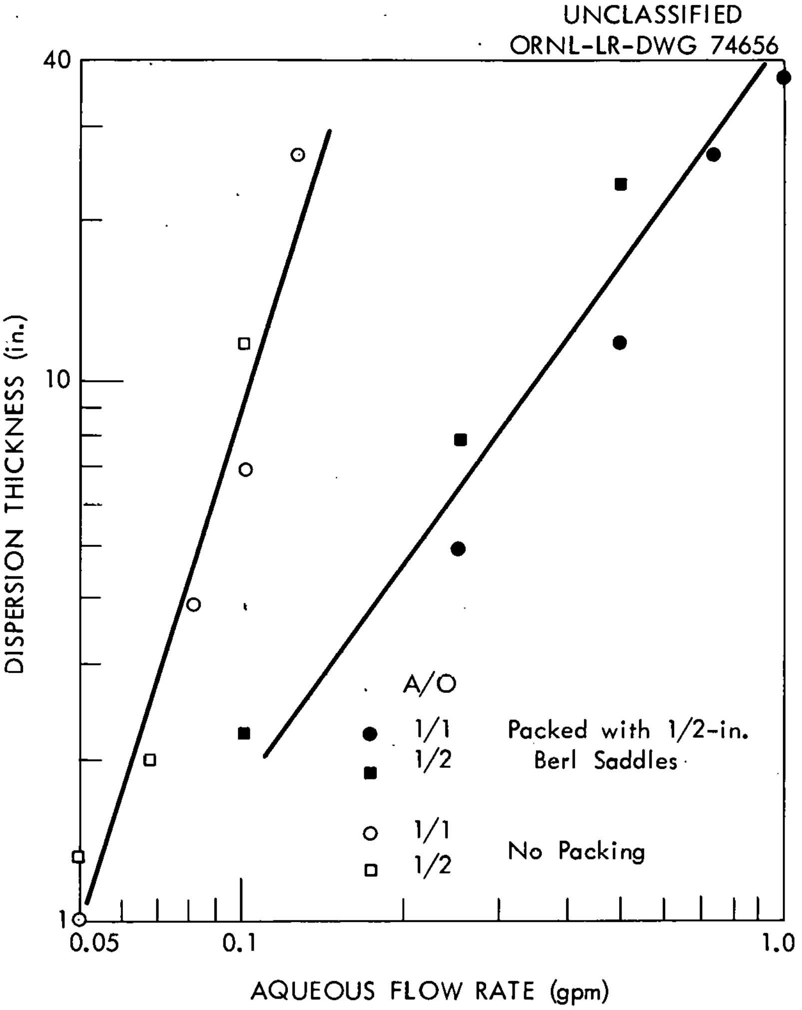

Fig. 21. Effect of Berl-Saddle Packing on Flow Capacity of 6-in.-diam Settler, with Organic-Continuous Dispersions.

Organic-continuous countercurrent tests showed that some emulsion accumulated at the interface in the settlers. After about 15 hr of operation, during which about 50 gal of silica feed liquor was processed, the accumulated emulsion was collected, measured, and centrifuged to obtain the volume percentage of trapped organic liquid. The results are shown in Table 36.

Organic-continuous mixing resulted in an accumulation of emulsion equivalent to 1.4 vol % of the feed when organic was recycled to give an A/O ratio of 1/3 in the mixer, compared with 4.7% without recycle (A/O of 3/1). The emulsion, which was aqueous continuous, although predominantly organic (70%), probably was formed because of localized aqueous-continuous mixing, particularly at the feed inlets to the mixers. Mixing at a low A/O ratio, which was attained by organic recycle, reduced the probability of local inversion to aqueous continuous, thereby decreasing the volume of emulsion formed.

Table 36. Emulsion Formation in Continuous-Flow Tests with Silica-Containing Liquor

Aqueous Feed: Synthetic leach liquor containing 4 g SiO_2 per liter
Organic: 0.1 M Amberlite LA-1 in kerosene

Additive	Mixing Conditions: Continuous Phase	Mixing Conditions: A/O	Emulsion[c] Formed (vol % of feed)	Organic in Emulsion (vol %)	Relative[d] Flow Capacity (%)
None	Org	1/3	1.4	72	25
None	Org	3/1	4.7	71	50
Carbon[a]	Org	3/1	0	0	50
Slime[b]	Org	1/3	0.8	27	75
Slime[b]	Aq	3/1	1.3	18	100

[a] Decolorizing carbon (-200 mesh) concentration was 10 g per liter of solvent.

[b] Ore slime (-200 mesh) concentration was 0.5 g/liter.

[c] Emulsion accumulation in settlers after an average of 15 hr operation.

[d] Based on flow capacity for nonsilica-bearing liquor with organic phase dispersed.

Addition of decolorizing carbon (10 g per liter of solvent) resulted in no emulsion formation even without organic recycle. The test was continued for about 20 cycles of the solvent, without any measurable loss of carbon from the solvent or any apparent loss of its effectiveness in preventing emulsification. However, a serious fault with carbon addition was discovered in subsequent testing with sodium carbonate regeneration of the solvent. The carbon stabilized an organic-continuous dispersion that separately slowly and frequently resulted in coagulation of the carbon, which settled out at the interface. Attempts to avoid the difficulty were not successful; consequently, regeneration, which at least in part is usually required, could not be done directly on solvent that contained carbon. Another minor problem with carbon is that it does settle out of the solvent on standing, which would complicate solvent storage and start-up procedure after several hours of shutdown.

Addition of ore slime (0.5 g per liter of feed) had virtually no effect on the quantity of emulsion formed with organic-continuous mixing. But, it did permit operation with aqueous-continuous mixing, resulting in an accumulation of emulsion equivalent to 1.3% of the feed, as compared, to complete emulsification without the presence of slimes. Virtually all of the slimes accumulated at the interface and eventually flowed out with the raffinate.

7.6 Secondary Settler for Recovery of Entrained Solvent

For aqueous-continuous mixing, the amount of solvent entrained in the aqueous phase after primary phase separation ranged up to 6 gal of solvent per 1000 gal of aqueous, which is not important as far as back-mixing is concerned but which would result in a significant loss of solvent in the raffinate. A secondary settler of the type used by the petroleum industry to remove oil from waste water decreased solvent entrainment to less than 0.2 gal per 1000 gal at an aqueous residence time of 2 hr (Table 37); the use of packing increased the settler efficiency so that less than 15 min of residence time was required. Organic-wetted packing (polyethylene Tellerettes) and aqueous wetted (ceramic Berl saddles) were equally effective, based on specific surface area; furthermore, entrainment was linearly dependent on flow rate per square feet of packing surface (Fig. 22). The use of Fiberglas cloth as a coalescing medium was more effective than packing in reducing entrainment but would be more limited in application because of possible blinding of the cloth by solids in the raffinate.

Table 37. Recovery of Entrained Solvent in Aqueous by Use of a Secondary Settler

Aqueous Phase: Sodium sulfate solution: 70 g SO_4/liter, pH 1.0
Solvent: 0.1 M Amberlite LA-1 in kerosene, no modifier

Aq. Flow Rate		Res.	Solvent Entrainment, gal/1000 gal of Aq.					
	Linear	Time	Entering	No	Tellerettes[a]	Berl Saddles[b]		Filter[c]
(gpm)	ft/min	(min)	Stream	Packing	2 ft^3	2 ft^3	4 ft^3	Cloth
0.16	0.03	180	0.25	< 0.04				
0.27	0.05	110	0.40	0.16				
0.50	0.09	60	0.50	0.27	0.10			
1.0	0.18	30	1.0	0.40	0.15	0.09	0.04	
2.0	0.36	15	1.5	0.60	0.31	0.15	0.07	0.04
4.0	0.72	7.5	6.0	1.5	0.48	0.36	0.22	0.13

[a] Polyethylene tower packing (surface area, 75 ft^2/ft^3), Harshaw Chemical Co.

[b] 1/2 in. ceramic Berl saddles (surface area, 150 ft^2/ft^3).

[c] Four sheets of Fiberglas cloth (Code N41A40, Owens-Corning Fiberglas Co.) mounted in vertical plane across the settler.

The aqueous feed to the secondary settler was obtained by operating a single mixer-settler unit at an A/O ratio of 4/1, with the aqueous phase continuous in the mixer. The secondary settler was a rectangular box (Fig. 23) with a settling section 4 x 1 x 1.5 ft high (liquid depth was 1 ft). The aqueous entered through a flow distributor to reduce turbulence in the settling section.

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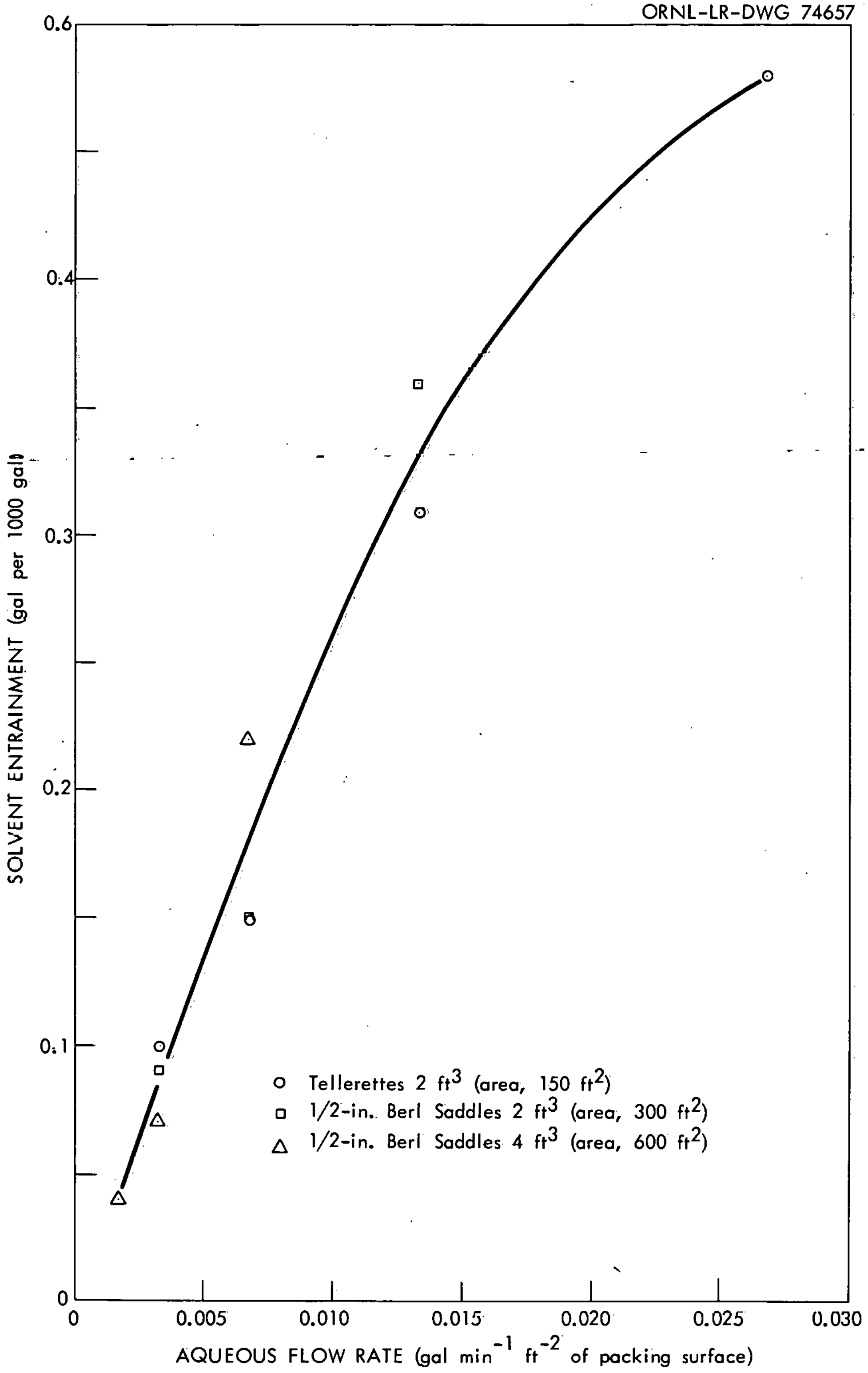

Fig. 22. Effect of Surface Area of Packing on Solvent Entrainment from Secondary Settler.

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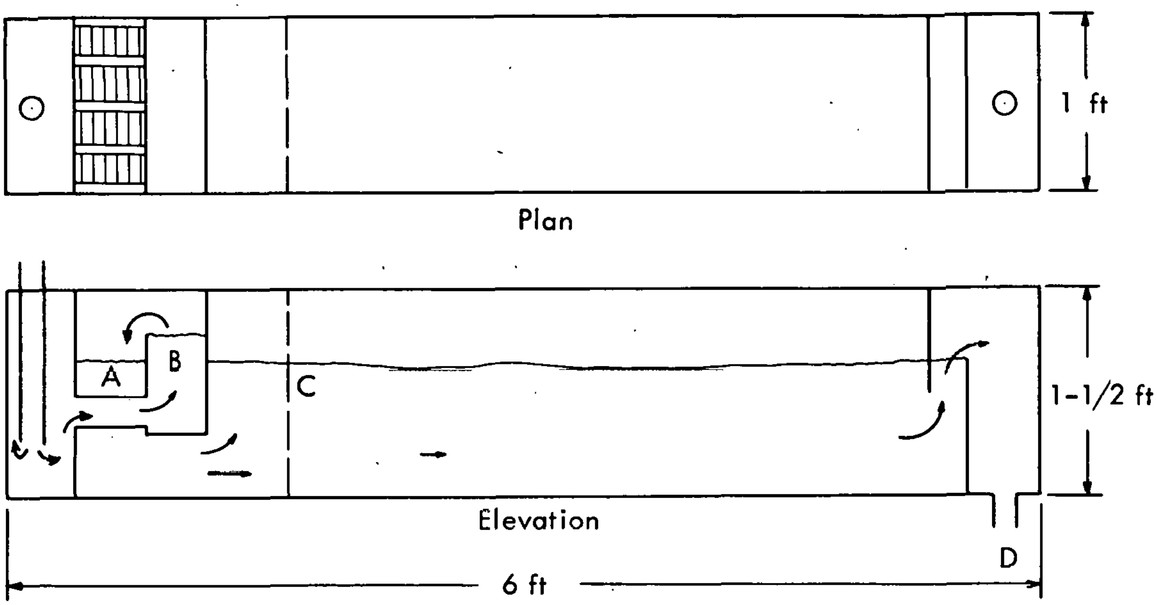

Fig. 23. American Petroleum Institute Type Secondary Settler. (A) Film Rupture Chamber; (B) Distribution Box and Adjustable Weir; (C) Filter Frame; (D) Sample Point.

APPENDIX A

Table A-1. Identification of Amines

Amine	Type	Equivalent Weight	Source
Amberlite LA-1	Secondary	350	Rohm and Haas Co., Philadelphia
Amberlite LA-2	Secondary	365	Rohm and Haas Co., Philadelphia
Di(tridecyl)	Secondary	380	Union Carbide Chemicals Co., New York
S-24	Secondary	350	Union Carbide Chemicals Co., New York
Triisooctyl	Tertiary	350	Union Carbide Chemicals Co., New York
Alamine 336	Tertiary	410	General Mills, Inc. Kankakee, Ill.
Trilauryl	Tertiary	520	Archer-Daniels-Midland Co., Minneapolis

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