UCRL-10625

University of California

Ernest O. Lawrence Radiation Laboratory

MECHANISM OF LIQUID-LIQUID SETTLING

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Research and Development

UCRL-10625
UC-4 Chemistry
TID 4500 (18th Ed.)

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

MECHANISM OF LIQUID-LIQUID SETTLING

Albert D. Epstein and C. R. Wilke

January 14, 1963

Printed in USA. Price $1.00. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D.C.

MECHANISM OF LIQUID-LIQUID SETTLING

Contents

Abstract v
I. Introduction 1
II. Factors that Govern Liquid-Liquid Separation by Gravity Settling
A. Stable vs Unstable Emulsions 2
B. Sedimentation 3
C. Coalescence 4
D. Particle-Size Distribution 4
E. Settler Flow Pattern and Velocity Profile 5
III. Equipment
A. Aroclor System 6
B. Water System 6
C. Mixing Section 6
D. Settling Section 11
E. Outlets 12
IV. Experimental Procedure 13
V. Experimental Data 14
VI. Observations 19
VII. Discussion of Data and Observations
A. Emulsion Layer 27
B. Concentration Profiles 29
C. Residence Times 34
VIII. Summary and Conclusions 38
Acknowledgments 41
Appendices
A. Calculation Procedure 42
B. Physical Properties of Aroclor 1248 43
C. Determination of Water in Aroclor 44
D. Nomenclature 45
References 46

MECHANISM OF LIQUID-LIQUID SETTLING

Albert D. Epstein and C. R. Wilke

Lawrence Radiation Laboratory
University of California
Berkeley, California

January 14, 1963

ABSTRACT

The separation of two immiscible liquids in a gravity settler was studied in a program to learn more about the mechanism of the settling process. The liquids used were water and Aroclor 1248 (sp gr 1.36). A mixture of the two liquids was fed into one end of a long horizontal tank in which the two phases were separated by gravity and were drawn off at the top and bottom of the opposite end. The liquids were introduced through a pipe narrow enough to assure a high degree of turbulent mixing. The effectiveness of the settling process was determined by measuring the concentration of water in the Aroclor phase resulting from (a) water dispersed during the initial mixing of the two phases and (b) water showered down into the Aroclor during the coalescence of the droplets into their respective phases from an emulsion layer at the settler interface. This emulsion layer moved toward the settler outlet at two to three times the velocity of the Aroclor phase. For the system investigated, the depth and length of the emulsion layer were found to depend upon the Reynolds number in the mixing section.

The settler flow patterns were also drawn for the cases in which the emulsion layer ended in the settler and those in which it extended the entire length of the section.

I. INTRODUCTION

The separation of two immiscible liquids may be accomplished continuously in a horizontal liquid-liquid gravity settler by making use of the density difference between the two phases. A dispersion of the two liquids is introduced into one end of a long horizontal chamber with a circular or rectangular cross section large enough to reduce turbulence to a minimum. After separation the lighter liquid is withdrawn at the top, and the heavier liquid is withdrawn from the bottom at the downstream end of the settler.

Gravity settlers are employed extensively in the oil and chemical industry, both in batch and in continuous operations. In many liquid-liquid solvent-extraction operations, settlers are used to separate the extract liquid from the raffinate liquid after the two have been contacted in a mixing tank. Refineries use settlers in many operations: for dewatering of crude oils, desalting of crude oils, caustic washing of light distillates, sulfuric-acid treatment, and solvent extraction.

Although many patents and articles have been devoted to settling, little progress has been made in devising a reliable design method that can be applied to their construction. The purpose of this paper is to provide some insight into the fundamental settling mechanism, and investigate some of the basic factors that control the extent of settling taking place under a given set of conditions. It is hoped that this analysis will provide some of the groundwork that will eventually lead to some practical rules for industrial design and scale-up of gravity settlers.

This investigation was a study of the separation of Aroclor and water by gravity settling.

II. FACTORS THAT GOVERN LIQUID-LIQUID SEPARATION BY GRAVITY SETTLING

A. Stable vs Unstable Emulsions

To accomplish a practical separation by means of a continuous gravity settler, the initial liquid-liquid dispersion must have the properties of an unstable emulsion. This emulsion is defined as one in which the rate of coalescence of the dispersed droplets is rapid and the emulsion more or less quickly breaks into two separate phases.

The breaking of an unstable emulsion described by Meissner and Chertow[1] closely resembles the separation of two immiscible liquids in a gravity settler. Two distinct stages are usually visible during this separation, and these are called the primary and secondary breaks. During the primary break three regions are briefly visible: a clear top layer of the lighter phase, a clear bottom layer of the denser phase, and a middle region composed of the dispersion itself. The primary break is considered complete when the middle region disappears and leaves a clearly defined interface, but a cloudy dispersion may be present in either the upper or lower phase. During the secondary break, the remaining small droplets move toward the interface and eventual clarification of both phases results. In most cases this second stage will take many times as long as the first and it therefore may be days before complete separation is obtained. Consequently, although the dispersion left after the primary break is strictly termed unstable, it must be considered "stable" in practical continuous liquid-liquid separation by gravity settling.

The stability of an emulsion depends on several factors:[2] (a) size of the dispersed globules, (b) density difference between the two phases, (c) viscosity of the continuous phase, and (d) stability of the liquid-liquid interface. These factors combine to determine the rates of sedimentation and coalescence which in turn control the overall rate of settling.

B. Sedimentation

In an unstable emulsion, dispersed droplets rise or fall through the continuous medium. Basically, the rate of this motion can be described by Stokes' Law or by one of its proposed modifications.[3, 4, 5] Bond and Newton's modification[3] illustrates the parameters that determine the settling velocity:

$$U_\infty = \left(\frac{2\Delta\rho g r^2}{g\,\mu_c}\right) f\left(\frac{\mu_d}{\mu_c}\ ,\ \frac{r\sigma_I}{w}\right),$$

where

U_∞ = terminal settling velocity of dispersed droplets (cm/sec),

μ_c = viscosity of continuous liquid phase,

μ_d = viscosity of dispersed liquid phase,

r = dispersed droplet radius (cm),

$\Delta\rho$ = density difference between dispersed and continuous phases,

g = acceleration due to gravity,

w = apparent weight of drop,

and

σ_I = interfacial tension.

For small values of $(r\,\sigma_I)/w$, i.e. large droplets,

$$f\left(\frac{\mu_d}{\mu_c}\ ,\ \frac{r\sigma_I}{w}\right) \rightarrow \left(\frac{(1 + \mu_d/\mu_c)}{(2/3 + \mu_d/\mu_c)}\right).$$

For large values of $(r\,\sigma_I)/w$, i.e. small droplets,

$$f\left(\frac{\mu_d}{\mu_c}\ ,\ \frac{r\,\sigma_I}{w}\right) \rightarrow 1.$$

From this equation we can conclude that high viscosity of the continuous phase, small density difference between the two phases, and small droplet size all hinder separation. An unfavorable combination of the above factors will produce a stable emulsion that cannot be separated by gravity settling methods.

C. Coalescence

The coalescence of the dispersed phase is a very important factor in liquid-liquid separation by the use of gravity settling. It is significant to the overall mechanism in two respects: (a) the coalescence of dispersed droplets with each other within the continuous phase, and (b) the eventual coalescence into the bulk phase at the liquid-liquid interface. The first of these factors affects the settling velocity of the droplets. It is evident from Bond and Newton's equation that larger droplets increase the settling rate.

The coalescence into the bulk phase at the liquid-liquid interface presents an entirely different problem. Many experimenters have observed that oil and water drops have a finite lifetime at an oil-water interface before they coalesce into the bulk phase.[6-9] Recently Lang found that this lifetime depended on the film that surrounds each droplet.[9] He showed that coalescence takes place only after the film is thinned sufficiently to be ruptured by random disturbances. This coalescing process may take as long as fifteen minutes, and prevents complete separation during this time. The droplet interface lifetime explains the stability of the emulsion layer observed by several experimenters during the settling process.[10, 11]

Graham[11] summarizes Lang's experiments with an Aroclor-water system.

D. Particle-Size Distribution

The size distribution of the dispersed particles entering the settling chamber is determined by two factors: (a) the conditions under which the two liquids are mixed and (b) the velocity at which the entering stream is injected. These two factors may be equally important or one may be controlling for a particular system.

The passage of two immiscible liquids through a pipe in violent turbulent motion results in the formation of a stable emulsion--particularly when the concentration of the dispersed phase is small so that the chance of coalescence is slight. Clay found that the particle-size distribution of this emulsion was a function of the Reynolds number.[12]

Increasing the Reynolds number intensifies the viscous shearing action and decreases the particle size -- thus stabilizing the emulsion.

Richardson observed the formation of an emulsion by the injection of one liquid into another at high velocities.[13] According to his experiments, increasing the velocity at the settler inlet decreases the particle size and, therefore, reduces the rate of separation.

E. Settler Flow Pattern and Velocity Distribution

In general, the flow of both phases through the settler must be free of turbulent eddies strong enough to overcome the movement of the dispersed droplets toward the interface.

The theoretical analysis of the stratified laminar flow of two immiscible liquids has been mentioned only briefly in the literature. Russell and Charles[14] present a mathematical analysis for a system consisting of two immiscible liquids flowing between parallel plates based on the equation of continuity and the Navier-Stokes equations of motion. Bird et al. derive similar equations for the special case in which the holdup of each phase was one-half of the total holdup,[15] and Forstrom presents equations without this restriction.[16]

These analyses are all based on the assumption of an infinitely long horizontal section in which flow can develop fully. This is not the case in practical settling equipment because of the low length-to-diameter ratio and the effects produced by the end conditions of injection at the center and by withdrawal at the top and bottom. The vertical movements of the dispersed droplets also distort the flow pattern and velocity profile.

It is of particular interest, in a study of settling, to predict the velocity at the liquid-liquid interface from a knowledge of the average velocity in each phase. For the case in which one fluid has an average velocity many times the other, as in this work, it is helpful to approximate the interface velocity by assuming that the entire settler is occupied by the fast fluid, and that Poiseuille's Law applies to this fluid. This approximation, though very rough, is of assistance in analyzing the velocity behavior observed in the settler.

III. EQUIPMENT

The equipment used in this experiment is represented in Figs. 1 through 4. The five main sections consisted of the Aroclor system, the water system, the mixing section, the settling section, and the outlet system.

A. Aroclor System

The Aroclor was stored in a 55-gal Bisonited drum equipped with a sight glass and two thermometers. A 1/4-hp mixer was used to agitate it, and three 3750-W immersion heaters were used to heat it.

A 3/4-in. copper line connected the Aroclor tank with a 5-gpm gear pump. A needle valve on a bypass line was used to control the Aroclor flow rate.

Rust and dirt particles were removed from the liquid by a 25-micron Cuno filter downstream from the pump. Final adjustment of the flow rate was accomplished with a needle valve located upstream from a rotameter.

B. Water System

The water was stored in another 55-gal Bisonited tank equipped with a sight glass, a thermometer, and a 1/8-hp mixer.

The water was pumped by a 5-gpm centrifugal pump through 3/8-in. copper tubing. The water flow rate was maintained by a needle valve located in front of the water rotameter. A 10-micron Cuno filter was located upstream from the rotameter for removing dirt and rust particles.

C. Mixing Section

The Aroclor and water streams met at a 1-in. brass tee attached to the mixing pipe, which consisted of four 1/4-in. -i. d. $\times$ 12-in. -long copper tubes encased in a 1$\times$6-in. -long brass nipple. The liquid passed through the 1/4-in. tubes directly into the settler. Metal plugs were used to block off the tubes, as required, to give the desired Reynolds number for a given flow rate.

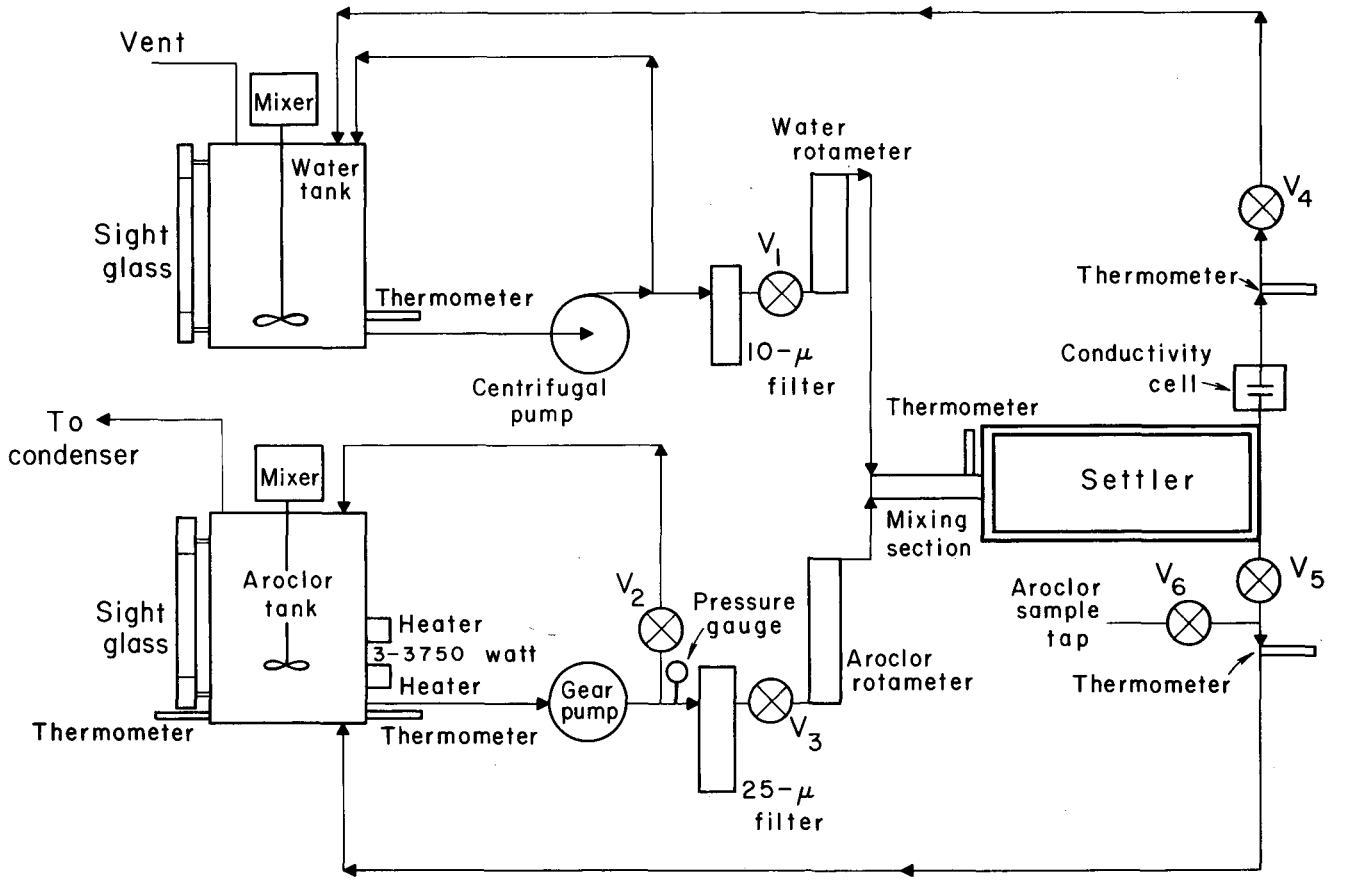


Fig. 1. Schematic diagram of settler apparatus.

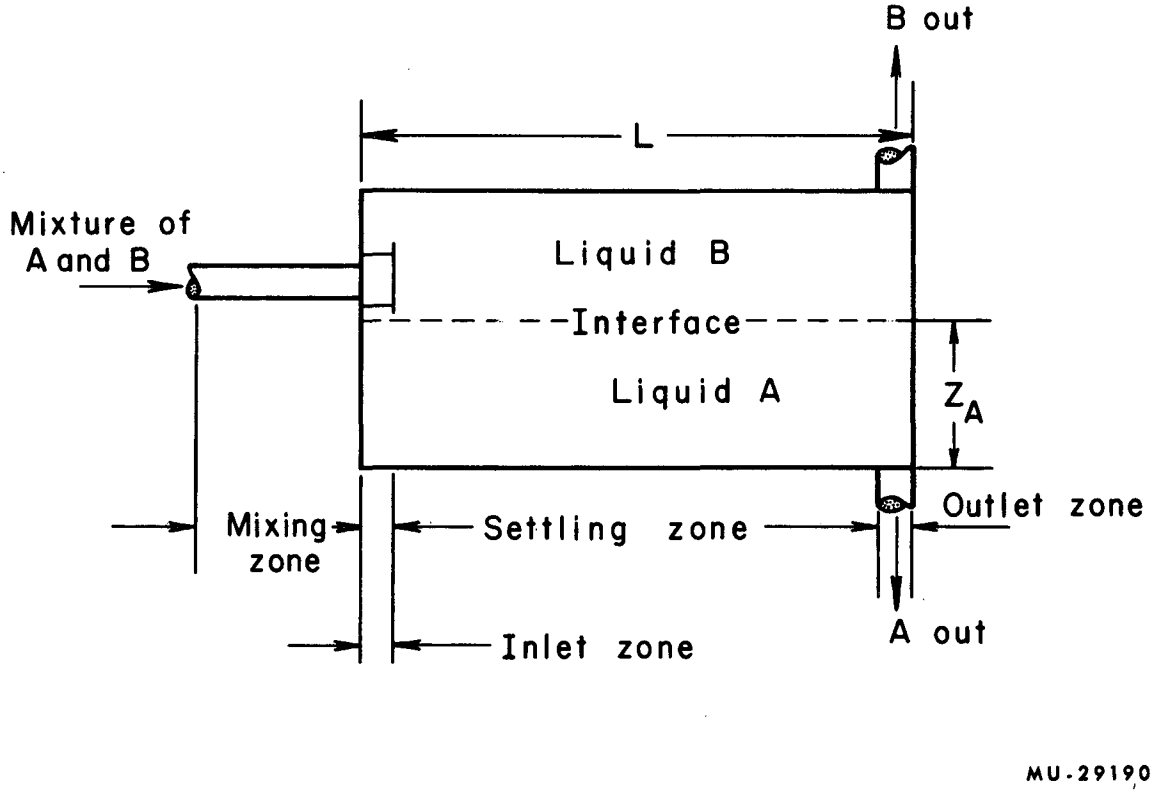
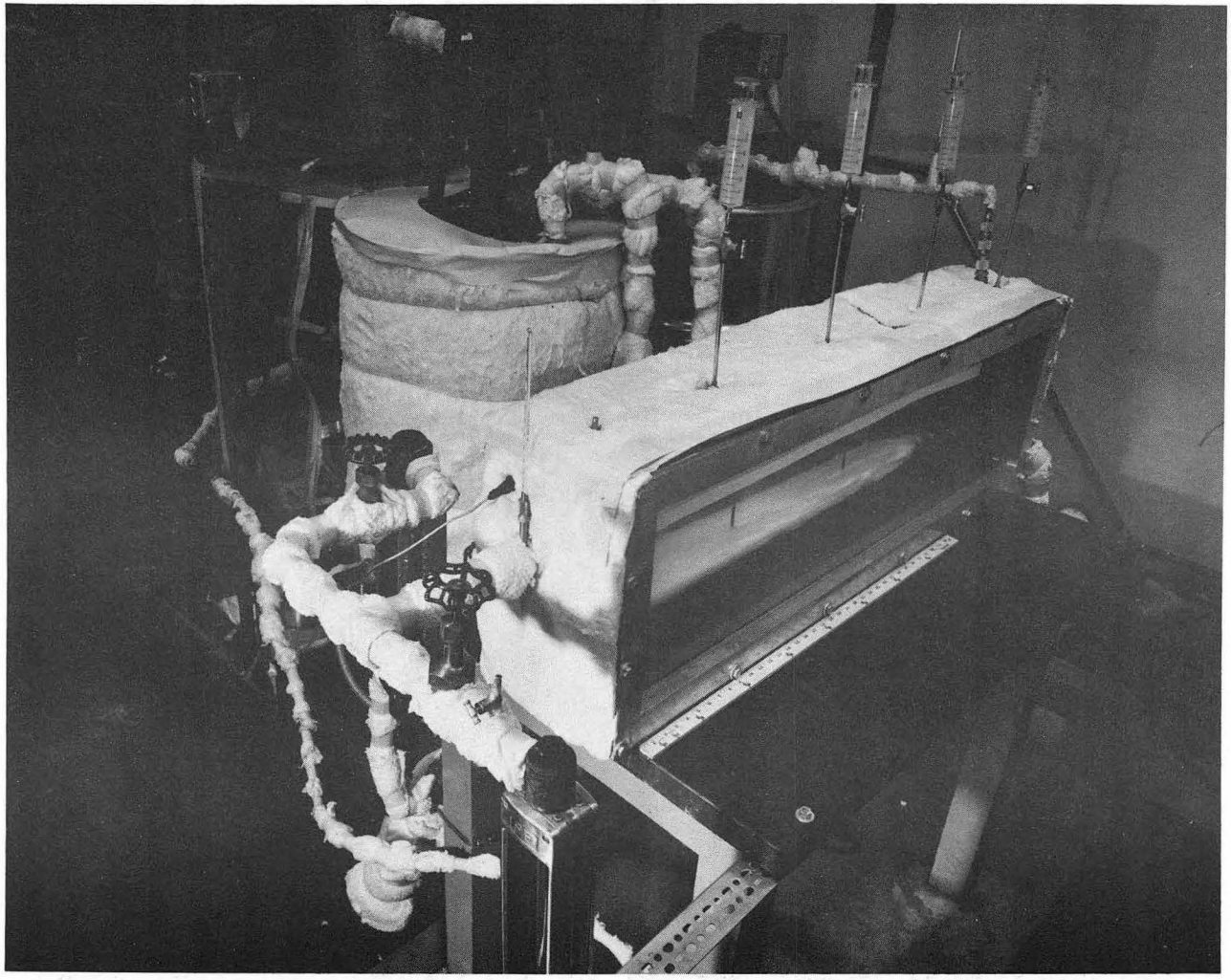
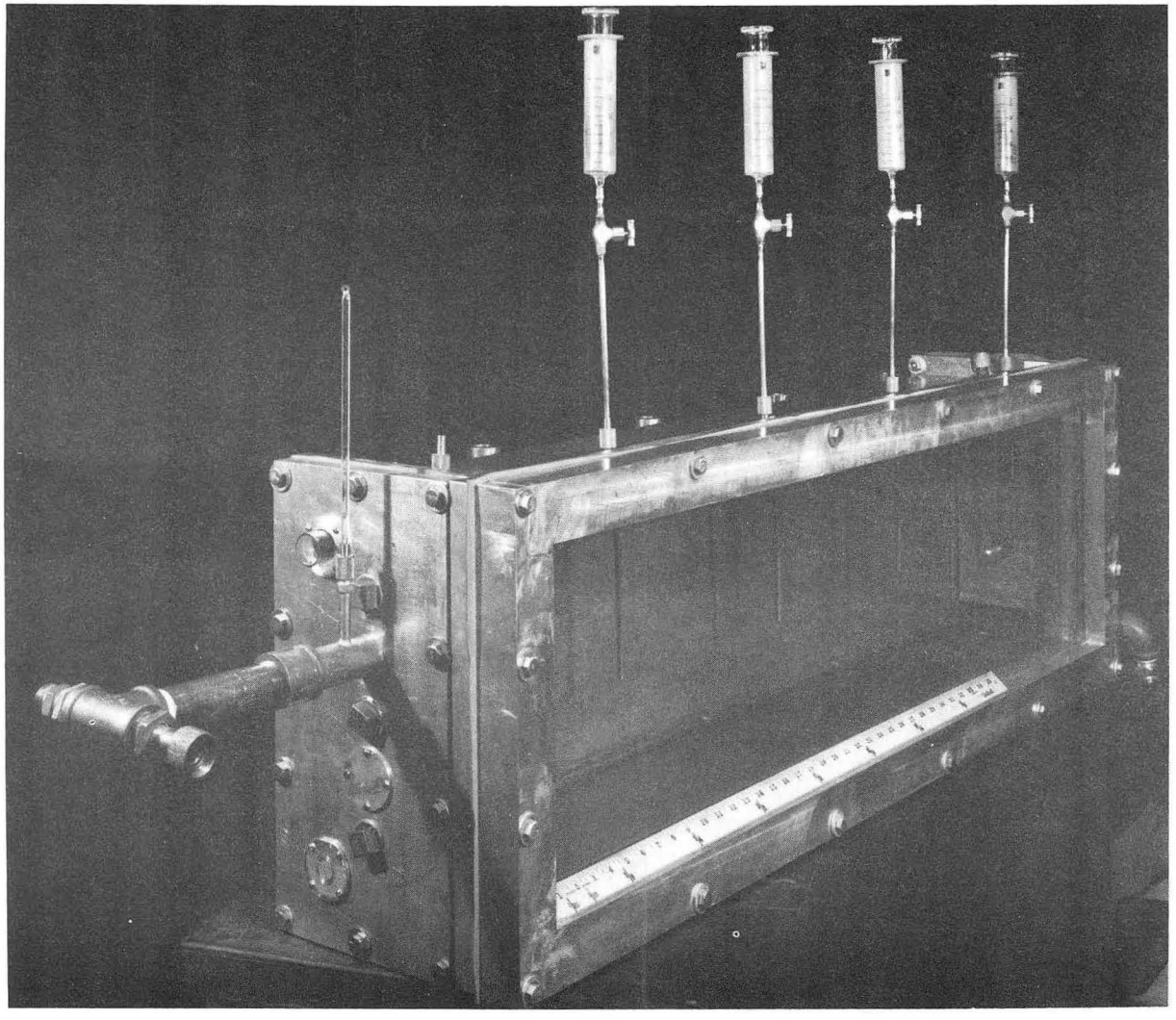


Fig. 2. Horizontal gravity settler.



ZN-3552

Fig. 3. Overall view of the experimental apparatus.



ZN-3553

Fig. 4. Gravity settler.

In runs 1A through 6A, a 1×12-in. brass nipple was inserted between the mixing section and the settler. This expansion section served to decrease the settler entrance velocity while the dispersion formed in the mixing pipes was maintained.

D. Settling Section

The settler was a 4-ft-long aluminum chamber with a rectangular cross section 12 in. high and 6 in. wide. A 0.5-in.-thick Pyrex glass window extended the entire length of the settler. It was attached by an aluminum frame bolted to a flange welded onto the main section. The entrance and exit plates were also bolted to flanges on the main section. Silicon rubber gaskets were used to seal the glass frame and the end plates.

A baffle 4 in. high and 2-in. wide was mounted 3 in. in front of the inlet to break up the incoming jet of liquid. The baffle was attached by two 3/8-in. tie rods threaded into the inside of the front plate on either side of the inlet pipe.

Four concentration probes were inserted at 1-ft intervals through fittings attached to the top of the settler. These probes consisted of 3/8×16-in.-long stainless steel tubes with 50-ml hypodermic syringes connected to the exposed ends of the probes. Each probe had free vertical motion, and could sample at any height in its particular cross section.

The settler was illuminated by a 42-in. 30-W fluorescent light installed inside a 30-mm o.d. Pyrex tube mounted in one of the upper corners of the chamber.

Constant temperature was maintained by four 384-W, 4-ft-long heating tapes wrapped uniformly around the settling section.

E. Outlets

For the Aroclor outlet a 1.25-in. pipe was welded to the bottom of the exit plate. The purpose of this large an outlet was to reduce turbulence at the Aroclor outlet. The Aroclor was returned to the top surface of the storage tank to facilitate rapid evaporation of the entrained water.

The water was withdrawn from a 3/4-in. outlet on the top end of the settler. The water outlet pipe contained an electrical conductivity cell connected to a Leeds & Northrup Speedomax recorder. This allowed continuous measurement of the electrical conductivity of the water stream at the settler exit.

The storage drums, mixing section, settling section, outlet section, and all connecting pipes were wrapped in 1/2-in. Fiberglass insulation.

IV. EXPERIMENTAL PROCEDURE

The agitator on the Aroclor storage drum was turned on, and the Aroclor was heated to 220°F. (See Fig. 1.) The water pump was started, and the settler was filled with water. While the settler was filling, the Aroclor outlet valve V_5 was closed, and the water outlet valve V_4 was left open.

When the settler was filled, valve V_2 was opened, and the Aroclor pump was started. Valve V_3 was opened, and the Aroclor flow rate was adjusted by valve V_1. When the Aroclor in the settler reached a depth of 6 in., the Aroclor outlet valve V_5 was opened, and the water outlet valve V_4 was adjusted to maintain the 6-in. interface height. Then both the Aroclor and water flow rates were readjusted to the desired values.

The Aroclor was allowed to raise the temperature of the water by direct-contact heat transfer until the temperatures of the incoming stream, water outlet stream, and Aroclor outlet stream were all constant and within the range of 185 to 190°F. Constant temperature was maintained by adjusting the heaters on the Aroclor storage tank and by using the heating tapes on the surface of the settling section.

Experimental data were taken approximately 30 min after the system reached steady state. Samples were taken from the Aroclor layer at 2, 4, and 6 in. below the interface with each of the four concentration probes. These samples were later analyzed for water content by the Karl Fischer method described in Appendix C.

Residence times of the water layer and the water in the Aroclor layer were measured after the concentration samples were removed. The electrical conductivity cell was connected to the recorder, and the pen was set on zero for the pure water passing through the outlet. After the pen had moved along the base line for a few minutes, a pulse of salt solution was injected from a syringe into the entering water stream. While the recorder traced the outlet response of the water layer, samples of the Aroclor outlet stream were taken every 15 sec from valve V_6. These samples were washed with water, and the

extracted salt in the washings was determined with an electrical conductivity cell.

The interface velocity profile was arrived at by timing droplets through a marked distance as they moved toward the outlet.

The height of the interface and the depth of the emulsion layer were read from clear plastic rules attached at 1-ft intervals along the length of the settler.

This procedure was repeated for various flow rates and mixing-section Reynolds numbers.

V. EXPERIMENTAL DATA

The experimental data and derived results are presented in Tables I through IV and discussed in detail in Sec. XII.

Table I. Experimental data and derived results for the separation of water from Aroclor 1248

Run number	Q (ft^3/min)	N_{Re}	Average velocity: Aroclor (ft/min)	Average velocity: Water (ft/min)	V_i (ft/min)	L_E (in.)	Aroclor: θ_{nm} (min)	Aroclor: θ_{exp} (min)	Water: θ_{nm} (min)	Water: θ_{exp} (min)	Depth of the emulsion layer (in.): 0 ft	1 ft	2 ft	3 ft	4 ft
1	0.3662	2990	1.17	0.292	2.75	30	3.41	3.13	13.7	1.5	1.50	0.65	0.20	-	-
2	0.3662	3620	1.17	0.292	3.20	36	3.41	2.87	13.7	1.0	1.75	1.0	0.40	-	-
3	0.3662	4470	1.17	0.292	3.86	48+	3.41	2.53	13.7	0.8	2.00	1.40	0.75	0.30	0.15
4	0.2838	2320	0.908	0.228	2.63	18	4.40	4.21	17.6	1.8	0.90	0.25	-	-	-
5	0.2838	2750	0.908	0.228	2.82	22	4.40	3.81	17.6	1.3	1.25	0.50	-	-	-
6	0.2838	3465	0.908	0.228	3.10	31	4.40	3.50	17.6	0.9	1.60	0.75	0.25	-	-
7	0.1900	1540	0.610	0.152	1.00	12	5.20	5.10	26.4	5.0	0.50	-	-	-	-
8	0.1900	1850	0.610	0.152	1.50	14	5.20	4.91	26.4	3.0	0.75	0.20	-	-	-
9	0.1900	2310	0.610	0.152	1.73	17	5.20	4.73	26.4	1.4	0.80	0.20	-	-	-

For all runs shown: C_0 = 15.2% water

Z_A = 6 in.

L = 4 ft

Temperature = 190°F

Table II. Concentration profile points (wt., % water).

Run number	Height (in.)	Length (ft) 1	2	3	4
	2	0.195	0.146	0.120	0.072
1	4	0.134	0.118	0.101	0.063
	6	0.113	0.104	0.092	0.059
	2	0.231	0.198	0.159	0.151
2	4	0.180	0.160	0.145	0.129
	6	0.169	0.148	0.139	0.125
	2	0.340	0.264	0.245	0.226
3	4	0.248	0.210	0.197	0.177
	6	0.210	0.167	0.170	0.158
	2	0.135	0.088	0.075	0.069
4	4	0.098	0.080	0.068	0.067
	6	0.091	0.077	0.066	0.065
	2	0.160	0.130	0.105	0.090
5	4	0.130	0.110	0.098	0.084
	6	0.121	0.102	0.091	0.079
	2	0.228	0.200	0.160	0.150
6	4	0.182	0.162	0.155	0.130
	6	0.170	0.150	0.140	0.118
	2	0.103	0.082	0.069	0.061
7	4	0.087	0.071	0.064	0.059
	6	0.080	0.067	0.062	0.057
	2	0.113	0.092	0.079	0.071
8	4	0.097	0.081	0.074	0.069
	6	0.090	0.077	0.072	0.067
	2	0.200	0.148	0.119	0.093
9	4	0.140	0.120	0.103	0.060
	6	0.123	0.099	0.083	0.058

Table III. Experimental data and derived results for the separation of water from Aroclor 1248 with reduced settler entrance velocity

Run number	Mixing section velocity (ft/min)	Settler entrance velocity (ft/min)	Average velocity Aroclor (ft/min)	Average velocity Water (ft/min)	V_i (ft/min)	L_E (in.)	Aroclor θ_{nm} (min)	Aroclor θ_{exp} (min)	Water θ_{nm} (min)	Water θ_{exp} (min)	Depth of the emulsion layer (in.) 0 ft	1 ft	2 ft	3 ft	4 ft
1A	5.99	0.992	1.17	0.292	2.65	32	3.41	3.20	13.7	1.45	1.40	0.50	0.20	-	-
3A	8.98	0.992	1.17	0.292	3.75	48+	3.41	2.60	13.7	0.85	2.00	1.50	0.70	0.25	0.10
4A	4.64	0.767	0.908	0.228	2.50	18	4.40	4.20	17.6	1.75	0.80	0.25	-	-	-
6A	6.95	0.767	0.908	0.228	3.00	30	4.40	3.55	17.6	0.90	1.50	0.70	0.25	-	-
7A	3.10	0.514	0.610	0.152	0.90	12	5.20	5.00	26.4	4.75	0.50	-	-	-	-
9A	4.65	0.514	0.610	0.152	1.70	16	5.20	4.70	26.4	1.30	0.75	0.20	-	-	-

For all runs shown: C_0 = 15.2% water

Z_A = 6 in.

L = 4 ft

Temperature = 190°F

Q and N_{Re} for 1A are identical to 1, for 3A are identical to 3, etc.

Table IV. Concentration profile points (wt., % water).

Run number	Height (in.)	Length (ft) 1	2	3	4
	2	0.193	0.140	0.110	0.070
1A	4	0.129	0.115	0.096	0.061
	6	0.110	0.100	0.087	0.047
	2	0.320	0.250	0.240	0.216
3A	4	0.231	0.200	0.190	0.170
	6	0.200	0.150	0.175	0.160
	2	0.129	0.086	0.071	0.067
4A	4	0.094	0.075	0.066	0.066
	6	0.090	0.072	0.065	0.065
	2	0.225	0.194	0.158	0.147
6A	4	0.180	0.160	0.153	0.131
	6	0.167	0.150	0.137	0.117
	2	0.101	0.080	0.067	0.060
7A	4	0.085	0.069	0.063	0.059
	6	0.076	0.065	0.061	0.057
	2	0.195	0.145	0.117	0.091
9A	4	0.137	0.118	0.098	0.061
	6	0.122	0.098	0.083	0.060

VI. OBSERVATIONS

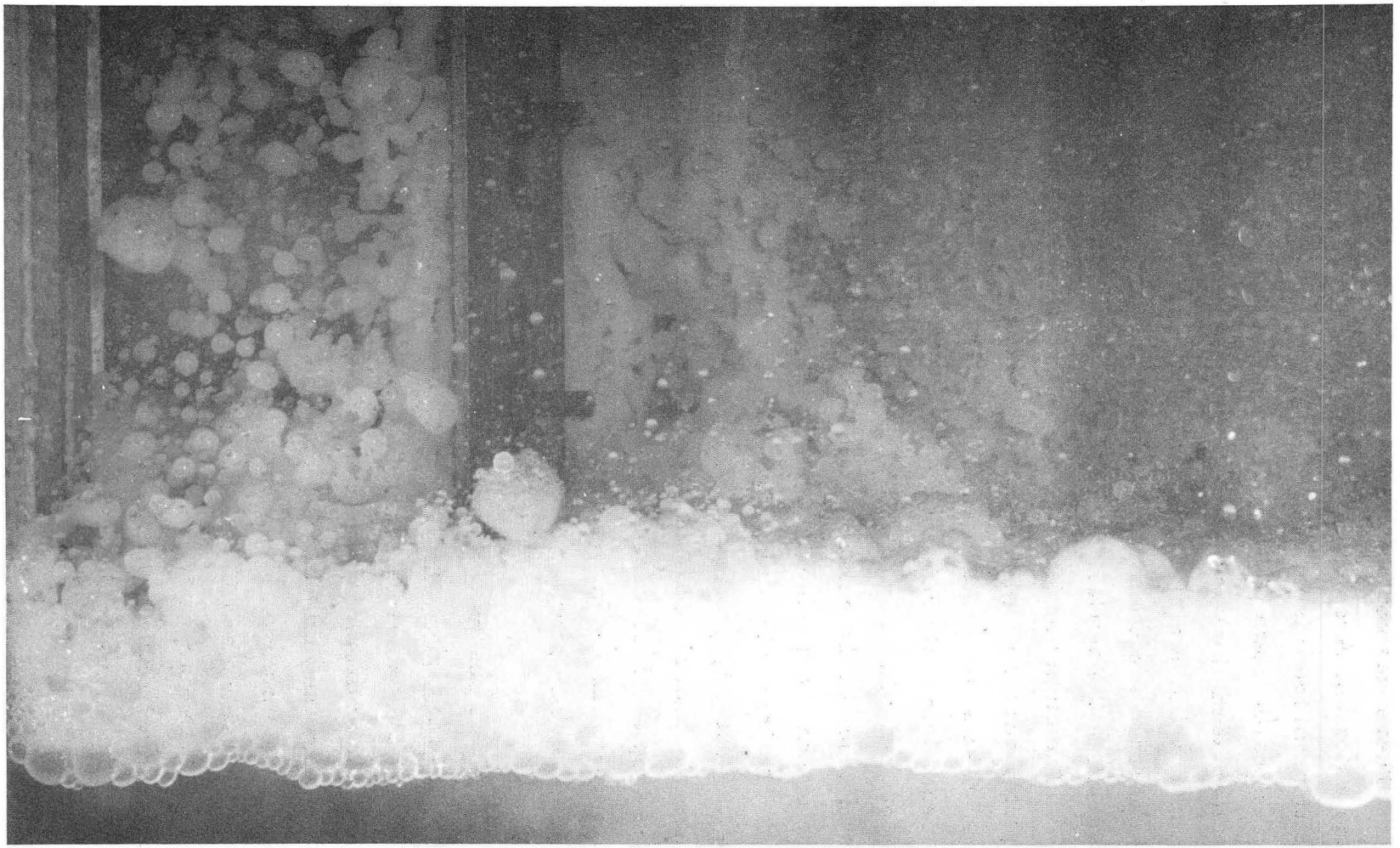
There was not a sharp interface between the two liquid phases as the water and Aroclor flowed through the settler. The turbulent conditions in the mixing section and the impact of the entering stream upon the baffle plate (Fig. 5) produced a mixture of the two phases that remained at the interface because of its intermediate density. This mixture, which hereafter will be referred to as an emulsion layer, was observed in its entirety through the glass window that extended the length of the settler.

The emulsion layer consisted not only of Aroclor and water droplets, but also of a complicated mixture of both Aroclor and water films; after a finite lifetime at the interface, the droplets and films coalesced into their respective phases. The interface lifetime of the droplets and films agreed with the observations made by Lang, and the existence of the emulsion layer was also consistent with observations made by other experimenters during the settling process.

The emulsion-layer droplets appeared to move along the interface at a velocity greater than the average velocity of either the water or Aroclor phase. Close to the end of the emulsion layer, the velocity of the droplets decreased rapidly and finally approached zero as the layer disappeared completely with the coalescence of the final droplets. Typical velocity profiles of the emulsion-layer droplets are shown in Fig. 6.

It was observed that droplets of the water and Aroclor combined to form bigger droplets and then coalesced into their respective phases as they moved along the interface. This coalescence caused a decrease of droplet concentration in the emulsion layer and therefore a decrease in depth toward the outlet end of the settler. The depth of the emulsion layer at 1-ft intervals is given, for all the runs made, in Table I and II, and sample depth profiles are shown in Fig. 7.

The existence of the emulsion layer was particularly significant in the overall settling process because coalescence and collapse of the droplets and films in this layer resulted in showers of tiny water



ZN-3554

Fig. 5. Formation of the emulsion layer at the settler entrance, Run No. 3.

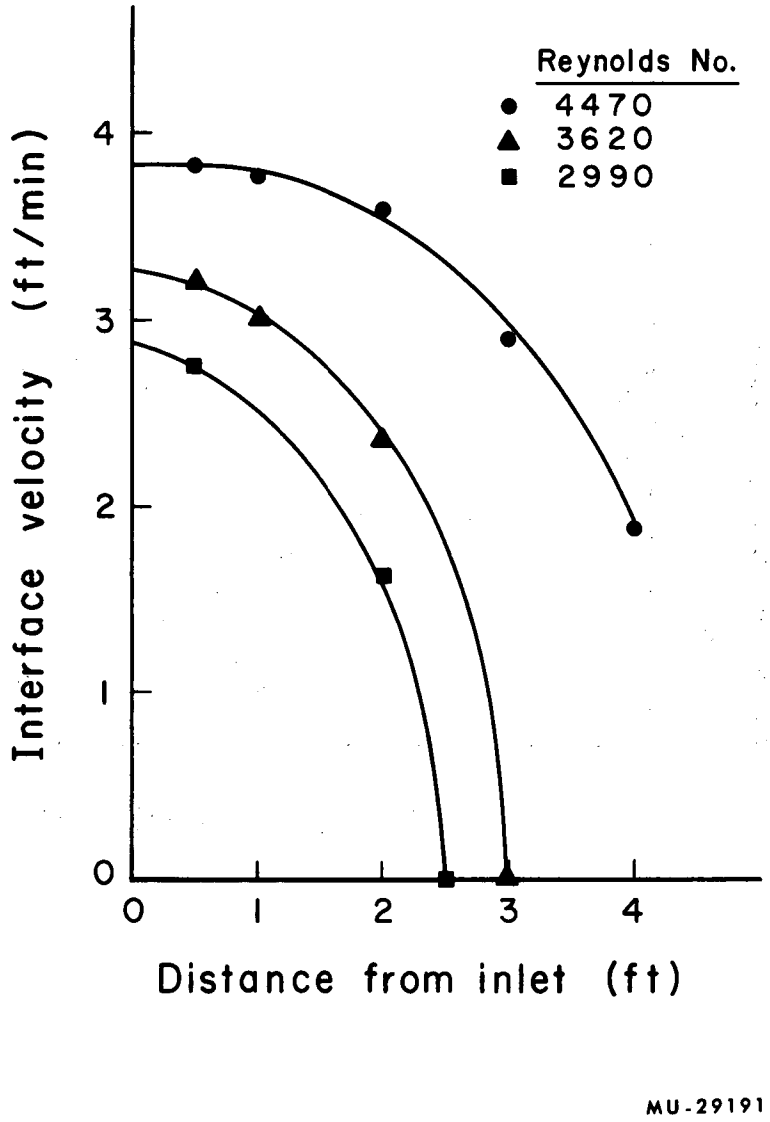


Fig. 6. Interface velocity profiles.

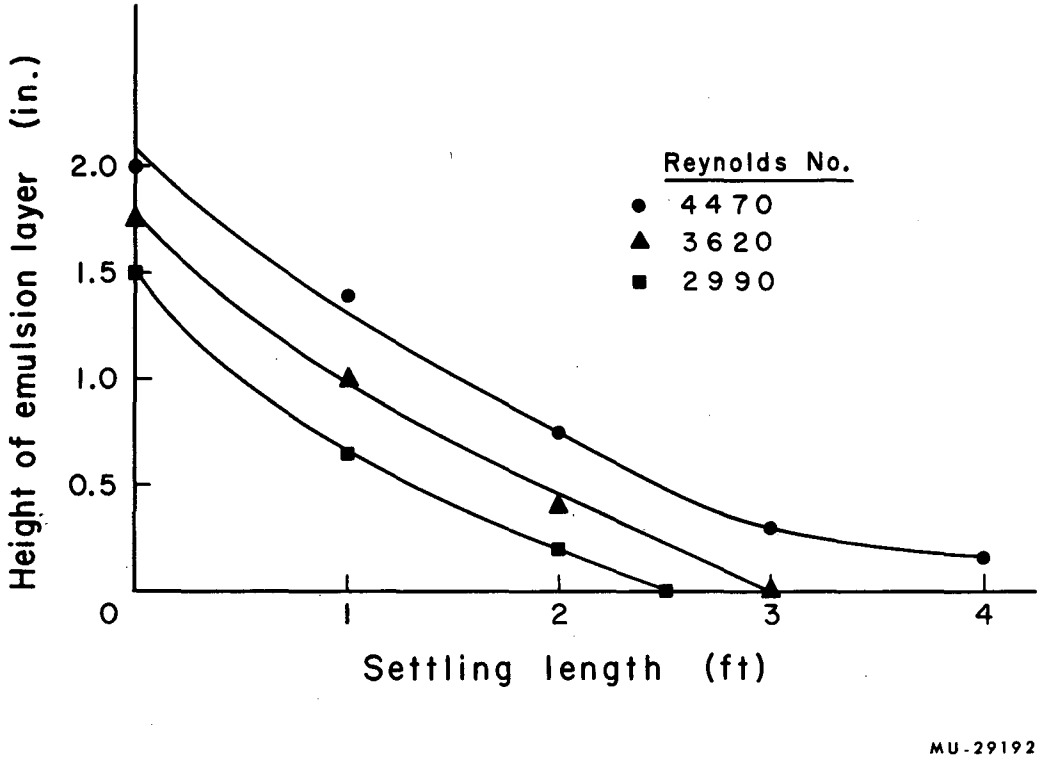
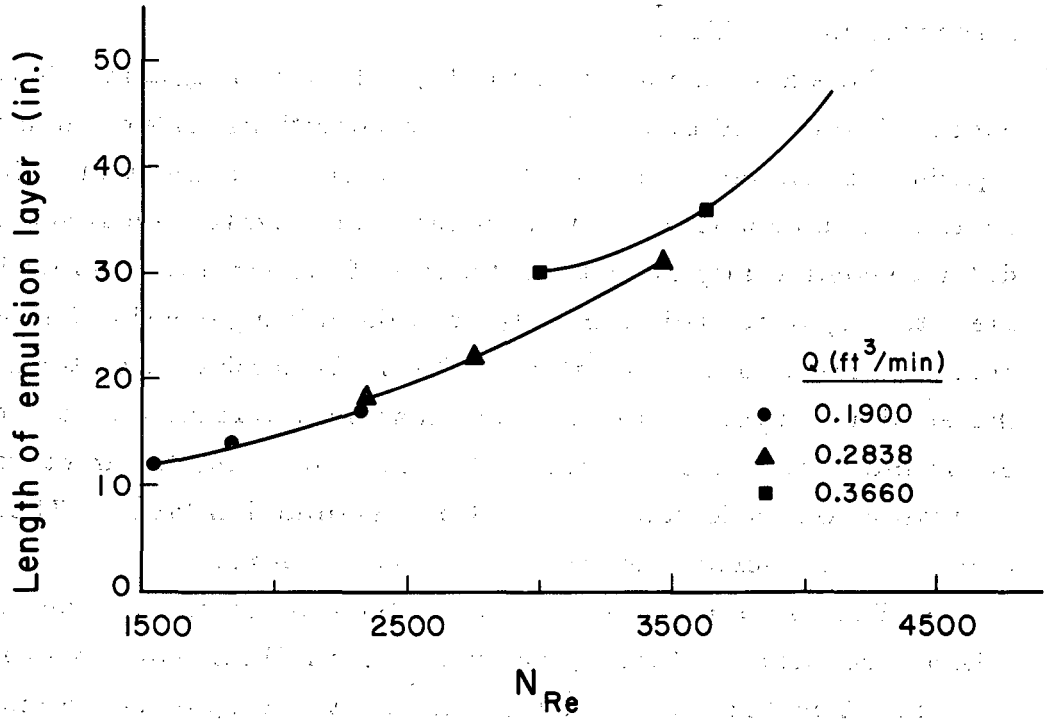


Fig. 7. Depth profiles of the emulsion layer.

droplets sent deep into the Aroclor layer. These droplets remained in the lower layer and were carried out through the Aroclor outlet, contributing greatly to the final concentration of water in the Aroclor. Further effects of these droplets on the overall settling mechanism are discussed in Sec. VII. A.

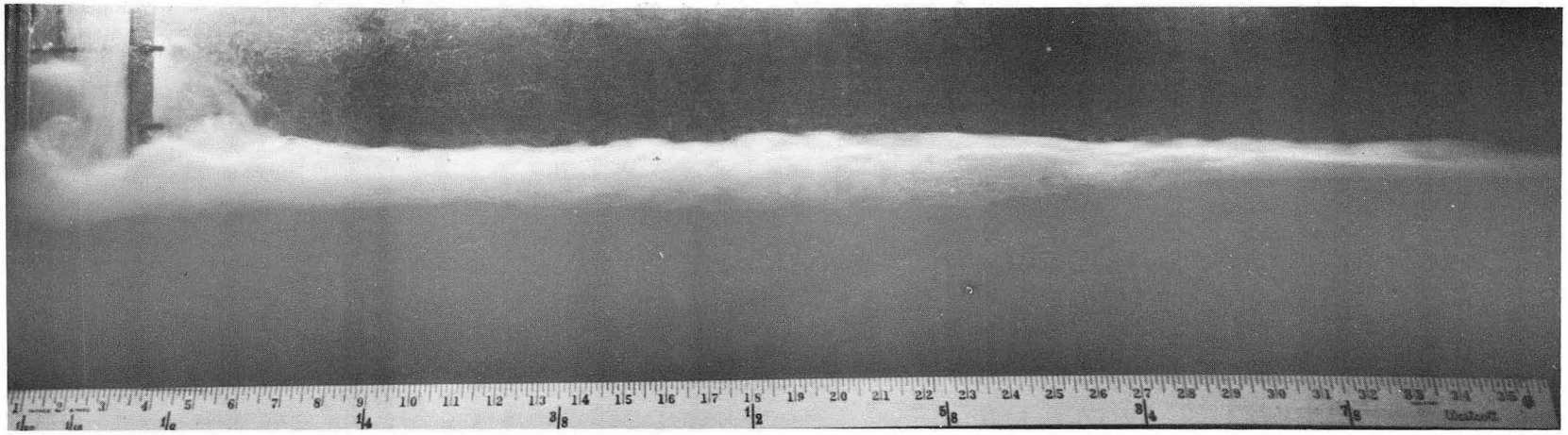
The extent of the emulsion layer both in length and depth was observed to depend primarily upon the conditions under which the two liquids were mixed, with all other variables held constant. The insertion of an expansion section to reduce the settler entrance velocity did not substantially alter the intensity of the emulsion layer; instead, the intensity depended primarily upon the mixing-section Reynolds number. Figure 8 shows the effect of Reynolds number upon the length of the emulsion layer. Graham found that the liquid flow rates, the height of the inlet above the Aroclor-water interface, and the inlet water concentration also affected the extent of the emulsion layer. These variables are not included in the study reported here.

The photographs show the emulsion layer formed under violent mixing conditions, Fig. 9, and relatively mild mixing conditions, Fig. 10. The Aroclor layer had a milky-white appearance caused by the small water droplets dispersed in it. The water layer was clear immediately after the inlet section because the heavy Aroclor droplets settled quickly. Close observation of the Aroclor revealed the unusual flow conditions that prevailed in this layer. The tiny water droplets moved toward the interface in small swirls, and eddies formed by the droplets were forced down into the Aroclor by the collapsing emulsion layer. Many of these droplets continued to move in circles until they were carried out through the Aroclor outlet. These droplets are seen in the photographs as a dense white cloud below the emulsion layer.



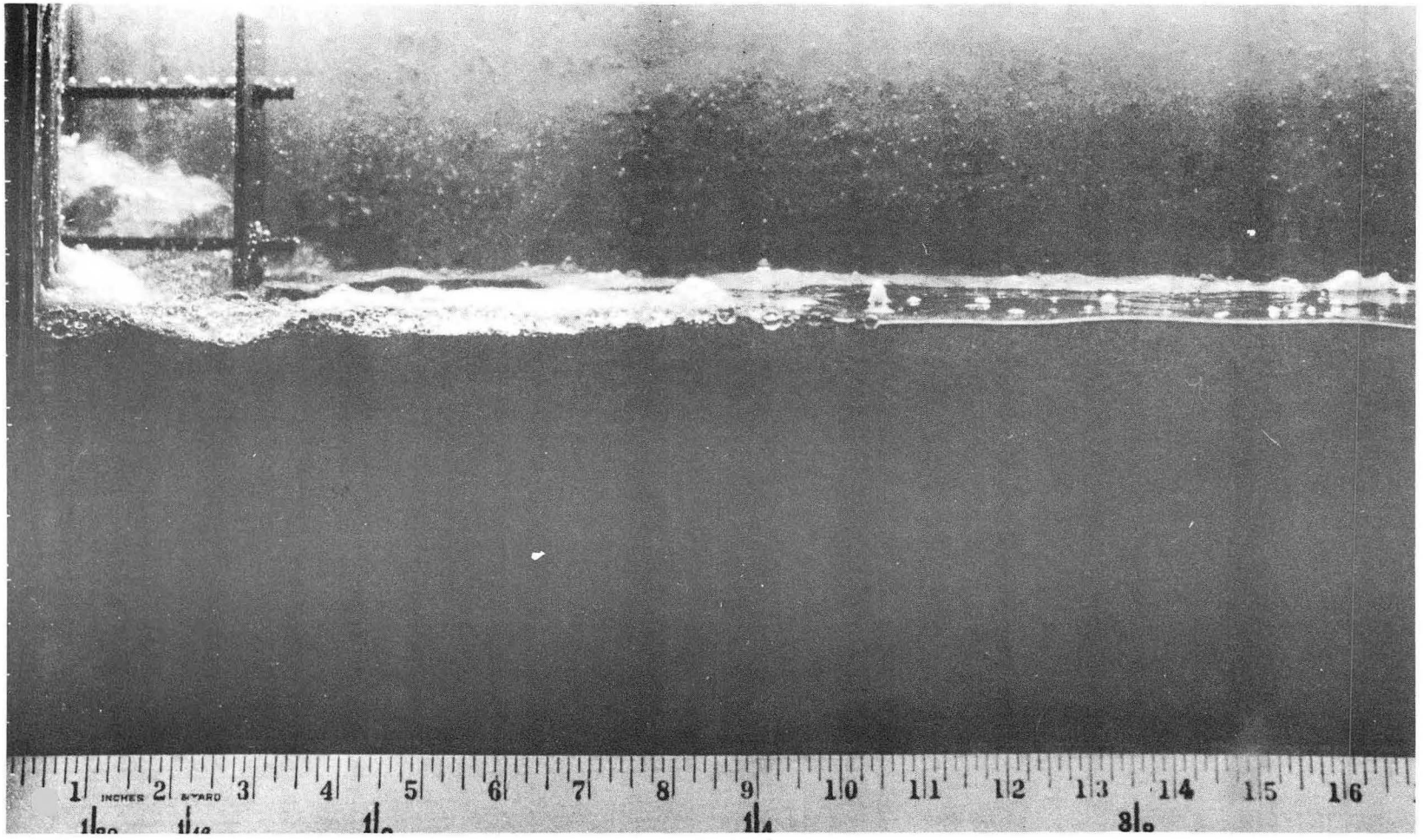
MU-29193

Fig. 8. Effect of mixing-section Reynolds number on the length of the emulsion.



ZN-3555

Fig. 9. Overall view of the emulsion layer at N_{Re} = 3620, Run No. 2.



ZN-3556

Fig. 10. Overall view of the emulsion layer at $N_{Re} = 1540$, Run No. 7.

VII. DISCUSSION OF DATA AND OF OBSERVATIONS

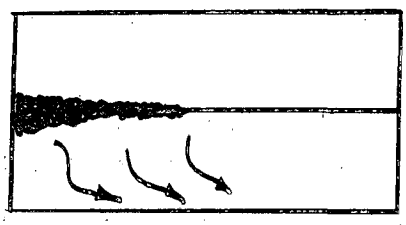
A. Emulsion Layer

Both the data and the observations indicate the significance of the emulsion layer in the overall settling mechanism. The small water droplets that were observed to originate in this layer contributed to the water present throughout the Aroclor phase and to the final contamination in the effluent stream. The mechanism and magnitude of this contamination were controlled by several factors, which are discussed in the following paragraphs.

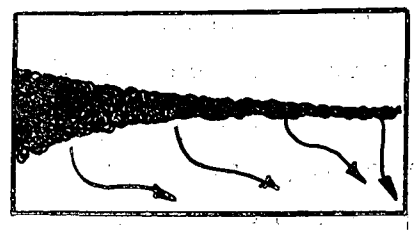
Among the variables studied, the length and depth of the emulsion layer depended mainly on the conditions under which the two liquids were mixed or, more specifically, upon the mixing-section Reynolds number. From the results of Richardson, discussed in Sec. II. D, one would expect the settler entrance velocity to have an effect on the intensity of the emulsion layer formed. A comparison of Table I with III shows this not to be the case, and the insertion of an expansion section to reduce the entrance velocity had no effect on either the length or depth of the emulsion layer. This can be explained by considering the violent mixing that took place between the two liquids before they entered the settler. This turbulent mixing was extreme enough to be the controlling factor for determining the size distribution of the entering particles, and so long as these conditions were maintained, a decrease in the settler entrance velocity did not affect the emulsion layer. Richardson injected a pure liquid into a stagnant phase, and therefore, in the absence of any turbulent mixing of the two phases, the injection velocity was critical. The entrance velocity would undoubtedly be more important for settling in which the mixing conditions are less extreme than those studied in this paper.

The disappearance of the interface velocity at the end of the emulsion layer leads to two different mechanisms by which contamination can enter the effluent Aroclor stream. When the emulsion layer does not extend the length of the settling section, the emulsion layer cannot

be drawn through the Aroclor outlet, but only contributes to the contamination through the water dispersed upon coalescence (Case I). On the other hand, when the emulsion layer does extend the total length of the section, the contamination is caused both by water dispersion and by the actual flow of the emulsion layer through the Aroclor outlet (Case II).

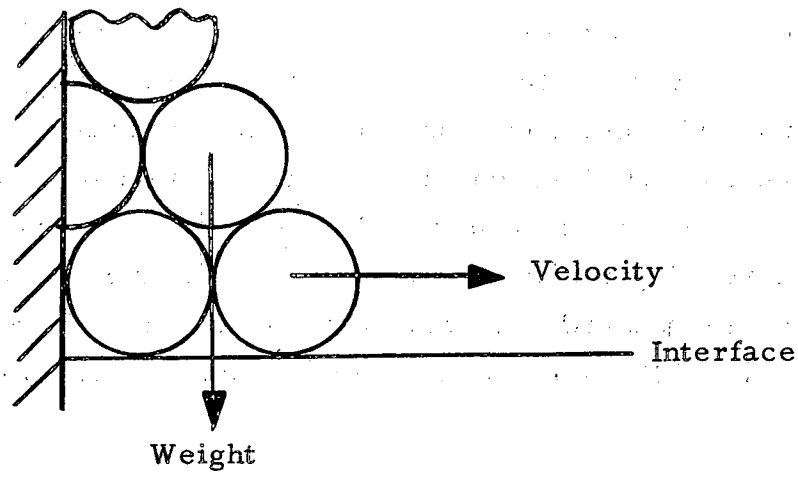


Case I



Case II

Table I shows the maximum interface velocity to be two to three times the average velocity of the Aroclor phase calculated by dividing the flow rate by the cross-sectional area. This increase in velocity can be attributed to a combination of two factors. Firstly, since the depth of the emulsion layer slowly decreases along the length of the settler, there is a hydrostatic force exerted on the droplets that causes them to slip along the interface toward the settler outlet.



Secondly, from the discussion of velocity profiles in Sec. II. E, one would expect the velocity at the interface to be approximately twice the average velocity of the Aroclor phase. In some cases the velocity of the emulsion layer is slightly less than twice the average velocity of the Aroclor. This can be explained by considering the shearing force acting on the interface by the slow-moving water phase. When the emulsion layer is thin, the hydrostatic force is small and is overcome by the shearing force exerted by the water layer. Therefore the velocity of the emulsion layer is determined by the combined effects of the hydrostatic forces, velocity-distribution, and shearing forces.

B. Concentration Profiles

In general, the following observations were made when concentration profiles at cross sections of different settling lengths were compared, as shown in Fig. 11. The concentration of water in the Aroclor was greater nearer the interface for all settling lengths. This is what is expected because the water at every point in the Aroclor phase moves toward the interface; the larger droplets arrive there quickly, and thus account for the higher concentration. It was also observed that the profiles at small settling lengths were considerably steeper than those at the settler exit -- particularly at high mixing-section Reynolds numbers, as can be seen in Tables II and IV. This can be explained by again considering the droplets of water dispersed in the Aroclor. Most of the larger droplets moved toward the interface rapidly and therefore coalesced into the water phase at low residence times. Near the settler exit, the general settling rate was decreased by the absence of these large droplets and the presence of smaller droplets with low settling velocities. The steep slope of the concentration profiles at high mixing-section Reynolds numbers is attributed to the existence of the emulsion layer. This was particularly true at the settler entrance in which the emulsion layer was the largest.

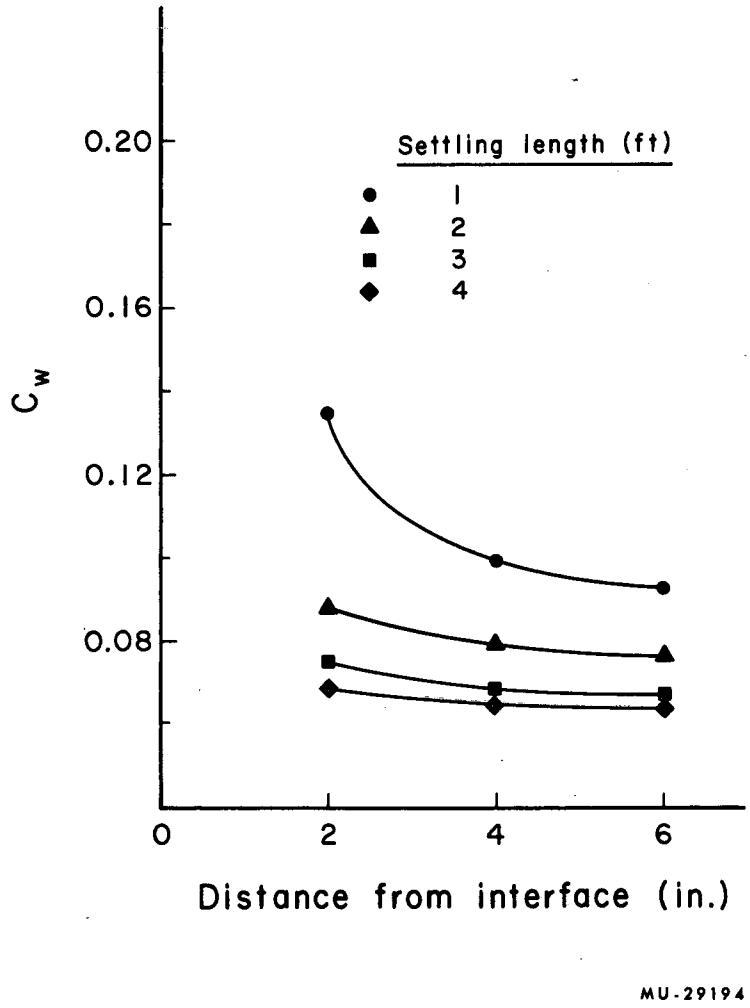


Fig. 11. Concentration profiles at cross sections of different settling lengths.

The concentration profiles at various distances from the interface, Fig. 12, illustrate the general decrease in water concentration with increasing settler length at all distances from the interface. That these profiles closer to the interface are much steeper indicates the increased settling rate there. Again, as in the previously discussed profiles, this was due primarily to the large water droplets closer to the interface because of their high settling velocity, and the droplets dispersed in the upper part of the Aroclor by the coalescence of the emulsion layer. At the bottom of the settler only very small droplets remained, and there was relatively little settling.

The velocity profiles (Figs. 11 and 12) indicate that the maximum settling takes place near the settler entrance and near the interface. An indication of the contaminating effect of the emulsion layer is also demonstrated.

Further evidence of the emulsion-layer contamination can be seen in the curves of water concentration vs Reynolds number plotted in Fig. 13. These demonstrate the effect upon conditions in the settler of the increased mixing-section turbulence with all other variables held constant. Each point on this plot represents the variation of this single point with mixing-section Reynolds number. For each of these runs all other variables (settling length, flow rates, interface positions, etc.) were held constant, so the slope of the lines in Fig. 13 must be due to some permanent effects of the mixing conditions or the entrance velocity. Since a comparison of Tables I and II shows no effect of entrance velocity, the variation in water concentration is due to the mixing-section Reynolds number. This Reynolds number controls the concentration throughout the settler by determining (a) the size distribution of the entering particles and (b) the depth and extent of the emulsion layer.

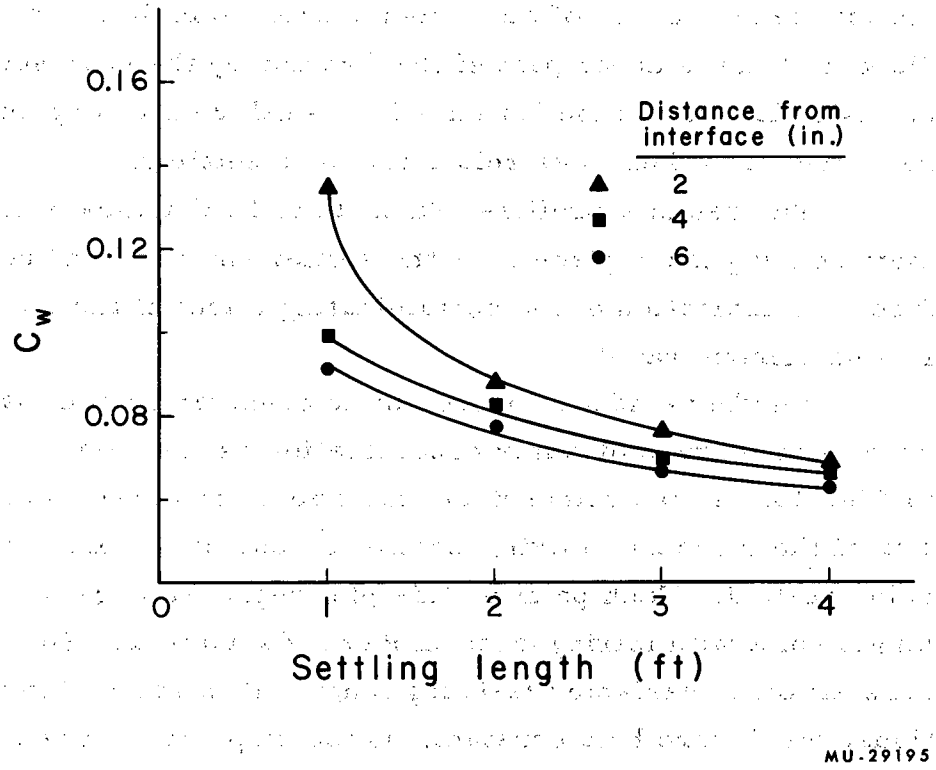


Fig. 12. Concentration profiles at various interface distances.

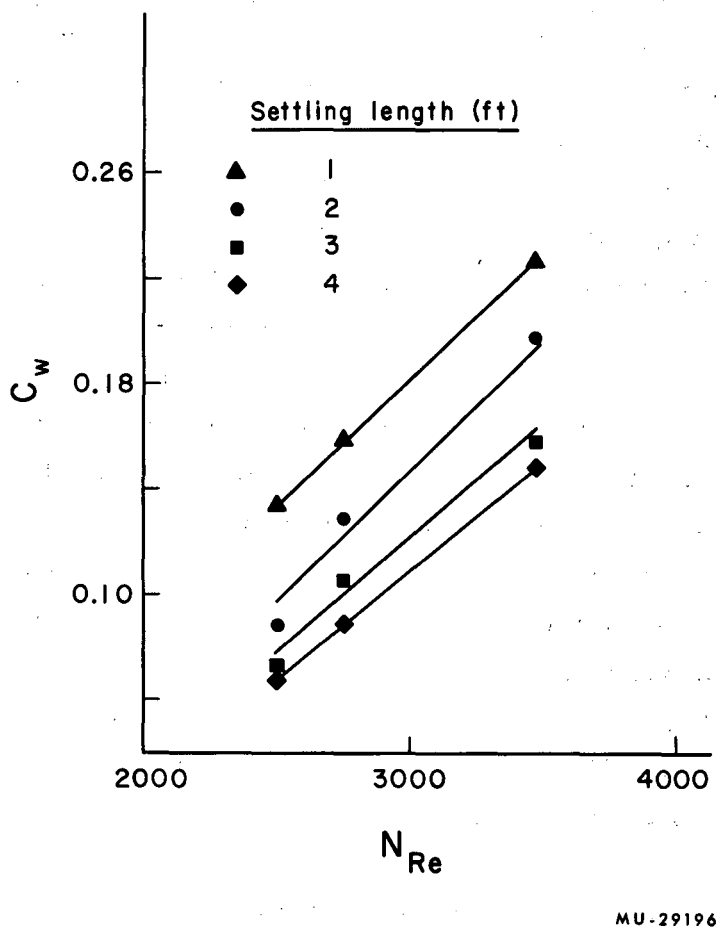
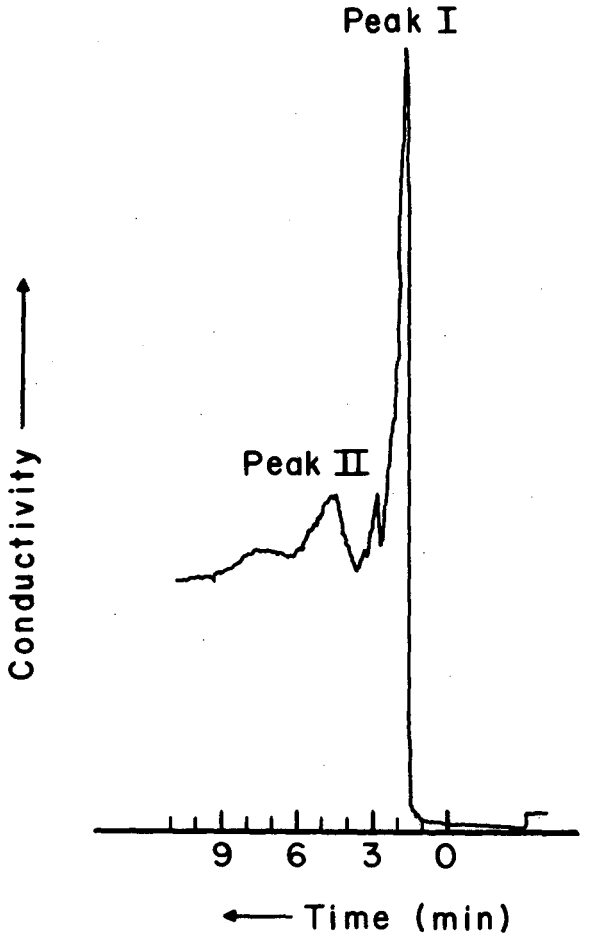


Fig. 13. Effect of Reynolds number on water concentration at various points in the Aroclor layer at interface distance = 2 in.

C. Residence Times

A pulse of saturated salt solution injected into the incoming water stream was used as a tracer for measuring the actual residence times of both the water phase and the droplets existing in the Aroclor phase. Both these times were considerably shorter than the no-mixing residence times predicted by dividing the volume of the phase by the volumetric flow rate. The deviation increased with increased mixing-section Reynolds number, indicating the effect of the increased depth and length of the emulsion layer. From the tracing of the recorder chart shown in Fig. 14, it is apparent that some of the water was carried along quickly at the interface and reached the end of the settler (Peak I) before the bulk of the liquid (Peak II). Much of this fast-moving water is trapped in the emulsion layer and is dispersed into the Aroclor phase; this explains the quick appearance of this water in the Aroclor outlet (Fig. 15). Of course, mixing of dispersed water droplets also contributed to the early appearance of the tracer solution in the exit stream. This high degree of mixing illustrates the presence of many turbulent areas in the settling section -- even at the low settling-section Reynolds numbers studied. These areas of circulation were also visually observed in the Aroclor phase by watching the movement of the tiny dispersed water droplets. These eddies tended to carry the small droplets formed by the coalescence of the emulsion layer deeply into the Aroclor layer, where they are drawn through the outlet.

Figure 16 compares the time of appearance of the tracer solution in the outlets with the average residence time of both phases. It shows the actual residence times in the settler to be much less than those predicted from the flow-rate volumes. This is due to a combination of intraphase mixing and the accelerating effect of the fast-moving emulsion layer.



MU-29197

Fig. 14. Response of injected salt pulse in the water phase.

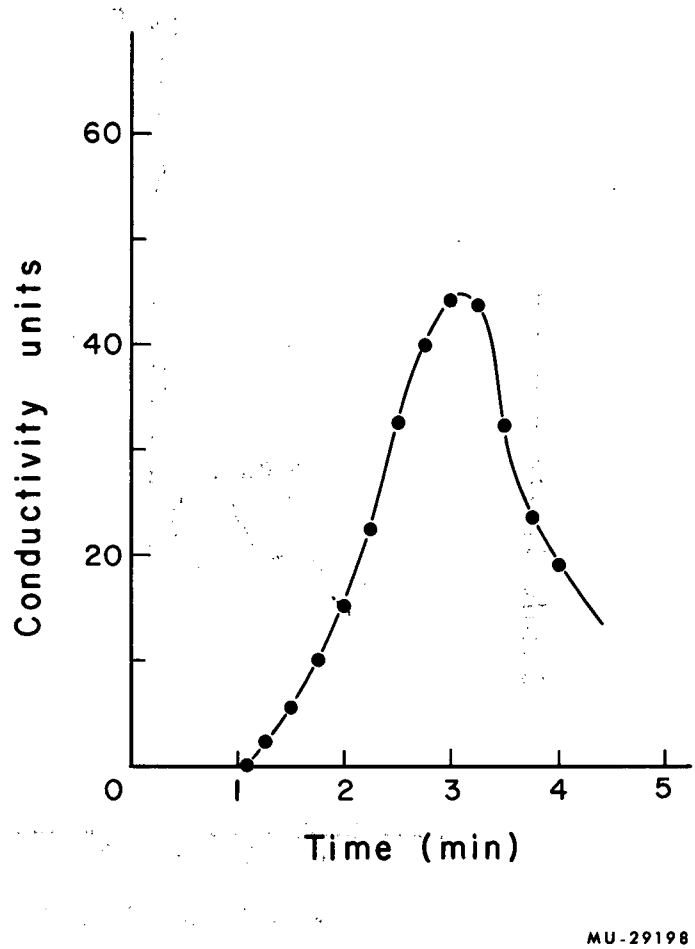


Fig. 15. Response of injected salt pulse in the Aroclor phase.

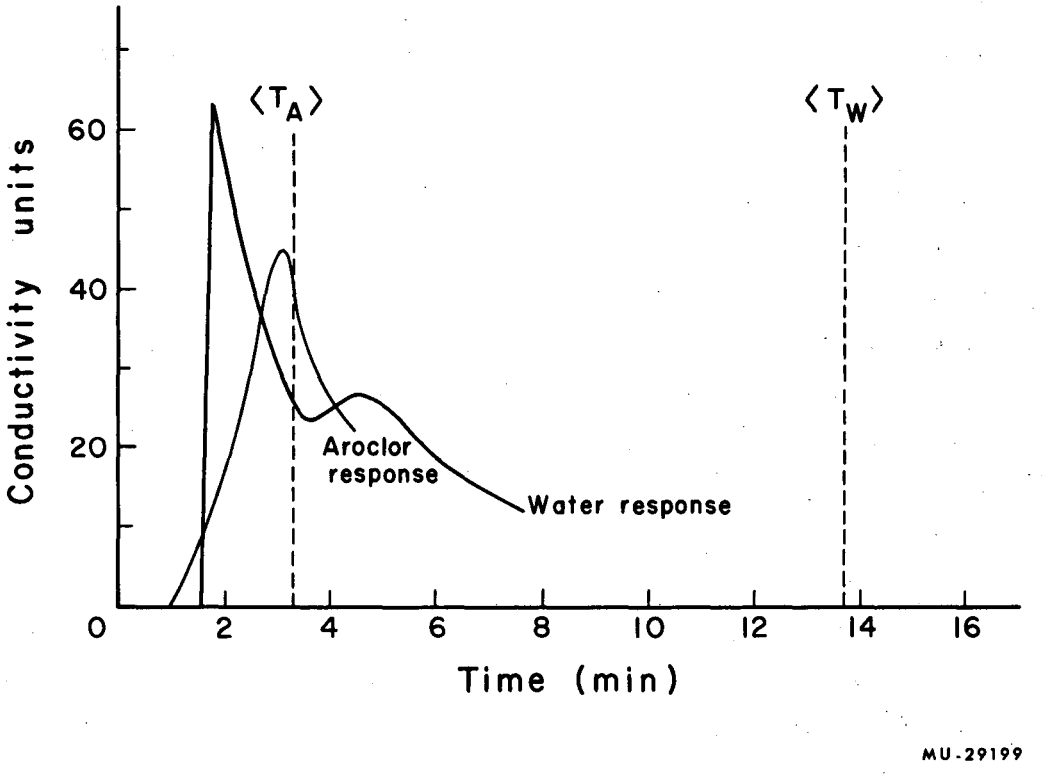


Fig. 16. Comparison of average phase residence times (computed from the volumetric flow data) with experimentally determined residence times.

$\langle T_A \rangle$: average residence time for Aroclor

$\langle T_W \rangle$: average residence time for water.

VIII. SUMMARY AND CONCLUSIONS

The overall mechanism of liquid-liquid settling depends on several factors including entrance, settling, and exit conditions. For a given set of conditions one or more of these factors may be controlling, but in general they all are important in determining the overall extent of settling.

In explaining the settling mechanism, it is helpful to consider a single water droplet dispersed in the continuous Aroclor phase at the settler entrance. This droplet can take one of several random paths, depending on its size and on the entrance conditions.

If the droplet is small, there is a high probability that it will be carried deeply into the Aroclor layer to become part of the milky-white cloud observed in this phase. When the droplet has lost the downward momentum imparted at the inlet, it will begin to rise owing to the buoyant force exerted by the Aroclor. As the droplet rises it will collide with other droplets and coalesce, thus increasing its size and velocity as it progresses through the settling zone. In the outlet zone a droplet that is rising is simultaneously acted upon by a downward-drag force, as the Aroclor flows downward toward its outlet. If the buoyant force is large enough, the droplet will move to the interface; otherwise, it will be entrained in the effluent Aroclor. When the droplet reaches the interface, it becomes part of the emulsion layer and then coalesces into the bulk water phase after its interface lifetime has expired.

A second path that an entering water particle may take is to become part of the emulsion layer formed at the settler inlet. In this case, the water is carried ahead rapidly along the interface until coalescence causes it to shower many small droplets down into the Aroclor phase.

The overall settling mechanism can be summarized by referring to the flow patterns shown in Fig. 17. As already mentioned, there is an important difference in the settler flow patterns between the case in which the emulsion layer ends in the settling section (Fig. 17a), and the case in which it extends the entire length of the settler (Fig. 17b).

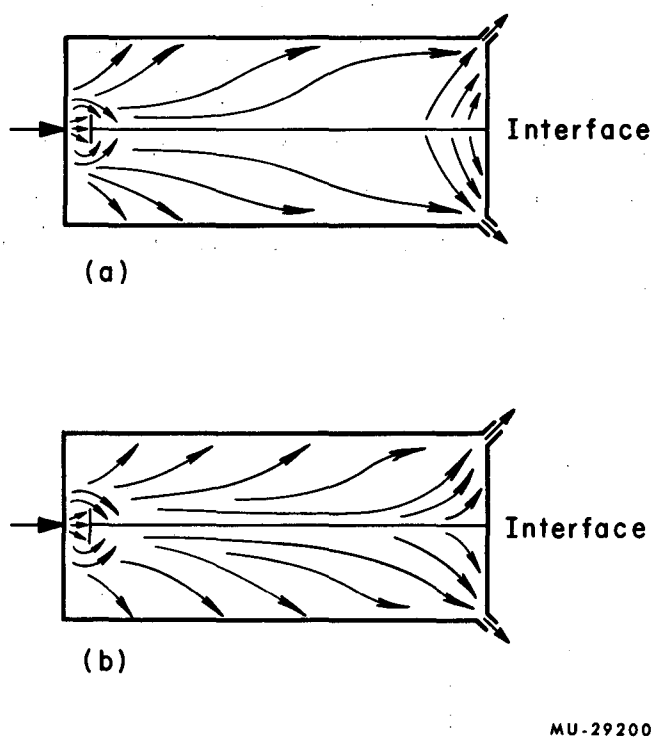


Fig. 17. Schematic diagrams of settler flow patterns.

The shaded portions of these diagrams represent relatively stagnant areas, where the droplets move randomly until caught in the currents of the leaving streams.

It can be concluded that the final water contamination is caused by (a) the droplets dispersed in the Aroclor in the mixing section and (b) droplets showered down during the emulsion-layer coalescence. When the entrance conditions are mild, the emulsion layer is small, and the dispersion formed in the mixing section is controlling; but when the entrance conditions are violent, the emulsion layer is extensive, and it becomes the controlling factor in determining the final water concentration in the Aroclor.

ACKNOWLEDGMENTS

We would like to thank Mr. G. G. Young; and his co-workers of the Mechanics Shop of Building 70 for the advice and help they have given us.

This work was done under the auspices of the U. S. Atomic Energy Commission.

APPENDICES

A. Calculation Procedure

The velocity and the density used in the calculation of the mixing-section Reynolds number were based on both the Aroclor and water phases; but since the viscosity of the mixture could not be determined, the viscosity of the continuous phase (Aroclor) was used for this calculation.

For Run No. 1 the values were

$Q_A = 0.293\ ft^3/min,$ $\quad D = 0.0208\ ft,$

$Q_W = 0.0732\ ft^3/min,$ $\quad \rho_A = 85.5\ lb/ft^3,$

$Q = 0.3662\ ft^3/min,$ $\quad \rho_W = 61.2\ lb/ft^3,$

$A = 1.02 \times 10^{-3}\ ft^2,$ $\quad \mu_A = 3.36 \times 10^{-3}\ lb/ft/sec.$

The results are

$$u_{av} = Q/A$$

$$= 0.3662\ \frac{ft^3}{min} \times \frac{min}{60\ sec} \times \frac{1}{1.02 \times 10^{-3} ft^2} = 5.99\ ft/sec;$$

$$\rho_{av} = \frac{1}{\frac{C_0}{\rho_W} + \frac{1-C_0}{\rho_A}}$$

$$= \frac{1}{\frac{15.2}{61.2} + \frac{84.8}{85.5}} = 80.5\ lb/ft^3\ ;$$

$$N_{Re} = \frac{Du\rho}{\mu}$$

$$= 0.0208\ ft \times 5.99\ \frac{ft}{sec} \times 80.5\ \frac{lb}{ft^3} \times \frac{1\ ft\ sec}{3.36 \times 10^{-3}\ lb.}$$

$$= 2990.$$

B. Physical Properties of Aroclor 1248

Aroclor 1248 is a heat-transfer medium made by the Monsanto Chemical Company. It is essentially tetrachlorobinphenyl with very small amounts of both lower and higher chlorinated biphenyls. Its physical properties are as follows.

(a) Density:[17]

Temperature (°C)	Density (g/cm^3)
30	1.44
60	1.41
88 (190°F)	1.382
100	1.37

(b) Viscosity:[17]

Temperature (°C)	Viscosity (cp)
30	112
60	17.5
88 (190°F)	6.0
100	4.2

(c) Interfacial Tension

The interfacial tension was determined by Graham with an interfacial tension meter.[11]

Interfacial tension of Aroclor against water at 20°C equals 44.6 dynes/cm.

(d) Solubility

Graham determined the solubility of water in Aroclor 1248 by titrating with Karl Fischer reagent. He presents a plot of concentration of water (mole %) as a function of temperature. From this plot one finds the solubility of water at 190°F is 1.3 mole %.

C. Determination of Water in Aroclor

Karl Fischer reagent was used to analytically determine the concentration of water in the samples taken from the Aroclor phase. The general procedure for preparing this reagent and its use in the determination of water are presented in detail by Mitchell and Smith.[18] Graham[11] summarizes their method and applies it to the Aroclor-water system. He discusses the important aspects of:

(a) the nature of the Karl Fischer reagent,

(b) the preparation of the Karl Fischer reagent,

(c) apparatus,

(d) standardization of the Karl Fischer reagent, and

(e) titration of water in Aroclor.

The procedure outlined by Graham was followed in the experiment reported here.

D. Nomenclature

A = total cross-sectional area of the mixing section (ft^2)

C_W = insoluble water concentration in the Aroclor phase (wt %)

C_0 = initial water concentration present in feed to the settler (wt %)

D = diameter of each of the mixing section tubes (ft)

g = gravitational acceleration

L = settler length (ft)

L_E = emulsion layer length (in.)

N_{Re} = Reynolds number in the mixing section

Q_A = Aroclor flow rate (ft^3/min)

Q_W = water flow rate (ft^3/min)

Q = $Q_A + Q_W$, total flow rate to settler (ft^3/min)

r = dispersed droplet radium (cm)

u = average velocity in mixing pipes (ft/min)

u_∞ = terminal settling velocity of dispersed droplets (cm/sec)

V_i = maximum emulsion layer velocity (ft/min)

w = apparent weight of drop

Z_A = depth of Aroclor layer in settling section (in.)

θ_{nm} = no-mixing residence time, (volume of phase)/(volumetric flow rate) (min)

θ_{exp} = minimum time for injected salt to reach settler exit (min)

μ = viscosity of injected liquid

μ_c = viscosity of continuous phase

μ_d = viscosity of dispersed phase

σ_I = interfacial tension

ρ_A = density of Aroclor (lb/ft^3)

ρ = density of water (lb/ft^3)

$\Delta\rho$ = difference in density between dispersed and continuous phases

REFERENCES

1. H. P. Meissner and B. Chertow, Ind. Eng. Chem. 38, 856 (1946).
2. W. Clayton, The Theory of Emulsions and their Technical Treatment (The Blakiston Company, Inc., New York, 1954), Chapter XI.
3. W. N. Bond and D. A. Newton, Phil. Mag. 5 series 7, 794 (1928).
4. S. Hu and R. C. Kinter, Am. Inst. Chem. Engrs. J. 1, 42 (1955).
5. A. J. Klee and R. E. Treybal, Am. Inst. Chem. Engrs. J. 2, 444 (1956).
6. J. J. Bickerman, J. Phys. Chem. 56, 164 (1952).
7. E. G. Cockbane and T. S. Roberts, J. Colloid Sci. 18, 440 (1953).
8. L. E. Nielsen, R. Wall, and G. Adams, J. Colloid Sci. 13, 441 (1958).
9. Sidney B. Lang, A Hydrodynamic Mechanism for the Coalescence of Liquid Drops (Ph. D. Thesis), UCRL-10097, May 1962.
10. D. H. Putney, Sulfuric Acid Alkylation of Paraffins, in Advances In Petroleum Chemistry and Refining, K. A. Kobe and J. J. McKetta, Jr., Eds. (Interscience Publishers, Inc., New York, 1959), p. 220.
11. Robert J. Graham, Separation of Immiscible Liquids by Gravity Settling and Induced Coalescence (M. S. Thesis), UCRL-10048, Feb. 1962.
12. J. O. Hinze, Am. Inst. Chem. Engrs. J. 1, 289 (1955).
13. E. G. Richardson, J. Colloid Sci. 5, 404 (1950).
14. T. W. F. Russell and M. E. Charles, Can. J. Chem. Eng. 37, 18 (1959).
15. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenoma (John Wiley & Sons, New York, 1960), p. 54.
16. R. W. Forstrom, Liquid Holdup and Pressure Drop in Two-Phase Flow (M. S. Thesis) University of California, Berkeley, California, May 1961.
17. Aroclor 1248, Monsanto Chemical Company, St. Louis, Mo., 1955.
18. J. Mitchell and D. Smith, Aquametry (Interscience Publishers, Inc., New York, 1948), Chap. 2.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.