FLOTATION AND WASHING OF SLIMY GELATINOUS PRECIPITATES OF OXYGENATED METALS

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Donald Robert Parker
1958

This is to certify that the

thesis entitled

Flotation and Washing of Slimy Gelatinous
Precipitates of Oxygenated Metals

presented by

Donald Robert Parker

has been accepted towards fulfillment
of the requirements for

Master of Science degree in Chemical Engineering

C. C. DeWitt
Major professor

Date July 8, 1958

O-169

FLOTATION AND WASHING OF SLIMY GELATINOUS PRECIPITATES OF OXYGENATED METALS

by

DONALD ROBERT PARKER

AN ABSTRACT

Submitted to the School for Advanced Graduate Studies of
Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1958

Approved: C Fred Gurnham

ABSTRACT

This is a report of an investigation to examine the feasibility of using flotation as a method for washing slimy gelatinous precipitates. The precipitates studied were the hydroxides of magnesium, nickel, copper, cadmium, and zinc, and the hydrous oxides of aluminum, iron, manganese, chromium, and cobalt. Particular emphasis was placed upon the flotation and washing properties of gelatinous magnesium and aluminum.

Flotation of the precipitates was accomplished in a machine designed to cause flotation by release of dissolved air. The machine was similar in principle to the Sveen-Pedersen Saveall used in the paper industry for white water clarification.

Oleic acid was found to be effective as a collector for all the precipitates studied with the exception of cupric hydroxide. Cupric hydroxide was floated using eosin red dye as an activator and emulsified light machine oil as a collector.

Data are presented to show the relative efficiency of several organic acids as collector reagents. The influence of temperature upon collector efficiency and adherence during washing was also studied. Results indicate that at temperatures exceeding 120° F the gelatinous precipitates of aluminum and magnesium may be floated and washed three times with no appreciable loss of precipitate.

FLOTATION AND WASHING OF SLIMY GELATINOUS PRECIPITATES OF OXYGENATED METALS

by

DONALD ROBERT PARKER

A THESIS

Submitted to the School for Advanced Graduate Studies of
Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1958

ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. Clyde C. Dewitt for the guidance and encouragement which he gave throughout the course of this investigation.

Thanks are also due to the Dura-Metallic Corporation of Kalamazoo, Michigan, for their generous donation of a Dura-Seal air tight bearing for this work.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

The separation, grading, and purification of materials, is a problem with which engineers and in particular mining and chemical engineers are frequently confronted. To solve these problems vast sums are invested annually by many industries for milling and screening plants, filters, fractionation columns, settling basins, and many other types of separation equipment. The separation and purification of materials is a primary justification for the employment of thousands of chemical engineers. There is a continual search for more effective and economical means for the separation and purification of materials.

The principal of flotation provides in some industries, and in particular the mining industry, an effective, and in many cases, a very efficient means for the separation of materials. In the mining industry, where this principle is currently finding its primary application, it is being used, each year, for the concentration of 150,000,000 tons of non-ferrous ore in the Western Hemisphere alone.(4)

The application of this principle is no longer limited to the minerals industry however. The number of materials separated or concentrated by flotation has, in recent years, grown rapidly. Such diverse materials as coal, diamonds, sulfur, collodial oil, peas, seeds, paper mill white water wastes, dyes, certain bacteria, viruses, many types of industrial wastes, and sewage are being separated by flotation.(7) It appears that the method will come into even greater use as the horizons of technology and imagination are extended.

All materials which are not chemically inert may theoretically be concentrated by air flotation from liquids in which the finely divided materials are suspended. However, as is often the case, the breach between that which is theoretically possible, and that which is at present technologically feasible, is great.

The primary problem usually associated with flotation systems is a problem involving surface chemistry. In order to separate a desired particle by flotation, it is necessary to form on at least a portion of that particle, a surface which is sufficiently hydrophobic as to cause the particle to be held at a gas-liquid interface. It is often necessary that similar hydrophobic surfaces be absent from such foreign particles that are present as impurities. The technique for bringing about such a condition in the suspended material being separated is, in essence, the science of flotation.

The flotation technique, now known as gross flotation, was first demonstrated by the Norwegian engineer, Nils Pedersen, and patented in the United States in 1921(11). Pedersen's machine was also patented in Norway in 1924 and in Germany in 1925. Pedersen's machine was designed to recover white water waste from the Fourdrinier machines of the paper industry. This white water contained suspended fibers, rosin size, glue, casein, clay, and mineral pigments.

In Pedersen's machine, air at 30-45 p.s.i.g. was dissolved in the white water suspension. After a short time the pressure was released and the air coming out of solution as myriads of submicroscopic bubbles adsorbed on the surface of the white water particles, floating them, in a bubble-like blanket, to the surface of the liquid from whence they were removed mechanically. Pedersen's development was not immediately successful.

Pedersen's invention did not prosper until the introduction by Karl Sveen, another Scandinavian engineer, of an agglomerating material which came to be known as Sveen's glue. This glue was made from animal glue, rosin size, alum, and formaldehyde; the formaldehyde serving to prevent decomposition of the mixture. Sveen glue, when used in the Pedersen machine, materially aided the flotation process and the Sveen-Pedersen Saveall, as it became known, was soon adopted by the paper industry throughout much of Europe.

The Sveen-Pedersen Saveall was introduced into the United States in 1937. Two years later, August 17, 1939, Ward D. Harrison(11) presented a very complete description of the commercial operation of the Sveen-Pedersen Saveall before an assembly of the Technical Association of the Pulp and Paper Industries. He reported reduction in white water solids from 9 pounds to 0.3 pounds per thousand gallons in some cases. The utilization of the Sveen-Pedersen machine is now common in the United States paper industry. Its use effects a very considerable economy in material losses and avoids resultant stream pollution.

New uses are rapidly being found for the Sveen-Pedersen Saveall.

> Among these new usages are: the removal of oil from brines and water, recovery of fines from synthetic rubber polymerizing processes, concentration of citrus pulp, recovery of soap spills, recovery of fish protein, hydration of fruit skins, seeds, and stems; removal of emulsified oil from railroad round house waste water, removal of carbon from airplane engine cleaning water, removal of grease from meat packing wastes, removal of solids from beet sugar waste waters, removal of starch from water, removal of stillage solids from winery waste water, removal of fines from fermentation slops, removal of albuminoids from beet and cane sugar solutions, and removal of fine solids from sewage.(4)

Flotation Applied to Problem of Washing Slimy Precipitates

It is necessary in certain processes to filter and wash the slimy gelatinous precipitates of metallic oxides or hydroxides. This operation is a very difficult and time consuming task. Filtration of such precipitates is necessarily costly. Flotation of these precipitates would allow simultaneous separation from solution and washing to be combined in one operation. The demonstration of such a flotation procedure based on known flotation principles was a part of the main objective of the present investigation.

Scope of the Investigation

The purpose of this investigation was to examine the possibility of using the gross flotation technique for the washing of slimy precipitates of metallic hydroxides and hydrated metallic oxides. This work involved a study of the kind and amount of effective collector reagents for the efficient flotation of such precipitates in a machine designed to effect the release of air dissolved in water suspensions of such precipitates at pressures higher than atmospheric.

The gelatinous precipitates of magnesium hydroxide and hydrated aluminum oxide were chosen for a detailed study; these materials were considered to be representative of oxygenated slimy precipitates. Other hydrated metallic oxide precipitates were shown to be amenable to washing by the gross flotation technique.

CHAPTER II

EXPERIMENTAL EQUIPMENT

The primary item of equipment used in this investigation was a flotation machine especially designed for the project. (See Figures 1, 2, and 3).

This machine consisted of a pressure chamber built of standard pyrex glass pipe; this chamber was provided with an internal agitator. Air, under pressure, was applied to the base of the machine and bubbled up through the agitated suspension. The air at 80 p.s.i.g. was brought to the machine through copper tubing. An air filter preceded the valve regulating the air supply to the machine. This filter prevented the introduction of entrained oil into the pressure chamber of the machine.

Air pressure in the machine was regulated by means of a specially built relief valve. (See Figure 4). This valve consisted of a steel ball bearing which rode on a brass seat; it was weighted by means of a lever arm resting upon it. A sliding weight on the lever arm, held in place by a set screw, served as a pressure adjustment. During operation of the machine there was a continual flow of air through the chamber and contents, since the air supplied to the machine was at 80 p.s.i.g., whereas pressure in the chamber was held constant throughout all of the experimental work at 35 p.s.i.g.

The flotation machine and auxilary equipment.

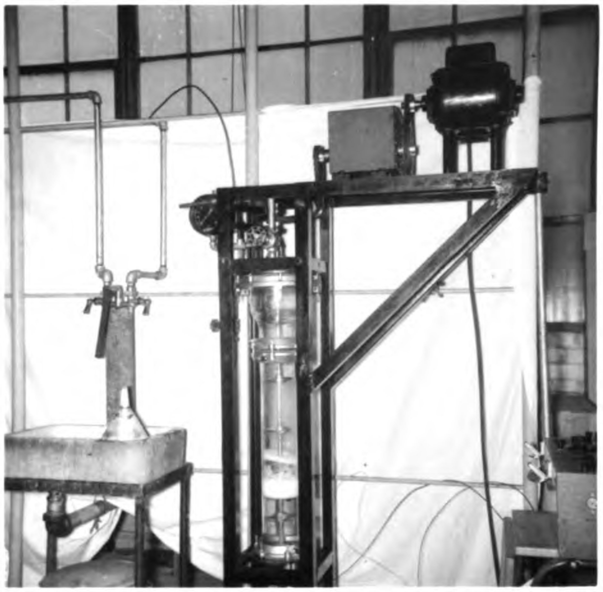


Figure 1.

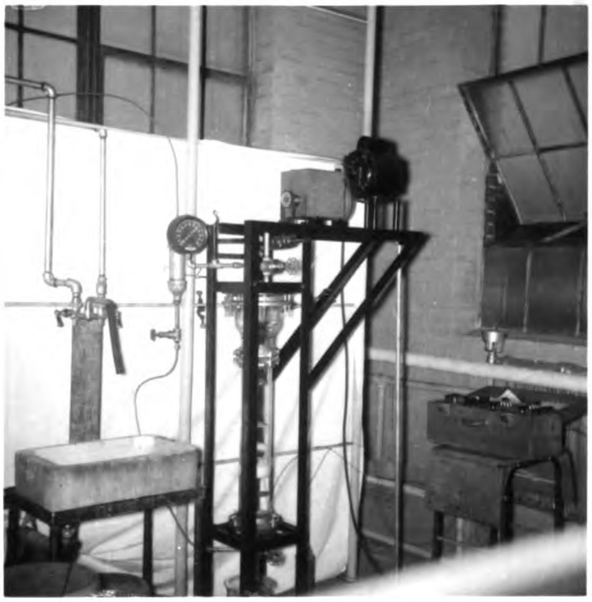


Figure 2.

Close-up of lower section of flotation machine.

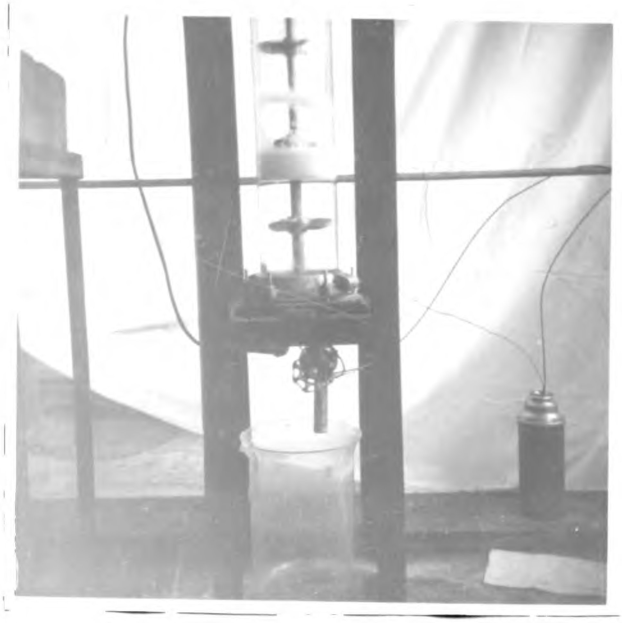


Figure 3.

Notice clarity of water beneath floated layer. The copper tubing air connection and thermocouple wires are shown here. The thermos flask containing ice and used as a reference junction with the potentiometer is also evident.

AIR PRESSURE RELIEF VALVE

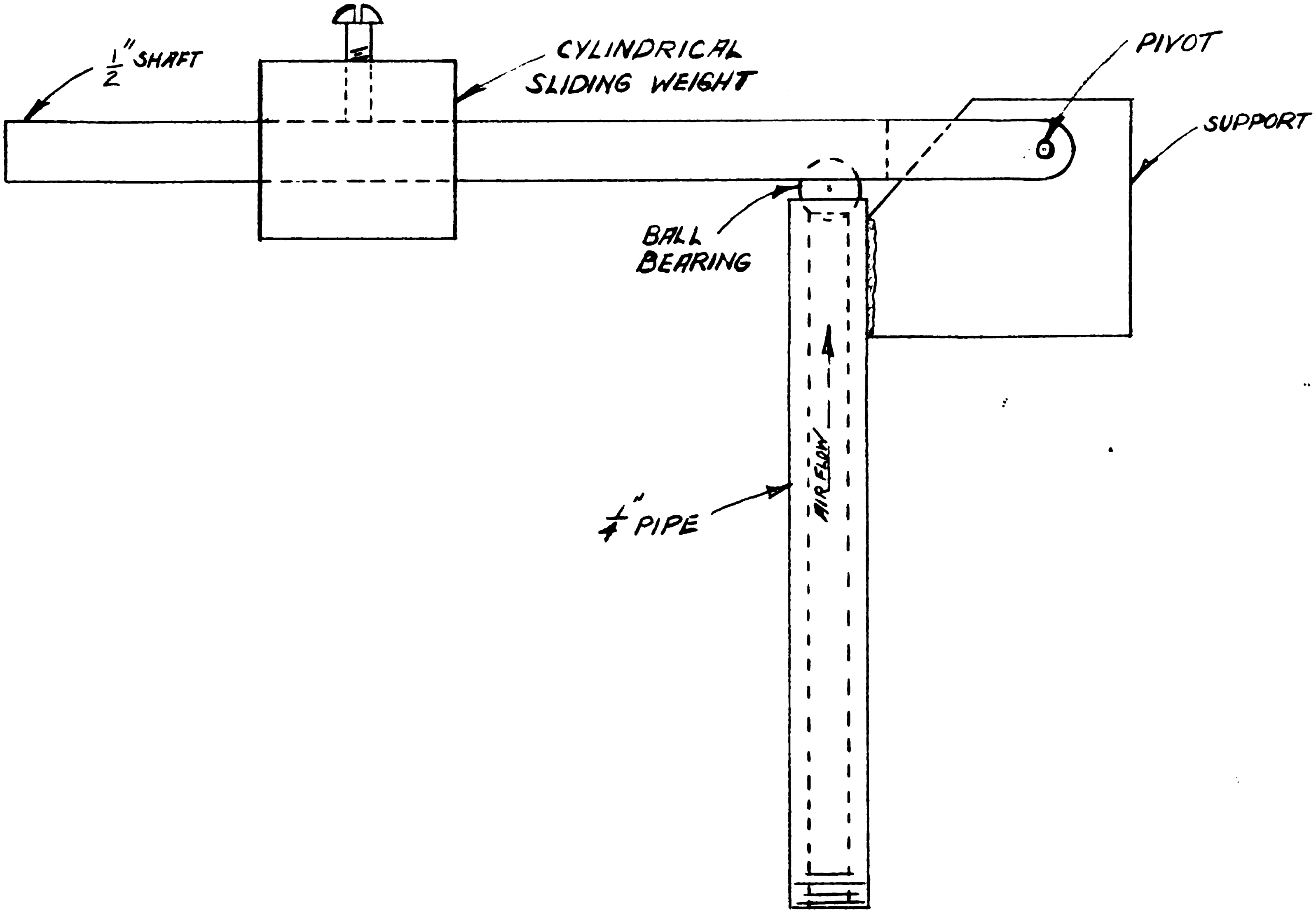


FIGURE 4

The internal agitator assembly consisted of a $\frac{1}{2}$" stainless steel shaft fitted with four stainless steel impellers equi-spaced along the shaft. The shaft was supported at the bottom end by a nylon bearing, and at the top end by a special pressure sealed bearing(5) through which it extended to the outside of the pressure chamber. Outside, and immediately above the chamber top, the agitator shaft was supported by a pillow block bearing which prevented the application of a lateral stress upon the sealed bearing. The agitator shaft was driven through a V-belt connection by means of a hydraulic speed reducer, which was in turn connected by a V-belt drive to a $\frac{1}{2}$ h.p. electric motor. The agitator was driven at approximately 300 R.P.M.

Materials entered the machine through a $\frac{1}{2}$" stainless steel pipe fitted with a $\frac{1}{2}$" stainless steel valve. A funnel served to direct liquids into the entrance pipe. Liquids were removed by gravity through a valved $\frac{1}{2}$" stainless steel pipe at the bottom of the pressure chamber. Both the top and the bottom of the pressure chamber were sealed by stainless steel plates, fitted with rubber gaskets. These plates held the pipes and the agitator shaft bearings. The pressurized air connection was attached to the bottom plate. The Pyrex pipe aluminum flanges were standard size.

CHAPTER III

PRELIMINARY EXPERIMENTAL WORK

Survey of Metallic Hydroxides and Hydrated Oxides

The first work undertaken was a survey to determine the floatability of many of the metals forming hydroxides and hydrated oxides.(17) It was found (see Table I) that the precipitated hydroxides of aluminum, magnesium, manganese, chromium, cobalt, cadmium, nickel, zinc, and iron could be floated using oleic acid as a collector. In the case of iron, it was found necessary to add a small quantity of activated silica, in order to make the oleic acid an effective collector. The hydrous hydroxide of bi-valent copper was floated with an emulsion of light machine oil in methanol after first activating the precipitate with eosin red dye which it adsorbs.(18) The flotation was difficult in this case.

Flotation Experiments with Digested Bauxite

Attempts were also made to float the residual red mud from the digestion of bauxite with caustic. A 50 pound sample of Suriname bauxite was generously donated for this work by the Aluminum Company of America.

The digestion was performed in an autoclave according to directions outlined by Dr. J. W. Newsome,(14) Chief of the Alumina and Chemicals Division, of the Aluminum Company of America. Several reagents were tried as collectors for the red mud but none of those tried was found to be effective.

TABLE I

Metallic hydroxides and hydrated oxides floated and reagent used.

Metal	Form of Precipitate	Precipitating Reagent	pH	Collector	Other Reagents (Activator)
Al^{+++}	Hydrous Hydrated Oxide	28% NH_4OH	9.8	Oleic Acid	
Mg^{++}	Hydrous Hydroxide	28% NH_4OH	11	Oleic Acid	
Fe^{+++}	Hydrous Oxide	28% NH_4OH	8	Oleic Acid	Activated Silica
Mn^{++++}	Hydrous Oxide	28% NH_4OH	9	Oleic Acid	
Cr^{+++}	Hydrous Oxide	28% NH_4OH	8	Oleic Acid	
Co^{++}	Hydrous Oxide	NaOH	8	Oleic Acid	
Ni^{++}	Hydrous Hydroxide	NaOH	8	Oleic Acid	
Cu^{++}	Hydrous Hydroxide	NaOH	8	Emulsified light oil in methanol	Eosin red dye in methanol
Cd^{++}	Hydrous Hydroxide	NaOH	8	Oleic Acid	
Zn^{++}	Hydrous Hydroxide	NH_4OH	8	Oleic Acid	

During all of this preliminary work few measurements were taken of such variables as the quantity of reagent used, amount of material floated, or temperature. The purpose of this phase of the investigation was to determine whether or not these materials could be floated without undue difficulty, and with moderate reagent usage.

Experimental Variables

The primary experimental variables in this investigation were expected to be the following:

1. Concentration or total amount of precipitate
2. Type of collector reagent
3. Quantity of collector reagent
4. pH of suspension
5. Air pressure in the chamber
6. Air flow through the chamber
7. Speed of agitator
8. Temperature
9. Manner of release of air pressure
10. Manner of addition of reagent
11. Variations in tap water impurities content

The most important variables were expected to be the first five listed above. However, from the difficulties experienced in obtaining reproducible results, it became obvious that many of the significant variables are not listed above. The method of attack on this problem was essentially to maintain constant all known variables, with the exception of the one being tested.

The following is taken from Sutherland and Wark.(15)

> The number of flotation variables is large, and possible combinations of them are almost innumerable. The investigator must therefore elect to study those which he considers are most important. With little data to go on, different experimenters have stressed

the importance of different variables, and as a consequence there is available a considerable amount of reliable information. It is an unfortunate fact, however, that many researches have not only been valueless, but have actually hindered progress because of the failure of investigators to design experiments in which only one factor at a time was varied, or to demonstrate, by means of control tests, that one factor alone was responsible for the variations observed.

CHAPTER IV

PROCEDURE

Usual Procedure Followed in Making Individual Trial Flotation Tests on Gelatinous Aluminum and Magnesium

The magnesium hydroxide suspension was prepared by precipitating 9 grams of $MgCl_2.6H_2O$ dissolved in 1500 mls. of water, with 35 mls. of 28% ammonia. The hydrated aluminum oxide was prepared in similar fashion, using 9 grams of $Al_2(SO_4)_3.18H_2O$ dissolved in 1500 c.c. of water, and precipitated with 25 mls. of 28% ammonia. From this point on, the procedure used was the same with both materials.

The precipitated suspension was placed in the machine with the aid of a 5" funnel. A quantity of collector was then measured out into a 150 mls. beaker with a pipette graduated in tenths of a mililiter.

The measured quantity of reagent was then diluted with 100 mls. of warm water and added to the suspension already in the machine. To ensure that all of the reagent drained into the suspension, an additional 100 mls. of warm water was also added to the machine bringing the total volume to 1700 mls.

The $\frac{1}{2}$" valve was then closed and the ball bearing was put into place on the pop-off valve. Air was admitted into the machine by completely opening the air line valve. In this manner, a constant flow of air was obtained.

The air pressure in the chamber rapidly built up to the maximum allowed by the pop-off (relief) valve which throughout these experiments was set at 35 p.s.i.g. When this maximum pressure was reached the ball bearing was forced off its seat allowing excess air to escape. In operation, the action of the valve was intermittent, but regular, resulting in a sound not unlike that of a distant steam locomotive running at constant speed.

Immediately after opening the air valve, the agitator motor was switched on, and ninety seconds later a temperature reading was taken, by means of a potentiometer connected to a thermocouple placed in a thermocouple well situated at the base of the machine and extending 2" into the body of the fluid suspension.

The machine was then allowed to operate for a total period of ten minutes. The air inlet valve was then closed, the agitator motor was stopped, and the air pressure allowed to escape, by lifting, slightly, the weight lever arm on the pop-off valve. Another temperature reading was then taken, and the suspension was allowed to settle for ten minutes, at the end of which time a sample was withdrawn at the bottom, into a mason jar, which was immediately sealed to prevent the escape of ammonia from the sample. The escape of ammonia would have resulted in a change of pH, and consequently a change in the quantity of precipitate found in the sample upon analysis. A turbidity measurement was then made upon the sample by means of a Coleman(1a) Model 14 spectrophotometer to determine the concentration of the unfloated precipitate.

In this manner the effects of the type of reagent used, reagent quantity, and temperature upon flotation efficiency were determined.

CHAPTER V

EXPERIMENTAL SECTION

Reagents Tested as Collectors

The following (Table II) is a tabulation of reagents tested as collectors for gelatinous magnesium hydroxide and gelatinous aluminum oxide at an average temperature of 115°F.

All of the above reagents were added to suspensions in the machine as solutions in methanol with the exception of those marked with an asterisk. Those marked with an asterisk were added in water solution. The average temperature in these runs was 115°F.

The results presented in Table II indicate that under these test conditions [redacted] the organic acids were effective as collectors for magnesium hydroxide and hydrated aluminum oxide. It was therefore decided to concentrate further effort upon the determination of the quantity, of those acids listed in Table II, which would be required for effective flotation.

Water Emulsions of Oleic and Linoleic Acid

As it was a purpose of this investigation to determine the feasibility of using repeated flotation and washing as a means of purifying slimy precipitates, emulsions of the collector acids were first used for these tests in preference to the sodium soaps of the acids, as is quite commonly done in flotation practice, even though the collector would very

TABLE II

Reagents tested as collectors.

Reagent	Chemical Formula	Molecular Weight	Melting Point °C	Flotation Results
Acids				
Stearic	$CH_3(CH_2)_{16}COOH$	284.47	70	Very poor
Oleic	$C_8H_{17}CH{:}CH(CH_2)_7COOH$	282.45	14	Excellent
Linoleic	$C_{17}H_{31}COOH$	280.44	-9.5	Excellent
Myristic	$CH_3(CH_2)_{12}COOH$	228.36		Poor
Lauric	$CH_3(CH_2)_{10}COOH$	200.31	48	Good
10-Undecylenic	$CH_2{:}CH(CH_2)_8COOH$	184.27		Good in sufficient quantity
Capric	$CH_3(CH_2)_8COOH$	172.26	31.5	Good in sufficient quantity
Caprylic-n	$CH_3(CH_2)_6COOH$	144.21	16	Did not float
Caproic-n	$CH_3(CH_2)_4COOH$	116.16	-1.5	" " "
Other				
Stearyl alcohol				Did not float
Amyl alcohol				" " "
Phenol*				" " "
Dodecyl phenol				" " "
Cresol*				" " "
Diamylene				" " "
Pinene				" " "
Benzyl-trimethyl-ammonium hydroxide*				" " "
*Sodium lauryl sulphate				" " "
Potassium amyl xanthate				" " "

*Those marked with an * were added in water solution.

likely only account for a very small percentage of the total weight, if present as an impurity. This would allow the acid impurity to be driven out by combustion if the washed precipitate was subsequently calcined, whereas a sodium oxide might remain after calcination if a sodium soap of the acid were used as a collector.

Water emulsions of oleic and linoleic acid were prepared by first dissolving a small quantity of the acid in a large volume of methanol, and then adding water in small quantities with vigorous shaking of the mixture until a phase inversion occurred, resulting in an emulsion of the acid in water stabilized by methanol.

It was found to be almost impossible to duplicate the composition of these emulsions. The emulsions were never stable for any length of time and some acid always floated to the top upon standing. Some emulsions prepared would break down almost immediately and others would appear to remain stable for several days.

Turbidity Determination to Measure Flotation Results

Due to the large number of determinations which had to be made throughout this investigation it soon became apparent that a rapid means of measuring flotation results would have to be developed. Attempts were made initially to filter a known volume of a sample, taken from beneath the floated layer, through an asbestos matted Gooch crucible. However this method of determining unfloated residue was much too time consuming due to the gelatinous nature of the precipitate. It was therefore decided to use an indirect method consisting of a turbidity measurement with a Coleman(14) Model 14 spectrophotometer. This was feasible due to the lack of color of the precipitated gels of aluminum and magnesium.

The turbidity measurement was made using a tap water sample as a reference and assigning to this reference a value of 100% on the transmittance scale of the spectrophotometer. Distilled water gave a reading of 103% against the tap water reference. In cases of excellent flotation it was not unusual to obtain a value in excess of 102% with samples taken from beneath the floated layer. The explanation is, of course, that most of the colloidal material present in the tap water used (having been adsorbed or trapped by the floc particles) was removed by flotation.(2)

One objection to this method of analysis was that obvious differences existed in the floc particle size depending largely upon the time which the material was allowed to stand after agitation and also due in part to flotation conditions. As would be expected, particle size was found to have a large influence upon the spectrophotometer reading obtained with a given sample.

However this difficulty was easily overcome by the simple expedient of shaking the cuvette tubes to break up the flocculated precipitate into finer particles just before a spectrophotometer reading was taken. In this manner a turbidity reading could, with few exceptions, be duplicated within reasonable limits of error. Thorough shaking of the samples prior to reading the spectrophotometer was therefore absolutely essential. This was true of both the aluminum and the magnesium precipitates. It was also necessary to shake the sample bottles immediately prior to the pouring of a sample into a cuvette for analysis, to insure that a representative sample was obtained. All recorded readings were taken immediately after shaking the samples.

The cuvettes used in this work were standard Coleman Class B and the wavelength found most suitable was 500 A. This wavelength was used throughout the tests for both the magnesium and the aluminum precipitates. Care was taken to insure that the cuvettes were clean and free of moisture on the outside, and that they were properly aligned within the instrument before a reading was taken.

After establishing that the turbidity method might be a satisfactory means for measuring the concentration of unfloated precipitate, it was next necessary to determine the correlation between per cent transmittance measured and the actual quantity of suspended precipitate.

This was done by filtering measured volumes of samples, taken at various transmittance readings, through weighed asbestos matted Gooch crucibles. The filtered precipitate was oven dried at 100° C for approximately 48 hours and allowed to cool to room temperature in a desiccator. The

Gooch crucibles were then reweighed and the ratio of weight to volume filtered was computed.

The results were plotted with per cent transmittance along the vertical axis and the weight of unfloated precipitate per 1500 mls. of sample was plotted along the horizontal axis as shown in Figures 5 and 6. The volume of 1500 mls. was chosen because it was found that the total volume occupied by the floated material was approximately 200 mls. which when subtracted from the total volume of 1700 mls. in the machine, left a volume of 1500 mls. representing clarified water.

It was anticipated that a determination of the degree of hydration of the dried precipitate in the Gooch crucibles might be difficult. It was necessary to know the formula weight of the dried precipitate in order to calculate the equivalent amount of suspended material which it represented.

Examination of Figure 5 indicates that the dried precipitate corresponds quite closely to $Al_2O_3 \cdot 3H_2O$. This conclusion is drawn from the fact that 3.3 grams of $Al_2O_3 \cdot 3H_2O$ is equivalent to 9.0 grams of $Al_2(SO_4)_3 \cdot 18H_2O$ and that the curve corresponds closely to a weight in suspension of 3.3 grams at the no float point of about 10% transmittance. This result is not precise but is sufficiently indicative that calculations based upon it should have a fair degree of reliability.

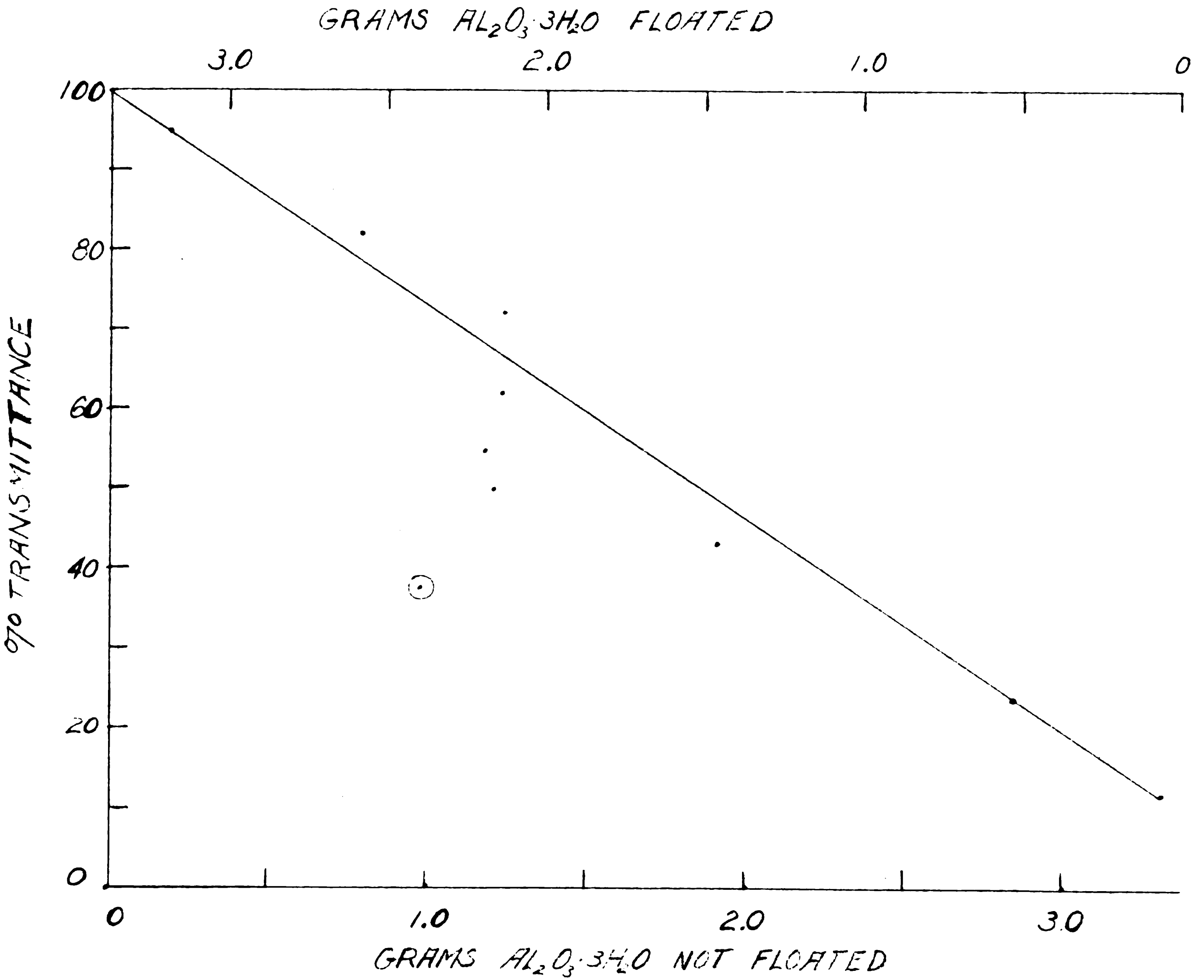

GRAMS $AL_2O_3 \cdot 3H_2O$ FLOATED
3.0
2.0
1.0
0
100
80
60
40
20
0
% TRANSMITTANCE
0
1.0
2.0
3.0
GRAMS $AL_2O_3 \cdot 3H_2O$ NOT FLOATED

FIGURE 5

TABLE III.

Hydrated aluminum oxide transmittance data.

Per Cent Trans-mittance	Volume Filtered (mls.)	Weight of Precipitate (Grams)	Weight per 100 mls. (Grams)	Weight per 1500 mls. (Grams)
95	75	0.0092	0.0123	0.19
81	50	0.0261	0.0522	0.78
72	50	0.0408	0.0816	1.22
62	50	0.0406	0.0813	1.21
55	50	0.0393	0.0786	1.18
50	50	0.0400	0.0800	1.20
43	50	0.0638	0.1276	1.91
38	50	0.0319	0.0638	0.96
24	25	0.0474	0.190	2.84

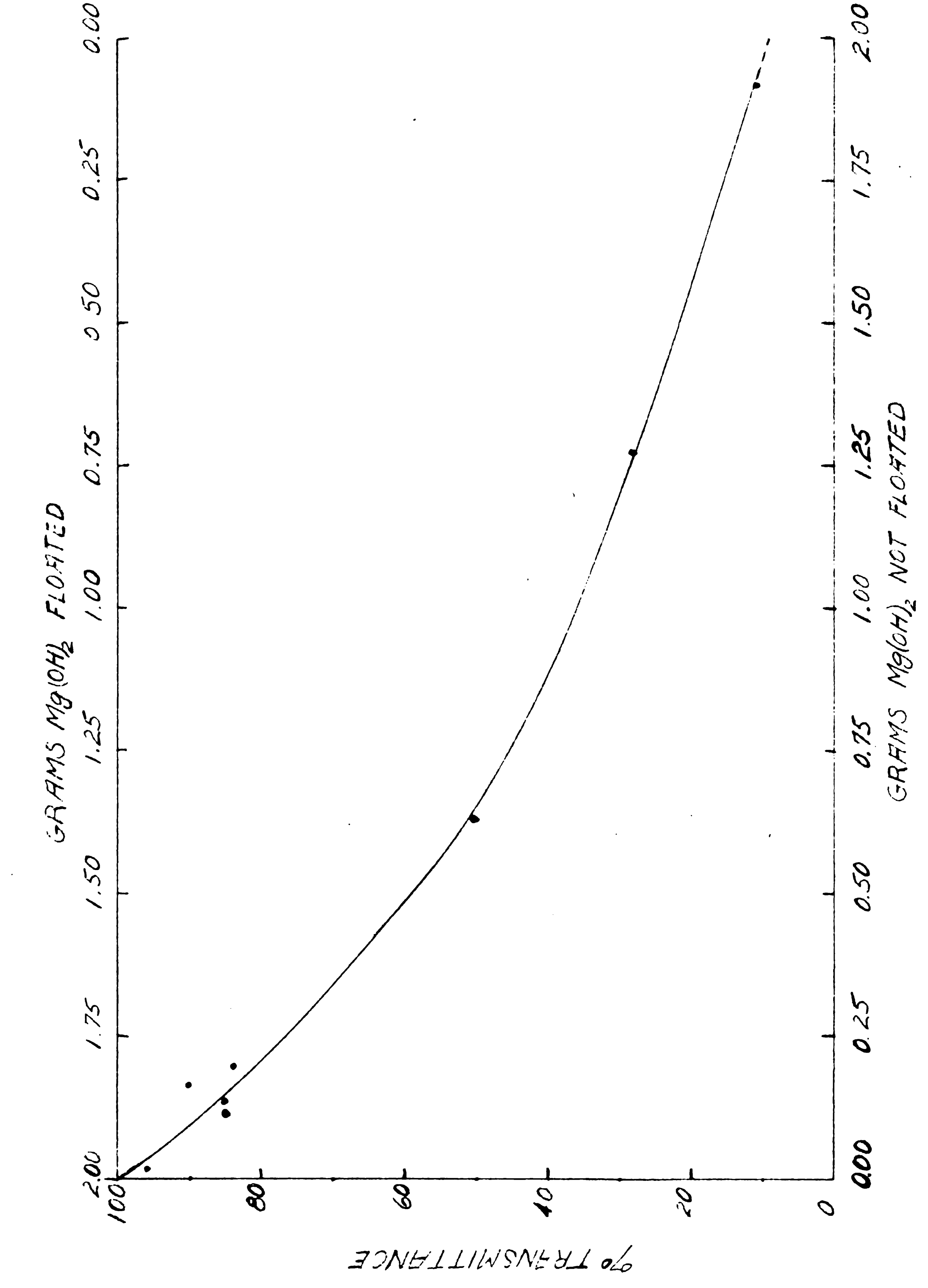

GRAMS Mg(OH)2 FLOATED
0.00
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
GRAMS Mg(OH)2 NOT FLOATED
0.00
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
% TRANSMITTANCE
100
80
60
40
20
0

FIGURE 6

TABLE IV.

Magnesium hydroxide transmittance data

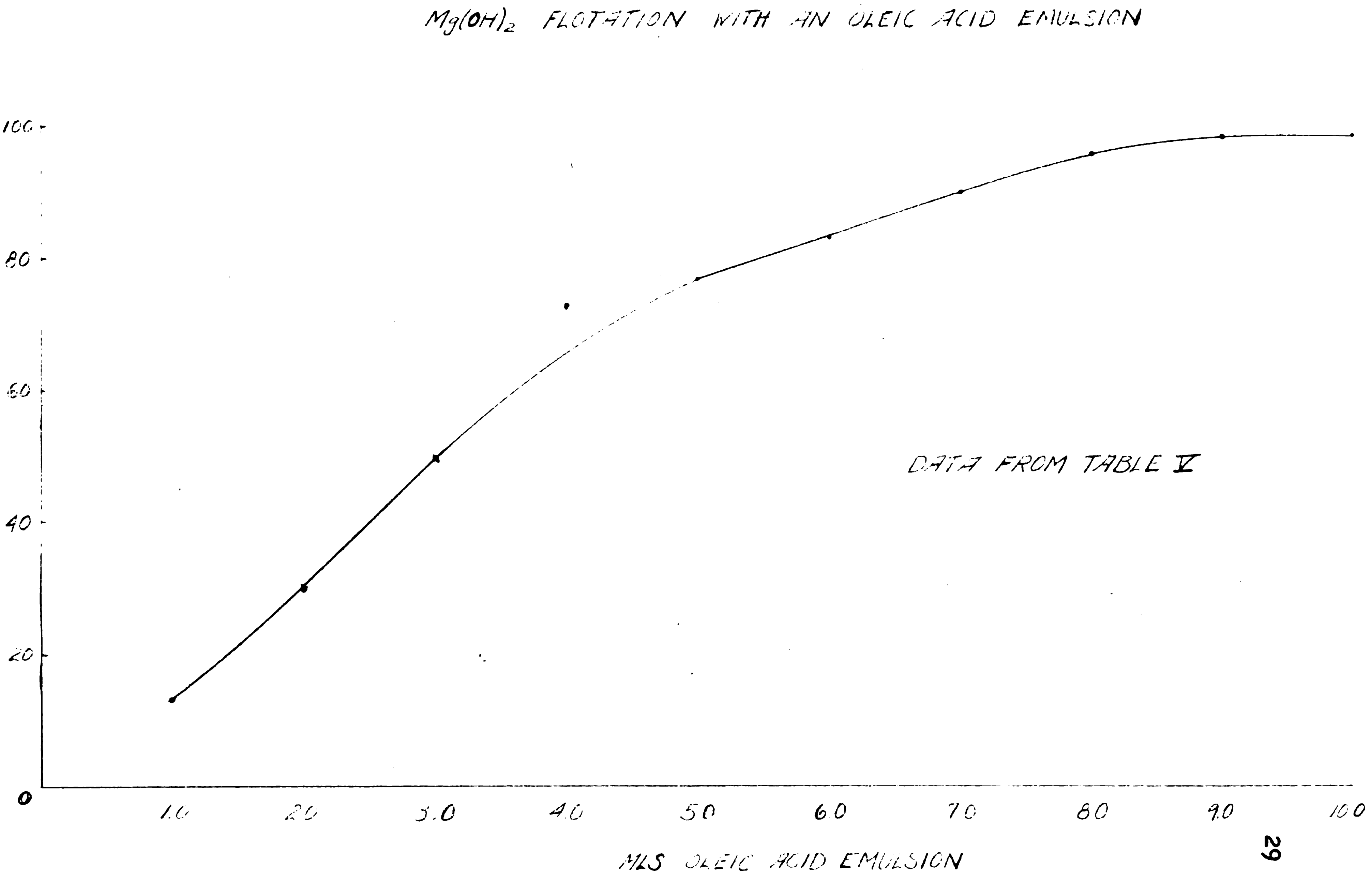
Per Cent Trans-mittance	Volume Filtered (mls.)	Weight of Precipitate (Grams)	Weight per 100 mls. (Grams)	Weight per 1500 mls. (Grams)
96	125	0.0015	0.0012	0.018
90	100	0.0105	0.0105	0.158
85	125	0.0100	0.0080	0.120
85	75	0.0057	0.0076	0.114
83	75	0.0128	0.0171	0.192
51	50	0.0209	0.0418	0.627
28	25	0.0212	0.0848	1.272
11	50	0.0639	0.1278	1.917

The transmittance curve of Figure 6 indicates a total weight equivalent to 2.0 grams at the no float point of about 10% transmittance. Since 9.0 grams of $MgCl_2.6H_2O$ is equivalent to 2.58 grams of $Mg(OH)_2$ it is apparent that some weight has been lost either by solubility or by partial dehydration of the $Mg(OH)_2$ to MgO. It is more likely that most of the weight lost represents a solubility loss since $Mg(OH)_2$ precipitates at a pH of 10.4 and a pH higher than this was difficult to maintain with ammonia, due to losses to the air which passed through the machine during agitation. Assuming that all the weight loss was due to solubility and further assuming that all hydrous water was removed by the oven drying, all calculations will be based upon the formula $Mg(OH)_2$ and the assumption of 2.0 grams of $Mg(OH)_2$ in suspension.

Flotation of Magnesium Hydroxide at 115° F Using an Oleic Acid Emulsion

Figure 7 shows the flotation results obtained using an oleic acid emulsion in floating magnesium hydroxide. The per cent transmittance measured on the spectrophotometer as previously described was plotted along the ordinate and the number of mls. of the oleic acid emulsion was plotted along the abscissa. The average initial temperature was 117° F.

Figure 8 illustrates the basic data of Figure 7 replotted to indicate the per cent $Mg(OH)_2$ floated as a function of the weight ratio of oleic acid to $Mg(OH)_2$.

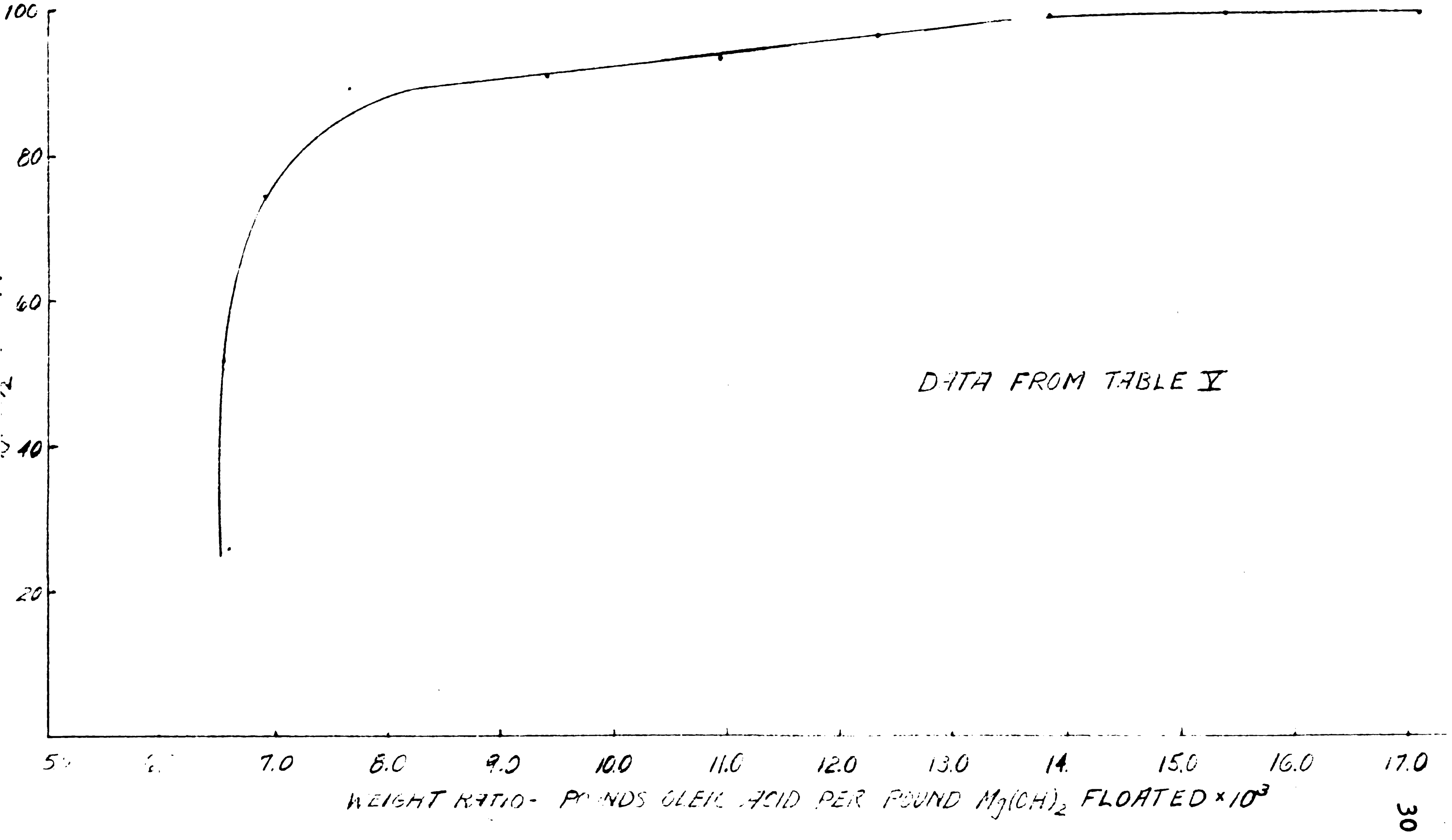


$Mg(OH)_2$ FLOTATION WITH AN OLEIC ACID EMULSION

DATA FROM TABLE V

FIGURE 7

$Mg(OH)_2$ FLOTATION WITH AN OLEIC ACID EMULSION



DATA FROM TABLE V

FIGURE- 8

TABLE V.

Magnesium hydroxide flotation with an oleic acid emulsion containing approximately 1.0 ml. per 200 mls. solution.

Average temperature - 117°F

Reagent Mls.	Equivalent Oleic Acid (Grams) x10^3	Initial Temper-ature	Per Cent Trans-mittance	Total $Mg(oH)_2$ Floated (Grams)	Per Cent of Total Floated	Weight Ratio Oleic/$Mg(oH)_2$ x10^3
1	4.3	126	13	0.65	26.0	6.6
2	8.5	107	30	1.30	52.0	6.6
3	12.8	115	50	1.85	74.0	6.9
4	17.1	116	73	2.22	88.8	7.7
5	21.4	116	77	2.27	90.8	9.4
6	25.6	112	83	2.34	98.5	11.0
7	29.9	116	90	2.42	96.7	12.4
8	34.2	118	96	2.47	98.7	13.9
8	34.2	108	96	2.47	98.7	13.9
9	38.4	113	98.5	2.49	99.6	15.4
10	42.7	120	98.5	2.49	99.6	17.1

The data was converted by means of the transmittance curve for $Mg(OH)_2$ given in Figure 6.

The oleic acid emulsion used had an approximate oleic acid concentration of one part acid per two hundred parts by volume. It was made by the procedure previously described, using 5.0 mls. of oleic acid, 300 mls. of methanol, and with sufficient water to bring the final volume to 1000 mls. It was not stable as previously noted.

Figure 9 shows flotation results obtained with an oleic acid soap solution which was prepared by dissolving 10 mls. of oleic acid in 250 mls. of methanol, adding 2.0 grams of sodium hydroxide, and then adding water slowly and with mixing until a final volume of 1000 mls. was reached. A portion of this soap solution was then diluted by mixing 200 mls. of it with 200 mls. of water resulting in a sodium oleate solution containing the equivalent of 1 ml. of oleic acid in 200 mls., or one part per two hundred parts by volume. This solution was stable as would be expected.

Figure 10 illustrates the basic data of Figure 9 replotted to indicate the per cent $Mg(OH)_2$ floated as a function of the weight ratio of oleic acid to $Mg(OH)_2$. The data was converted by means of the transmittance curve of Figure 6.

Figures 11 and 12 show the flotation results obtained in floating $Al_2O_3.nH_2O$ with a lauric acid soap prepared by dissolving 2.0 grams of lauric acid in 100 mls. of methanol,

MG(OH)$_2$ FLOTATION WITH AN OLEIC ACID SOAP **SOLUTION**

(SOLUTION CONTAINED 1 ML. OLEIC ACID PER 200 MLS. OF SOLUTION)

AVERAGE TEMPERATURE 114°F

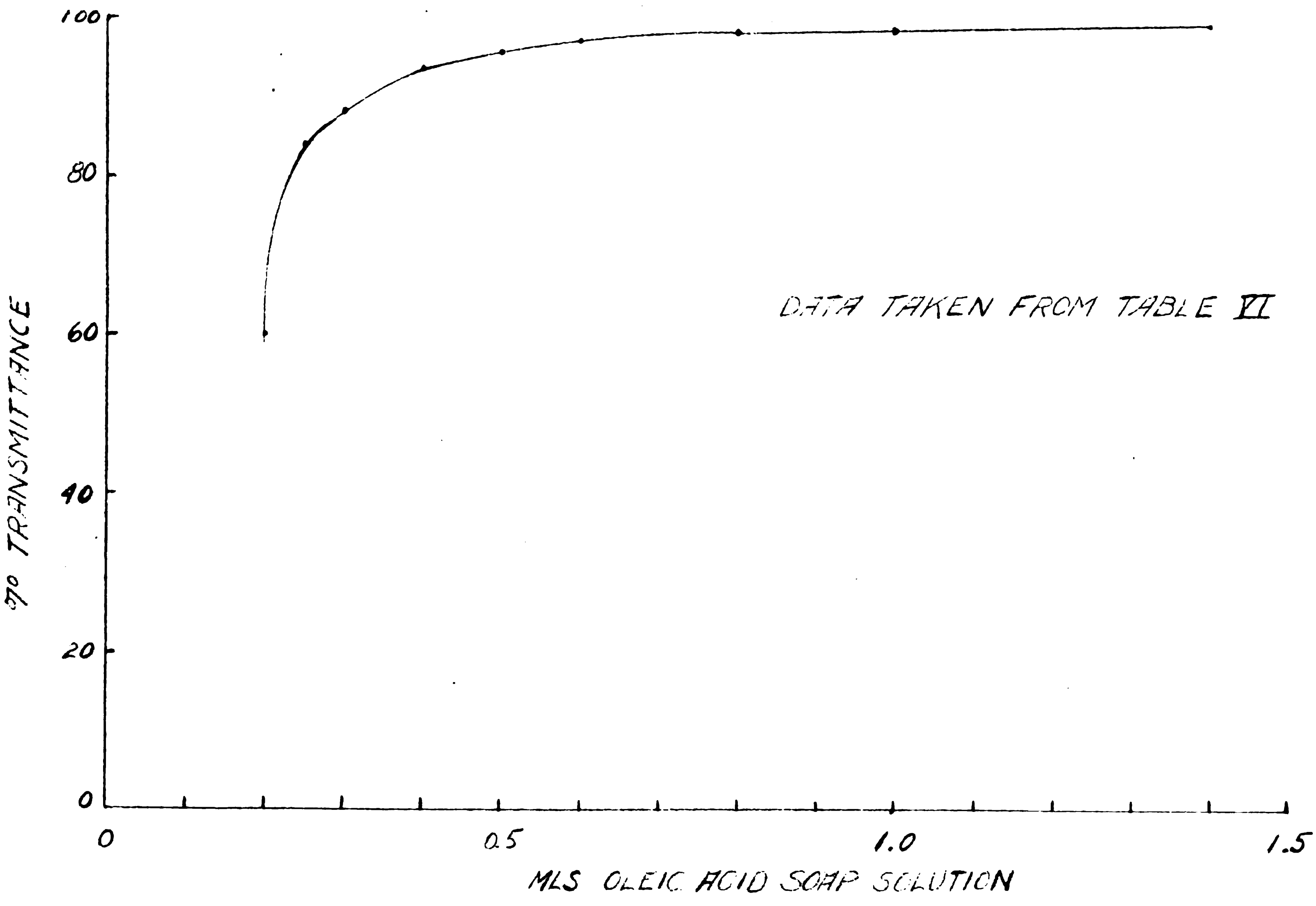


FIGURE 9

$Mg(OH)_2$ FLOTATION WITH AN OLEIC ACID SOAP SOLUTION
(CONTAINED 1ML OLEIC ACID PER 200 MLS. SOLUTION)

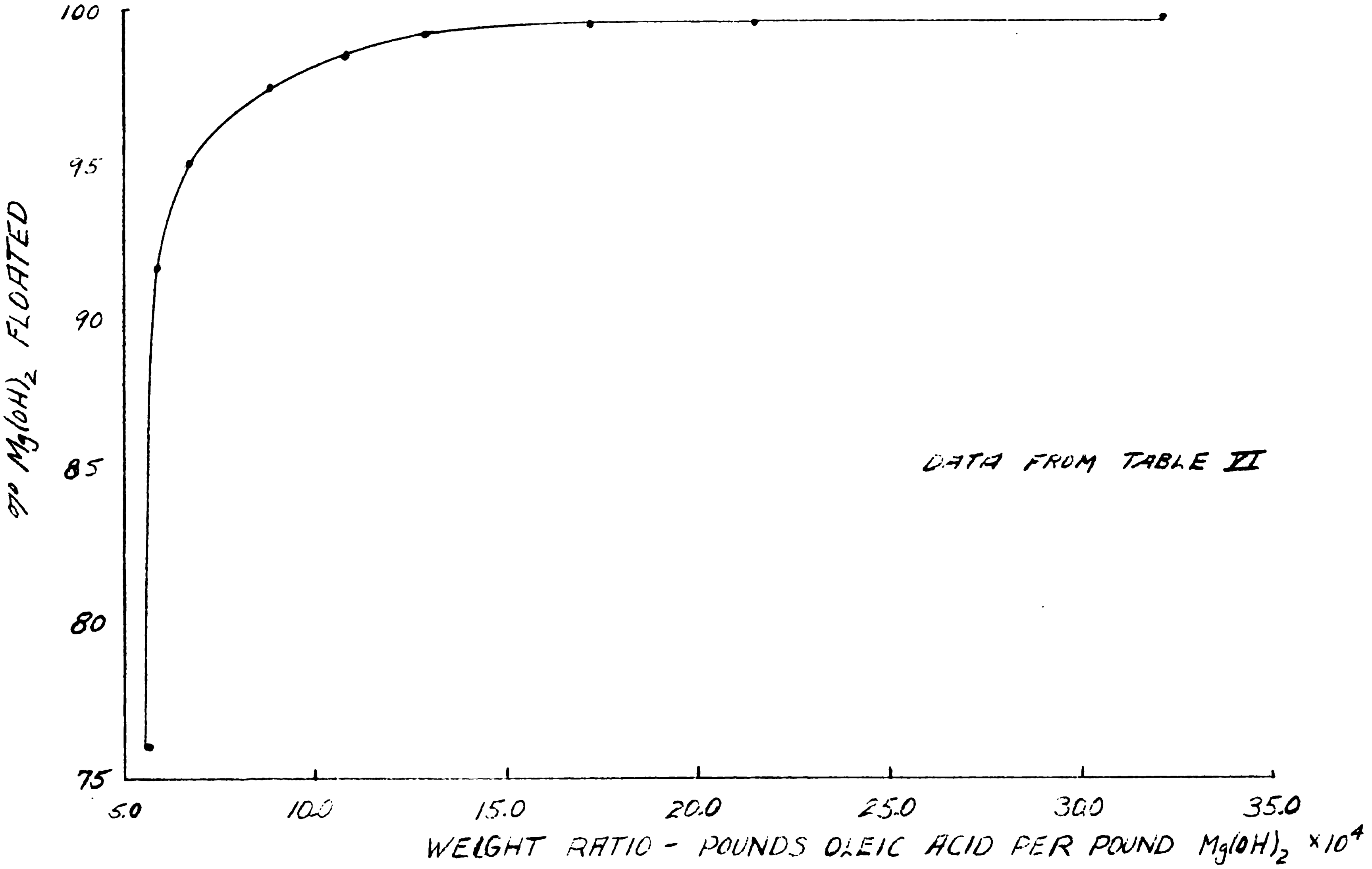


FIGURE 10

TABLE VI.

Magnesium hydroxide flotation with an oleic acid soap containing 1.0 ml. oleic acid per 200 mls. solution.

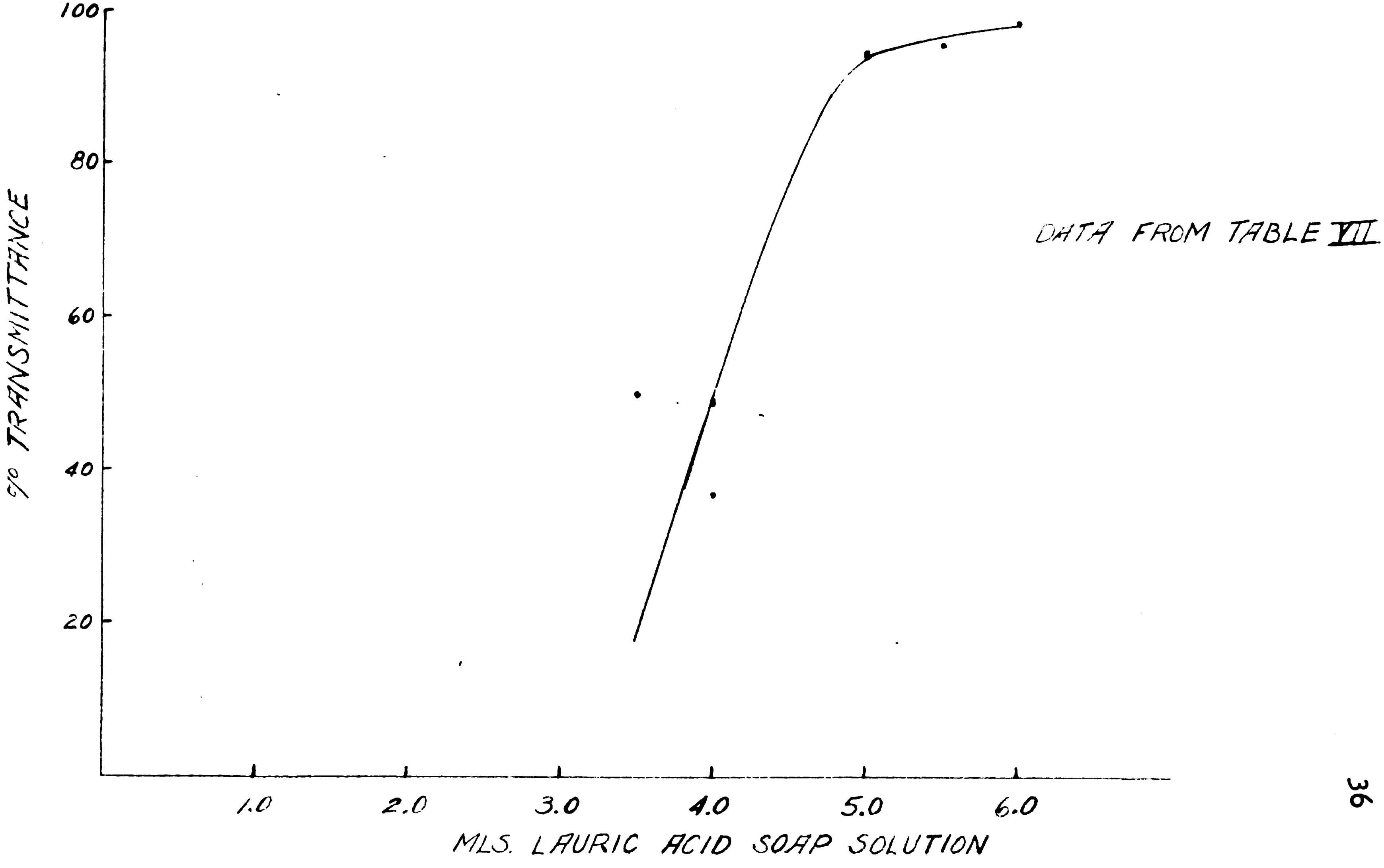
Average temperature - 114° F

Reagent Mls.	Equivalent Oleic Acid (Grams) x10⁴	Initial Temperature (°F)	Per Cent Transmittance	Total $Mg(oH)_2$ Floated (Grams)	Per Cent of Total Floated	Weight Ratio Oleic/$Mg(oH)_2$ x10⁴
0.20	8.5	114	60	1.53	76.5	5.6
0.25	10.7	112	83	1.84	92.0	5.8
0.30	12.8	114	88	1.90	95.0	6.7
0.40	17.1	114	93.6	1.95	97.5	8.8
0.50	21.3	115	95.7	1.97	98.5	10.8
0.60	25.6	115	97.2	1.98	99.0	12.9
0.80	34.1	115	98.5	1.99	99.5	17.2
1.00	42.7	113	98.5	1.99	99.5	21.5
1.00	42.7	116	98.5	1.99	99.5	21.5
1.50	64.0	108	99.0	1.99	99.5	32.1

$Al_2O_3 \cdot 3H_2O$ FLOTATION WITH A LAURIC ACID SOAP SOLUTION

(SOLUTION CONTAINED 10 GRAM LAURIC ACID PER 200 MLS.)

AVERAGE TEMPERATURE - 121°F



DATA FROM TABLE VII

FIGURE 11

$AL_2O_3 \cdot 3H_2O$ FLOTATION WITH A LAURIC ACID SOAP SOLUTION

(SOLUTION CONTAINED 1.0 GRAM LAURIC ACID PER 200 MLS.)

AVERAGE TEMPERATURE - 121°F

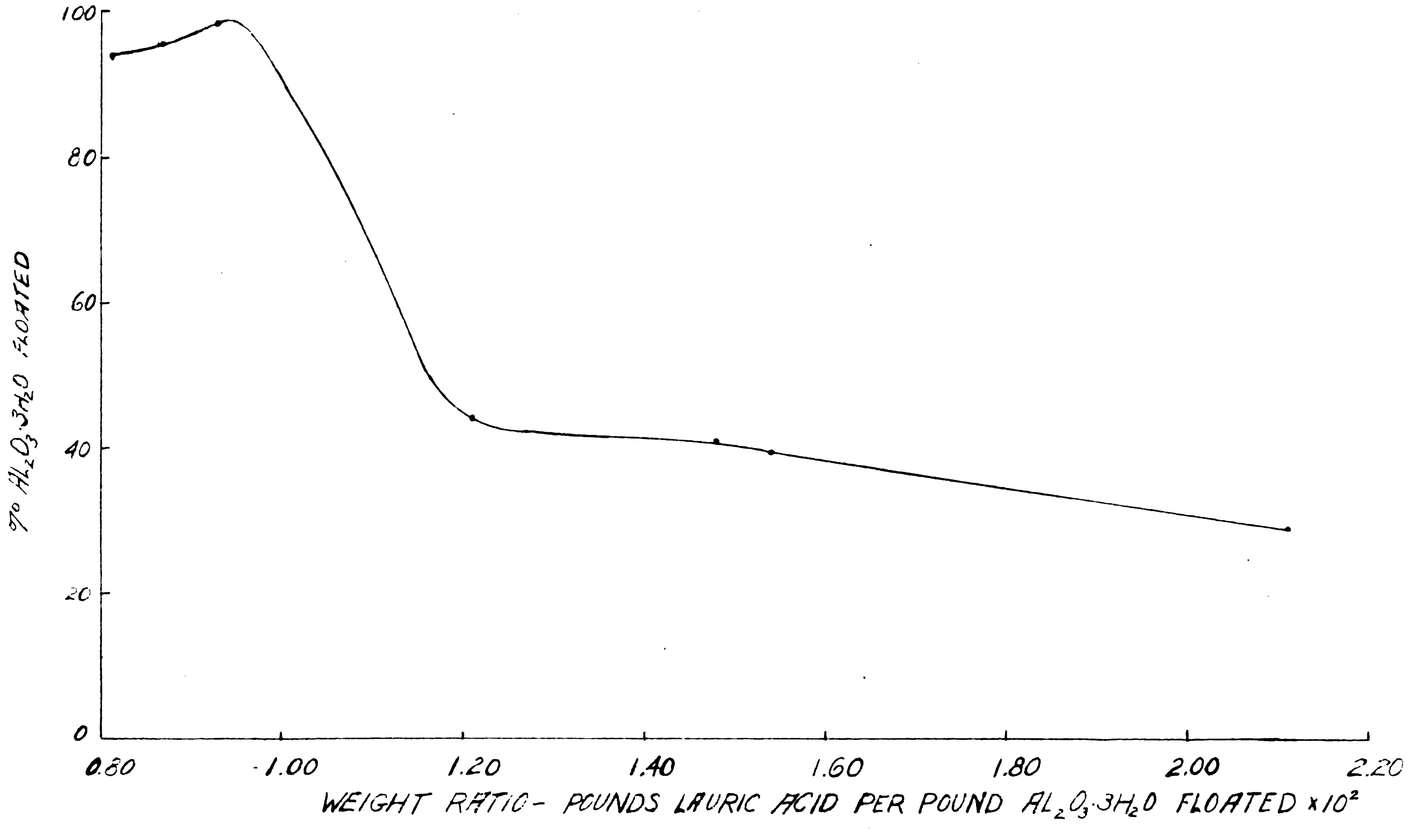


FIGURE 12

TABLE VII.

Hydrated aluminum oxide flotation using a lauric acid soap containing 1.0 gram lauric acid per 200 mls. of solution.

Average temperature - 121° F

Reagent Mls.	Equivalent Lauric Acid (Grams) x10^2	Initial Temperature (°F)	Per Cent Transmittance	Total $Al_2O_3.3H_2O$ Floated (Grams)	Per Cent of Total Floated	Weight Ratio Lauric/$Mg(OH)_2$
3.5	1.75	120	50	1.45	43.9	1.21
4.0	2.00	122	37	0.95	28.8	2.11
4.0	2.00	125	48	1.35	40.8	1.48
4.0	2.00	120	47	1.30	39.4	1.54
5.0	2.50	122	94.5	3.10	93.9	0.81
5.5	2.75	120	96	3.15	95.5	0.87
6.0	3.00	121	98	3.23	98.5	0.93

adding 2.0 grams of sodium hydroxide, and adding water slowly with mixing until all of the lauric acid had been saponified and a final volume of 400 mls. was reached. This lauric acid sodium soap solution therefore contained 1.0 gram of lauric acid per 200 mls.

The curve of Figure 12 is somewhat misleading and requires explanation. The curve might be interpreted to indicate that flotation improved as the ratio of lauric acid to $Mg(OH)_2$ decreased. All the evidence available however, strongly suggests that the ratio of lauric acid to $Mg(OH)_2$ floated is high when the total amount of lauric acid present is low due to the relatively large solubility of lauric acid in the water solution, and that after the solubility requirement of lauric acid in water has been satisifed the behavior is analogous to that of oleic acid as shown in Figure 10. In both cases a maximum of flotation is indicated at definite reagent concentrations.

Figures 13 and 14 show the flotation results obtained in floating $Mg(OH)_2$ with the same lauric acid soap used in floating the $Al_2O_3.mH_2O$ of Figures 11 and 12.

<u>Effect of Temperature on Efficiency of Collector</u>

Figure 15 shows the effect of varying temperature upon the flotation of $Mg(OH)_2$ using the same emulsion used previously in obtaining the curves of Figures 7 and 8 for the flotation of $Mg(OH)_2$. The effectiveness of 5.0 mls. of the

$Mg(OH)_2$ FLOTATION WITH A LAURIC ACID SOAP SOLUTION

(SOLUTION CONTAINED 10 GRAM LAURIC ACID PER 200 MLS.)

AVERAGE TEMPERATURE
120°F

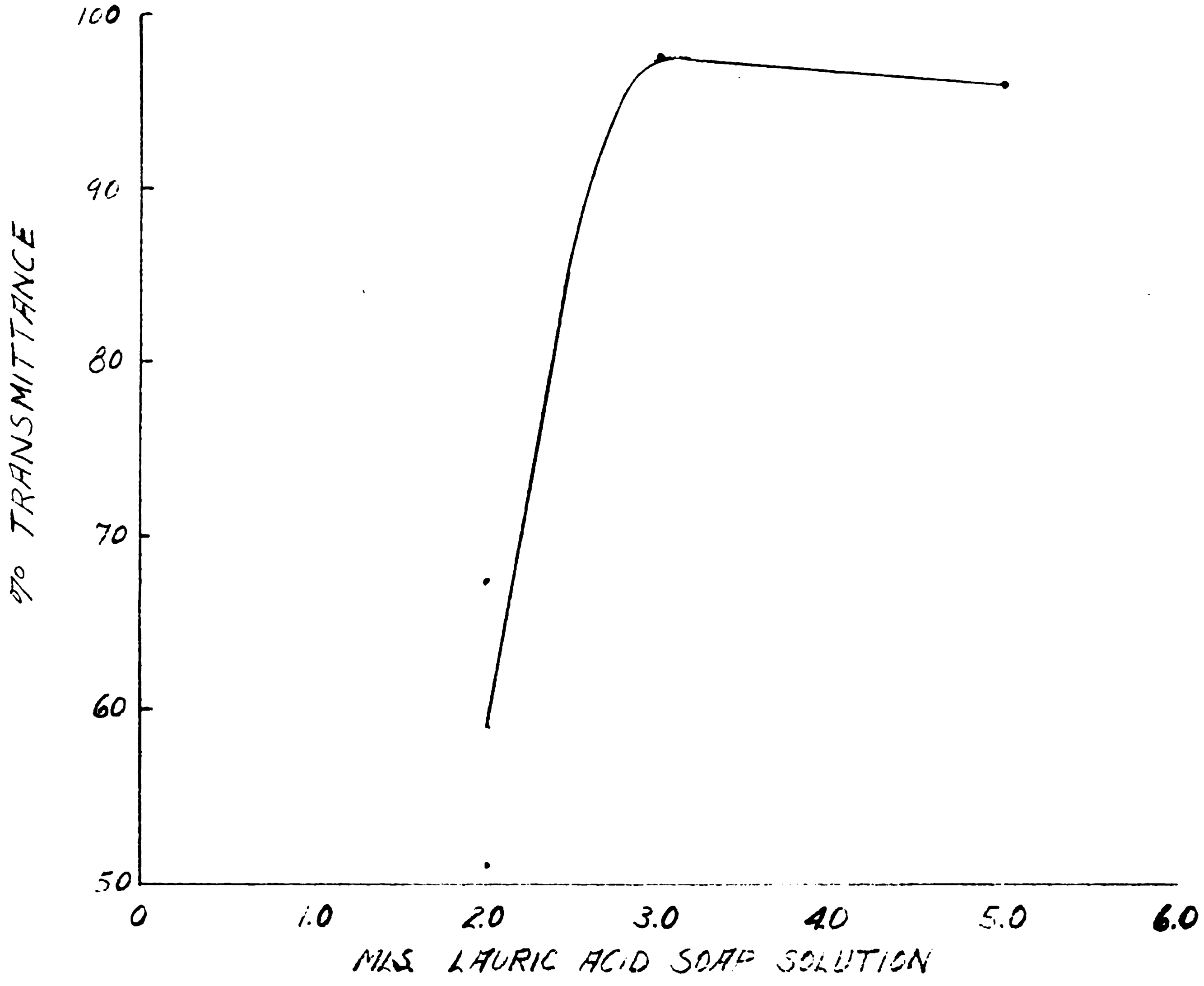


FIGURE - 13

$Mg(OH)_2$ FLOTATION WITH A LAURIC ACID SOAP SOLUTION

(SOLUTION CONTAINED 1.0 GRAM LAURIC ACID PER 200 MLS.)

AVERAGE TEMPERATURE - 120°F

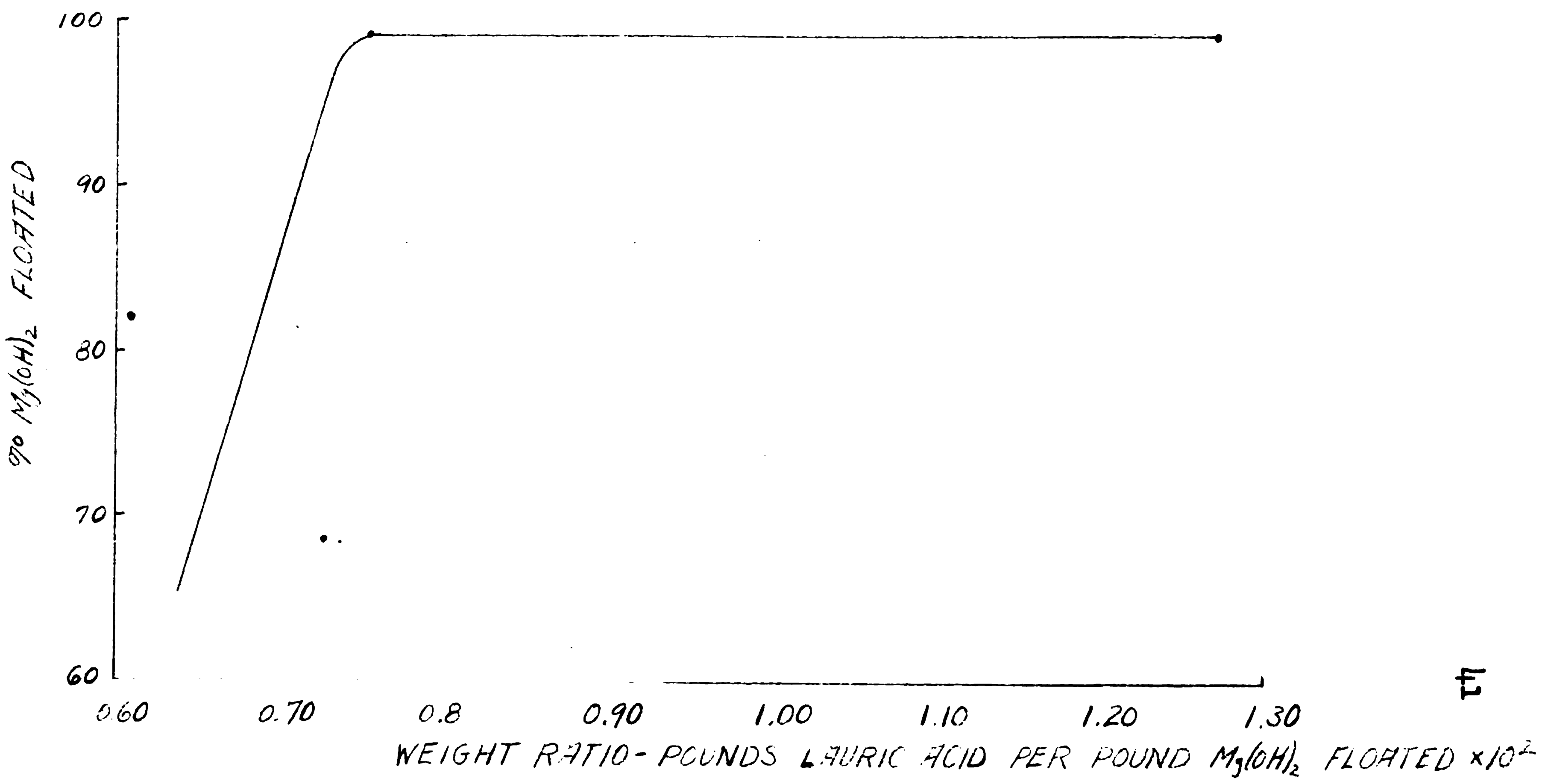


FIGURE 14

TABLE VIII.

Magnesium hydroxide flotation using a lauric acid soap solution containing 1.0 gram of lauric acid per 200 mls. of solution.

Average temperature - 120°F

Reagent Mls.	Equivalent Lauric Acid (Grams) $x10^2$	Initial Temperature	Per Cent Transmittance	Total $Mg(oH)_2$ Floated (Grams)	Per Cent of Total Floated	Weight Ratio Lauric/$Mg(oH)_2$ $x10^2$
5.0	2.5	118	96	1.97	98.5	1.27
3.0	1.5	121	97.5	1.98	99.0	0.76
2.0	1.0	121	51.0	1.37	68.5	0.73
2.0	1.0	118	67.5	1.64	82.0	0.61

EFFECT OF TEMPERATURE ON FLOTATION OF $Mg(OH)_2$

(REAGENT - OLEIC ACID EMULSION CONTAINING APPROXIMATELY 1 ML OLEIC ACID PER 200 MLS.)

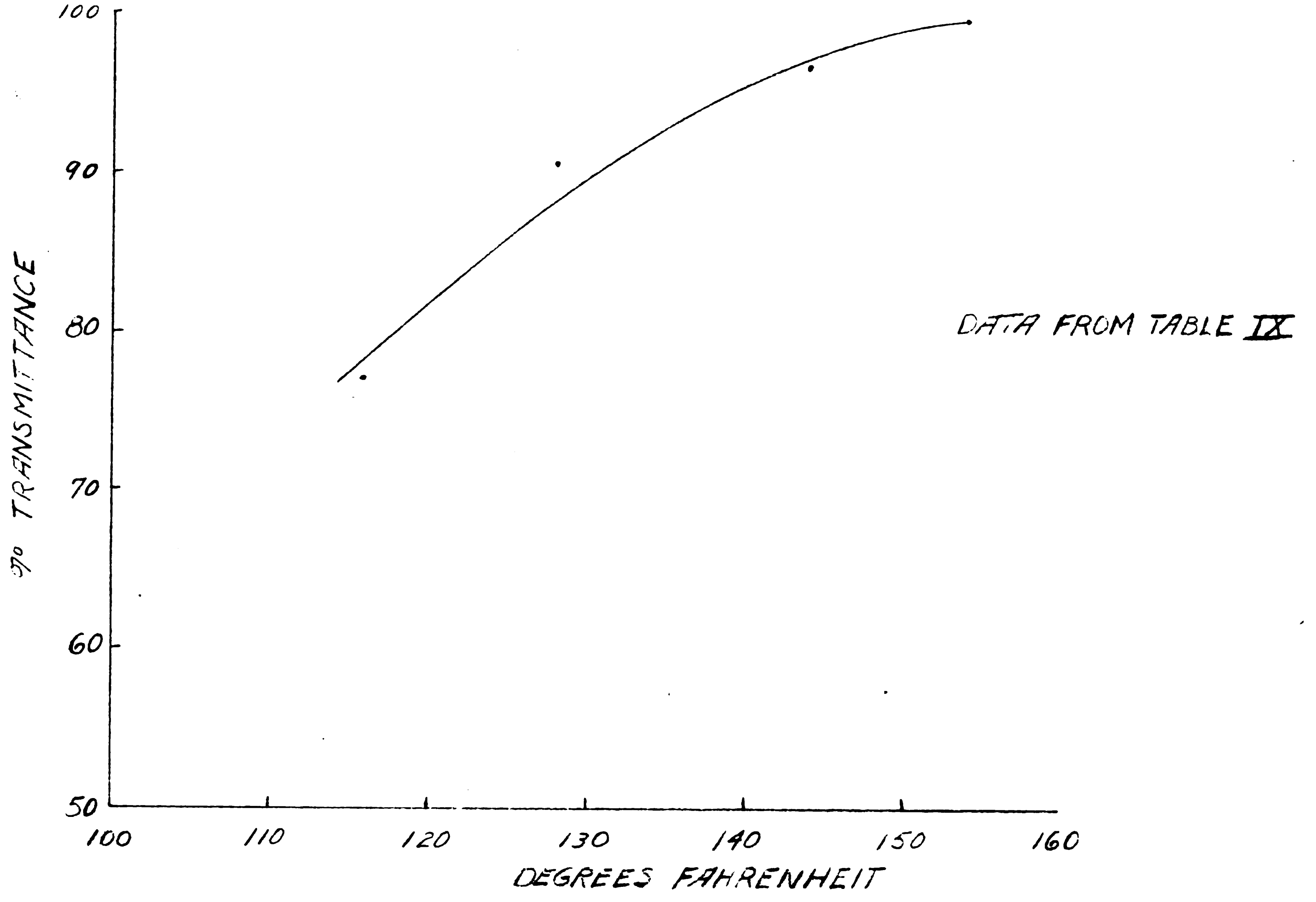


FIGURE 15

EFFECT OF TEMPERATURE ON FLOTATION OF $Mg(OH)_2$

(REAGENT- OLEIC ACID EMULSION CONTAINING APPROXIMATELY 1 ML OLEIC ACID PER 200 MLS.)

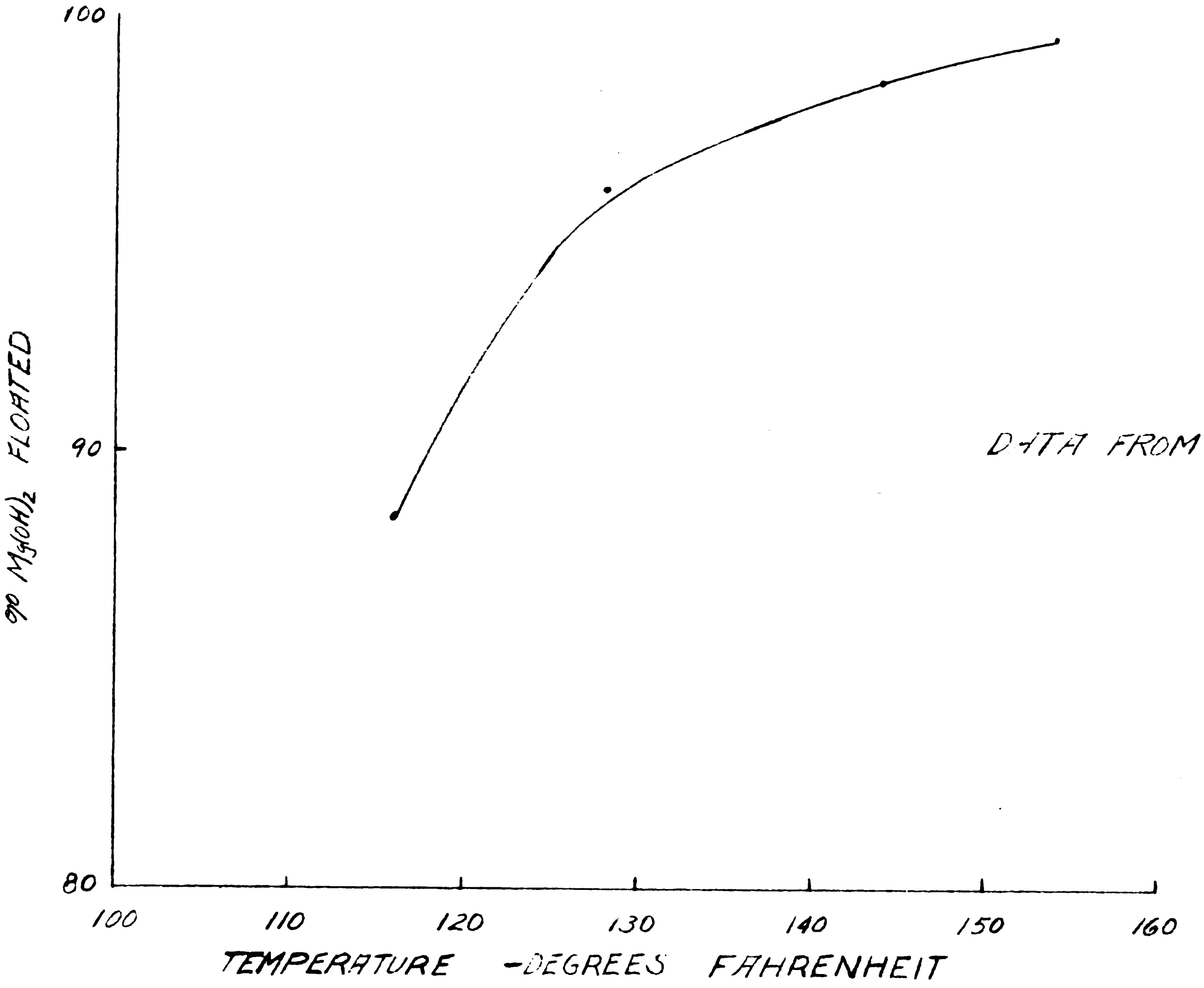


FIGURE 16

TABLE IX.

Effect of temperature on flotation of $Mg(OH)_2$ using 5.0 mls. of an oleic acid emulsion containing approximately 1.0 ml. oleic acid per 200 mls.

Initial Temperature (°F)	Per Cent Transmittance	Total $Mg(OH)_2$ Floated (Grams)	Per Cent of Total Floated
116	77	1.77	88.5
128	90.5	1.92	96.0
144	96.5	1.97	98.5
154	99.6	1.99	99.5

emulsion was determined at several different temperatures and as Figures 17 and 18 indicate the variation of collector efficiency with temperature is great.

A corresponding temperature effect is shown in Figure 17 in floating hydrated aluminum oxide using the same sodium soap solution of oleic acid as was used in obtaining the curves of Figures 9 and 10 for $Mg(OH)_2$. The preparation of this oleic acid soap solution has been previously described. Shown also in Figure 17 is a similar curve obtained with a linoleic acid sodium soap solution prepared in exactly the same manner as the previously described oleic acid soap solution was prepared. The results are shown on the same plot for comparative purposes.

Repeated Flotation and Washing of the Aluminum Oxide and Magnesium Hydroxide Precipitates

Washing of the aluminum and magnesium precipitates was accomplished by the following stepwise procedure:

1. The suspended precipitate was first floated in the usual manner.
2. One-half of the total volume, or 850 mls. of the water layer beneath the floated material was then drained out of the machine.
3. An equal quantity (850 mls.) of fresh water was then added to the machine. (In the case of $Mg(OH)_2$ an additional 20 mls. of 28% ammonia was also added to maintain pH above 10.4).
4. The material was then refloated in the usual manner using a ten minute agitation and a ten minute settling period to complete the cycle.

EFFECT OF TEMPERATURE ON FLOTATION OF $Al_2O_3 \cdot 3H_2O$

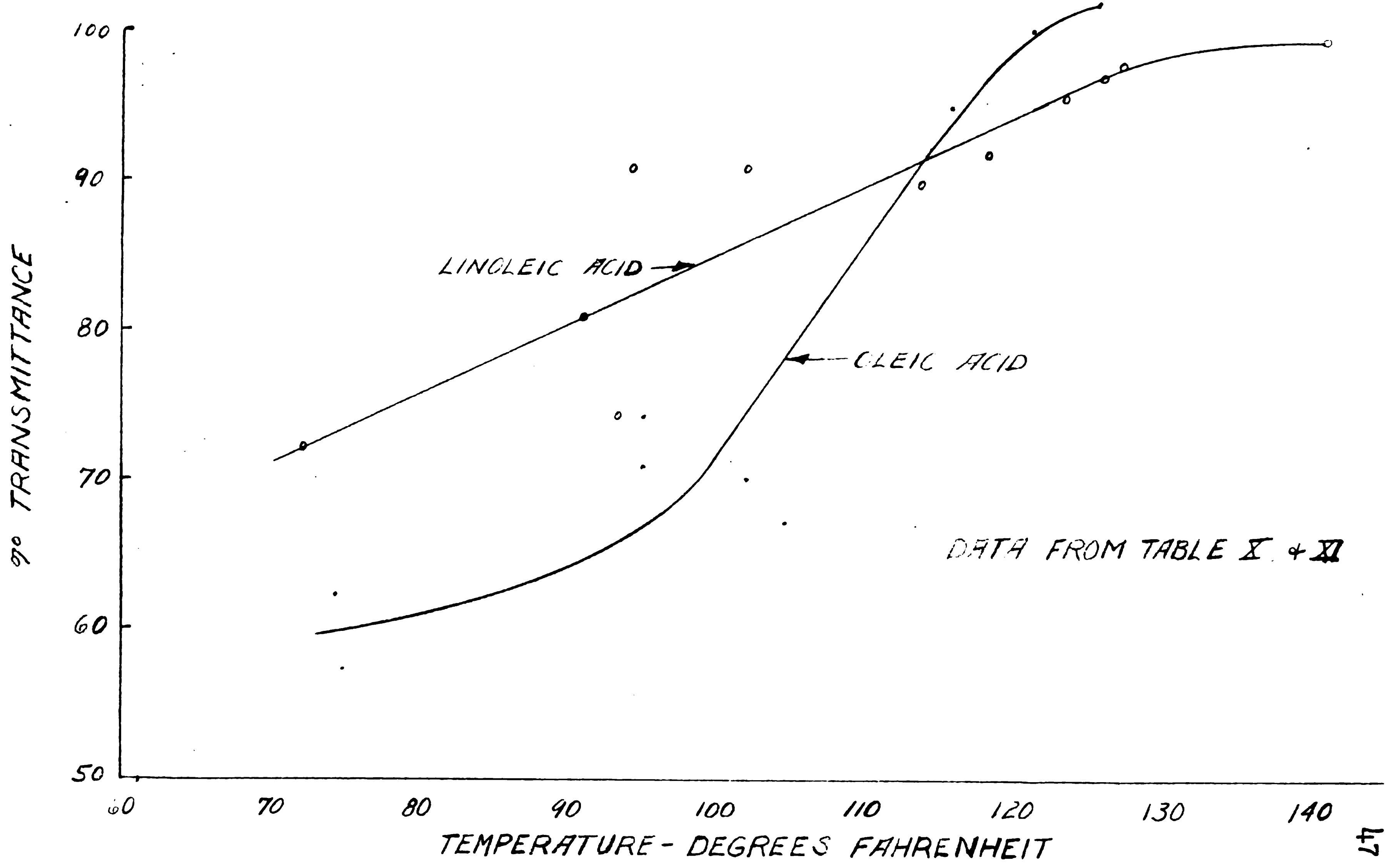


FIGURE 17

TABLE X.

Effect of temperature on flotation of gelatinous aluminum oxide using 0.6 mls. of oleic acid soap containing one part per 200 parts by volume.

Initial Temperature (°F)	Per Cent Transmittance	Total $Al_2O_3.3H_2O$ Floated (Grams)	Per Cent of Total Floated
74	62	1.90	57.6
75	57	1.70	51.5
95	71	2.23	67.6
95	74	2.35	71.2
102	70	2.20	66.7
104	67	2.07	62.8
116	92	3.00	90.8
116	95	3.12	94.5
121	100	3.30	100.0
126	102	3.30	100.0

TABLE XI.

Effect of temperature on flotation of gelatinous aluminum oxide using 0.6 mls. of linoleic acid soap containing one part per 200 parts by volume.

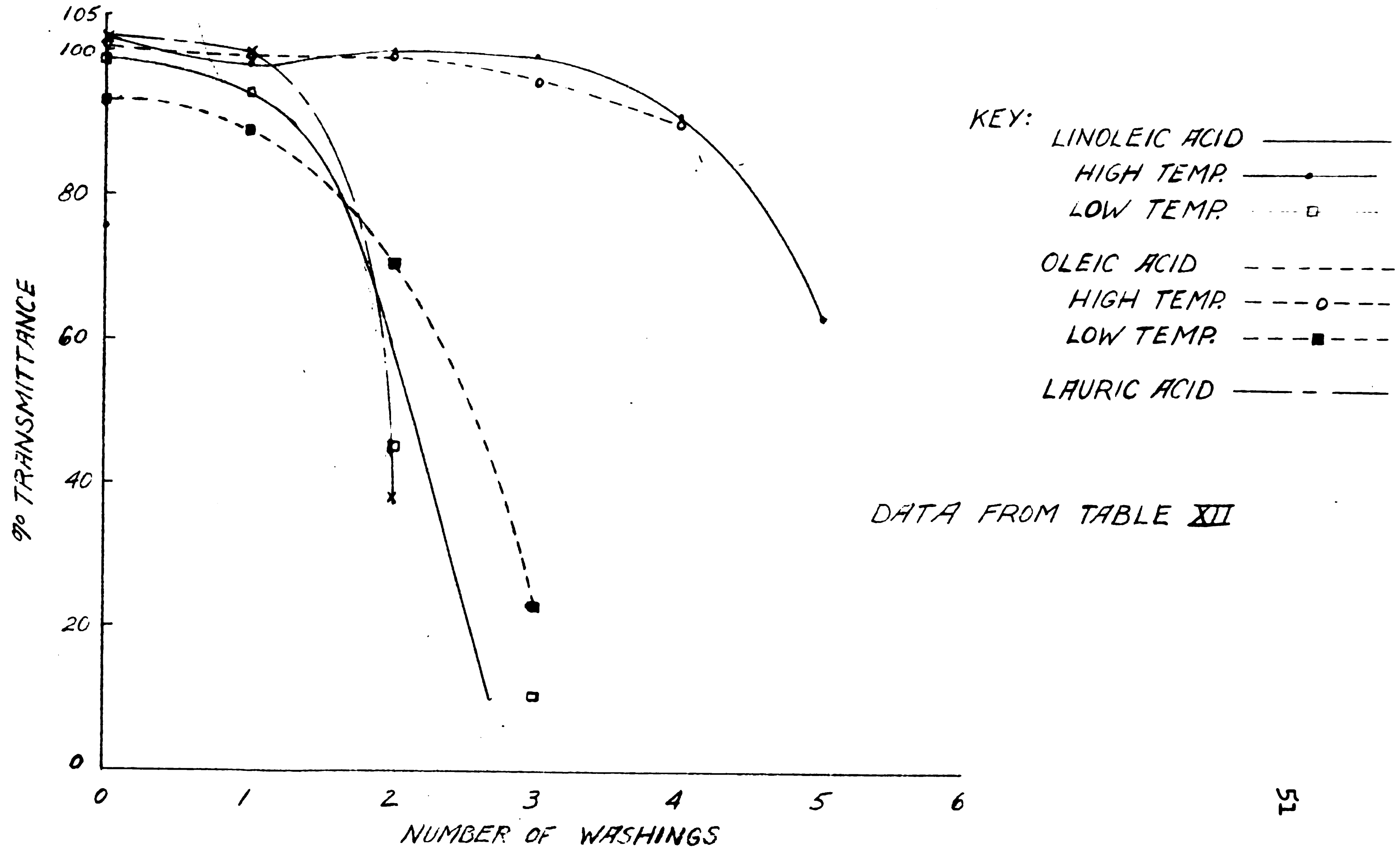
Initial Temperature (°F)	Per Cent Transmittance	Total $Al_2O_3.3H_2O$ Floated (Grams)	Per Cent of Total Floated
72	72	2.25	68.2
91	81	2.60	78.7
93	74	2.35	71.2
94	91	2.98	90.3
102	91	2.98	90.3
113	90	2.95	89.4
118	92	3.00	90.8
123	96	3.15	95.4
126	97	3.17	96.0
127	98	3.23	97.8
141	99.5	3.28	99.4

The curves of Figures 18 and 19 were obtained by sampling the lower water layer which was removed in Step 2 of the previously listed procedure. Test conditions for each curve, as marked, are given in Tables XII and XIII.

Notice the nearly parallel behavior of oleic acid as compared with linoleic acid and also how much better the collector film adheres to the magnesium precipitate as compared to the aluminum precipitate. Notice also the poor adherence of the lauric acid collector in both aluminum and magnesium flotation and that best results were obtained by heating the solutions before flotation. By running at higher temperatures, excellent flotation was assured with a near minimum of collector.

The dip indicated in the curves shown in Figures 18 and 19 suggest that possibly the first washing caused particles with collector deficiencies to drop out.

ADHERENCE OF VARIOUS COLLECTOR FILMS ON GELATINOUS ALUMINUM



DATA FROM TABLE XII

FIGURE 18

ADHERENCE OF LINOLEIC AND LAURIC ACID FILMS ON GELATINOUS MAGNESIUM

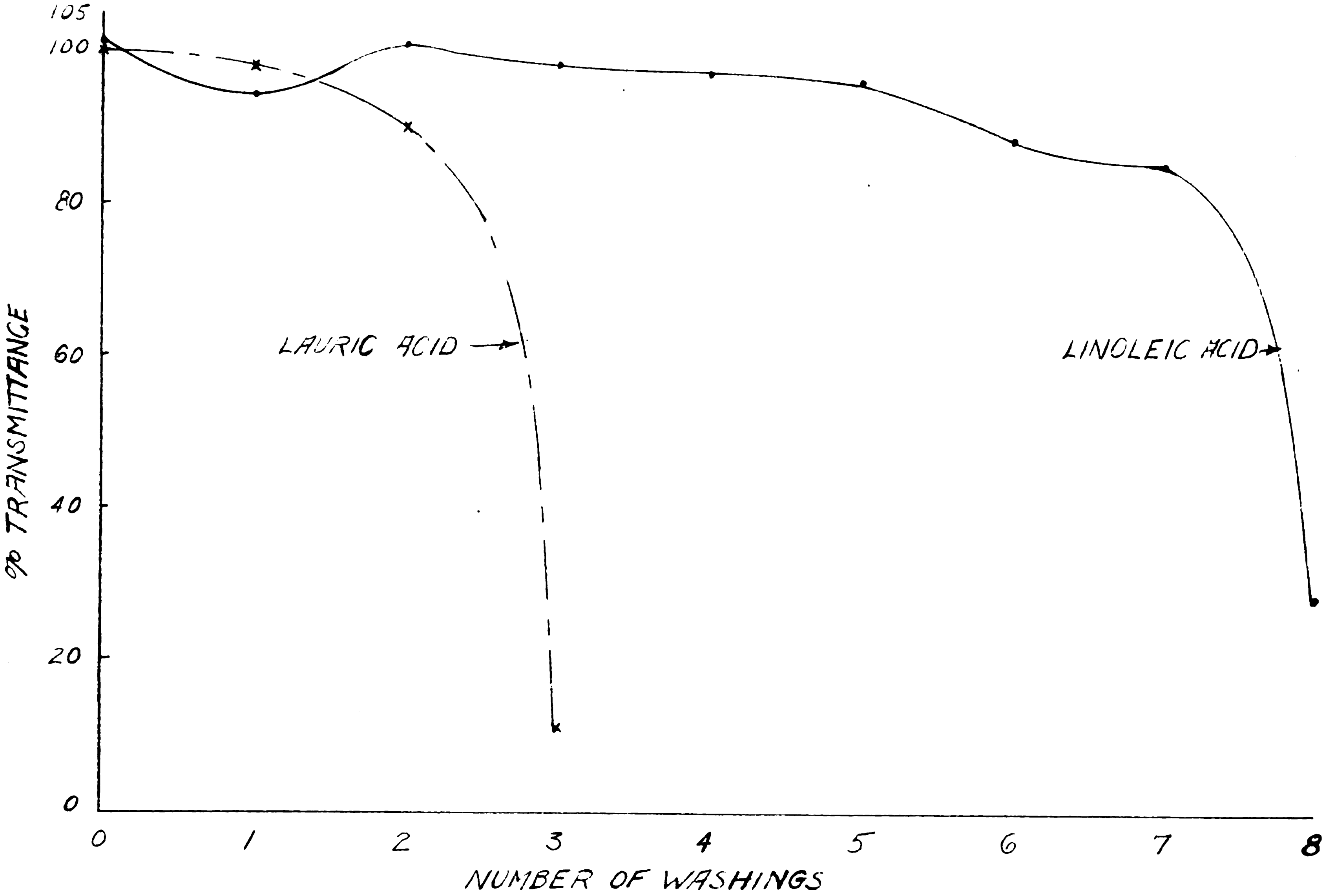


FIGURE 19

TABLE XII.

Repeated washing and flotation of gelatinous aluminum.

Test	Reagent	Used Reagent Mls.	Boiled ?	Washing No.	Initial Temperature (°F)	Per Cent Transmittance	Weight Lost (Grams)	Total Weight Lost	% Total Weight Lost
#1	Linoleic Acid soap, 1/200 by volume	0.7	Yes	0	158	102	Not measurable	0	0
				1	117	98	0.03	0.03	1.00
				2	101	100	Not measurable	0.03	1.00
				3	94	99	0.02	0.05	1.50
				4	92	91	0.18	0.23	6.97
				5	80	63	0.78	1.01	30.60
#2	Oleic Acid soap, 1/200 by volume	0.7	Yes	0	155	101	Not measurable	0	0
				1	114	99	0.02	0.02	0.60
				2	94	99	0.02	0.04	1.20
				3	84	96	0.08	0.12	3.63
				4	79	90	0.20	0.32	9.70
#3	Lauric Acid soap, 1 gram per 200 Mls.	3.0	Yes	0	150	102	Not measurable	0	0
					110	99.5	0.01	0.01	0.3
					99	38	1.35	1.36	41.2
#4	Oleic Acid soap, 1/200 by volume	0.7	No	0	124	93	0.14	0.14	4.2
				1	96	88.5	0.23	0.37	11.2
				2	86	71	0.61	0.98	29.7
				3	82	23	1.62	2.60	78.8
#5	Linoleic Acid soap, 1/200 by volume	0.7	No	0	126	99	0.02	0.02	1.5
				1	99	94	0.13	0.15	4.54
				2	84	45	1.16	1.31	39.7
				3	77	11	3.30	3.30	100.0

TABLE XIII.

Repeated washing and flotation of gelatinous magnesium.

Test	Reagent	Used Reagent Mls.	Boiled ?	Washing No.	Initial Temperature (°F)	Per Cent Transmittance	Weight Lost (Grams)	Total Weight Lost	% Total Weight Lost
#1	Linoleic Acid soap, 1/200 by volume	0.7	Yes	0	148	101	Not measurable	0	0
				1	110	94	0.03	0.03	1.50
				2	106	101	Not measurable	0.03	1.50
				3	102	98	0.01	0.04	2.00
				4	95	97	0.02	0.06	3.00
				5	86	96	0.02	0.08	4.00
				6	82	88	0.06	0.14	7.00
				7	81	85	0.08	0.22	11.00
				8	76	28	0.72	0.94	18.20
#2	Lauric Acid soap, 1 gram per 200 mls.	3.0	Yes	0	154	100	Not measurable	0	0
				1	119	98	0.01	0.01	0.50
				2	102	90	0.05	0.06	3.00
				3	91	11	1.09	1.15	57.50

CHAPTER VI

DISCUSSION

Bubble Attachment

The method of gross flotation as used in this work was different from the usual mineral froth flotation in that bubble attachment was the result, almost exclusively, of gas precipitation upon the surface of the floated particles. In the usual froth flotation of mineral particles, bubble attachment is the result primarily of collision between the bubble and mineral particles in the agitated suspension.(8) In such a system it can be shown that as particle size is reduced the chances for successful bubble-particle encounter become much less. As a consequence, systems containing very small particles are floated with difficulty.

Surprising as it might seem, very small particles are also difficult to float using the gas precipitation method, as it was used in these experiments. For example, experiments with the flotation of $CaCO_3$ and dried $Al_2O_3.nH_2O$ using linoleic acid soap as collector showed that the material could not be completely floated even though an excess of collector was used and it was run at a high temperature.

These materials, $CaCO_3$ and $Al_2O_3.nH_2O$ (dried), showed a marked difference in their floatability as compared with the previous gelatinous precipitates. The best results which could be obtained resulted in a transmittance reading of 87% in the case of dried $Al_2O_3.nH_2O$. Similar results were obtained with $CaCO_3$. It was observed in these cases that there was no appreciable flocculation and that many very fine particles remained in suspension upon release of the air pressure. It thus appears that flocculation is very essential to the gross flotation method.

Unfortunately the method of gross flotation is non-selective. All foreign material particles in the suspension which are not too heavy or dense are floated either by direct collector activity or indirectly by becoming trapped or adsorbed by the straining action of the floating floc.(2)

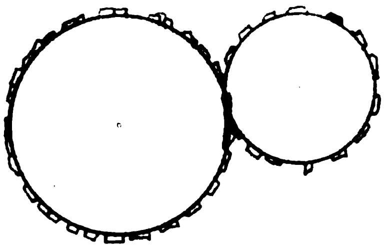
Bubbles are attached to the relatively large floc particles in gross flotation, whereas in mineral flotation the particles are attached to relatively large bubbles. These differences are illustrated below in Figure 20.

Relative Efficiency of Some Organic Acids as Collectors

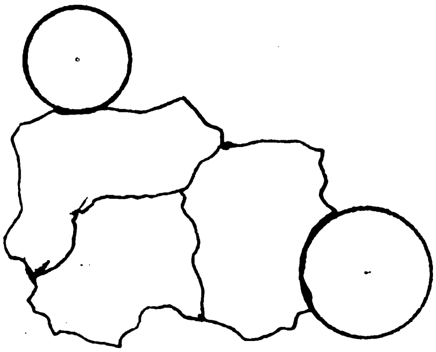
It appears, from the results given in Table II, that there are two primary factors to be considered in selecting a straight chain organic acid as a collector for the oxygenated metals; they are melting point and solubility.

The melting point of the acid determines, to a large extent, its dispersibility in solution whereas its solubility determines the quantity of the acid required. A more soluble acid is not so effective probably because the film which it forms is not so hydrophobic in comparison to films formed by the less soluble acids, and in addition more of the acid is necessary to satisfy the solubility requirements within the body of the fluid.

BUBBLE ATTACHMENT COMPARISON



MINERAL FLOTATION



GROSS FLOTATION

FIGURE 20

Keck and Jasberg(12) found from their studies on the flotative properties of magnetite, that with the saturated fatty acids valeric, caproic, caprylic, and stearic, flotation increased with the number of carbon atoms. Oleic acid was found to be a better collector than saturated stearic acid. They suggest that the inferiority of stearic acid was due to its lack of dispersion.(13) The results of Table II are in agreement with this suggestion. In Table II lauric acid was the last saturated acid in the series of increasing number of carbon atoms which had a low enough melting point to be sufficiently dispersible at 115° F to be effective as a collector at that temperature. However from the standpoint of quantity, lauric acid was only about one-tenth as effective as unsaturated oleic or unsaturated linoleic acid, due most probably to its greater solubility. This may be seen from a comparison of Figures 9 and 13.

It is interesting to note that at temperatures above 115° F oleic acid is equal to or superior to linoleic acid as a collector according to the results of Figure 17. The oleic acid film is probably more effective at higher temperatures because it is more hydrophobic. At temperatures below 115° linoleic acid is more effective as compared to oleic acid at the same temperature; linoleic acid appears to be more readily dispersed than is oleic acid. This increased effectiveness of linoleic acid may be due to its chemical constitution, or those physical properties which allow it to be more easily dispersed.

According to Gaudin(9)

> In practice where a carboxylic acid or its soap is required for collection, unsaturated acids such as oleic acid are preferred. The preference for unsaturated fatty acids has led to the search for cheap sources of multiply unsaturated fatty acids such as those of corn oil, cottonseed oil and fish oil foots. It is believed that these fatty acids have greater solubility in water and a lower melting point than saturated fatty acids with hydrocarbon chains of equivalent length.

That unsaturated acids are more effective than saturated acids may well be some function of their solubility. However, on the basis of these findings it is evident that solubility is a detriment to collector efficiency. It therefore appears that the effectiveness of the unsaturated acids such as oleic or linoleic acids must be explained in some other manner.

In some instances the multiply unsaturated acids are readily oxidized. To determine whether or not oxidation during flotation with oleic acid was responsible for its high efficiency as a collector, Gaudin and Cole(6) floated fluorite with highly refined oleic acid, extracted the floated mineral with solvents for oleic acid after inoxidative gentle acidification, and examined the extracts for the presence or absence of double bonds. They concluded that oleic acid was unchanged, even when the mineral which it coated was floated repeatedly, that linoleic acid which has two non-conjugated double bonds, was not effected appreciably more than oleic acid, but that linolenic acid (three non-conjugated bonds) was measurably altered, even after one single flotation step. They concluded that the extraordinary utility of these reagents is related to some property of the compounds other than the oxidizability of their double bonds.

The recent work of Hackerman and Makrides(10) suggests and supports another explanation for the superior results obtained with unsaturated acids. The only real difference between a saturated acid such as stearic acid and unsaturated acids such as oleic and linoleic acids is their comparative hydrogen deficiency. From the chemisorption viewpoint an unsaturated double bond possesses an extra pair of sharable electrons. The sharing of these electrons with positively charged surface atoms might well explain the greater efficiency of the unsaturated organic acids as flotation reagents.

Frothing

As has been suggested previously gross flotation is somewhat different from the usual froth flotation in the manner of bubble attachment as illustrated in Figure 20. The presence of excess froth is completely unnecessary in this type of flotation. It was observed that the degree of frothing of the agitated suspension with added collector was in no way directly related to the final flotation results obtained. The appearance of froth even with a collector such as oleic acid did not necessarily guarantee good final results, whereas good results were often obtained with a minimum of froth.

Frothing is related to the concentration of a potential frother in the solution as compared with its concentration at the gas-liquid interface. This relation is expressed by the Gibbs equation given here, which relates the two concentration factors to the rate of change of surface tension with concentration in the bulk of the fluid.

Gibbs equation:

$$\Gamma = \frac{-C}{RT} \cdot \frac{d\mu}{dc}$$

Where Γ = difference in concentration between bulk of liquid and concentration at gas liquid interface

C = concentration in bulk of liquid

μ = surface tension

R = gas constant

T = temperature

(Note: for greater precision activities should be used in place of the concentration factors in the above equation.)

If the rate of change of surface tension with respect to concentration is negative, then Γ is positive and surface tension is lowered with increasing concentration of material in the bulk of the fluid. Such a decrease in surface tension makes a froth or foam more stable, thermodynamically speaking, since less energy is required for an extension of the surface.

Generally, organic substances which are only slightly soluble are positively or preferentially adsorbed at the surface whereas inorganic salts are negatively adsorbed.

Organic substances which have both a hydrophobic portion and a polar hydrophylic portion in their molecules are often good frothing agents. Examples of such materials are pine oils, cresylic acid, and certain synthetic alcohols. The organic acids used in this work also acted as frothing agents.

When the minimum of the organic acid required for effective flotation was used, very little frothing was evident during agitation. The floated material gave the appearance of the usual froth as observed in traditional mineral flotation and only closer examination would reveal any distinction between the two types of flotation. The distinction is merely one of structure of the froth or bubble attachment as shown in Figure 20. Gross flotation, although different from the standpoint of bubble attachment, is, strictly speaking, a froth flotation.

pH as a Variable

Consideration has to be given to the effect of pH in almost every flotation system. In some systems it has been found that the difference between float and non-float is merely a matter of one pH unit whereas in other systems the range may be as great as six pH units.(16)

pH was not studied in this investigation primarily due to the solubility sensitivity of the materials to pH changes. The solubility consideration presented an obstacle to such a study since the method of analysis depended upon the assumption of constant concentration of the material being floated. To overcome this solubility obstacle different methods of analysis would have been required.

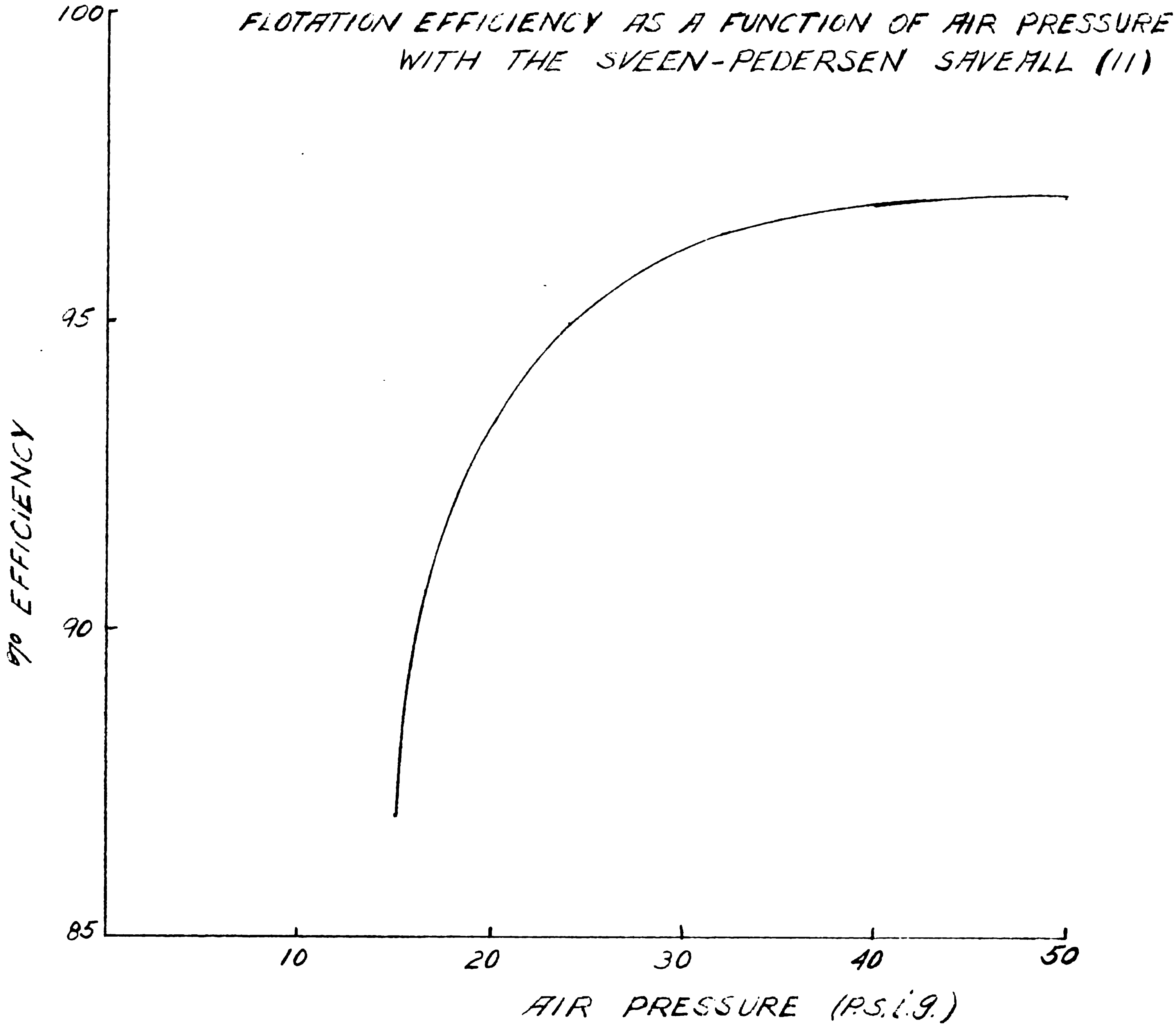
It is quite likely, that for the flotation of the aluminum precipitate, that a pH of about 7.0 would have been found to be optimum. Deshpande and Bhat(3) found that a pH of seven was optimum for the flotation of alumina and Harrison(11) reported a pH of about seven as being optimum for the flotation of white water in which gelatinous aluminum floc was one of the principal constituents floated.

Air Flow Through the Chamber

No attempt was made to regulate air flow through the agitated suspension but it was kept as constant as slight variations of the building's air supply would allow by opening the air inlet valve completely during all tests. It is felt that the total air flow was probably only important to the extent that it affected agitation of the suspension.

Air Pressure in the Chamber

Air pressure in the chamber was kept constant at 35 p.s.i.g. in order that other previously discussed effects could be studied. Harrison(11) gives the curve shown in Figure 21 for the relation between air pressure and per cent efficiency for the flotation of paper mill white water. It seems quite likely, in view of the fact that aluminum floc was one of the principal constitutents of the white water system, for which this curve is given, that this relation should also hold quite closely for the system of gelatinous



FLOTATION EFFICIENCY AS A FUNCTION OF AIR PRESSURE
WITH THE SVEEN-PEDERSEN SAVEALL (11)

FIGURE 21

aluminum used in these experiments. It would not be surprising to find that the same curve also predicted results for the flotation of gelatinous magnesium.

Release of Air Pressure

From observation of the suspension upon release of air pressure from the machine, it appeared that the results were not appreciably affected by the manner of release provided the release was not too violent or too slow. If the release was too rapid it appeared that much air escaped without effect due to violent agitation of the suspension after some of the gas had already precipitated upon the surface of particles, in which case the bubbles were broken loose and floated free. When the release of air pressure was too slow, a somewhat similar effect was evident, due to turbulence introduced by air escaping from the air tube entering the chamber at the bottom. Both of these difficulties were absent when air release was gradual but not too slow.

Agitation

Agitation was constant throughout these experiments. The flotation machine was equipped with a hydraulic variable speed reducer, but this was run at maximum speed at all times. A variation of agitator speed may have had an effect upon flotation results, especially in view of the assumed importance of dispersion to collector efficiency.

Time of agitation was kept constant at ten minutes. Both the speed of the agitator and the time of agitation may have reasonably had some bearing on the size of the floc which resulted, as well as upon the degree of dispersion of the collector. It was observed that a finer floc floated more readily than a course floc.

Washing the Precipitates

The procedure for repeated flotation and washing of the precipitate has been given previously and will not be repeated here.

The previous data shown in Figures 18 and 19 and tabulated in Tables XII and XIII indicate, the best results were obtained when the materials were floated at higher temperatures. When higher temperatures were used the loss of precipitate was held at its lowest level. Unfortunately the cost of heat is high and quite probably would preclude the use of heat in most commercial applications of this principle.

Examination of Figures 7, 9, 11, 13, and 15 indicate that in some cases the highest efficiencies are not attained even with excess collector at temperatures lower than 120°. Adherence of the collector film is poor at these lower temperatures.

The contamination caused by an adhering acid film such as oleic acid or linoleic acid would amount to approximately 0.09% in the case of gelatinous magnesium calculated as

$Mg(OH)_2$ and approximately 0.11% in the case of gelatinous $Al_2O_3.nH_2O$ calculated as $Al_2O_3.3H_2O$. Such a slight impurity would very likely be tolerable in most instances. An adhering acid film could of course be destroyed by calcination. Even in cases where it was found desirable to use the sodium soap of the acids as collectors no appreciable sodium should interfere since it seems reasonable that only the collector anion is responsible for film formation.

Gross flotation precludes the elimination of insoluble impurities by this washing procedure due to the non-specific nature of the gross flotation method. Only soluble impurities would be eliminated by such a procedure of repeated flotation and washing. It may be found possible to eliminate some impurities by proper control of pH to render them soluble. This could be a subject for further investigation.

Hardness of Water and Its Effect Upon Results

A typical analysis of the tap water used in these experiments is given in Table XIV. It is evident that there is an appreciable amount of hardness due to the presence of Ca^{++} Mg^{++}. This total hardness amounted to 339.0 parts per million as $CaCO_3$.

The Mg^{++} and Ca^{++} ions were both precipitated almost completely under the conditions of these tests. A turbidity of 74% was measured when the pH, of 1500 mls. of the tap water used in these experiments, was raised to 10.5 by the addition of 20 mls. of 28% ammonia.

Assuming all of the calcium and magnesium was precipitated, a simple calculation showed that 339 parts per million of $CaCO_3$ was equivalent to 0.345 grams per 1700 mls. as $Mg(OH)_2$.

Since it was known that $CaCO_3$ and $MgCO_3$ also floated under these test conditions it could only be concluded that interference by these materials, in this investigation, was significant. In spite of such interference it was decided to continue the use of tap water due to the difficulty of obtaining sufficient quantities of distilled water for these experiments.

TABLE XIV.

Analysis of service water supplied to buildings on the north campus of Michigan State University. This is a typical analysis.(1)

	P.P.M., $CaCO_3$ Equivalent
Silica	9.6
Iron	0.3
Calcium	221.0
Magnesium	118.0
Sodium	18.8
Potassium	1.6
Manganese	0
Carbonate	0
Bicarbonate	384.0
Sulfate	32.6
Chloride	8.6
Fluoride	0.2
Nitrate	1.4
Total Hardness as $CaCO_3$	339.0

CONCLUSIONS

CHAPTER VII

CONCLUSIONS

I. A machine, similar in principle to the Sveen-Pedersen Saveall, was shown to be an efficient device for the flotation of slimy gelatinous precipitates.

II. Oleic and linoleic acids are excellent collectors for many slimy gelatinous metallic precipitates.

III. The efficiency of the organic acids as collectors for these precipitates was shown to be temperature dependent.

IV. Repeated flotation and washing of the gelatinous precipitates of aluminum and magnesium was possible without the addition of more reagent at each flotation step.

V. It was found possible to float and wash the gelatinous precipitates of aluminum and magnesium three times without appreciable loss of the precipitates provided a temperature exceeding 120° F was used in the initial flotation step.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Campbell, J. M. Private Communication. (1958).

1a. Coleman Model 14. Spectrophotometer Instruction Manual.

2. D'Arcy, N. A. American Petroleum Institute, Tulsa, Okla. May 1, 1951.

3. Deshpande, F. K., and G. N. Bhat. "Bubble pick-up Studies with Alumina," J. Ind. Inst. Science, 37 A, 141-6 (1955).

4. Dewitt, C. C. Private Communication. (1957).

5. Dura-Metallic Corporation, Kalamazoo, Michigan

6. Gaudin, A. M., and Richard E. Cole. "Double-bond Reactivity of Oleic Acid During Flotation," Trans. A.I.M.M.E., 196, Tech. Note 144-B. (1953).

7. Gaudin, A. M. Flotation. 2nd ed. New York: McGraw-Hill Book Company, Inc. 529-53. (1957).

8. Gaudin, A. M. Flotation. 2nd ed. New York: McGraw-Hill Book Company, Inc. 348. (1957)

9. Gaudin, A. M. Flotation. 2nd ed. New York: McGraw-Hill Book Company, Inc. 258. (1957)

10. Hackerman, Norman and A. C. Makrides. "Action of Polar Organic Inhibitors," Ind. Eng. Chem. 46. 523-527. (1954).

11. Harrison, W. D. "The commercial Operation of the Sveen-Pedersen Saveall," T.A.P/P.I., Paper Trade Journal 109. 67-74. (August 17, 1939).

12. Keck, W. C., and Paul Jasberg. "A Study of the Flotation Properties of Magnetite," Trans. A.I.M.M.E., Vol. 134. 129-45. (1937).

13. Keck, W. C., and Paul Jasberg. "A Study of the Flotation Properties of Magnetite," Trans. A.I.M.M.E., Vol. 134. 132. (1937).

14. Newsome, J. W. Private Communication. (1958).

15. Sutherland, K. L., and I. W. Wark. Principles of Flotation. Melbourne: Australasian Inst. Min. and Met. Inc. 51. (1955).

16. Sutherland, K. L., and I. W. Wark. Principles of Flotation. Melbourne: Australasian Inst. Min. and Met. Inc. 86. (1955).

17. Weiser, H. B. Inorganic Colloid Chemistry. New York: John Wiley and Sons, Inc., Vol. II. (1935).

18. Weiser, H. B. Inorganic Colloid Chemistry. New York: John Wiley and Sons, Inc., Vol. II. 376. (1935).