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### THE VISCOSITY CHARACTERISTICS OF CLAY

SUSPENSIONS

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Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science

from

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Dear Mr. Squires:

In partial fulfillment of the requirements of the Degree of Master of Science, we submit the following thesis, subject to your approval.

Very truly yours,

*^*.

## ACKNOWLEDGEMENT

The authors are deeply indebted to Mr. Lombard Squires and Dr. W. K. Lewis, who freely gave very helpful advice and suggestions in supervising this thesis. TABLE OF CONTENTS

4-7 mm - 1

	Page
SUBJECT	l
OBJECT	l
ABSTRACT	1
INTRODUCTION	3
SUMMARY OF PROCEDURE	9
RESULTS	13
DISCUSSION OF RESULTS	20
CONCLUS IONS	39
RECOMMENDATIONS	40
APPEND ICES	
PROCEDURE	42
EXPANSION OF INTRODUCTION	50
SUMMARY DATA SHEET	61
CALCULATIONS	62
DATA	64
LITERATURE CITED	65

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#### SUBJECT

The Viscosity Characteristics of Clay Suspensions.

#### OBJECT

To investigate some of the viscosity characteristics of clay suspensions with special emphasis of methods of reducing the viscosity by chemical treatment. January 1, to May 25, 1933.

### ABSTRACT

All viscosity measurements were made with a MacMichael viscosimeter. Three clay suspensions were investigated — Rabb's Ridge mud from above 3000 feet, Rabb's Ridge mud from below 3000 feet and Conroe mud from below 4000 feet. These muds are drilling fluids taken from the oil fields of the Humble Oil Company in Texas. The effect of several reagents on the viscosity of the muds was determined at various concentrations of the reagents and various pH values for each concentration.

Quebracho tannin and phosphoric acid gave the most favorable results, giving approximately 50 192015 per cent decrease in the viscosity of the original mud. Formaldehyde gave a slight decrease. Ferric chloride, chromic chloride, sulfite liquor and sodium phosphate were other reagents tried, all of which gave increases in viscosity. It was found necessary to carefully control the pH values if the best results were to be obtained, irregardless of the reagent used. Phosphoric acid gave the best results at a pH value of 6.5; Quebracho tannin gave best results at a pH value of about 10.5 It is the conclusion of the authors that the acids having three or more valent anions are most satisfactory for the reduction of the viscosity of clay suspensions.

- 2 -

### INTRODUCTION

There are two standard methods used in oil well drilling at the present time. The older of the two is known as the cable-tool method of drilling and is spoken of as the standard rig in oil field parlance. The cable-tool apparatus consists essentially of a bit which is alternately raised a few feet by means of a cable and then let The drilling is accomplished by the trip\_ drop. hammer-like action thus brought about. Water is introduced in small amounts into the drill hole to facilitate in the cutting of the rock strata and also to cool the bit. It is necessary to withdraw the bit frequently and bail out the cuttings from the bottom of the drill hole. It is obvious that in drilling deep wells there is a great loss of time brought about in withdrawing tools from and bailing out the drill hole.

There is also the fact that water bearing formations are encountered in drilling most oil wells, and consequently it is necessary to case off those formations with pipe. Excess water in the drill hole is a serious hindrance to this type of drilling,

- 3 -

since it slows up the fall of the bit, and thus slows down the drilling operations. It is obvious that if many of these water bearing strata are encountered the entire well must be cased and the upper part of the drill hole must be very large to compensate for the tapering effect in the casing.

dis There is further/advantage of the cabletool apparatus in that when high rock pressures are encountered large quantities of oil are often lost due to gushing when the oil-bearing stratum is first tapped, and often the drilling rig is completely demolished by the oil gusher. Such uncontrolled losses obviously bring about a reduction in the rock pressure in the field where they may occur. If this pressure can be maintained it is advantageous to do so since in many cases the pressure is sufficient to make pumping of the wells unnecessary. Hence if the pressure is preserved an appreciable saving may be made by eliminating pumping costs.

The rotary drilling apparatus has been devised to combat the above mentioned short comings of the cable-tool apparatus. The rotary drilling

- 4 -

tool consists of a hollow stem equipped with a suitable cutting head at its lower extremity. The tool is rotated from the surface, with pressure applied at the bit. A suitable drilling fluid, usually clay suspensions, is circulated down the inside of the hollow stem, out through orifices just above the cutting head or bit, and thence back to the surface through the annular space between the drill atem and the wall of the drill hole. The drilling fluid serves four distinct purposes, namely,

1. It serves to wash the strata clean from cuttings and carries them to the surface.

2. Water, gas and minor oil bearing formations are sealed off by the hydrostatic head of the fluid column, which is controlled by properly regulating the fluid density.

3. It also serves to seal off the pores of the drill hole and prevents caving of loose formations.

4. The fluid serves as a lubricant for the drill stem and in running casing into the drill hole due to its colloidal properties.

- 5 -

Thus it is seen that the latter method makes more or less continuous drilling possible. Nevertheless due care must be exercised in properly controlling the properties of the fluid lest the cuttings settle out before the mud can carry them to the surface, and consequently collect at the base of the drill hole and hopelessly jam the drilling tool.

Proper control and manipulation of the drilling fluid makes it possible to preserve the rock pressure in the oil fields. It is often necessary to add weighting materials to the fluid to obtain sufficient hydrostatic head to hold the pressure under control. Barium sulfate is often used as the weighting material.

Cases are known where as much as \$30,000. has been spent for drilling fluid for a single well. Thus the importance given to drilling fluids is realized, and also the economic necessity for reclaiming and using again as much of the fluid as is possible and as many times as is possible. Thus it is fitting that some of the required properties of these fluids should be mentioned here.<sup>12</sup>

- 6 -

<u>First</u>, carrying cuttings from the bottom of the drill hole requires alone or in combination,

1. High density and high velocity in the turbulent flow region.

2. High density and high velocity in the viscous flow region.

<u>Second</u>, Elutriation, or dropping of cuttings requires alone or in combination,

1. Low density of the fluid.

2. Low viscosity of the fluid.

3. Low velocity of the fluid in the settling ditch.

Third, the release of gas requires, 1. Low viscosity.

2. Time or reduction of path.

There are three chief constituents in a drilling fluid which help to obtain the above mentioned properties, namely, water, colloidal matter, both gel-forming and non-gel-forming, and larger particles suspended in the medium. The gelforming constituent is the most important of the two colloidal substances present, since it imparts the necessary properties to an efficient drilling fluid. It will be shown in the Expansion of the Introduction that viscosity plays only a minor part in controlling the pumping costs, but is an important factor in reclaiming drilling fluids, namely, in the settling out of the larger particles.

There has been very little work done until within the last two or three years on the chemical treatment of drilling fluids in an effort to decrease their viscosities. Consequently, the purpose of this thesis is to study some of the Viscosity Characteristics of Clay Suspensions, giving special emphasis to methods of reducing the viscosity of actual drilling muds by chemical means.

- 8 -

### SUMMARY OF PROCEDURE

All viscosity measurements were made with a MacMichael viscosimeter, using wire No. 26 for lower viscosities and No. 22 for higher viscosities. The wires were calibrated with glycerine solution. The large inner cup and disc plunger were used in all determinations, and 100 cc. of suspension for each measurement.

Three samples of actual drilling fluids as taken from the fields of Humble Oil Company in Texas were used in this investigation. These muds were Rabb's Ridge mud from above 3000 feet, Rabb's Ridge mud from below 3000 feet, and Conroe mud from below 4000 feet.

Universal indicator was used to determine pH values.

Caustic soda and hydrochloric acid were used to vary the pH values.

The effect of the following reagents was measured:

Chromium chloride
 Ferric chloride
 Formaldehyde
 Quebracho tannin
 Phosphoric acid
 Sodium phosphate
 Sulfite liquor
 Sodium hydroxide
 Hydrochloric acid.

### - 9 -

Chromium chloride and ferric chloride were tried with concentrations varying from 0.05 to 2.00 cc. of 50 per cent solution to 100 cc. of each of the three muds investigated. The pH values of the samples were varied before and after adding the reagents, the viscosities being taken for various concentrations of the reagents and various pH values for each concentration.

Concentrations of Quebracho tanning ranging from 0.05 to 2.00 cc. of 28 per cent water solution of tannin to 100 cc. of mud were tried. Separate samples were made using different concentrations of tannin, and the pH raised to 11 or above by adding caustic. The wiscosity was determined at various pH values for each sample.

The effect of sulfite liquor was tried with Rabb's Ridge mud from above 3000 feet, the procedure being similar to that for chromic and ferric chlorides. It was found to act similar to those samples in which chromic and ferric chlorides had been added, so no other muds were tried.

When testing for the effect of formaldehyde, the pH of the muds were raised to approximately 10,

- 10 -

and different concentrations of formaldehyde were added. The samples were then allowed to stand for several days, during which time, no further treatment was given the mud except the determinations of the viscosities at various intervals of time. Finally, before discarding the samples, the pH values of all samples were raised to 11 or above (while standing, the pH values of the muds lowered, apparently due to the reaction of the formaldehyde).

Various concentrations ranging from 0.10 to 1.0 cc. of 85 per cent ortho-phosphoric acid per 100 cc. of mud were added to different samples. The muds were then thoroughly shaken and allowed to stand for one night. The viscosities were then taken before and after shaking. The samples were then allowed to stand two more days, and although some water separated out during the last two days, the viscosities were found to change very little, so the pH values were raised, the viscosities being The effect taken at various pH values up to 7.5. of phosphoric acid on a bentonite (5 per cent by was also determined weight) suspension, the procedure being similar to that for the other three muds.

- 11 -

The effect of sodium phosphate was also tried, the technique being similar to that for ferric chloride and chromic chloride. Only a few samples were run.

The effect of stirring was determined by using a constant speed mechanical stirrer, the viscosity being taken at the end of 0.05, 1.0, 2.0, etc. minutes until constant viscosity was obtained.

A 50 cc. sample of Conroe mud was dried, the density determined and the effect of dilution upon the viscosity of the mud at concentrations ranging from 7.0 to 9.0 volume per cent was tried in order to see if this suspension followed the Hatschek formula.

All data was recorded as deflection produced at a given r.p.m. The actual r.p.m's. recorded were 50, 54, 110, and 143. This data was plotted as "deflection" against "r.p.m's.".

## RESULTS

The results given below were obtained by experimenting with Rabb's Ridge Mud from above 3000 Results for Rabb's Ridge mud from below 3000 feet. feet and Conroe mud from below 4000 feet are given in the Appendix, accompanying the plots on which the data is presented. (Figures 39 to 82).

Effect of Stirring Rabbie 3000 fe		Mud from	above
Minutes Stirred	<b>z</b> _84	<b>z-1</b> 43	Z-I
0 0.5 1.0 2.0 3.0 4.0	146 51 28 23 22	101 37 26 20 19 18	37 17 14 10 12 12

Effect of pH on the Viscos	sity of	Rabb's	Ridge Mud
from Above	<u>3000 Fee</u>	et.	
pH	<b>z_</b> 84	<b>Z-1</b> 43	Z-I
5.0 6.0 7.0 8.0	108 117 137 235	72 77 91 154	18•3 18•3 24•9 38•6
9.0 9.5 10.5 11.0 11	261 22 16 13 93	18 14 12 59	12.4 12.4 10.5 10.5

- 13 -

Conc.*	pH	<b>z</b> _84	<b>z-1</b> 43	Z-I
0 <b>.05**</b>	8.5	17	14	10.5
	9.5	13	12	10.0
	11.0	21	16	9.8
	11***	59	42	16.4
0.10	8.5	16	14	12.1
	10.0	11	11	11.1
	11	18	15	11.8
0.25	8.5	14	13	12.1
	10.5	11	11	10.5
1.00	8.54	27	20	10.5
	8.5 <sup>5</sup>	14	13	12.1
	10.0	11	11	11.1
	11.0	10	10	10.0
	11	23	18	11.1
2.00	8.54	50	34	10.5
	8.5 <sup>5</sup>	57	39	13.8
	10.0	24	20	13.4
	11.0	15	13	11.8
	11	54	38	13.4

Effect of Quebracho Tannin on Rabb's Ridge Mud from Above 3000 Feet.

\* cc. of reagent per 100 cc. of mud

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 Concentration of reagents is given in the Procedure
 The dashes after 11 means that the pH is above 11, but it was not possible to tell pH values above 11 with Universal Indicator
 Immediately after preparation

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**5** Five days after preparation.

# Effect of Formaldehyde

Conc.	pH	<b>Z-8</b> 4	<b>z-1</b> 43	Z-I
0.05*	10.5*	25	21	15.7
	10.5**	15	14	12.4
	11.0	29	21	9.5
0.10	10.5*	21	18	16.0
	10.5**	12	12	11.8
0.25	10.5*	19.	18	15.5
	10.5**	15	13	9.8
1.00	10.5 <del>*</del>	23	19	13.0
	10.5**	30	21	8.5

## Effect of Chromic Chloride

The mud was treated previously with HCl until pH equals 4.

Conc.	pH	<b>Z-8</b> 4	<b>z-1</b> 43	Z-I
0.05	4.0	66	45	17
	7.5	70	48	16
	8.0	\$7	58	17
	11.0	177	113	16
0.10	4.0	67	47	18
	6.0	69	48	17
	8.5	78	53	17
	9.5	91	61	18
	11.0	156	101	22
0.50	3	69	49	20
	7.0	83	59	24
	8.0	87	60	21
	9.0	92	64	22
	11.0	178	113	19
1.00	3 6.5 7.5 8.5 9.5 11	64 76 82 98 190	47 53 58 61 68 122	24 21 23 26 26

	Effect of	Chromic C	Chloride (Cont	<u>t'd)</u> .
Conc.	pH	<b>Z-</b> 84	<b>Z-</b> 143	Z-I
2.00	3 7.0 8.0 9.0 10.0 11	50 68 77 94 98 178	39 49 54 65 67 116	22 20 21 24 22 27

# Effect of Ferric Chloride

.

The mud was treated previously until pH equals 3

Conc.	рН	<b>Z_</b> 84	<b>221</b> 43	Z-I
0.10	3.0 7.0 10.0 11.0	72 72 99 165	51 51 66 104	19 19 18 17
0.25	3. 6.0 8.5 10.5	74 79 82 122	51 54 56	17 19 18 19
1.00	3.0 6.0 7.0 8.0 10.0	67 71 76 86 98	47 48 59 66	17 17 18 18 18

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# Effect of Chromic Chloride

The mud was not treated previous to the addition of the chromium chloride.

Conc.	pH	<b>Z–</b> 3 <sup>1</sup> +	<b>z-1</b> 43	Z-I
0.05	9.0	183	121	30
	10.0	127	81	16
	11.0	71	43	12
	11	76	52	18
0.10	8.5	122	78	16
	11.0	90	59	14
	11	108	68	11
0.25	7.5	148	96	22
	8.5	114	77	26
	9.5	58	41	15
	11.0	79	55	20
	11	245	147	9
0.50	6.0	116	76	<b>21</b>
	7.5	114	77	25
	9.0	95	65	24
	10.0	92	64	24
	11.0	118	78	23
1.00	5.0	158	105	26
	7.0	167	110	26
	7.5	159	107	30
	9.5	174	114	27
	11.0	220	141	24

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## Effect of Ferric Chloride

The mud was not treated previous to the addition of the ferric chloride.

Conc.	pH	Z-84	<b>z-</b> 143	Z-I
0 <b>.0</b> 5	8.5 10.0 11.0	233 134 425	139 98 286	49 45 87
0.10	8.0 9.5 11.0	307 166 400	203 120 270	56 53 83
0.25	9.0 10.	346 620	222 380	42 38
1.00	5.0 7.5 9.0 10	685 570 486 out of ra	444 355 304 ange	98 45 41
	Effect of	Sulfite I	iquor	
Conc.	pHq	<b>Z-</b> 84	<b>Z-1</b> 43	Z-I
0.05	8.5 11.0 10.0	161 150 91	107 100 58	28 28 9
1.5	8.0 9.0 10.0	227 155 out of r	144 98 ange	25 17

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E. P

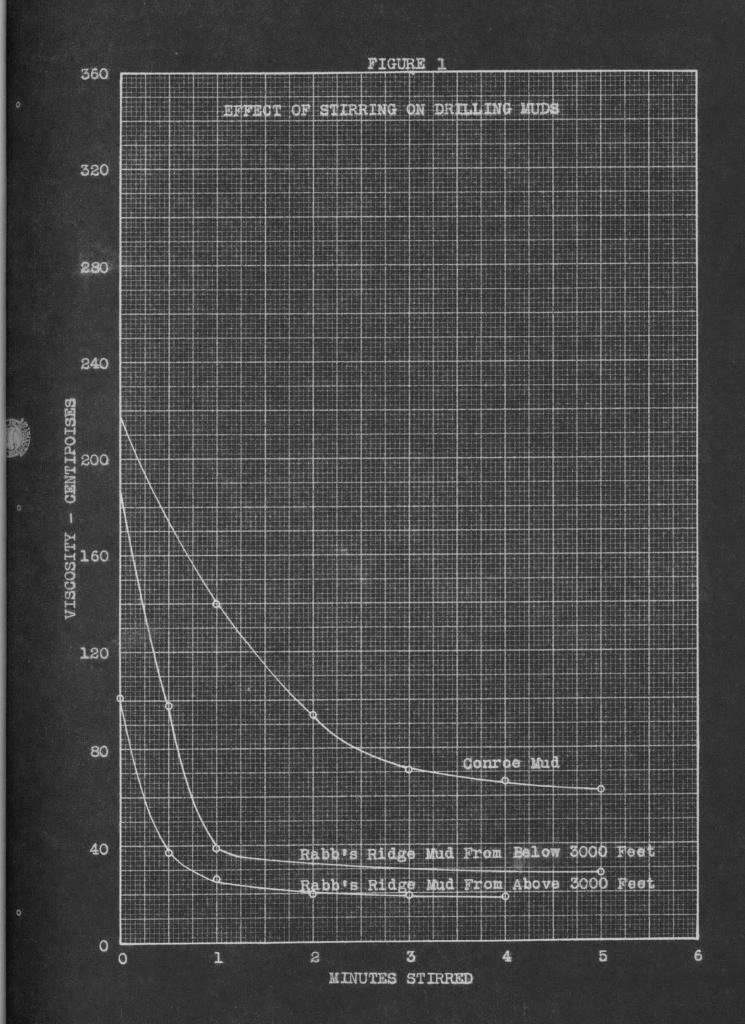
# Effect of Sodium Phosphate

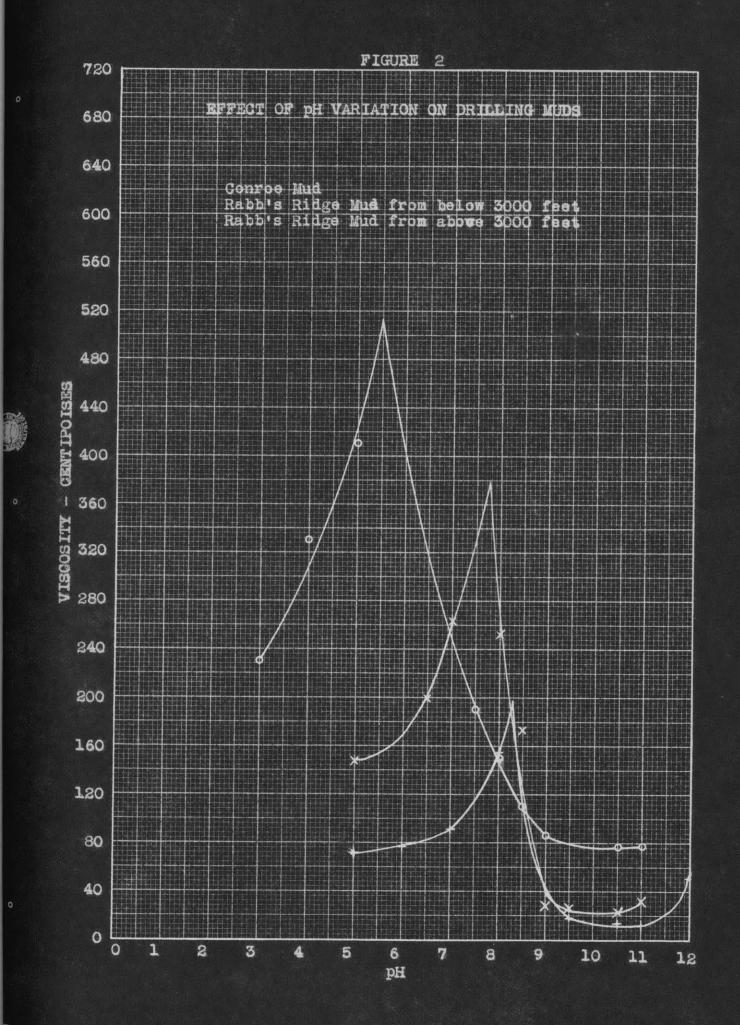
Conc.	pH	<b>Z-</b> 84	<b>Z-1</b> 43	Z-I
0.10	9•5	43	30	11
0.25	9•5	43	31	- 15

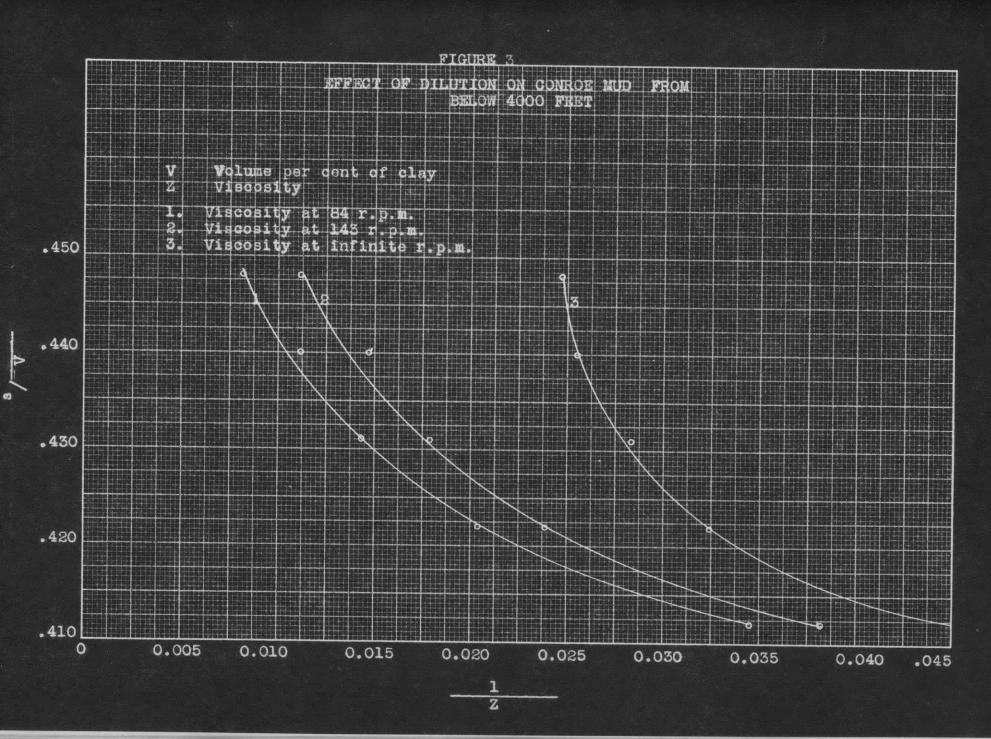
# Effect of Phosphoric Acie

Conc.	pH	<b>Z_</b> 84	<b>z-1</b> 43	Z-I
0.20	7.0	18	15	క•0
	7.5	25	18	క•0
0.50	3	100	66	18
	5.0	29	22	11.0
	7.	21	16	9.2
	6.0	17	14	8.5
	6.5	15	12	8.5

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### DISCUSSION OF RESULTS

When viscosities of true liquids are determined with a MacMichael viscosimeter, the deflection is a linear function of the angular velocity of the revolving cylinder for a constant viscosity. Also, the deflection is a linear function of the viscosity for a constant angular velocity. (Angular velocity will be referred to as r.p.m. hereafter in this thesis). Therefore, the viscosity may be expressed by the following equation:

$$Z = K \frac{d(deflection)}{d(R.p.m.)}$$

where,

Z is the viscosity expressed in centipoises

K is a constant for any one wire

Deflection is the deflection in degrees MacMichael

r.p.m. is the revolutions per minute of the rotating cylinder.

The wires were calibrated with glycerine solution. When using a true liquid of constant viscosity, the results plotted as r.p.m. against deflection gives a straight line passing through the origin. From the slope of this line, the constant, K, was calculated and found to be 93.5 for wire number 26 (Figure 84), and 537 for wire number 22 (Figure 85). From these values of K plots were drawn for viscosity against deflection at constant r.p.m. As mentioned in the Procedure the deflection for the viscosities of the various muds were determined at 50, 84, 110, and 143 r.p.m. The plots of viscosity against deflection were constructed for 84 and 143 r.p.m. (Figures 87 and 88).

When determining the viscosities of suspensions of the colloidal type, it is found that considerable force can be exerted on the suspensions without causing a permanent displacement. It follows that when determining the viscosity of these suspensions, a certain portion of the shearing force is used up in overcoming this resistance. In other words, when using a viscosimeter of the MacMichael type, a deflection is obtained at zero r.p.m. Bingham<sup>4</sup> has suggested that this resistance be called the internal friction of the material.

- 21 -

It follows that a plot of deflection versus r.p.m. of suspensions of the colloidal type will not give a line passing through the origin. However, the points do lie on a straight line, as shown on all plots of r.p.m. versus deflection given in the Appendix (Figures 4 to 82). For convenience, these lines will be called the viscosity characteristic lines. Bingham has suggested that the reciprocal of the slope of the r.p.m. versus deflection line be called the coefficient of mobility. corresponding to the coefficient of fluidity in the case of true liquids. If the line be extrapolated to r.p.m. equals zero, the value for deflection at this point is an indication of the magnitude of the internal friction of the sample under consideration, i.e. the yield point.

Thus it is seen that the viscosity of suspensions of this type involves two factors p internal friction and the reciprocal of the coefficient of mobility. Therefore, if the viscosity, as defined for a true liquid, is to be determined for suspensions of this type, it is found to change with r.p.m. This is the reason for giving the different values of viscosities in the results. It has already been

- 22 -

mentioned that for a constant r.p.m., the viscosity is a linear function of the deflection. Therefore, a line drawn through any coordinate and the origin on a r.p.m. versus deflection plot represents a definite viscosity. Z-84 is the viscosity represented by a line drawn through the origin and the point where the viscosity characteristic line cuts the line, r.p.m. = 84. The Z-143 values were calculated similarly. Z-I is the viscosity represented by the slope of the viscosity characteristic line, or the viscosity at infinite rate of shear, i.e. a line drawn through the origin, cutting the viscosity characteristic line at r.p.m. = infinity. Unless otherwise stated, the term viscosity in the following discussion will refer to the viscosity at 143 r.p.m.

It was found that all three muds, Rabb's Ridge mud from above 3000 feet, Rabb's Ridge mud from below 3000 feet and Conroe mud from below 4000 feet, gave qualitatively similar results. If the results were presented for all three muds, it would be very confusing because of the multiplicity of the results and of very little benefit. Therefore, for purposes

- 23 -

of discussion, the results of only one mud, Rabb's Ridge mud from above 3000 feet, are presented in the Result section proper. The results of determinations for all three muds are presented in tables accompanying plots of the data given in the Appendix (Figures 4 to 82).

### Stirring

Several characteristics of the viscosity of the muds were explained when the effect of stirring on the viscosity of the muds was inves-Previous to making these determinations, tigated. several experiments had been run using different reagents, and it was impossible to get check re-The viscosities would change as the samples sults. were being handled. It was impossible to evade this phenomena as considerable handling was given to the samples when working with them. Also, the viscosities of the samples would slowly dhange when allowed to run in the viscosimeter at a constant When a sample of a mud was stirred with a r.p.m. constant speed stirrer, the viscosity was found to decrease and approach an asymptotic value (Figure 1). Kuhn<sup>11</sup> suggests that variations of the viscosity of suspensions is due to the loose aggregation of the suspensoid particles to form chains or networks which break up when the suspension is stirred, and tend to assume a particle orientation in relation to the direction of flow when stirred. This point is also verified by Dubrisay<sup>7</sup>. When further tests were run, the asymptotic value of the viscosity of the untreated muds were used as a standard of reference. It was found that shaking the muds produced a very close approximation of these values, and was much less time consuming than stirring. All samples, unless otherwise stated, were thoroughly shaken before viscosity determinations were made.

### Quebracho Tannin

It has been known for some time that tannin would reduce the viscosity of drilling muds, and it has been used in this capacity to a considerable extent. It was not known to the authors what concentrations of tannin were used or to what extent the viscosities were reduced, by this reagent. Therefore,

- 25 -

several determinations were made using this reagent in order to (1) find to what extent the viscosities were reduced, (2) concentrations necessary, and (3) to have quantitative data to compare the effect of other chemicals.

It was found that the best results were obtained with from 0.50 to 1.00 cc. of tannin solution (See Procedure) per 100 cc. of mud. If the

samples containing 1.00 or more cc. of tannin were allowed to stand for a day or two, the results were much more favorable. Concentrations of more than 1.00 cc. per 100 cc. of mud caused a rise in the viscosity.

An inspection of the results above will show that the pH value is one of the controlling factors. The minimum viscosities for each concentration occur when the pH value is approximately 10. If the samples were allowed to stand, they showed a distinct tendency to gel, which is a rather unfavorable characteristic of drilling fluids.

Upon the addition of small quantities (0.05 to 0.25 cc.) of tannin to Conroe mud, the viscosity showed a distinct rise (Figures 60-63). However, when the concentration of tannin was raised to 1.0 cc., the viscosity dropped to a value considerably below that of the original mud. This was the only mud which showed this effect.

### Formaldehyde

As formaldehyde tans best at higher pH values, the pH of the muds was raised to about 10.0 to 10.5 before adding the formaldehyde. It was found necessary to allow the samples to stand for some time before any appreciable results were obtained, the reaction with formaldehyde being very slow. When allowed to stand, it was found that the pH value of the muds lowered, apparently due to some reaction of the formaldehyde. It is possible that the formaldehyde formed acid polymers. Be that as it may, when the pH was again raised, the muds slowed a slightly lower viscosity than the original muds. The change was more appreciable with Conroe mud than the others (Figures 75 to 79). It is interesting to note that the minimum viscosities were obtained when the pH was about 10.5, as was also the case with tannin.

Formaldehyde, when in basic solution, forms

acidic polymers. It is possible that this reaction took place in the samples to which it was added.

### Ferric Chloride and Chromic Chloride

Ferric chloride and chromic chloride are known to have certain tanning properties, and it was thought that because of this similarity with tannin, these might have a similar effect in reducing the viscosities of the muds as did tannin. Sodium sulfite was tried for the same reason.

The muds were treated similarly with regard to chromic chloride and ferric chloride. One set of samples were treated with each reagent without previously adding any caustic soda or hydrochloric acid to the muds to affect the pH value. After ferric chloride or chromium chloride had been added, hydrochloric acid was added to a few samples, and the viscosity showed a rise. This procedure was therefore discontinued. If, however, after adding the reagents, the pH was raised by adding caustic soda, the viscosity was found to go through a minimum. The value of the minimum was more or less dependent upon the amount of ferric chloride or chromic chloride added. If the results are inspected, it will be noticed that the minimum continually rises as the concentration of ferric chloride or chromic chloride is raised. This effect is more conspicuous if one inspects the plots on which these same results are shown (Figures 68-72, 48-51, 15-18). Further, it will be noticed that the minimum viscosities for the samples were obtained at progressively lower pH values as the concentrations of the ferric chloride and chromic chloride were increased.

As negative results, as far as lowering the viscosity was concerned, were obtained when ferric chloride, and chromic chloride were added to the mud, it is possible that the ferric hydroxide and chromic hydroxide were precipitated due to the alkalinity of the muds, which were distinctly basic. Therefore another set of samples were run in which the pH of the muds was lowered with hydrochloric acid before adding the ferric chloride and chromic chloride.

In the set of samples where the pH values were lowered by adding hydrochloric acid, the addition of chromic chloride and ferric chloride had little further effect upon the viscosity of the muds. Also,

- 29 -

as the pH was raised after the addition of these salts, the viscosities of all samples show a general rise. It is interesting to note the comparative constancy of Z-I for any one sample, irregardless of how much Z-S4 and Z-143 changed.

Inspection of the results given above and the data given in graphical form in the Appendix (Figures 4 to 82 ) will show that the viscosities represented by the slope of the characteristic viscosity lines (Z-I) does not change as rapidly as the viscosities at 84 and 143 r.p.m. Also, it will be noted that in some cases the viscosities at 143 and 84 r.p.m. will increase and the viscosities represented by the slope of the line will decrease. It seems that there is very little correlation between the relative values of Z-I with Z-143 and Z-84. However, it does indicate that the greatest changes in viscosity are due to the changes in internal friction. A little consideration will show that after this resistance is overcome, it takes comparatively little change in force to vary the rate of shear.

### Sulfite Liquor

Sulfite liquor gave qualitatively the same results as ferric chloride and chromic chloride. Since

- 30 -

these results were negative, insofar as reducing the viscosity is concerned, very few samples were run.

## pH

The fact that the pH value is a determining factor in the control of the viscosity of drilling muds is shown in Figure 2. From an inspection of these curves it will be observed that a very sharp maximum occurs when the pH is decreased slightly below that of the original mud. Ambrose and Loomis<sup>2</sup> observed similar characteristics to exist when working with bentonite suspensions. It is possible that the maximums observed with these drilling muds have some relation to the isoelectric points of these muds. However, no attempts were made to determine whether or not this is true. It is recommended that future investigators interested in this problem should attempt to test the validity of this possibility.

All of the muds passed through a minimum as the pH value was raised. Also, in every sample tested, irregardless of how it was treated previously, when excess caustic was added the viscosities showed a distinct and fairly sharp rise. Keppeler<sup>10</sup> explains that when clay particles are mixed with water the particles become negatively charged with reference to the water and hence repel each other. In other words, the particles show a tendency to be self-stabilizing in water. This writer further explains that when alkali are added to the suspension the clay particles adsorb the hydroxyl ion and hence become strongly negative. This causes the particles to repel each other and hence the clay remains in suspension for a longer period of time.

The minimum through which the viscosities of the muds passed when the pH was increased is probably due to the presence of amphoteric materials, such as alumina or silicon hydroxides, in the suspensions. The viscosity of colloidal solutions of these materials is known to pass through a minimum at the isoelectric point. The minimum is thus explained by the presence of such materials, and conversely the minimum is offered as evidence that such materials are present in the drilling muds investigated.

# Phosphoric Acid

From the above discussion, it would seem probable that the effect of tannin/and the effect of reducing the viscosities is due to entirely different

- 32 -

properties of the reagents. Since formaldehyde polymerizes in a basic solution to form acidic polymers, and since tannic acid reacts as an acid, it would seem that the acidic properties of the reagents might play an important roll in the reduction of viscosity of the muds.

It will also be noticed from the discussion of the effect of pH on the viscosities of the muds that this is the same qualitative results as those which are obtained when the effect of pH on colloidal solutions of amphoteric materials, such as aluminum hydroxide is determined. If such materials are present in the muds it is probable that either aluminum hydroxide or silicon hydroxide, or both. is present. Assuming that aluminum hydroxide were present, an acid having a high valence anion which forms an insoluble salt of aluminum would be expected to reduce the viscosity. The mechanism of such a reaction would be to form a dehydrated, insoluble salt, and to decrease the charge on the particles. While this is entirely problematical, it is quite possible that such a reaction took place in the case of tannin and formaldehyde. In order to verify this theory, the effect of a trivalent, inorganic acid was

- 33 -

investigated -- phosphoric acid.

Phosphoric acid was found to be quite satisfactory for reducing the viscosity of the muds. It was necessary to allow the samples to stand for a day. Apparently, when the acid was first added, the only effect was to lower the pH value of the samples. As has been mentioned above, lowering the pH values of the muds raised the viscosity several fold. This phenomena was evident from the fact that immediately after adding the acid, it was impossible to pour the samples out of the bottle. However, after standing for a/day, it was evident that the viscosity of the samples had lowered from the fact that the muds would then flow from one end of the bottle to the other very readily. Also, if the plots (Figures 80, 35, and 54) are inspected, it is found that upon determining the viscosities of the samples before and after shaking, there is very little change in viscosity, which is quite a contrast to the results obtained with untreated mud, and samples treated with tannin or formaldehyde. The untreated mud showed viscosities several times larger before shaking than after shaking (Figure 1). This is at least a qualitative measure of the amount of gellation of the samples.

When the samples to which phosphoric acid had been added were allowed to stand for two days. water separated out. It was found to be roughly proportional to the amount of acid added. This is an indication that the clay particles are flocculated and desolvated by the acid. Keppeler<sup>9</sup> also found similar results when certain acids were added to clay suspensions. When the viscosity of the muds containing phosphoric acid was determined after thorough shaking of the samples, it was found to differ very little from that of the samples before shaking. The sample which contained 0.2 cc. of the acid, however, did show a slight drop. When the pH values of the samples were raised by adding caustic soda, the viscosity of all samples which contained more than 0.2 cc. of the acid was lowered. A minimum viscosity was reached with the sample containing 0.5 cc. of the acid per 100 Rabb's Ridg<sup>e</sup> mud from below 3000 feet cc. of mud. was tested with 1.00 cc. of the acid, and the per cent reduction in viscosity was found to be the same as for 0.50 cc., the minimum viscosity coming at the same pH value. It is interesting to note that the minimum viscosity for all muds when phosphoric

- 35 -

acid was used came when the pH values were approximately 6.5. When 0.2 cc. of the acid was added. it was not sufficient to lower the pH value to 6.5. When the pH of samples with 0.2 cc. of phosphoric acid was increased, it was found that the viscosity of these samples increased as the pH was It should be noted that the 0.2 cc. conraised. centration of phosphoric acid lowered the pH of each sample to approximately 7,5, whereas, the higher concentrations lowered the pH to approximately 3. Hence, since the pH of the 0.2 cc. sample was more nearly 6.5 than those of higher concentrations it appears that this fact accounts for the lowest viscosity which was obtained without varying the pH of the samples containing phosphoric acid. Therefore the authors believe that the following conclusion is justified, namely, that a concentration of phosphoric acid slightly above 0.2 cc. per 100 cc. of mud, which is just sufficient to give a pH equal to 6.5 will give as satisfactory results as the higher concentrations, the pH values of which must be increased to 6.5 to produce the most satisfactory results.

The fact that the minimum viscosities of the samples to which phosphoric acid was added appeared at a pH value of 6.5 raises another interesting point. It was mentioned above that the behavior of tannin and formaldehyde might be due to aluminum hydroxide gel, which reacted with the formaldehyde and tannin to form an insoluble, de-The aluminum hydroxide might have hydrated salt. been the predominant factor in the case of these reagents. But, it is also quite possible that silicon hydroxide was present also. Aluminum hydroxide is a much stronger electrolyte than silicon hydroxide. T herefore, the isoelectric point would appear at a higher pH value than for silicon hydroxide. Upon the reaction of the aluminum hydroxide with phosphoric acid, the concentration of aluminum hydroxide concentration might be reduced to such a low value that silicon hydroxide was the determining factor. It seems a quite plausible conclusion that the pH at which the minimum viscosity of this set of samples was the isoelectric point of the silicon It is the recommendation of the authors hydroxide. that future investigators interested in the viscosity

- 37 -

chafacteristics of clay suspensions determine the isoelectric point of the muds under the various conditions at which minimum viscosities were obtained with each reagent in an effort to correlate its effect with the theory given above.

Sodium phosphate, as would be expected from the results using ferric and chromic chlorides, increases the viscosity, although not as much as the other agents since it is a neutral salt in solution.

Hatscheck proposed the following formula for the relation between volume percent of a suspended material and the viscosity:

$$Z = \frac{Z}{1 - \sqrt{hV}}$$

where

Z = viscosity of suspension Zo = viscosity of dispersing liquid V = volume percent of suspended material h = constant

Therefore when  $\frac{Z}{Z_0}$  is plotted against  $\sqrt[3]{V}$ , a straight line should result. As is noticed on the plot (Figure 3), given in the results, this formula does not fit the facts.

## CONCLUSIONS

1. The pH value of a clay suspension is one of the most important factors controlling the viscosity.

2. Minimum viscosities/occur at the isoelectric point of the mud.

may

3. Acids having three or more valent anions which react with the amphoteric materials to form an insoluble precipitate are most satisfactory reagents for reducing the viscosity of clay suspensions.

4. The high viscosities of muds are due to some gel forming amphoteric material such as hydroxide or silicon hydroxide.

5. The anion of the polyvalent acid reacts with the cation of the amphoteric hydroxide present in the muds to form an insoluble, dehydrated salt.

6. The drilling muds investigated do not follow Hatschek's equation.

## **RECOMMENDATIONS**

1. For investigators interested in the viscosity characteristics of clay suspensions, the authors make the following recommendations:

a. Determine the isoelectric point of the suspensions, with emphasis on its relationship on the minimum and maximum viscosities of the suspensions.

b. Investigate the effect of other trivalent or tetra-valent acids on the viscosity of clay suspensions.

2. The use of phosphoric acid as a treating agent for the reduction of the viscosity of drilling fluids should be investigated from the standpoint of practicability and economics.



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# - 41 -

## PROCEDURE

All viscosity measurements were made with a MacMichael Viscometer. It consists essentially of an outer revolving cylinder and an inner stationary cylinder supported by a wire. The torque produced upon the wire is a linear function of the displacement, and read as degrees MacMichael (300 degrees per revolution) of displacement about a vertical axis. Each wire has a limited viscosity range in which it can be used. Therefore, different sized wires are used for different ranges of viscosity. Two wires, No. 26 and No. 22, were used in this investigation.

The wires were calibrated with glycerine solution. The viscosity of glycerine solution is a function of the specific gravity and the temperature of the solution. These relationships are shown in Figure 86. The specific gravity of the solution used was 1.2500 at 20° Centigrade. The viscosity corresponding to this specific gravity and temperature is 523 centipoises. By using a liquid of constant viscosity, the fieflection produced upon the wire is a

- 42 -

straight line function of the revolution per minute. The results of these calibrations are shown in graphical form on Figures 54 and 55.

The viscosity (Z) is given by the following equation:

 $Z = \frac{(K)d(Deflection)}{d r \cdot p \cdot m}$ 

'K' for wires No. 26 and No. 22 were found to be 93.5 and 537 respectively.

Considerable preliminary work was done with Conroe mud in an attempt to get check results on different sample treated by the same method. However, it was impossible to get check results due to the changing of the viscosity of the mud as it was being handled. Several minutes were necessary to determine the r.p.m. of the revolving cylinder. During this time, the deflection would drop several degrees. Also, the viscosity would change while pouring the mud from one vessel to another. A method for determining the deflection at four different r.p.m. was developed which required only 15 to 20 seconds to make all four determinations. This was done by tightening the speed control screw of the viscosimeter against slugs of different size. By this method, 143, 84, 110, and 50 r.p.m. were obtained with very little effort, and with excellent consistency. The change in viscosity from handling was eliminated by stirring the muds for several minutes, after which further stirring did not effect the viscosity. Later, it was found that shaking the samples would produce the same results in much less time. All samples, unless otherwise stated, were treated by this method.

The effect of stirring (Figure 1) was determined by taking the viscosity of the muds with as little handling as possible, then after stirring with a constant speed mechanical stirrer. The viscosity was taken at the end of 0.5, 1.0, 2.0 etc. minutes until further stirring caused no further decrease in viscosity.

To determine the dilution effect (Figures 3, and 82) on the viscosity, it was necessary to dry the muds, and determine the density of the clays resulting. The muds were dried by evaporating over a water bath in a watch glass. This required about ten hours. The density was determined by use of a pichnometer. A known weight of the clay was placed in the pichnometer, and the pichnometer filled with alcohol. The density of the alcohol was then determined by weighing the pichnometer empty, full of water, and full of alcohol. From these determinations, the density of the clay was computed. After this, by adding the calculated amount of water required, suspensions of Conroe mud containing 9.03, 8.5, 8.0, 7.5 and 7.0 per cent by volume were made and the viscosity determined.

The effect of pH was determined by taking two samples of each mud, and lowering the pH by the addition of hydrochloric acid, to one, and raising the pH by adding caustic to the other. Viscosities were determined at various pH values as different quantities of acid and base were added.

Universal Indicator was used to determine the pH values.

The effect of different reagents (Figures 4 to S1) were tried on Rabb's Ridge mud from below 3000 feet, and Rabb's Ridge Mud from above 3000 feet, and Conroe mud from below 4000 feet. All three muds were treated similarly in order to compare the properties of the fhree.

## The following reagents were used:

1.	Chromium chloride	<b>50%(</b> by	weight)of	$CrCl_3.2H_2O$
2.	Ferric Chloride	50%	of	FeCl3.6H20
3.	Formaldehyde	40%		
4.	Quebracho tannin	28%		
5.	Phosphoric acid (ortho)	<b>8</b> 5%		
6.	Sodium phosphate	28%		
7.	Sulfite liquor			

8. Sodium hydroxide (caustic) 40%

The Quebracho tannin solution was prepared by adding 100 cc. of water to 40 grams of the tannin. All of the solid tannin extract did not dissolve. The liquid above the solid was used as the reagent. The sulfite liquor was mother liquor obtained in the production of sodium sulfite crystals. Phosphoric acid and formaldehyde solutions were attained made up at the concentrations mentioned above. All other reagents were made by adding the required volume of water to 25 grams of the crystals.

The effect of ferric chloride was tried by two different methods. The first was to add the ferric chloride to the mud directly, and the second to lower the pH of the mud to about 4 by the addition of hydrochloric acid, then add the ferric chloride. Concentrations of 0.05, 0.10, 0.25, 0.50 and 1.00 cc. of 50 per cent ferric chloride per 100 cc. of mud were used. Each concentration was made up separately, and the pH raised to 11 or above by adding caustic. By this method data for the effect of concentration of ferric chloride and the effect of pH on the different concentrations were obtained.

The effect of chromium chloride was determined by the same methods as for ferric chloride. Sulfite liquor was tried on Rabb's Ridge mud from above 3000 feet, and found to act similar to chromic chloride and ferric chloride, so further determinations were not made with this reagent.

The effect of Quebracho tannin was determined by preparing samples containing 0.05, 0.10, 0.25, 1.00 and 2.00 cc. of 28 per cent solution per 100 cc. of the mud. In no case were the muds treated to change the pH before adding the tannin. After adding tannin, the pH was raised to 11 or above with caustic solution. The viscosity of the muds were determined at different pH values for each sample as the caustic was intermittently added.

Previously to adding formaldehyde to different samples, the pH value of the muds were raised to 9.5 or 10 by adding caustic solution. Then different concentrations of formaldehyde were added and the viscosity determined immediately. The samples were then allowed to stand, for several days, the viscosities being taken at different intervals, as noted on the graphs on which the data is recorded (Figures 31 to 34 and 75 to 79). The pH value of the muds were found to lower to as much as 8.5 after standing several days. The pH values were then raised to 11 or above by adding more caustic before the samples were discarded.

The effect of phosphoric acid was determined on all three muds at concentrations ranging from 0.10 to 1.0 cc. of 85 per cent phosphoric acid per 100 cc. of mud. The samples were made up, shaken thoroughly, and allowed to stand over night. The viscosities were then taken <u>before</u> and <u>after</u> shaking. The samples were again set away for a couple of days and water separated out over the mud. This water was siphoned off, measured and returned to the mud. The samples were then shaken up well and the viscosity again determined. The pH values were then maised by adding caustic and the viscosity determined at various pH values ranging from less than 3 to 7.5.

- 48 -

The effect of phosphoric acid on a suspension of bentonite (5 per cent by weight), was also determined by the method used for the three muds mentioned above, except that the mud was allowed to stand only one night.

The effect of sodium phosphate was tried on the two Rabb's Ridge muds. No treatment was given the mud previous to adding the sodium phosphate solution. The pH values were changed on two samples, but after no lowering of the viscosity was observed either before or after varying the pH, no further work was done with the sodium phosphate samples.

#### EXPANSION OF INTRODUCTION

The fact that control of the viscosity of drilling fluids is a very important factor in present day rotary drilling operations was mentioned in the Introduction. It will now be shown just what part viscosity does play, and why it is important to decrease the viscosity of drilling fluids as much as possible.

Lawton, Ambrose, and Loomis<sup>1</sup> use the following form of the Pfanning equation to show the relation between pump pressure and viscosity,

 $p = K_1 z^{0.2} (v_c + K_2)^{1.8} = K_3 z^{0.2}$ , for constant carrying capacity, where,

p = pump pressure z = viscosity  $v_{c} = v - v_{s}$ where,

v = velocity of flow of the mud fluid  $v_s = velocity$  of slip of the cuttings.

It is seen from the above equation that any variation in the viscosity will result in only a small relatively/change in the pump pressure.

Lawton, Ambrose and Loomis assume the mud particles to be in two sizes, large and small, and then make use of this assumption to show that the viscosity of the drilling fluid is a very important factor in the rate of settling of the cuttings. The formula derived by these investigators from Stoke's law and the above assumption is as follows,

$$V_{L} - V_{S} = \frac{K r_{L}^{2}}{Z} (L - S)$$

where,

 $V_L$  = velocity of settling of large particles  $V_S$  = velocity of settling of small particles K = a constant in Stoke's law  $r_L$  = radius of large particles z = viscosity of the suspension L = density of the large particles s = density of the small particles

It is obvious that if the above equation truly represents the conditions which exist in the settling ditch, there is only one variable on the right hand side of the equation, the viscosity, and since it is in the denominator it should be made as small as possible in order to obtain the largest possible difference between  $V_L$  and  $V_S$ . The small particles

should remain in the suspension, and therefore a decrease in the viscosity of the suspension will result in an increase in the settling rate of the large particles. This is the chief object of decreasing the viscosity of drilling fluids, since it is generally highly advantageous to recover the fluid and use it over and over again for economic reasons pointed out in the Introduction.

The MacMichael viscosimeter is widely used for viscosity, determinations of such materials. The MacMichael viscosimeter operates on the torsion principles. A plunger of standard dimensions is suspended by a torsion wire of exact length from the top of the instrument. The material is placed in the cup which is revolved at a constant rate of speed on a motor driven platform. The angular velocity of the platform, expressed in revolutions per minute, can be readily varied to any desired speed up to approximately 140 by a small thumb screw, which in turn regulates the motor governor. The amount of twist imparted to the wire, depending on the viscosity of the material, is read on the graduated scale of the The disc is attached to a spindle, at the bottom disc.

of which the plunger is fastened. The angular twist given to the plunger by the rotating liquid causes the hollow spindle to turn around the wire as an The upper end of the wire is rigidly held in axis. place at the top of the instrument, and its lower end is clamped to the spindle at the point where the plunger is attached. The disc is thus carried around by the spindle through a certain number of divisions which can be read directly on the disc scale under the tip of the adjustable pointer. This reading indicates the force exerted by the rotating fluid on the plunger. These readings are readily interpreted in poises by calibrating the wires with a fluid of known viscosity characteristics, glycerine for example.

The concentric cylinder type of viscosimeter is used in measuring the viscosity of suspensions, emulsions and similar fluids since viscosity is essentially a phenomena of shearing, and the large particle size encountered in fluids of the suspension and emulsion type obviously eliminates the use of small capillaries for viscosity measurements of such fluids. The particle size in many such fluids is often of the

- 53 -

same order of magnitude as the diameter of the capillary, and hence may introduce an appreciable error in the results obtained, whereas in the case of the concentric cylinder type of apparatus the particle diameter is negligible in comparison with the difference in the radii of the two cylinders, and therefore introduces no error within the limits of the experimental accuracy of most such measurements.

As has been previously stated, there has been very little work done to devise methods of reducing the viscosity of drilling fluids. The best work which has been published on the subject, of which the writers are aware is that by Ambrose and Loomis<sup>2</sup> and a second by Lawton, Ambrose and Loomis<sup>1</sup>.

Drilling fluids, or drilling muds as they are often termed, are very effectively defined by Ambrose and Loomis<sup>2</sup> as exceptional clay mixtures which are not truly viscous. These investigators explain that drilling muds flow as a plug at low pressures with no shearing except at the walls of the tube, but at higher pressures the plug breaks up and shearing takes place in the main body of the fluid.

The plug effect spoken of by Ambrose and Loomis<sup>2</sup> shows up in measurements made with the MacMichael

- 54 -

viscosimeter as the yield point, or as Bingham<sup>4</sup> terms it, the internal friction of the material. This point is discussed in the Discussion of Results.

Clay suspensions are known to possess several unusual characteristics. Nikolaev<sup>14</sup> found, as have several other investigators, that the viscosity of clay suspensions increase on standing. Schofield and Blair<sup>15</sup> found that a solid wall may modify the consistency of clay suspensions at an appreciable distance from it, but further state that this point is still somewhat doubtful due to lack of available data. Dubrisay<sup>7</sup> and Kuhn<sup>11</sup> found that the viscosity of clay suspensions is decreased by stirring, and attribute this behavior to the lamellar structure of the particles and hence when the suspensions is stirred the particles orient themselves tangent to the vortex lines created by the agitation. Dubrisay in the same article explains the high viscosity of these suspensions in alkaline and acid solutions by the fact that the particles are agglomerated. Briggs<sup>6</sup> defined the water which is bound to the colloidal particles as that portion of the water in a system

containing colloid and crystalloid particles which is associated with the colloid together with the ions that form a part of the colloid complex. It is well known that the amount of bound water which is in a clay suspension depends on the amount of colloidal material present. Shmelev<sup>16</sup> found that the volume of certain Russian clays increased to as much as 44 per cent above that of their absolute volume. This was due to the hydration of the clay particles. Bradfield<sup>b</sup> states that the concentration of calcium cations at the surface of colloidal clay particles is greater than in the intermicellar liquid. This fact probably accounts for the fact that certain clays give off carbon dioxide when strong acids are added to them, since more or less carbonate is associated with the calcium ion in such materials.

Certain chemicals are known to affect the properties of colloidal clay suspensions. Dubrisay and Trillat<sup>8</sup> found that soda, lithia, potash, sulfuric acid, phosphoric acid, and hydrochloric acid caused suspensions of kaolin to flocculate, and explained the phenomenon by a change in structure of the pre-

- 56 -

cipitated particles, but the specific change in structure is not mentioned. These authors state that X-ray spectograms favor this explanation.

Bah<sup>3</sup> attributes the mutual flocculation of certain hydro-sols to the neutralization of opposite charges, the interaction of stabilizing ions and the presence of electrolytes.

The authors are aware of only two articles which have been published on the chemical treatment of drilling fluids to lower their viscosities. Nikolaev<sup>14</sup> found that the addition of ammonia to a certain drilling mud prepared from a Russian clay lowered the viscosity of the mud when added in excessive amounts. However, when added in small amounts the reverse effect was observed. Treatment of the mud with ammonia and hydrochloric acid yielded a product similar to aqua gel.

The most complete work described in the literature is that of Lawton, Ambrose, and Loomis<sup>12</sup>. These investigators used the following reagents, tannic acid and varying amounts of caustic, peat with varying amounts of caustic, sulfite waste liquor (a by-product of the paper industry), soda-black liquor (also a byproduct of the paper industry which contains mostly

- 57 -

lignins and carbohydrates and sodium carbonate), Sap-brown (a commercial product containing humates and lignates), Mud-it (a commercial product containing sodium aluminate with excess caustic) and Stabil-

ite which is another commercial product, the constituents of which are not known to the authors. It is stated in this article that Sap-brown and Stabilite are both superior to soda with respect to lowering the viscosity and elimination of the rapid increase in viscosity shown by caustic soda with increase in concentration. The results with tannic acid were that tannic acid with increasing amounts of soda is superior to Stabilite, but alone has little effect. Peat, which contains humic acid chiefly, also gave excellent results. Sulfite waste liquor gage good results, but somewhat greater concentrations were necessary. Soda-black liquor gave good results also.

As a result, these investigators conclude that organic uses are much superior to the inorganic reagents for the purpose of lowering the viscosity of clay drilling muds. Further the degree of eglling of the mud is almost entirely dependent upon the amount of caustic soda used with a given organic chemical. All chemicals used formed a light gel with the clay.

Often weighting materials such as barium sulfate<sup>13</sup> are used as weighting materials to increase the density of the drilling muds.

The muds used in the investigation of the authors were kindly furnished by the Humble Oil Company, and are described as follows:

## Rabb's Ridge Mud from above 3000 feet.

This mud was obtained at a depth of less than 3000 feet. This mud has a very low viscosity and a slow rate of gellation for a given density. It is considered a very satisfactory drilling mud.

#### Rabb's Ridge Mud from below 3000 feet.

This mud was obtained at a depth of more than 3000 feet. If the density of this mud is kept at 10 pounds per gallon or lower it has a relatively low viscosity but an extremely high rate of gellation, and it has been found that if is not satisfactory for use in high pressure gas areas. If the mud is diluted with water to a density of approximately 9.6 pounds per gallon, it is not easily gas cut, but does not have a sufficiently high density to overcome the gas pressure, and consequently, inert weighting material should be added to raise the density to the required value without affecting the rate of gellation and the tendency to gas out.

## Mud from the Conroe Field

This mud was obtained at a depth of more than 4000 feet. This mud has a high viscosity and very fast rate of gellation when the density is ten pounds per gallon or greater. This mud gas cuts readily unless it is treated with alkaline sodium tannate or diluted with water to decrease the viscosity and the density increased to 10 pounds per gallon by the addition of inert weighting material in order to drill high pressure gas areas. Because of the fast rate of gellation, it is considered a poor mud for drilling purposes unless it is treated.

## SUMMARY DATA SHEET

Weight of water to fill sp.gr. bottle - - - - - - 24.9315 gm Average weight of 24.99 cc of glycerine - - - - - - 31.2388 gm Weight of methyl alcohol to fill sp. gr. bottle - - - 19.7451 gm Weight of dried sample of Conroe Mud - - - - - - - 4.4941 gm Weight of methyl alcohol in bottle with dried sample

of Conroe Mud - - - - - - - - - - - 18,4491 g m

#### CALCULATIONS

Calibration of Specific Gravity Bottle

$$Capacity = \frac{24.9315}{0.998} = 24.99 \ cc$$

Specific Gravity of Glycerine

Specific gravity = 
$$\frac{31.2388}{24.99}$$
 = 1.2500

Density of Methyl Alcohol

Density = 
$$\frac{19.7451}{24.99} = 0.788$$

Specific Gravity of Dried Conroe Mud 19.7451 - 18.4491 = 1.2960 grams alcohol displaced by the

mud.  

$$\frac{1.2960}{0.788} = 1.645$$
 cc alcohol displaced by the mud.

Specific gravity of the mud =  $\frac{4.4941}{1.645}$  = 2.73

Calculation of the Wire Constants

Wire No. 26 -- at 50 r.p.m. deflection = 280 (Figure 84) Viscosity of Glycerine = 523  $K = \frac{523 \times 50}{280} = 93.5$ 

Wire No. 22 -- at 114 r.p.m. deflection = 122 (Figur e 85)

$$K = \frac{523 \times 50}{114} = 537$$

Calculation of Viscosity versus Deflection Plots

Wire No. 26 -- Deflection = 300

84 r.p.m.

$$Z = \frac{93 \cdot 5 \times 300}{84} = 334$$

$$\frac{Z = 93.5 \times 300}{143} = 196$$

180 r.p.m.

$$z = \frac{93.5 \times 300}{180} = 156$$

Wire No. 22 Deflection = 120 in each case except in the case of 84 r.p.m., where deflection = 100.

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$$\begin{array}{r} 84 \text{ r.p.m.} \\ Z = \frac{537 \times 100}{84} = 640 \end{array}$$

$$143 r \cdot p \cdot m \cdot Z = \frac{537 x 120}{143} = 451$$

180 r.p.m.

$$z = \frac{537 \times 120}{180} = 358$$

-64-

The original data as taken in the data book is in the possesson

of the Chemical Engineering Department c/o Mr. Squires. The viscosity data is presented here in the from of plots in which the authors believe/is best adapted to this case.

Specific Gravity of Glycerine Determination

Weight of sp. gr. bottle filled with water <b>50.7150</b> gm Weight of sp. gr. bottle <u>25.7835 gm</u> Weight of water 24.9315 gm
1.Weight of glycerine + sp. gr. bottle 57.0226 gm 2.Weight of sp. gr. bottle + glycerine 57.0275 gm 3.Weight of sp. gr. bottle + glycerine <u>57.0168 gm</u>
Average weight of sp. gr. bottle + glycer.57.0223 gm Weight of sp. gr. bottle 25.7835 gm Average weight of glycerine 31.2388 gm

Specific Gravity of Dried Conroe Mud

Specific gravity of methyl alcohol - - - -

	Weight of sp. gr. bottle + methyl alcohol Weight of sp. gr. bottle	25.78 <u>39 gm</u>
Weight Weight	of mud + sp. gr. bottle	25.7839 gm
Weight Weight	of alcohol + mud + sp. gr. bottle of sp. gr. bottle + mud	30.2780 gm

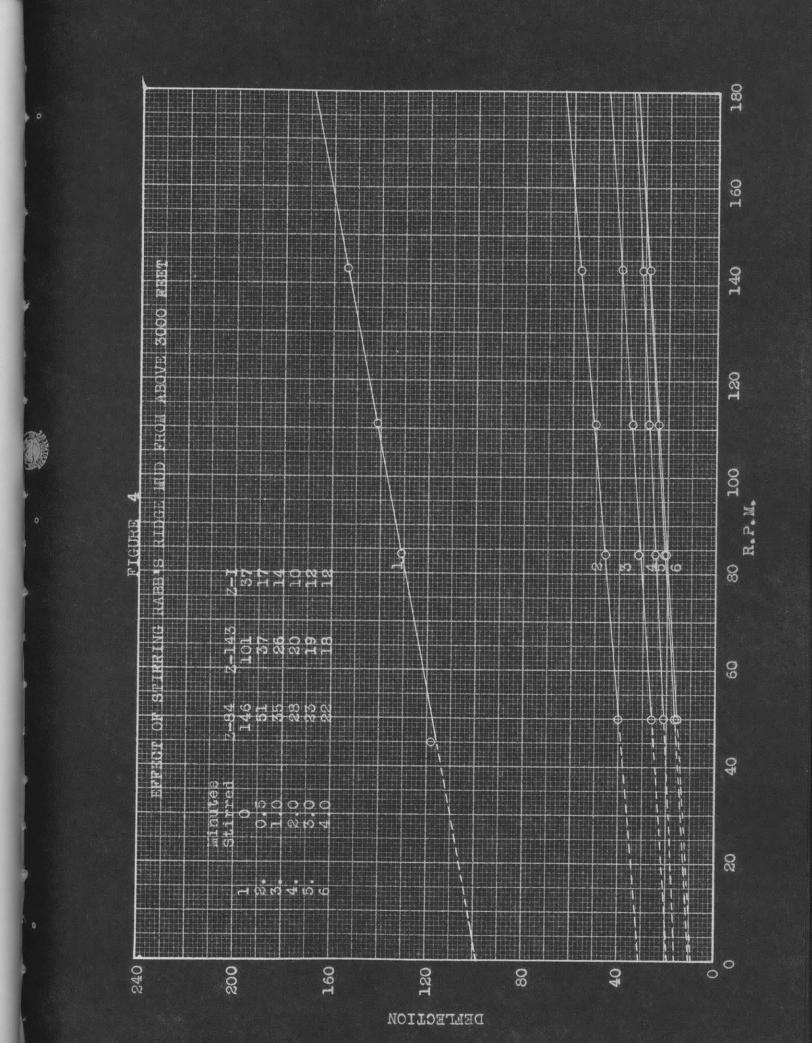
# LITERATURE CITED

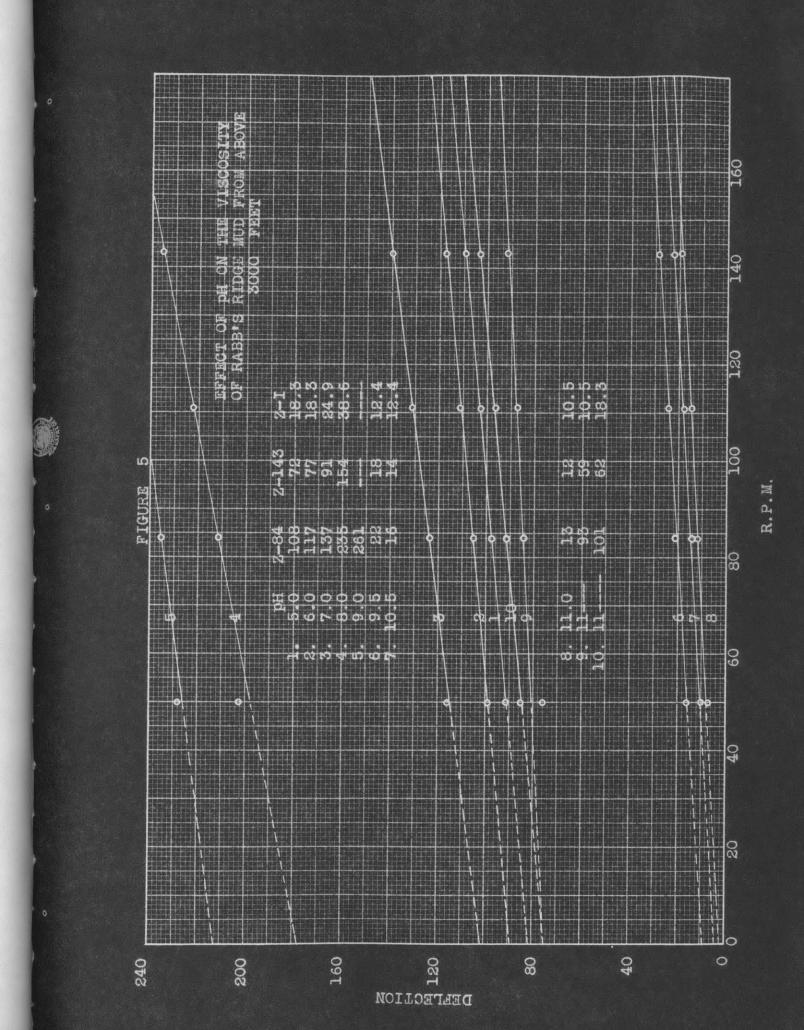
1. Ambrose, H.A. and Loomis, A.G., Oil and Gas Jour. 31. 30-31(1932) 2. Ambrose, H.A. and Loomis, A.G., Physics, 1, 129-136 (1931) 3. Bah, Diwan Chand, Kolloid-Z., 59, 60-68(1932) 4. Bingham, E.C., Fluidity and Plasticity, 1st. ed., McGraw-Hill, p.217(1922) 5. Bra dfield, Richard, J. Phys. Chem., 36, 340-347(1932) 6. Briggs, David R., J. Phys. Chem., 36, 367-386(1932); cf., C.A. 25, 5820 7. Dubrisay, R., Chimie and Industrie, Special No. 579-586 (March 1931); cf. C.A., <u>23</u>, 1,234,5081; <u>24</u>, 3413 8. Dubrisay, R. and Trillat, J.J., Rev. gen. colloides, 8. 1-9(1930) 9. Hatschek, E., Viscosity of Liquids, Chap. on Colloidal Solutions, D. Van Nostrand, (1923) 10. Keppeler, G., Ber. deut. keram. Ges., 10, 133-146 (1929) 11. Kuhn, W., Z. phys. chem., <u>A161</u>, 1-32(1932) cf. Boeder, C.A. 26, 3981 12. Lawton, H.C., Ambrose, H.A. and Loomis, A.G., Physics, 2, 365-375(1932) 13. Lu tzenko, N.and Letchenko, V. Azerbaidzhanskoe Neftyanoe Khozyaistvo, No. 4, 734(1931)

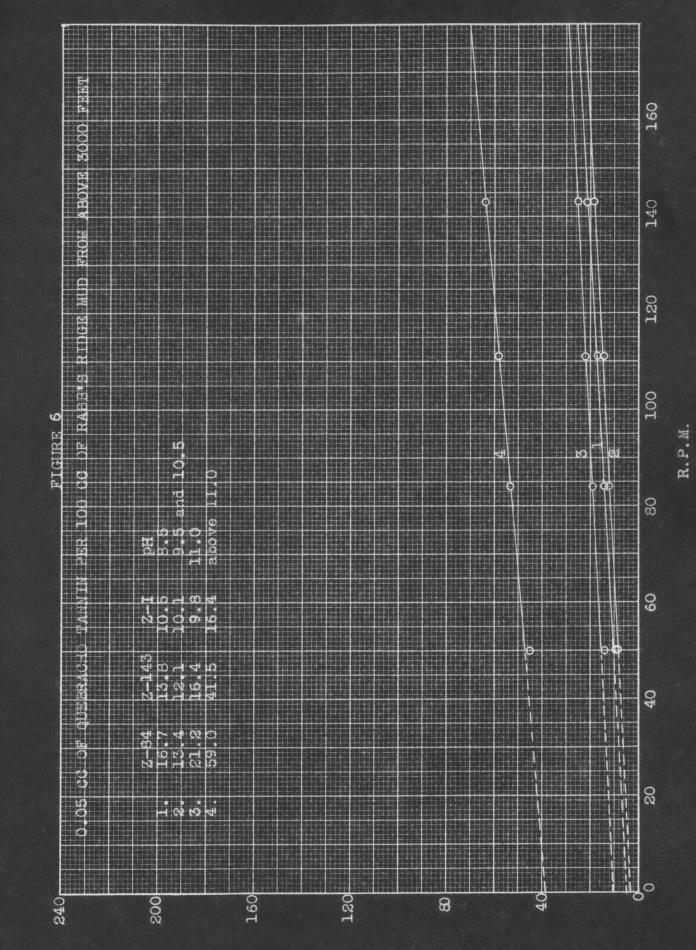
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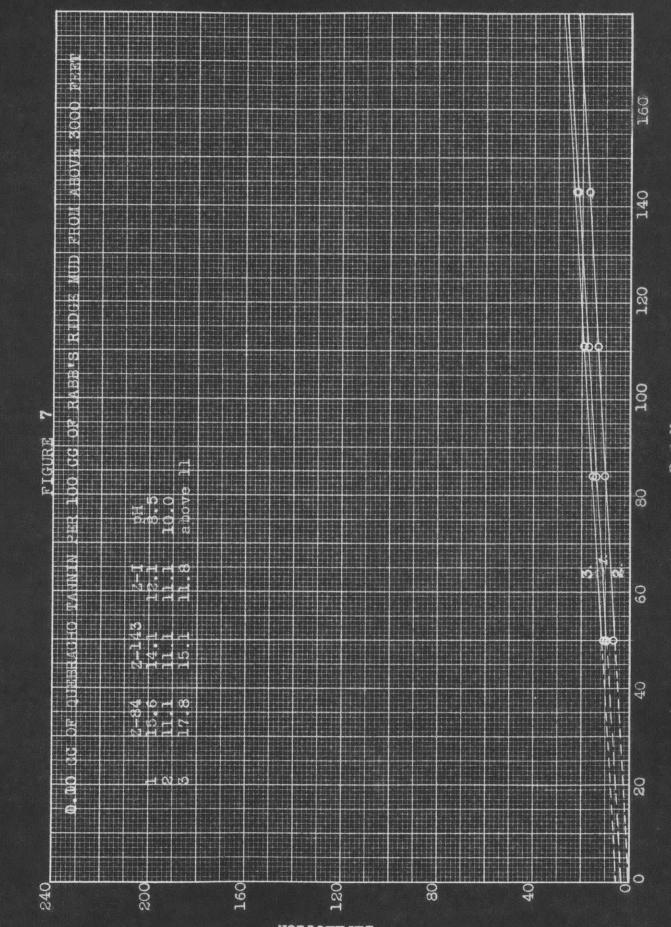
14. Nikolaev, V,,Azerbaidzhanskoe Neftyanoe Khozyaistvo, Nos. 9-10, 37-44(1931)

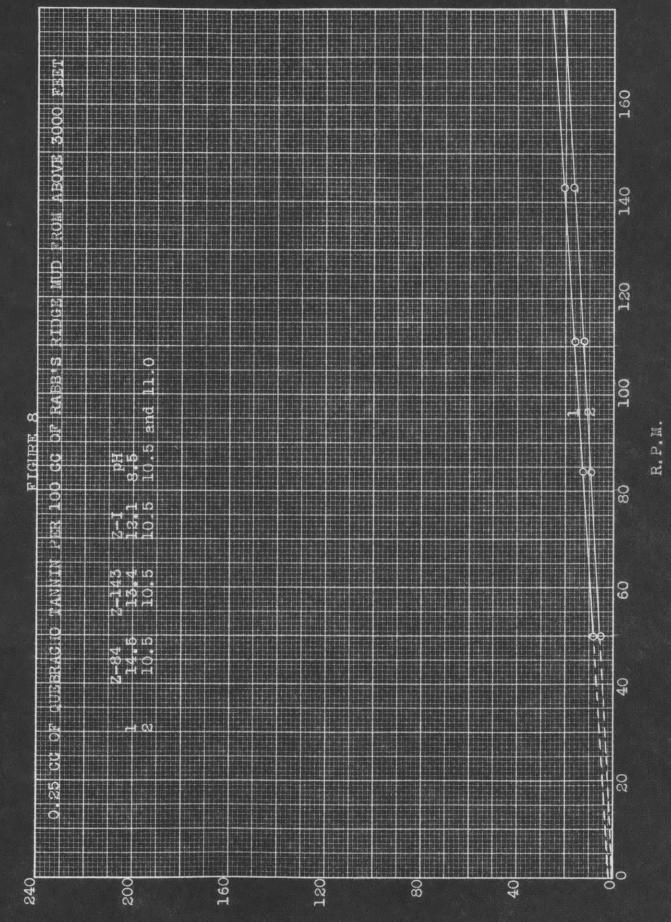
15. Schofield, R.K. and Blair, G.W.S., J.Phys.Chem., <u>35</u>, 1212-1215(1931)

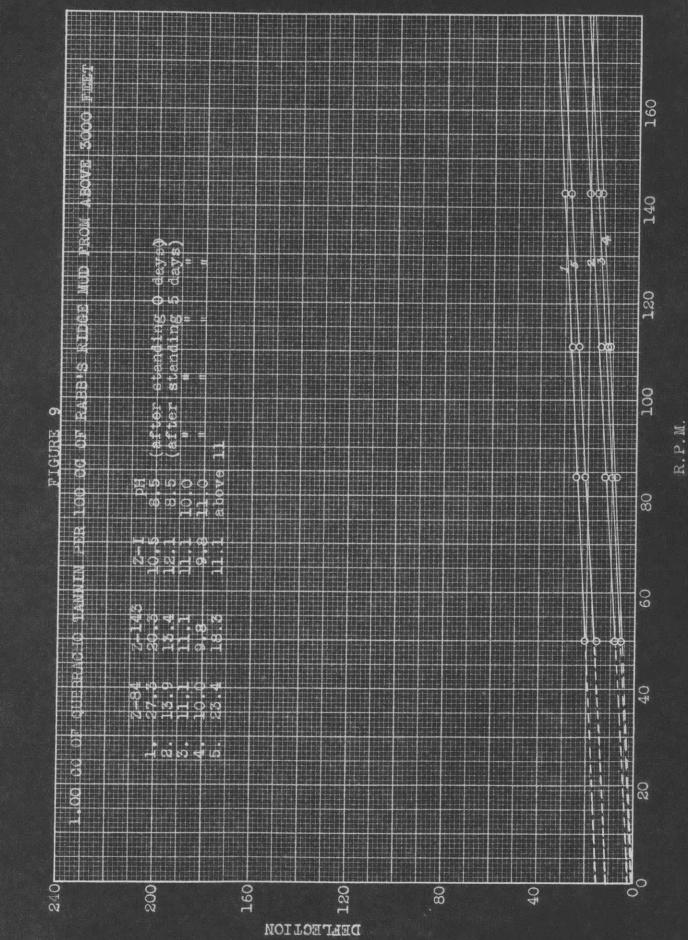


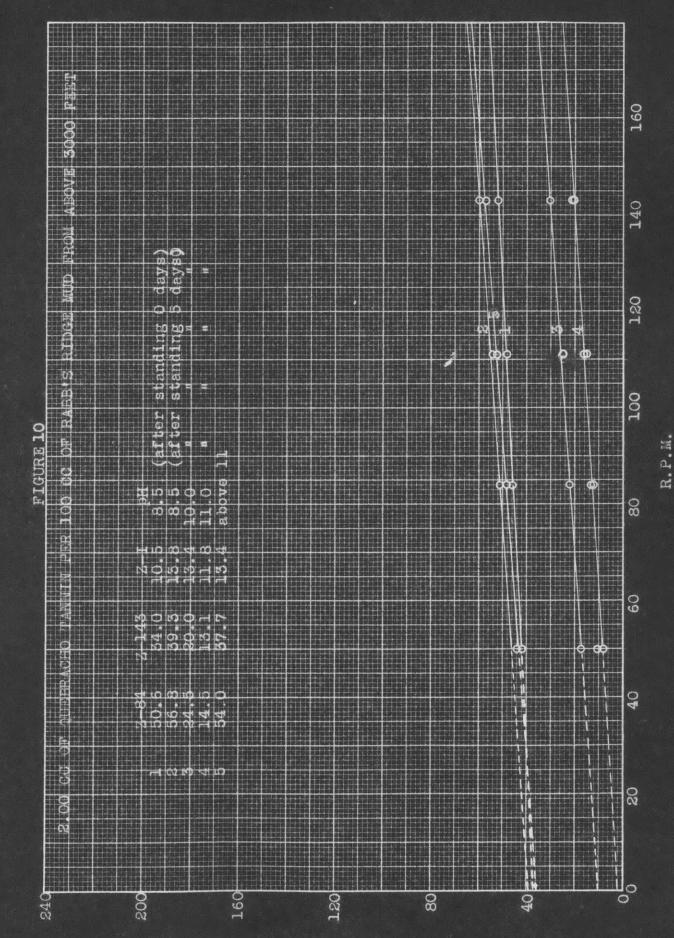


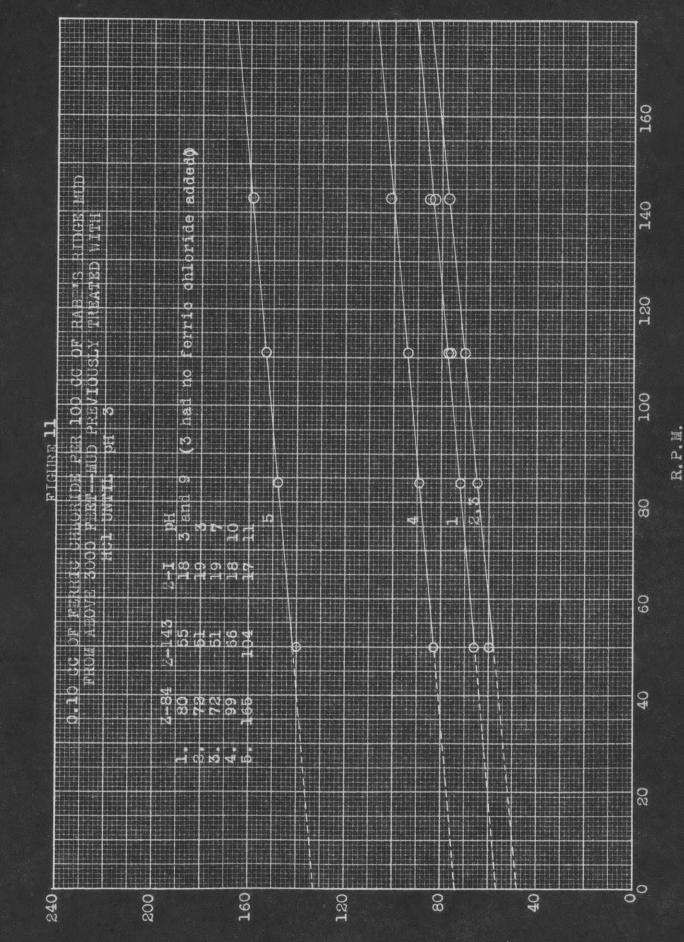


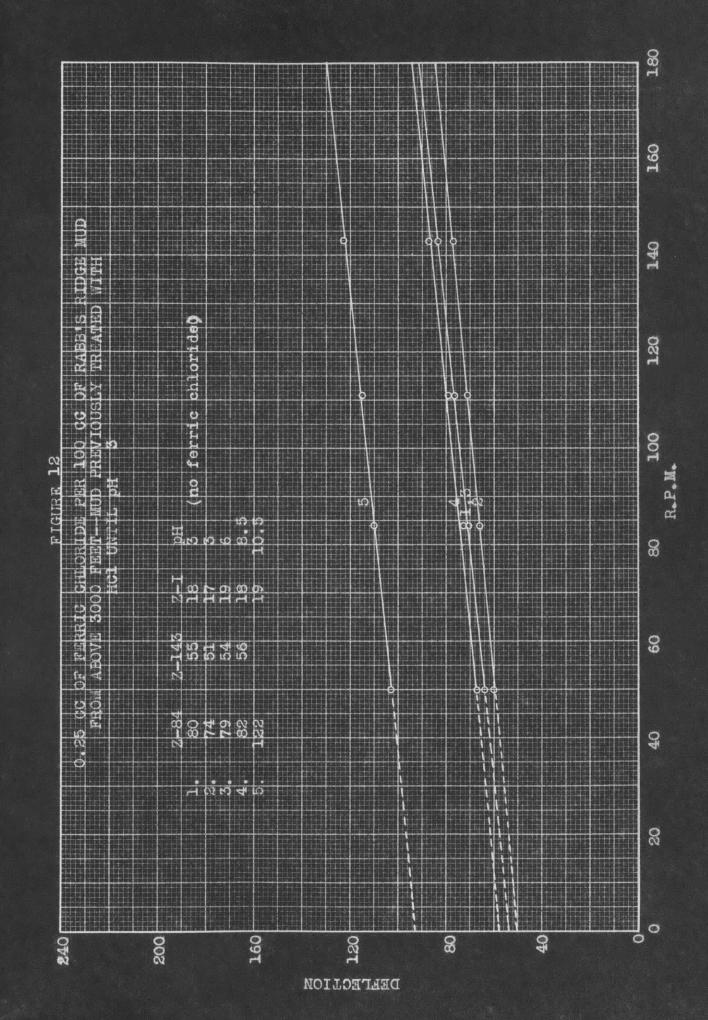


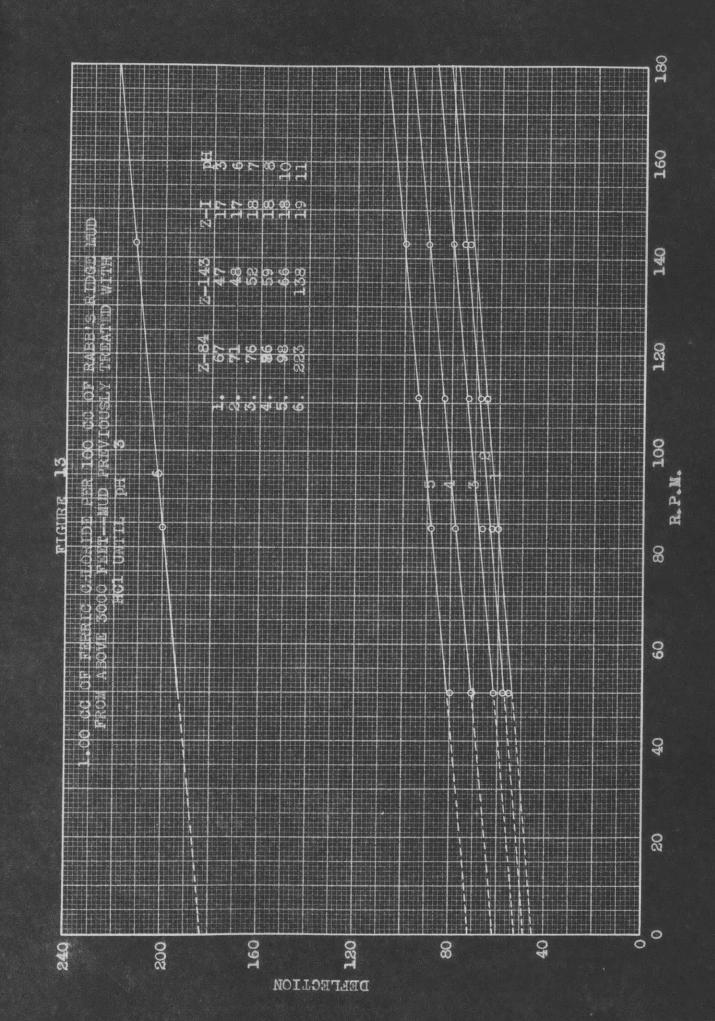


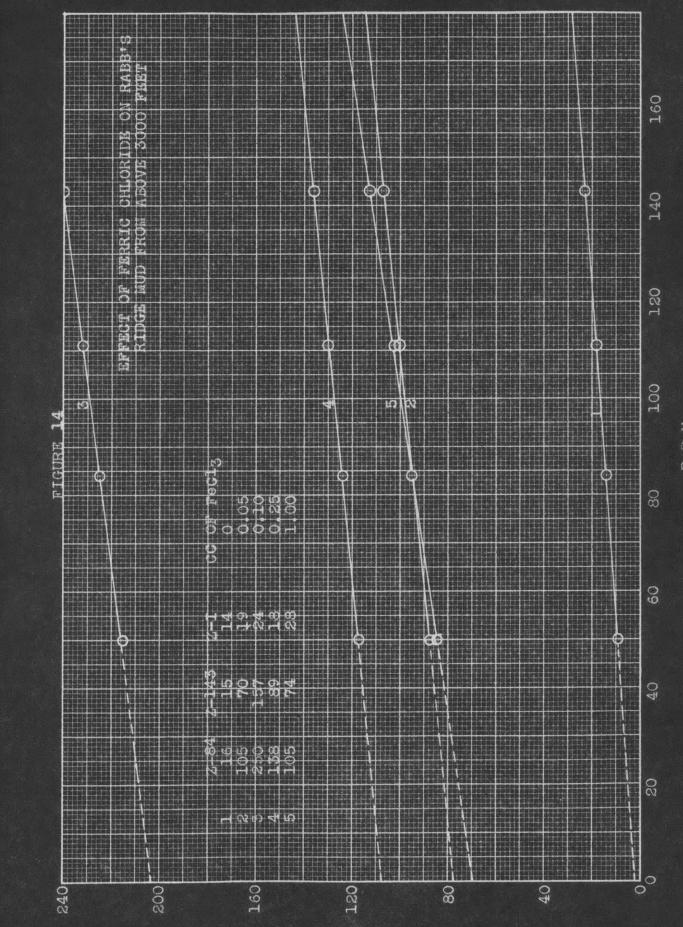






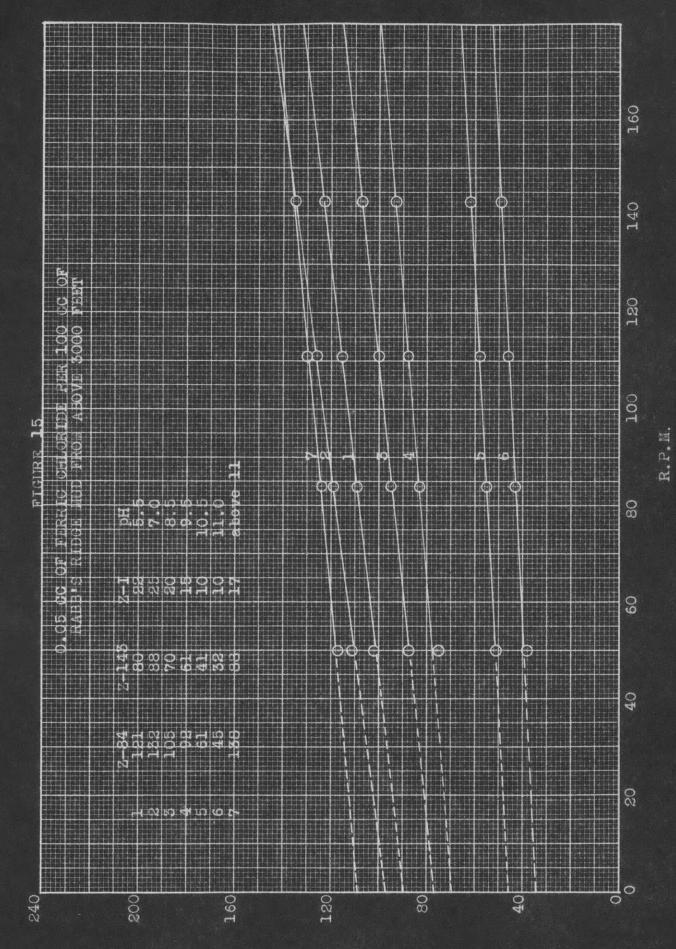


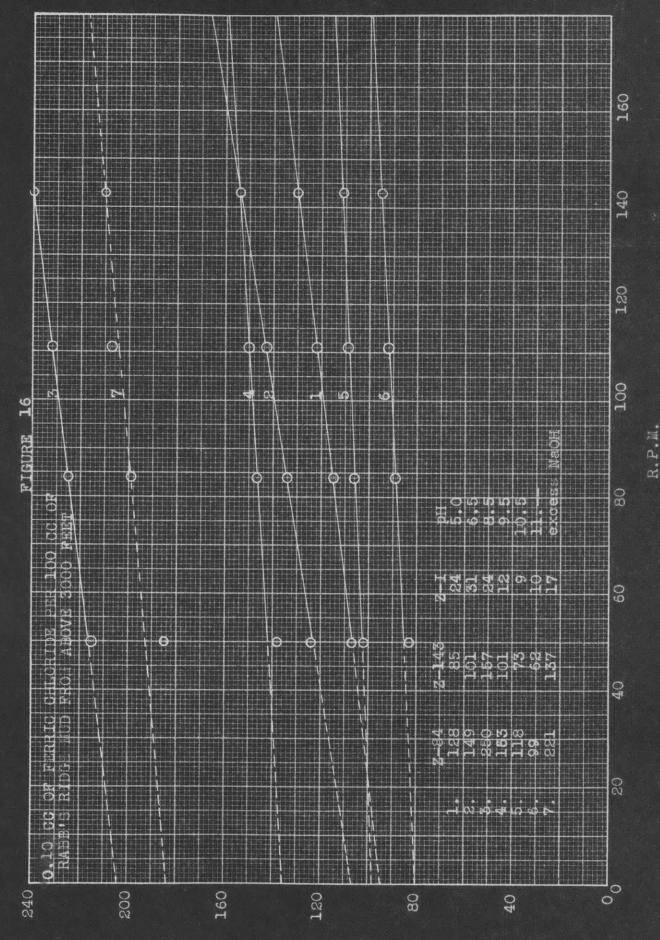


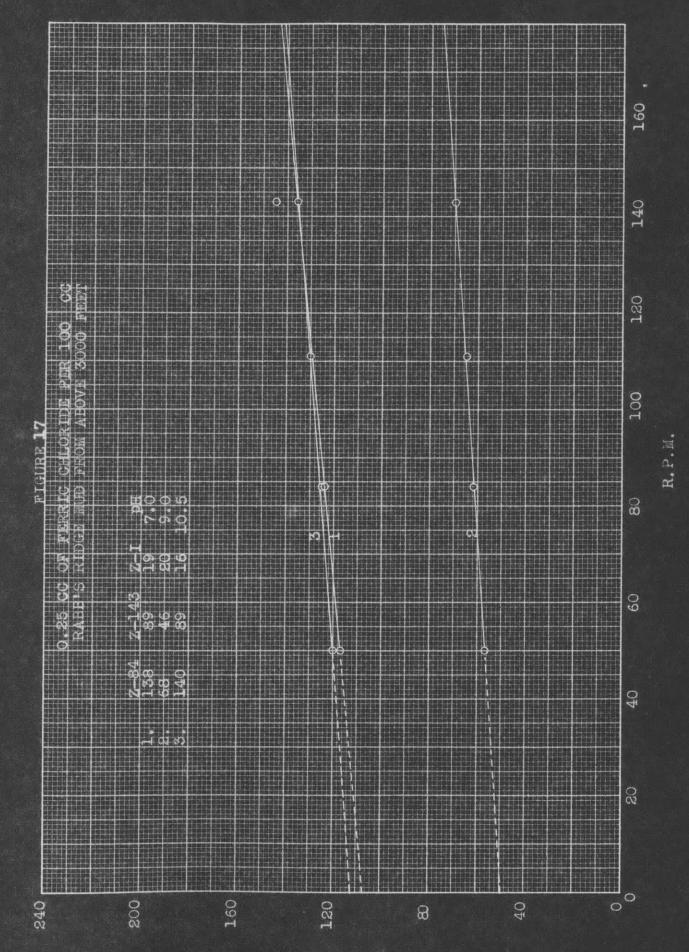


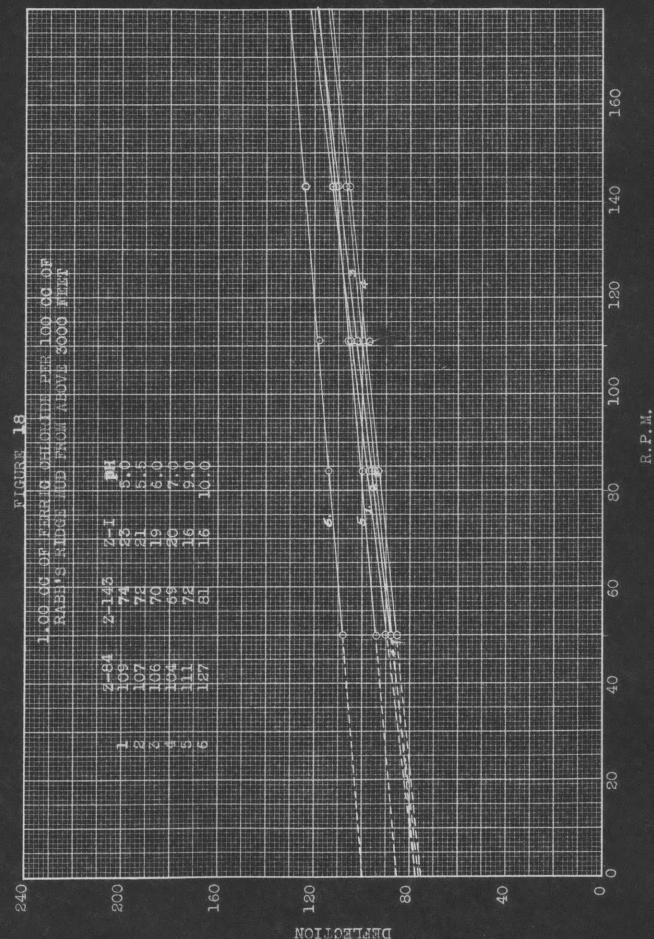
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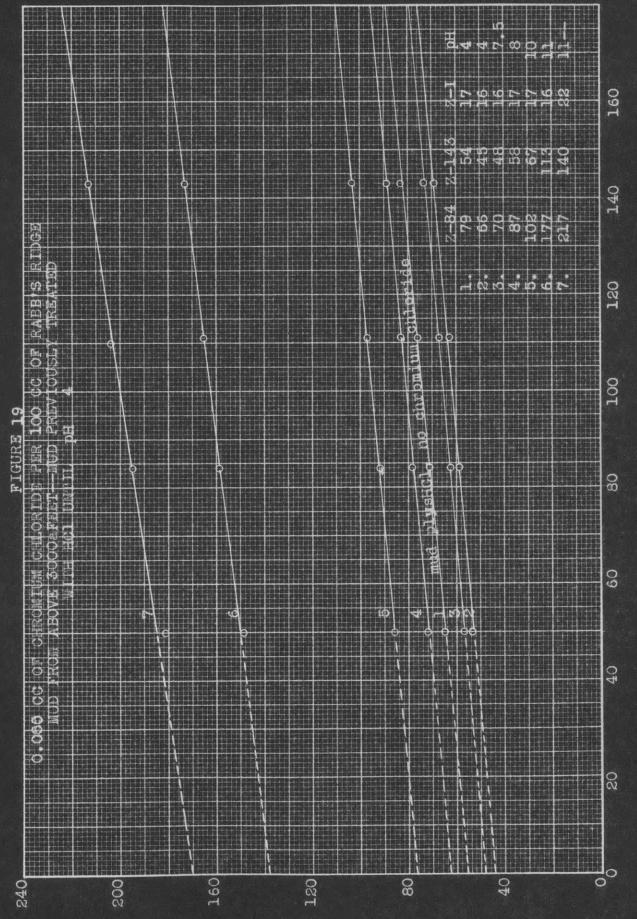
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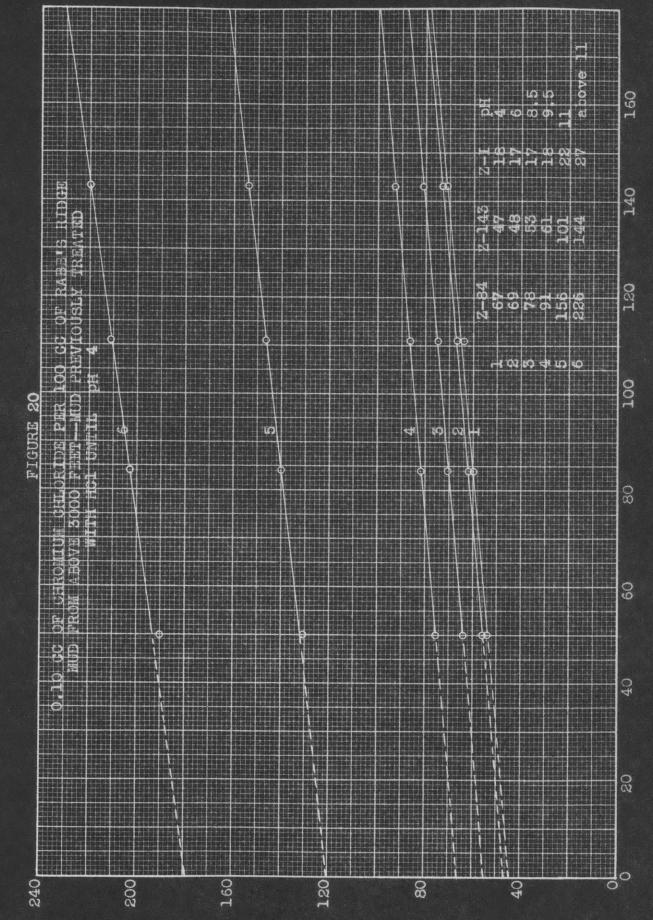


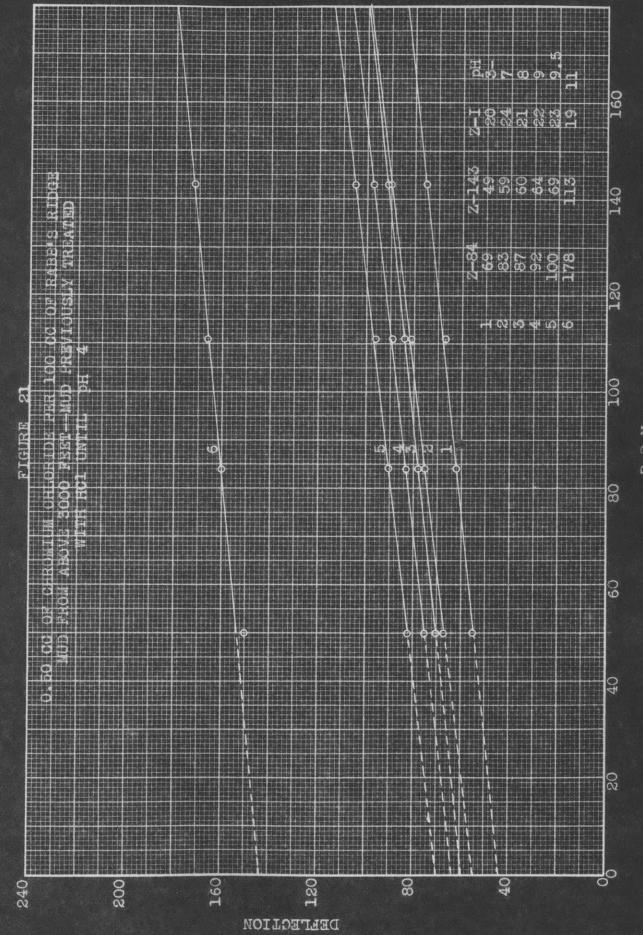


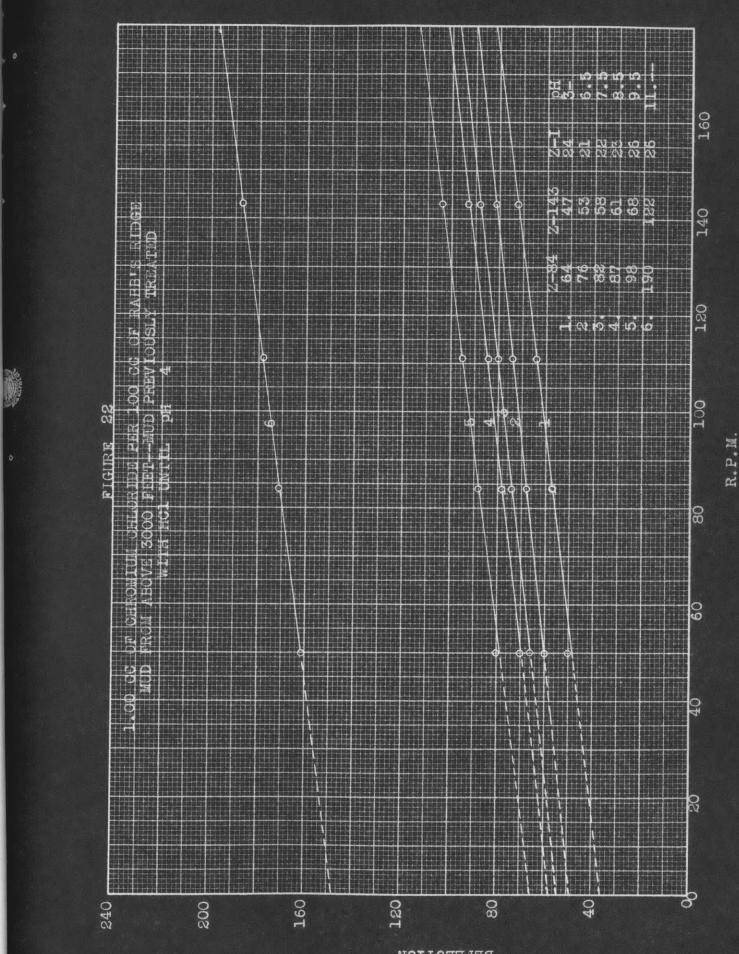


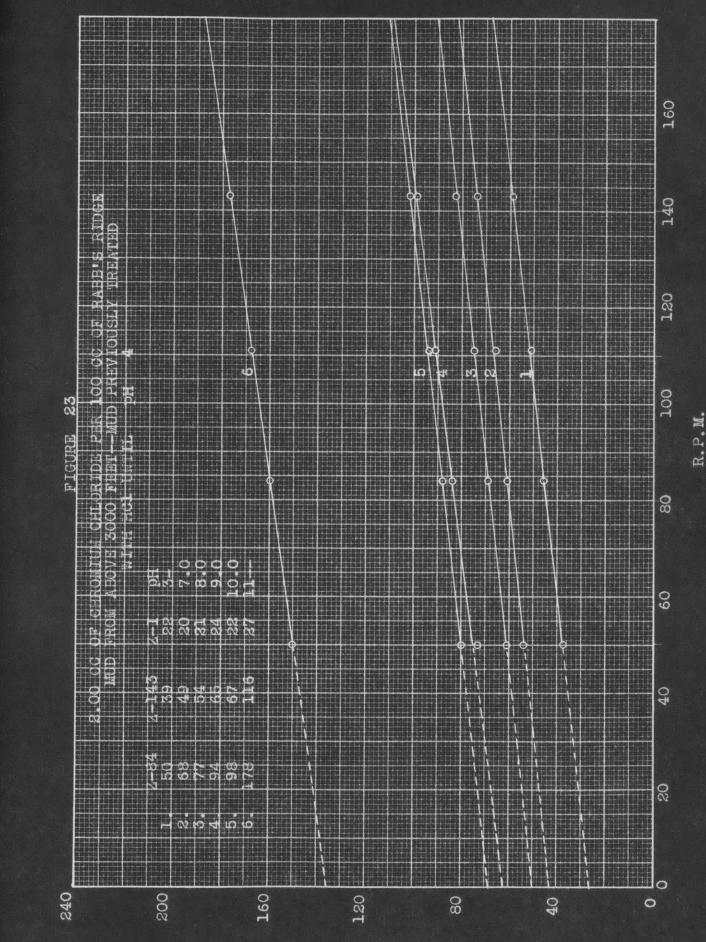


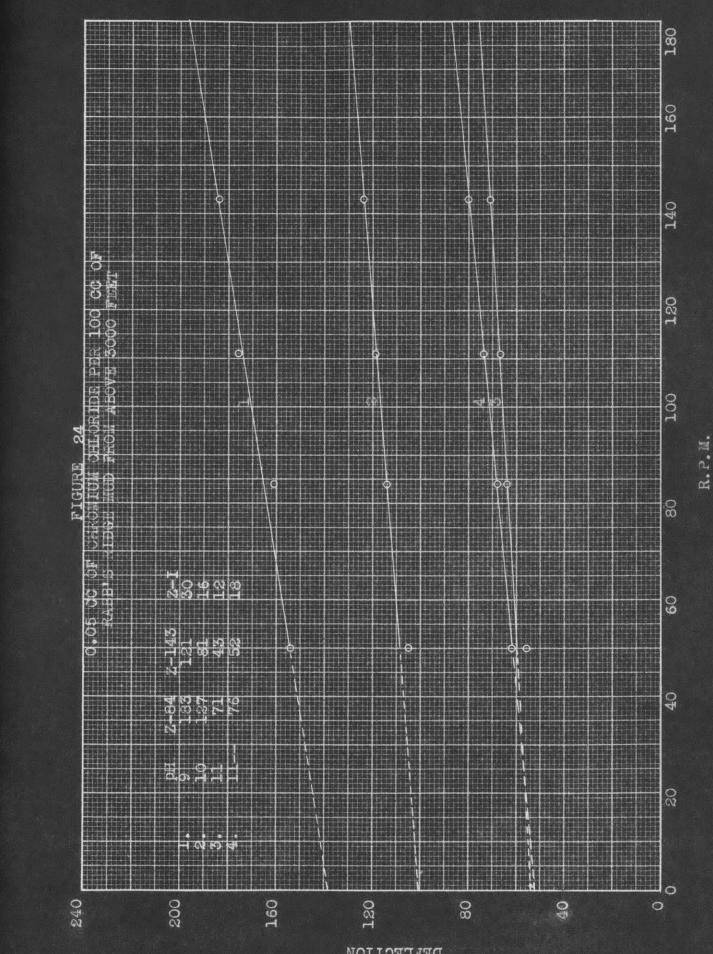


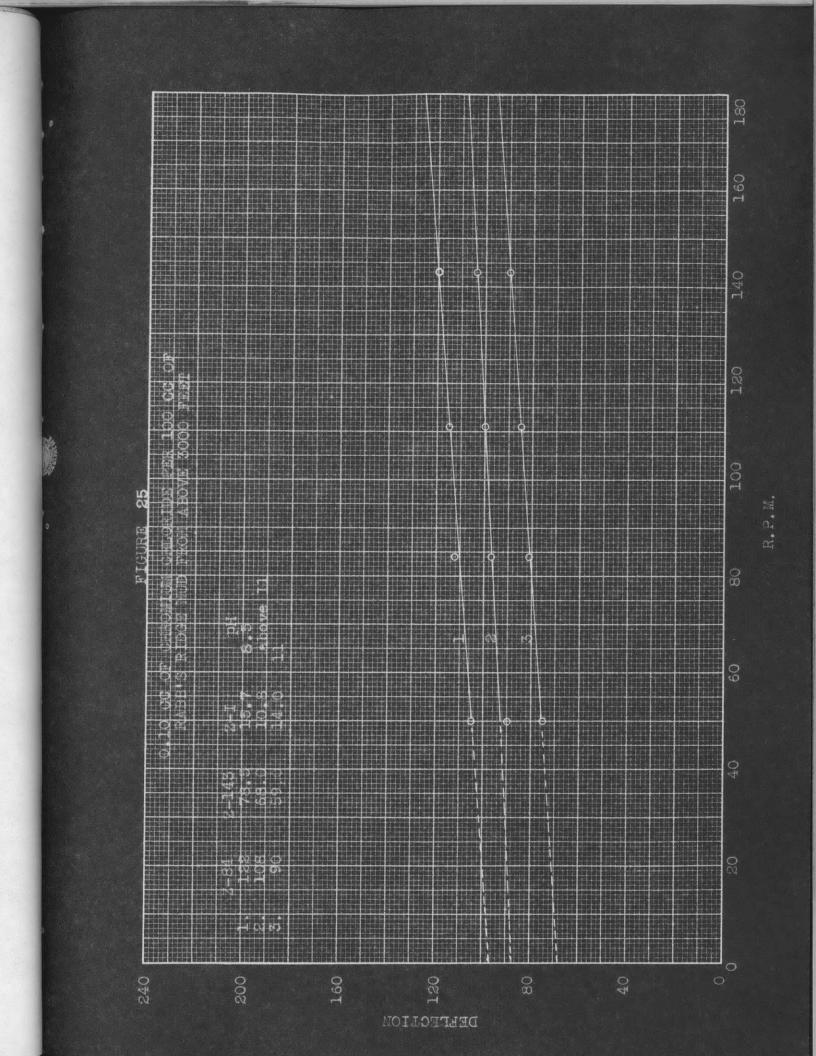


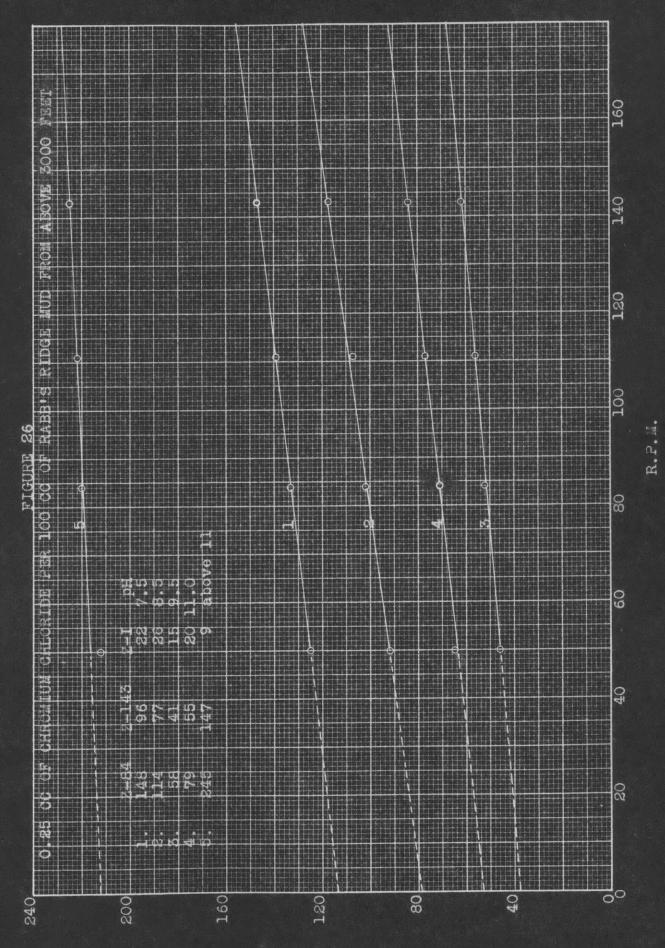




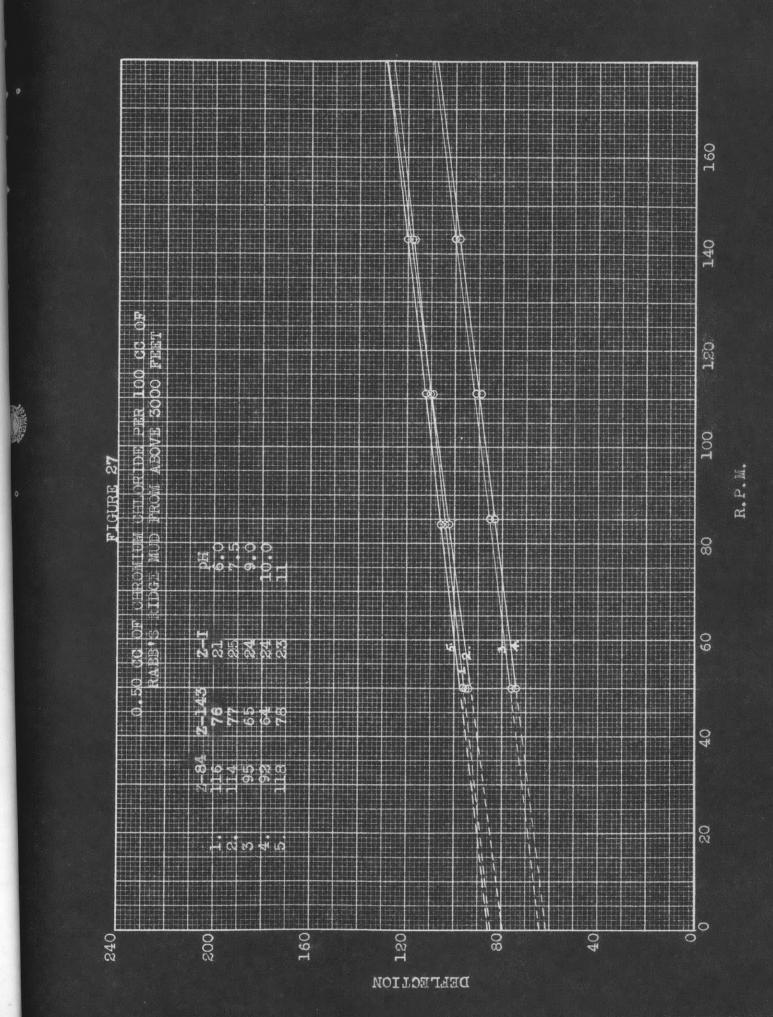


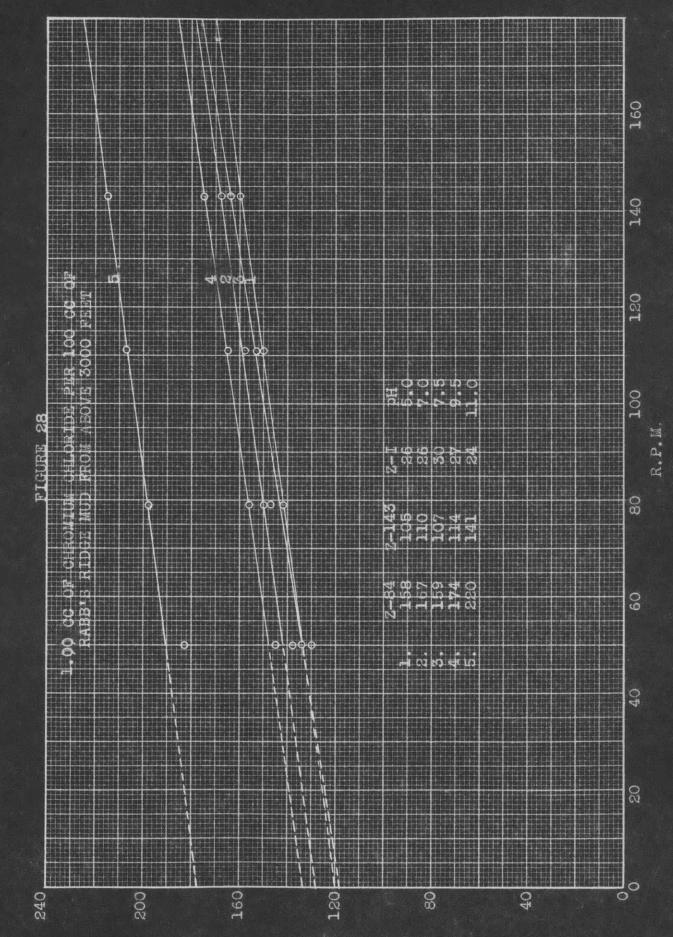




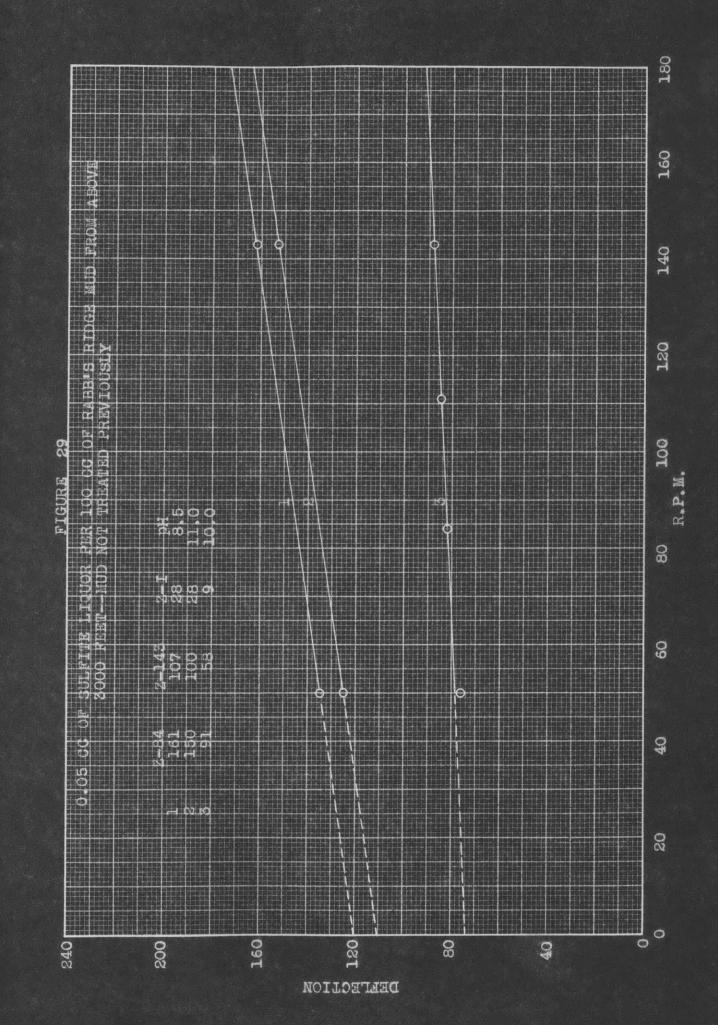


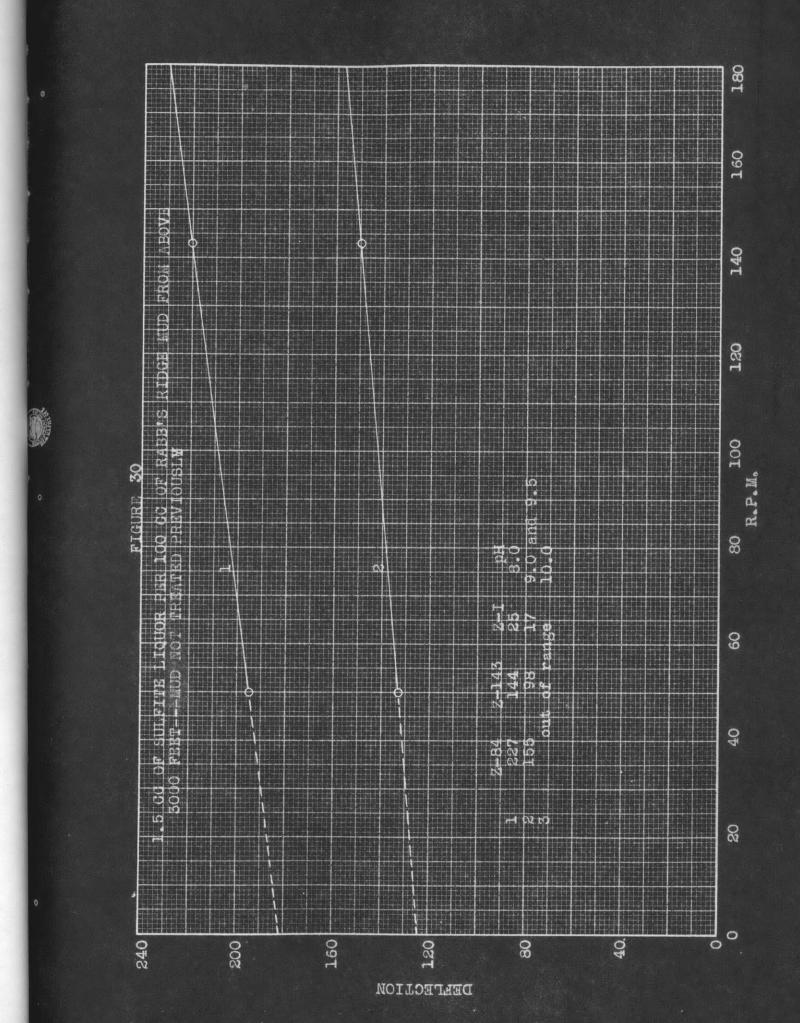
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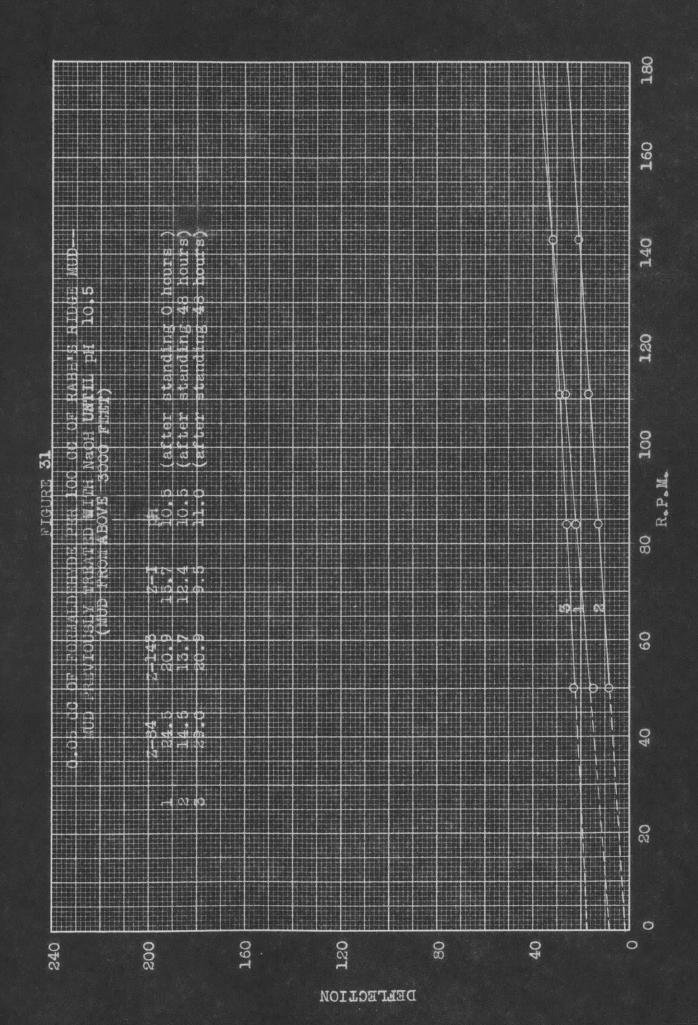


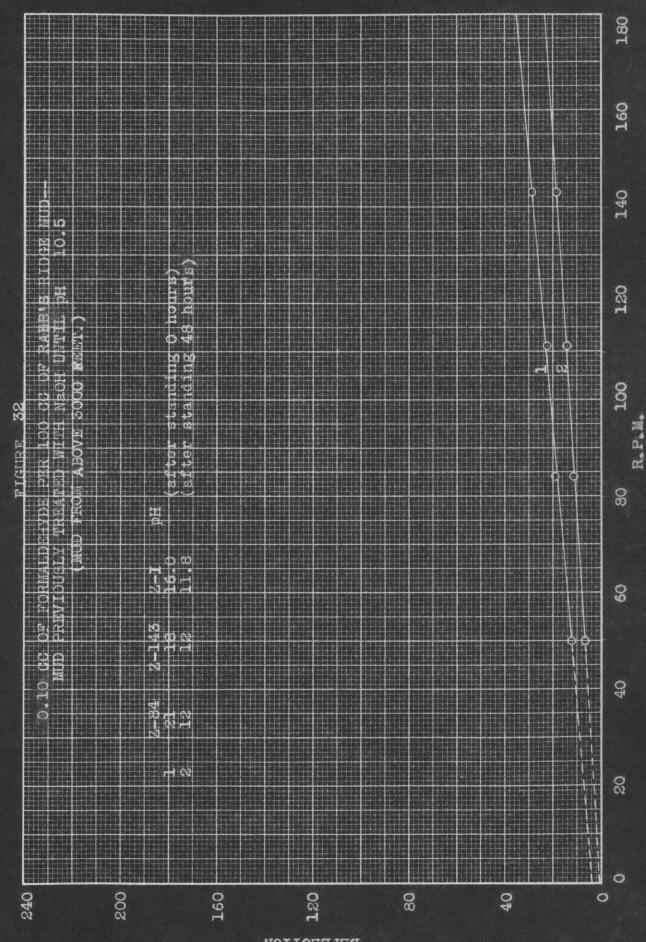


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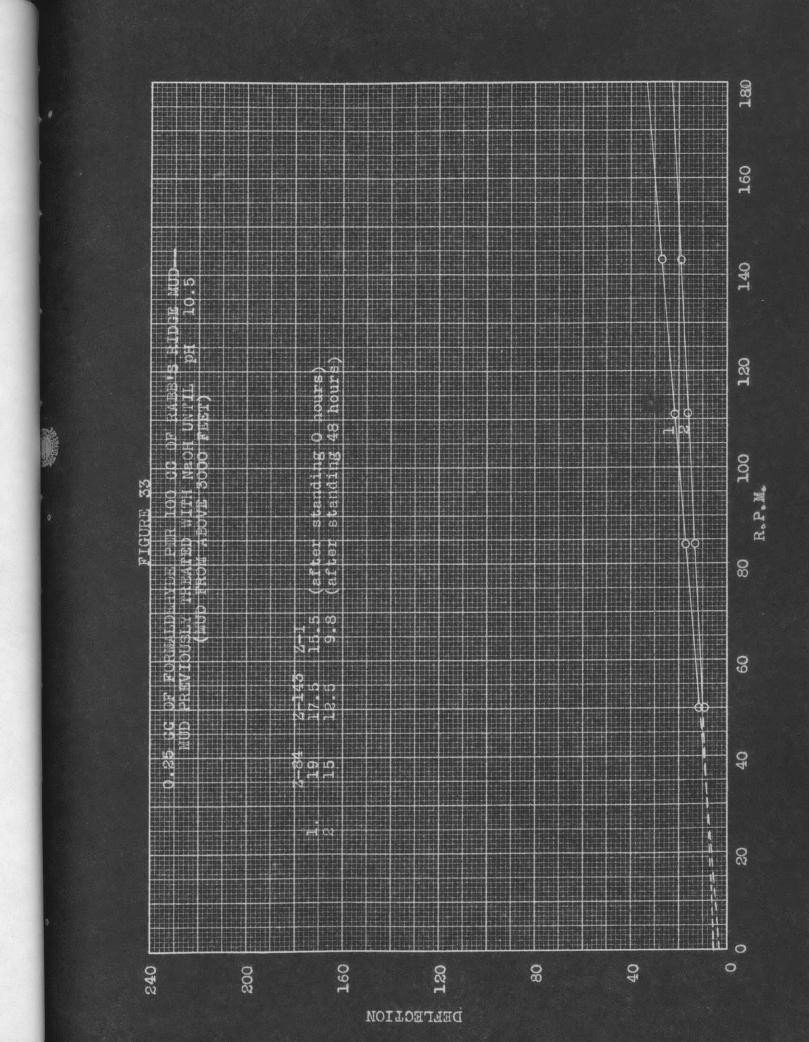


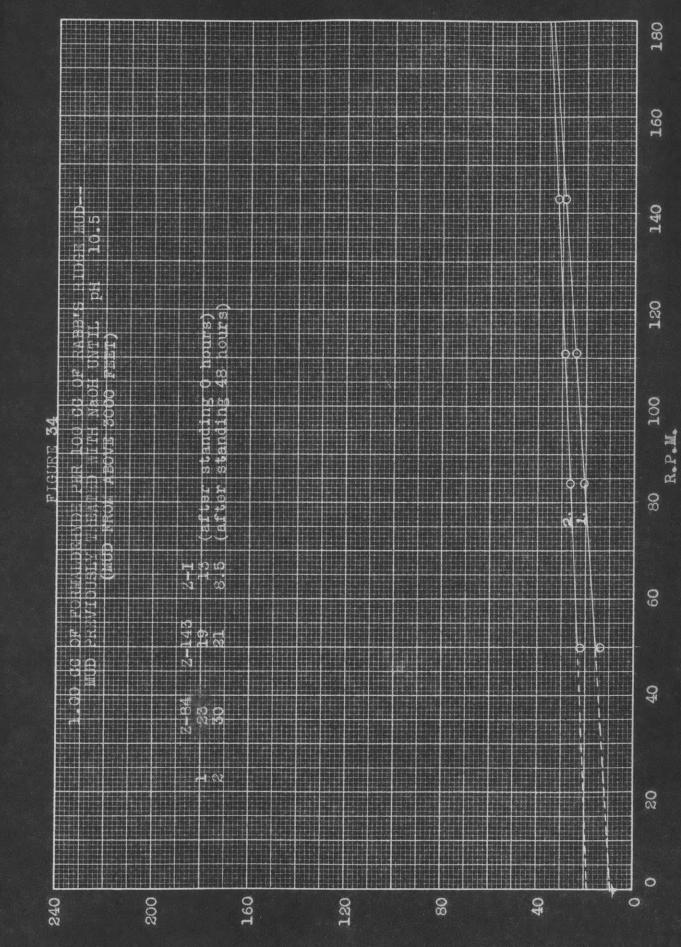




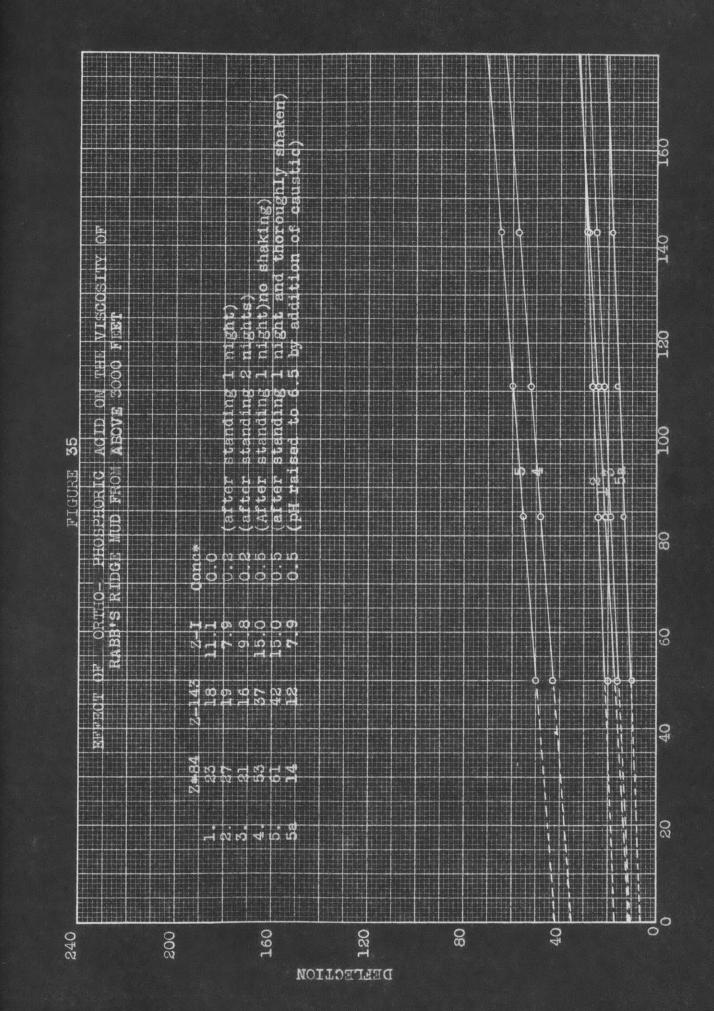


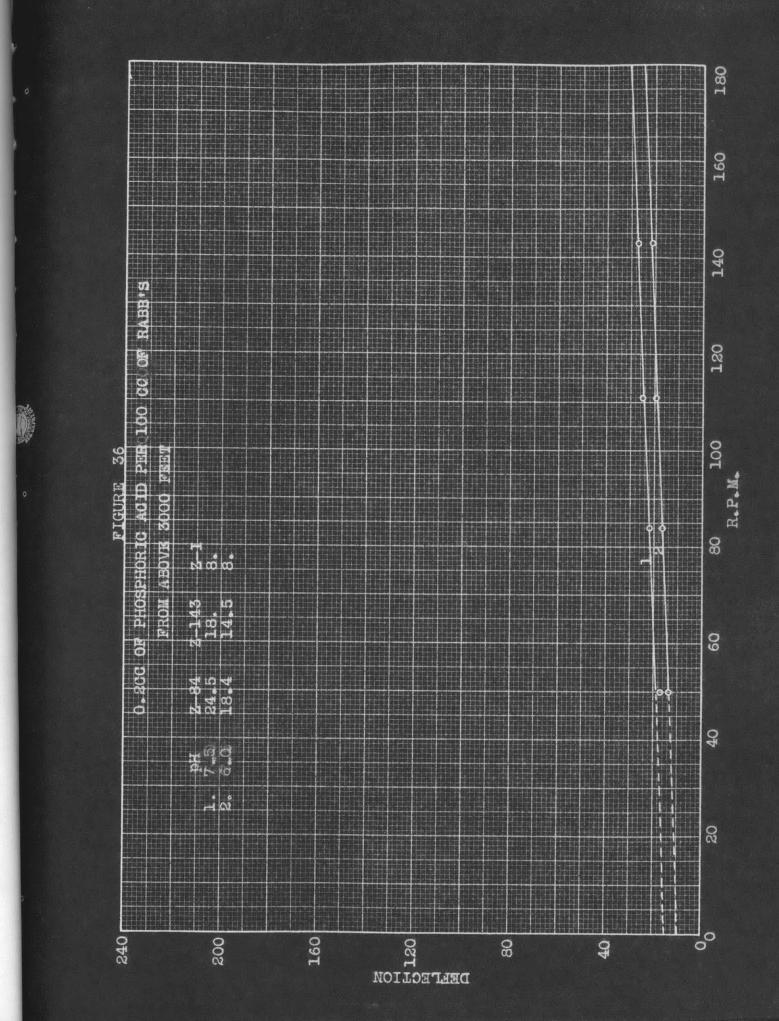
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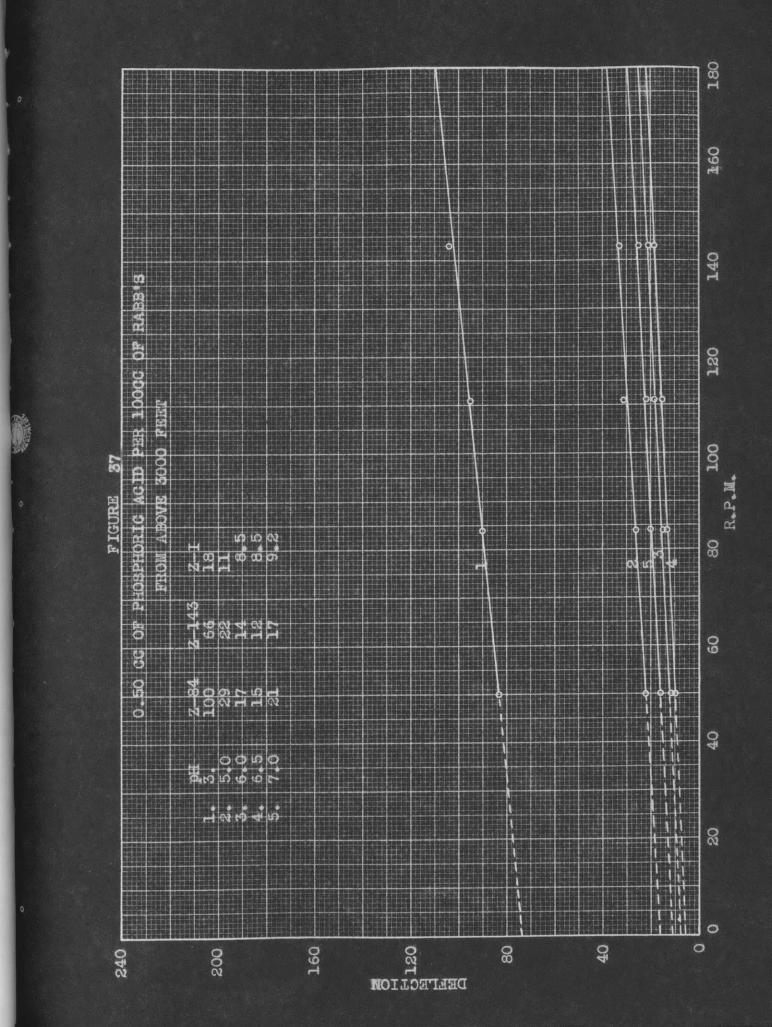


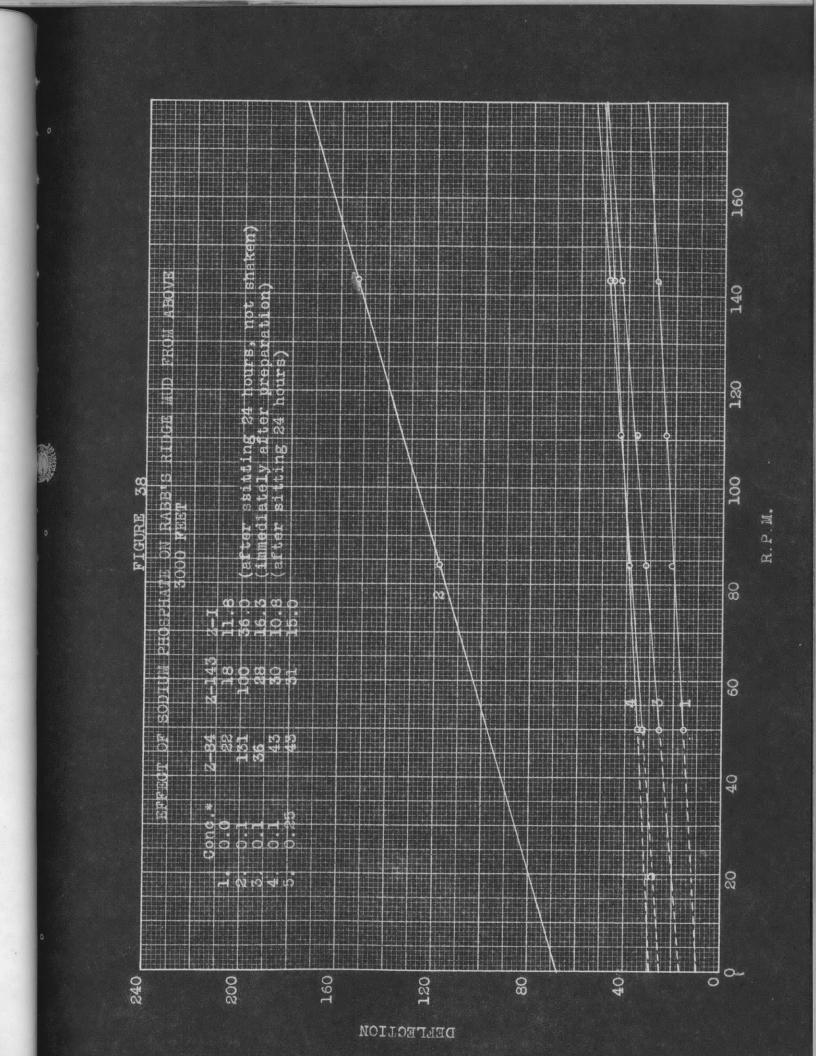


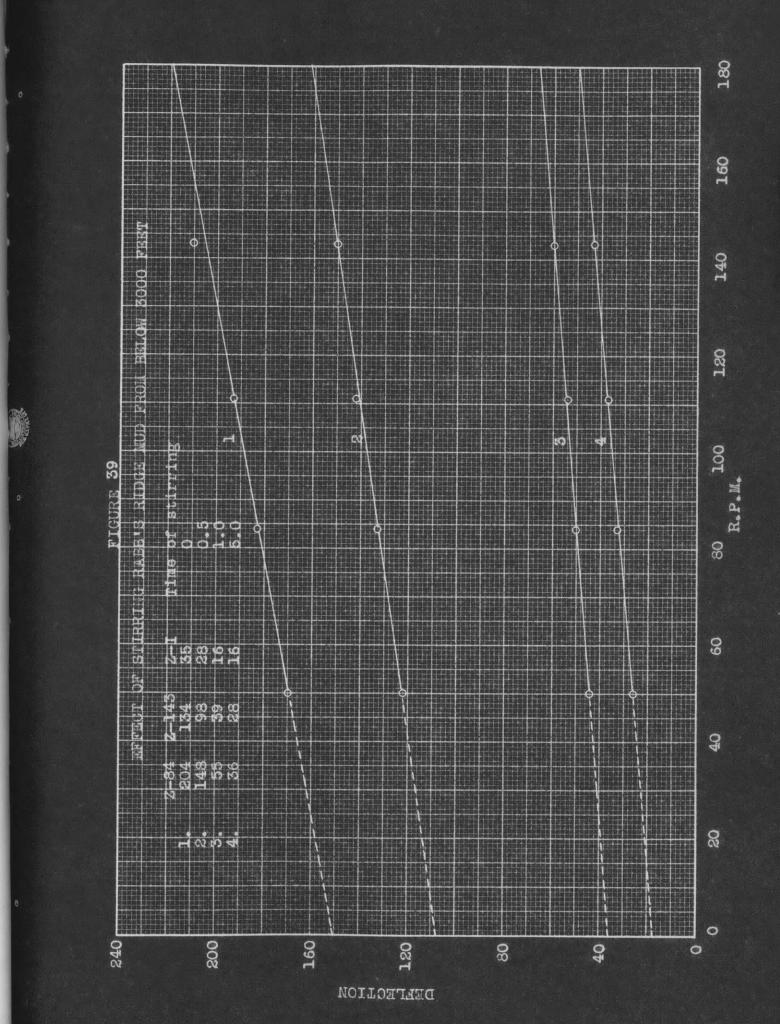
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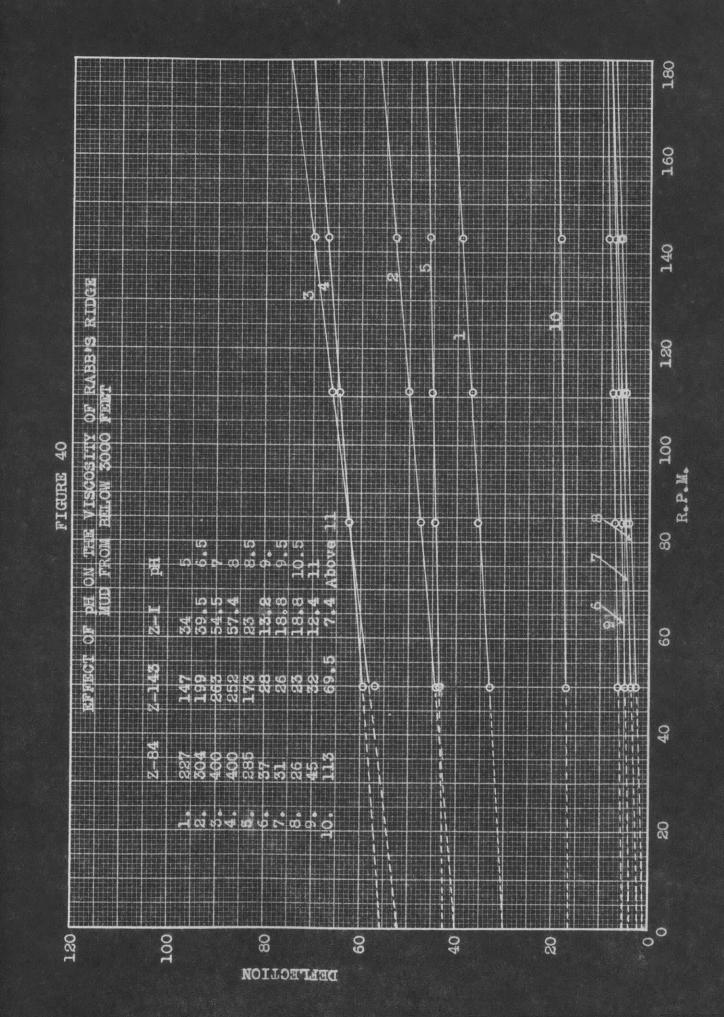


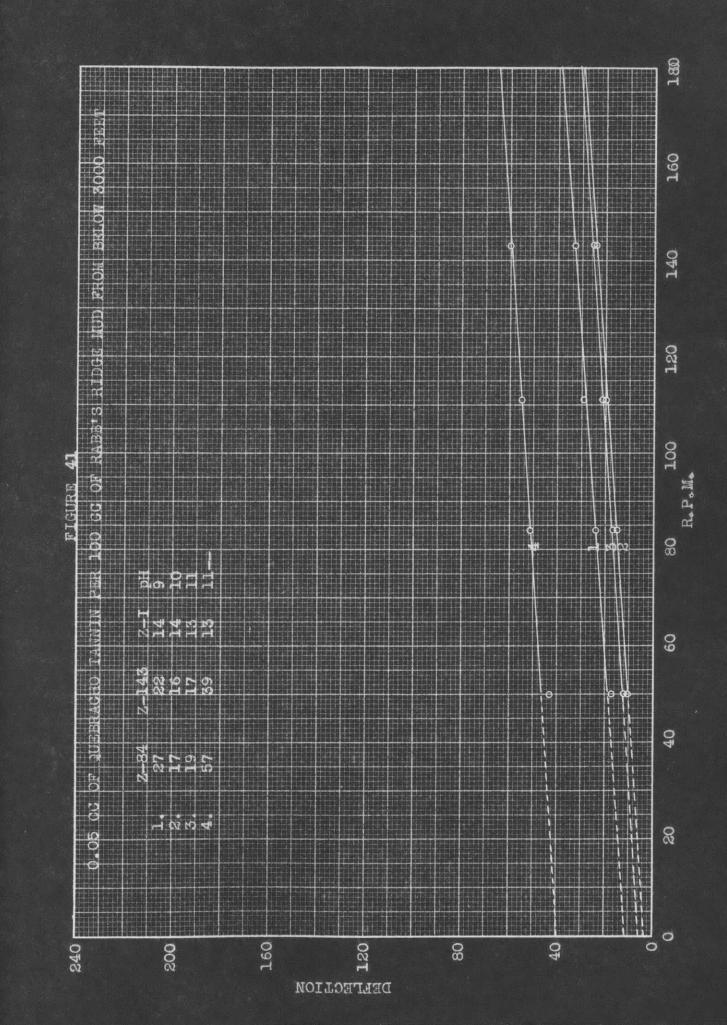


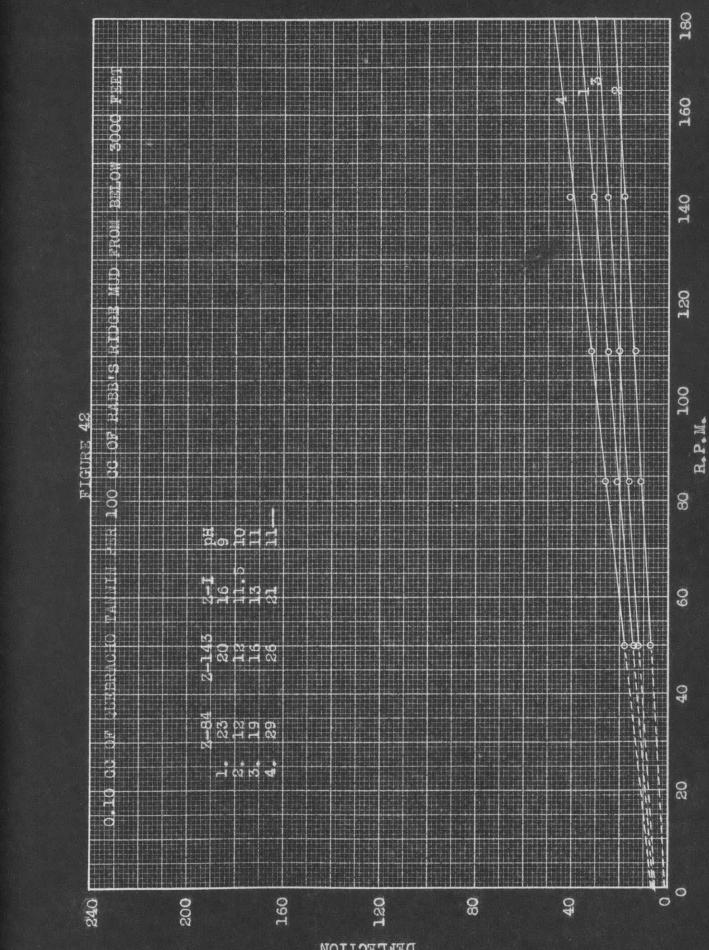




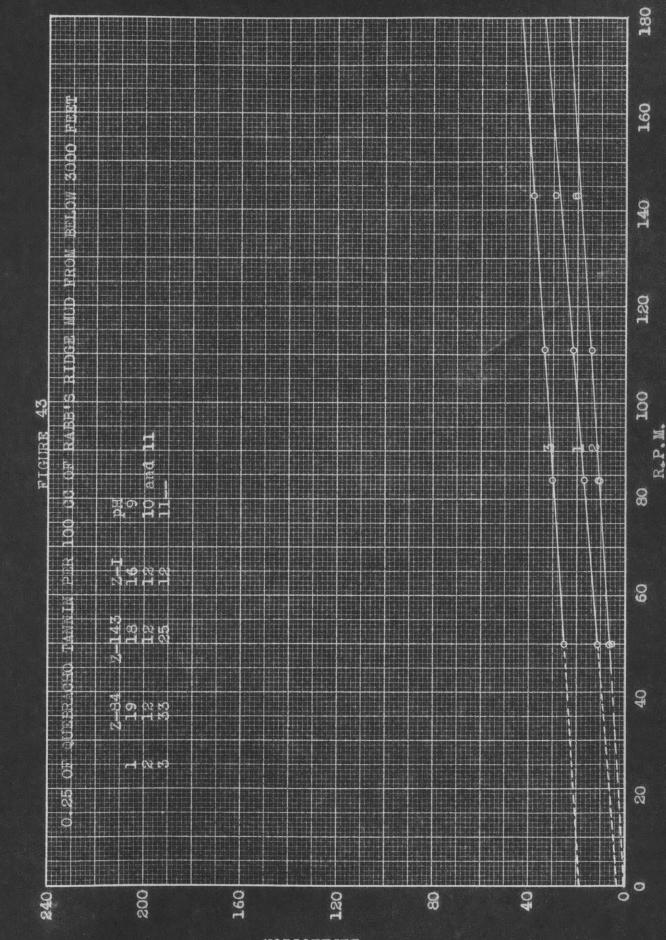


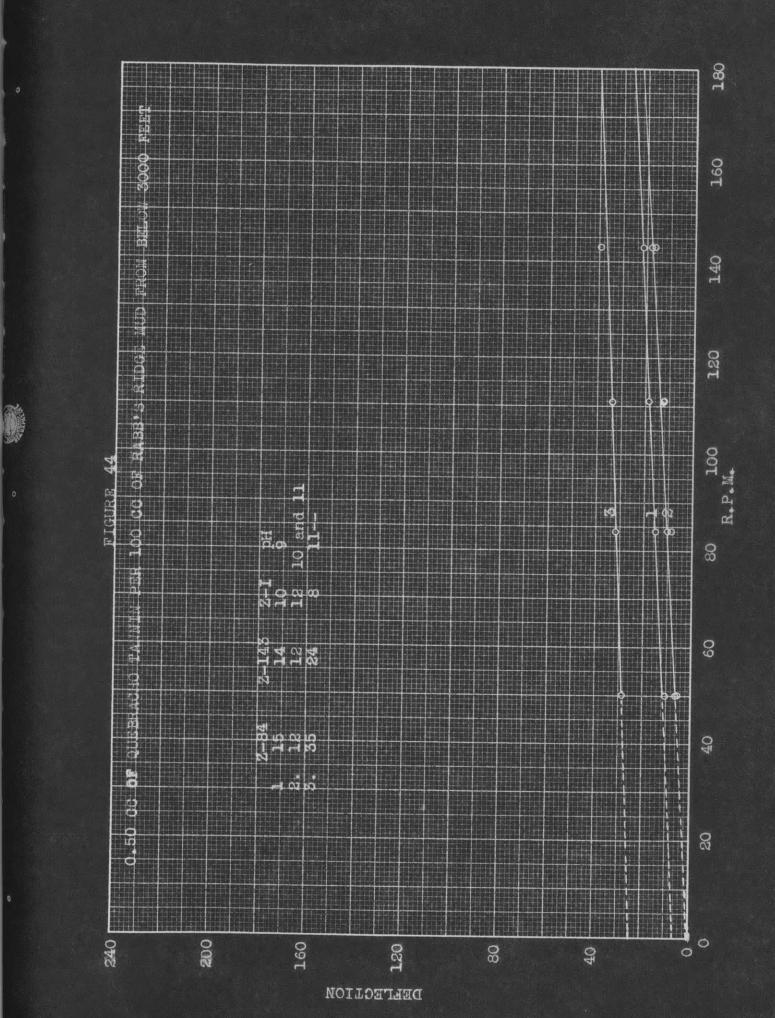


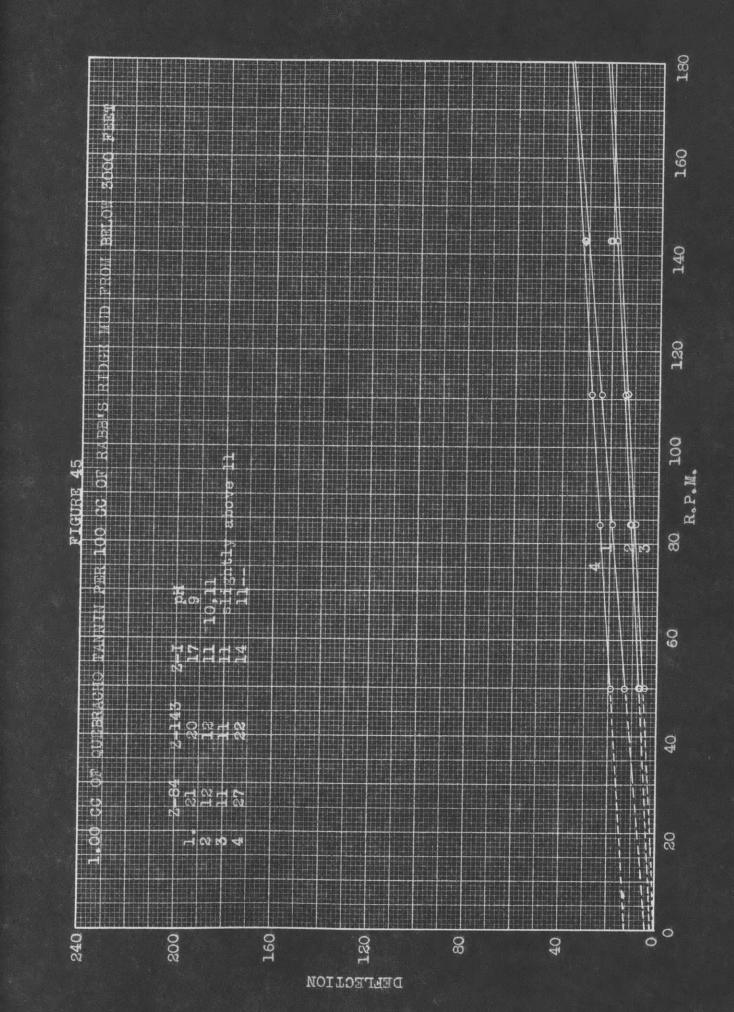


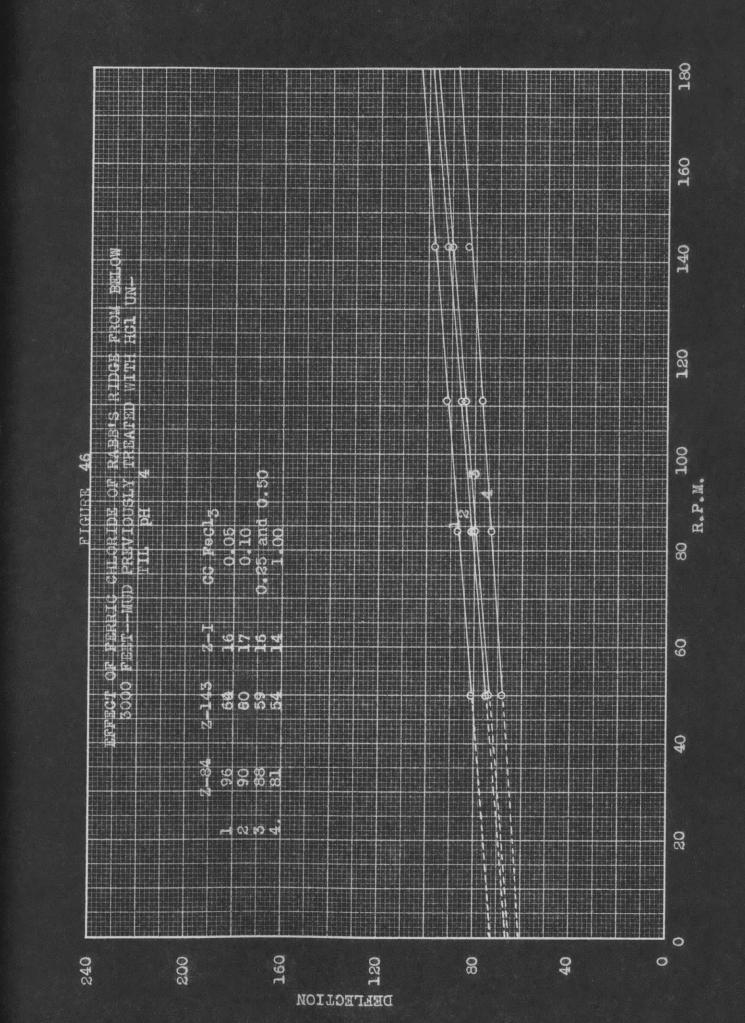


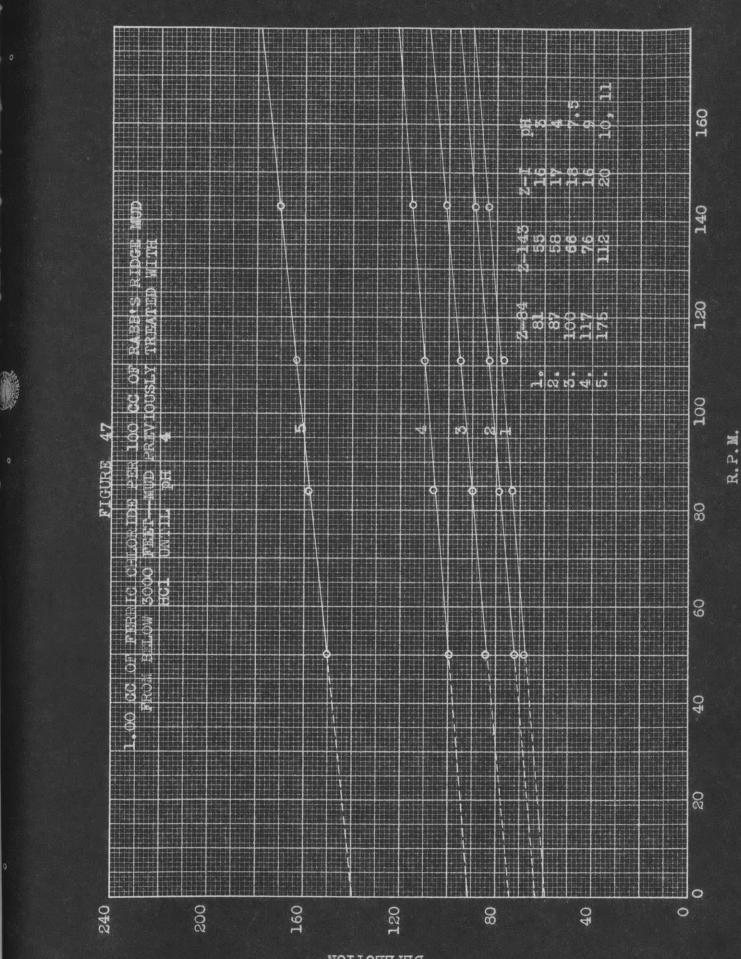
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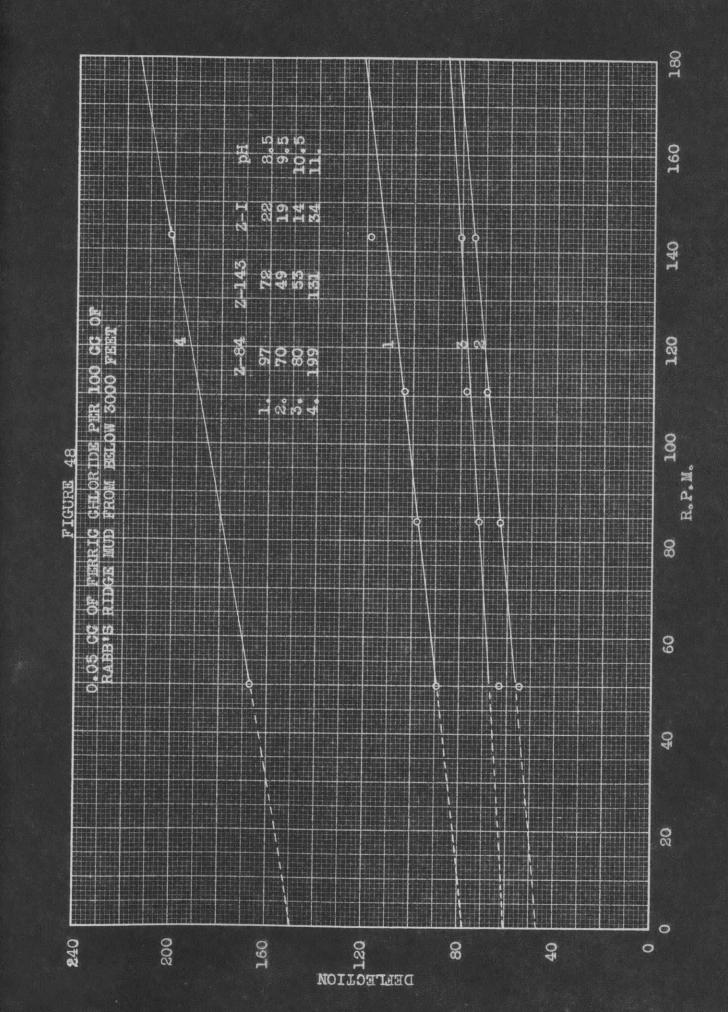


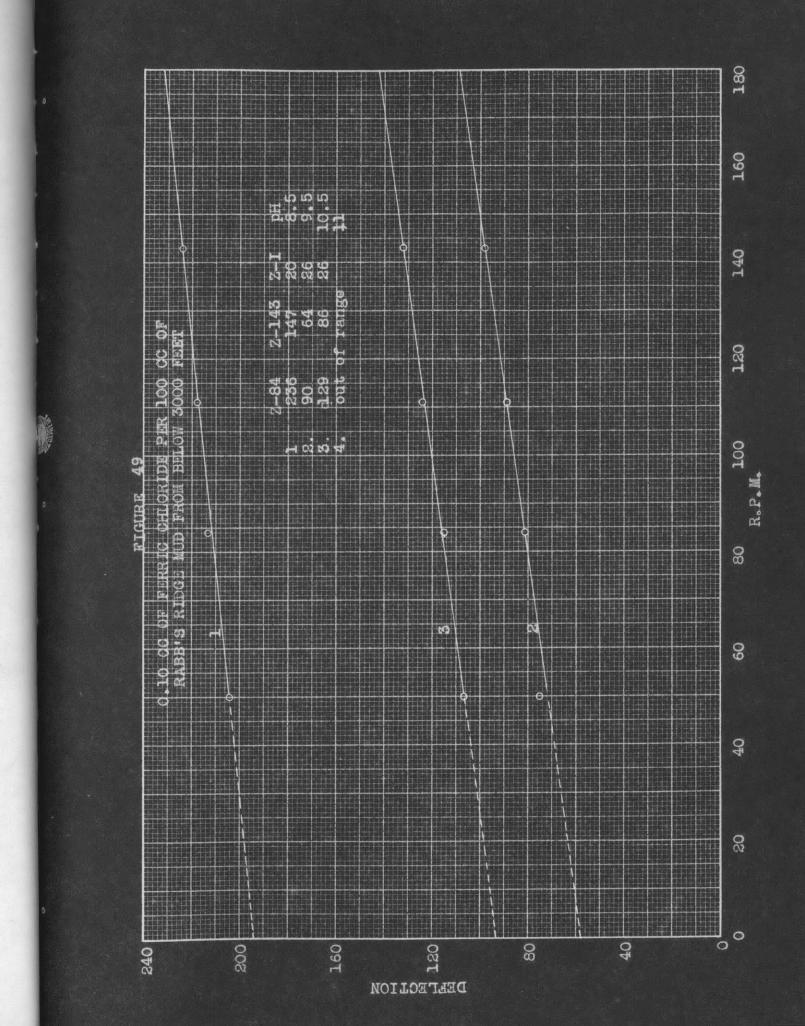


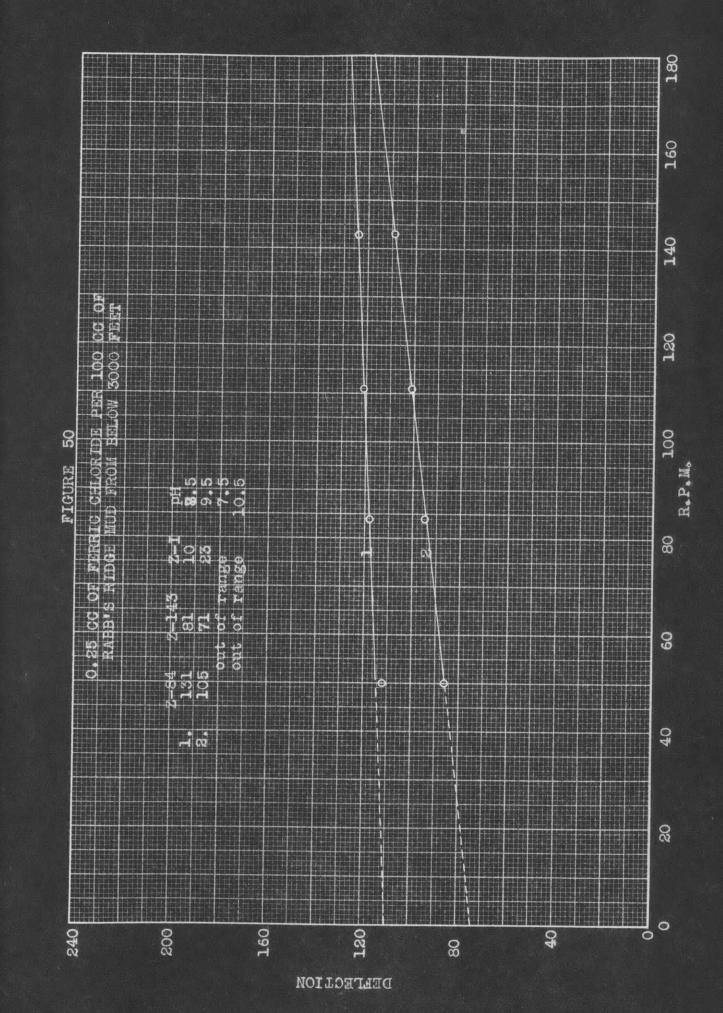




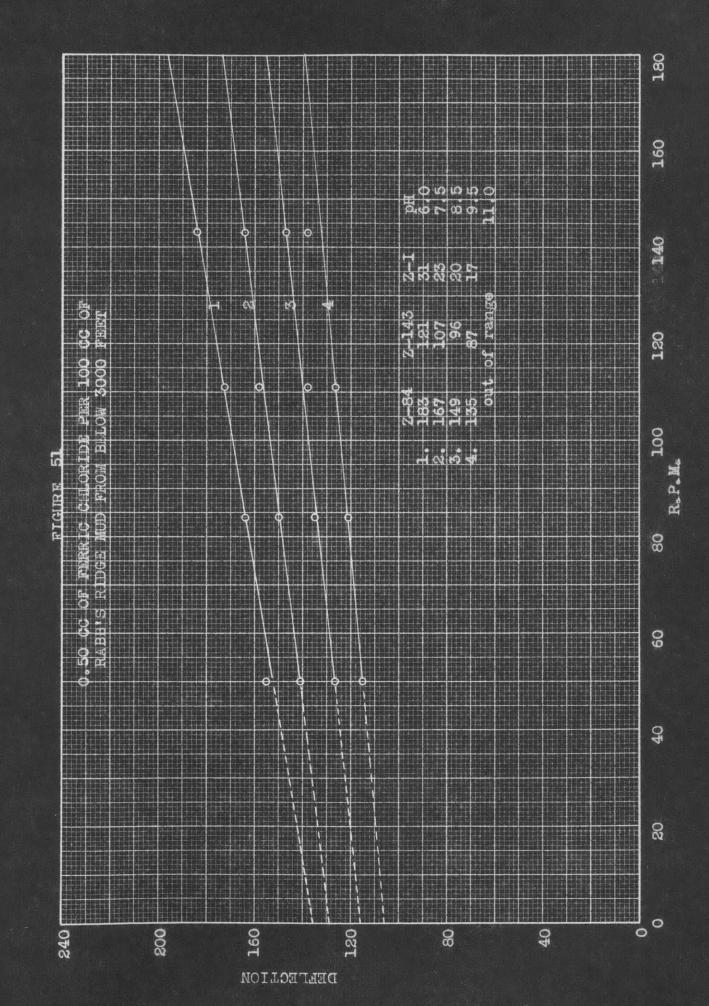
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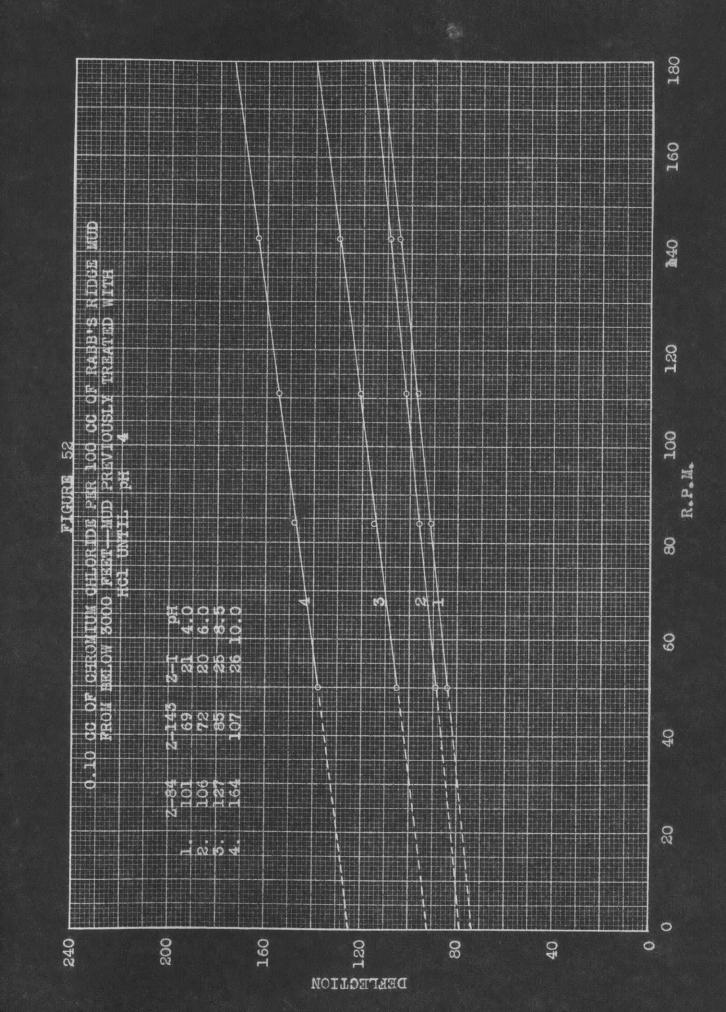


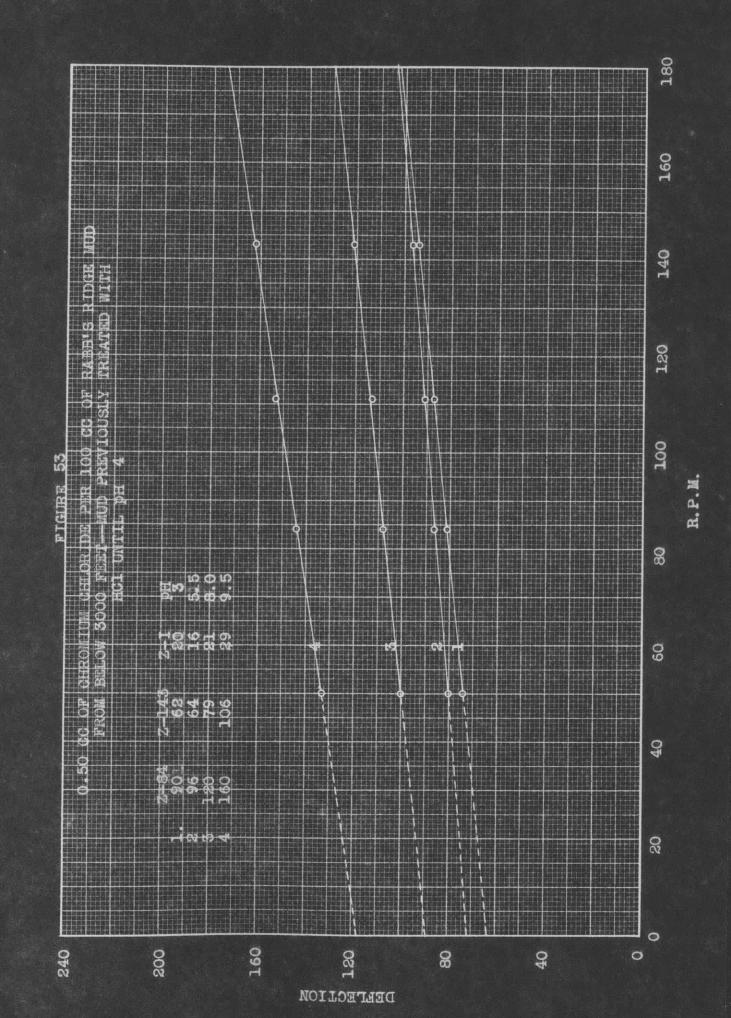


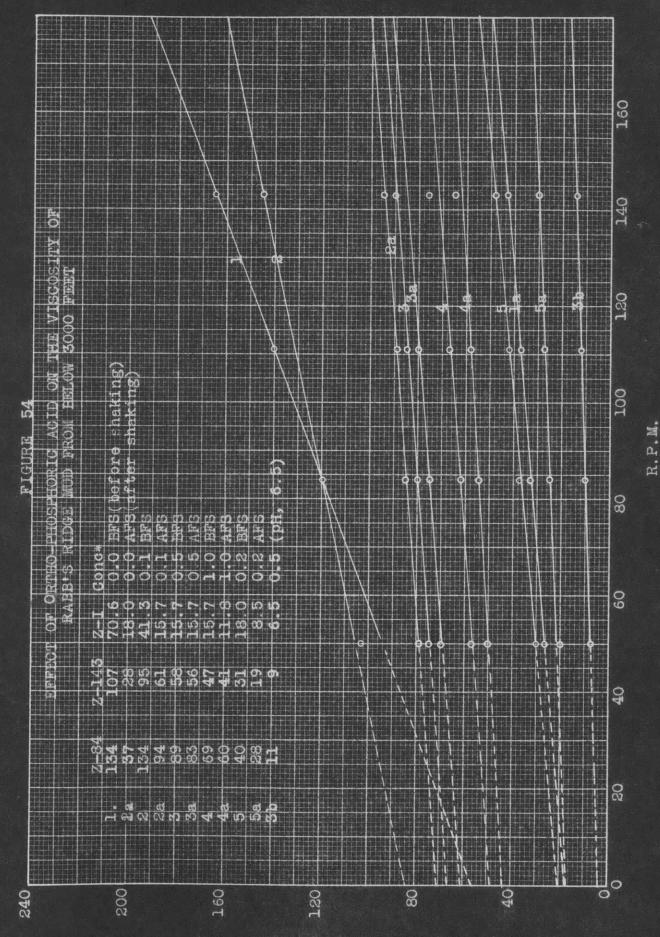
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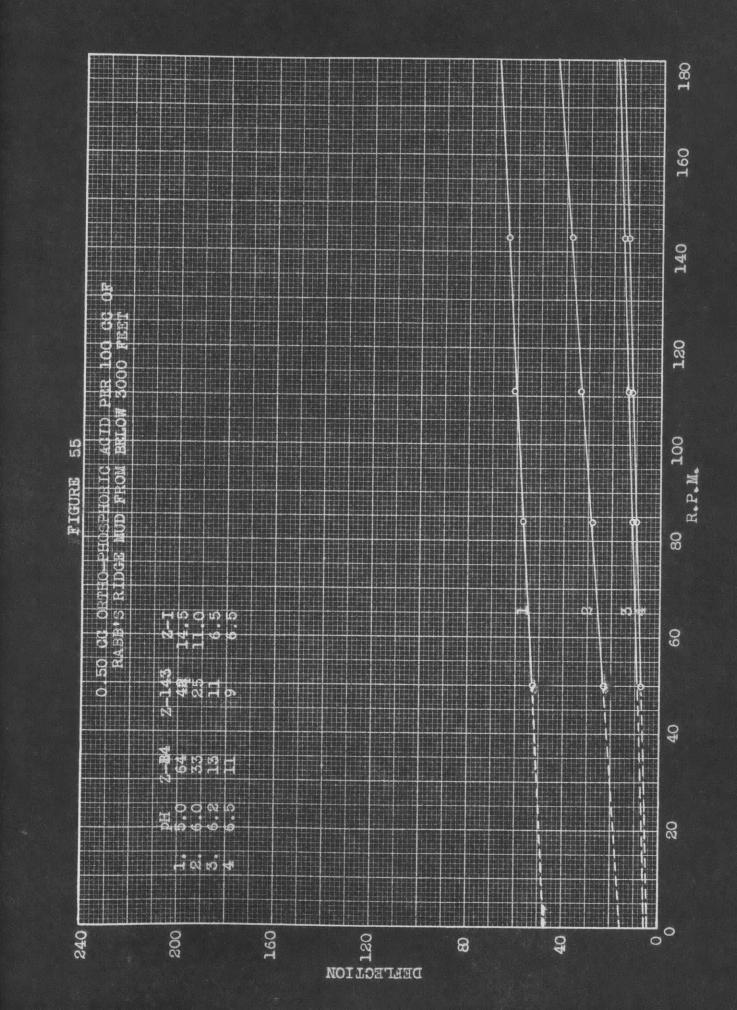
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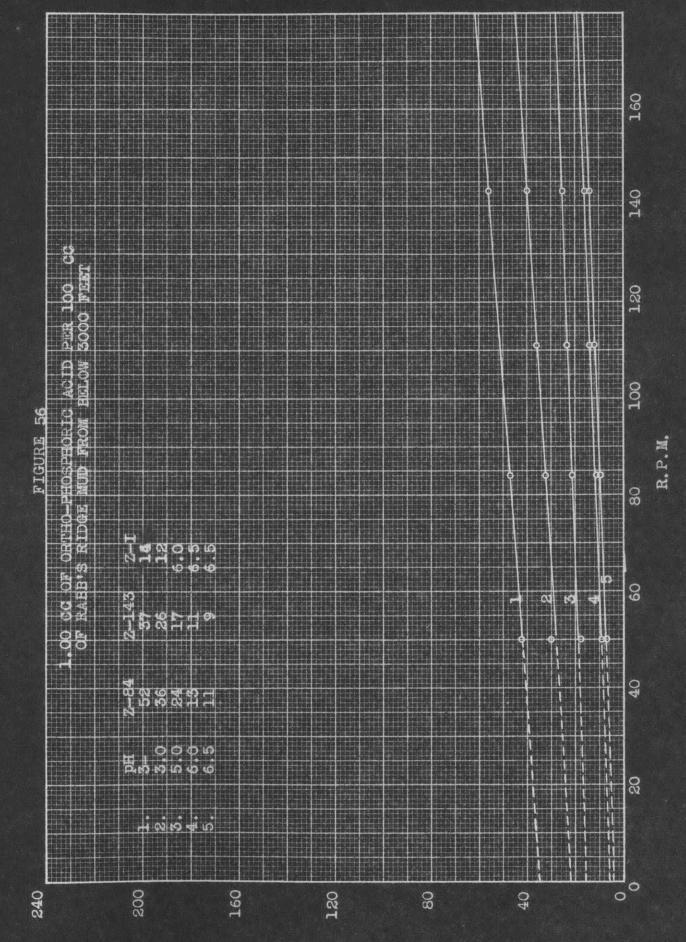


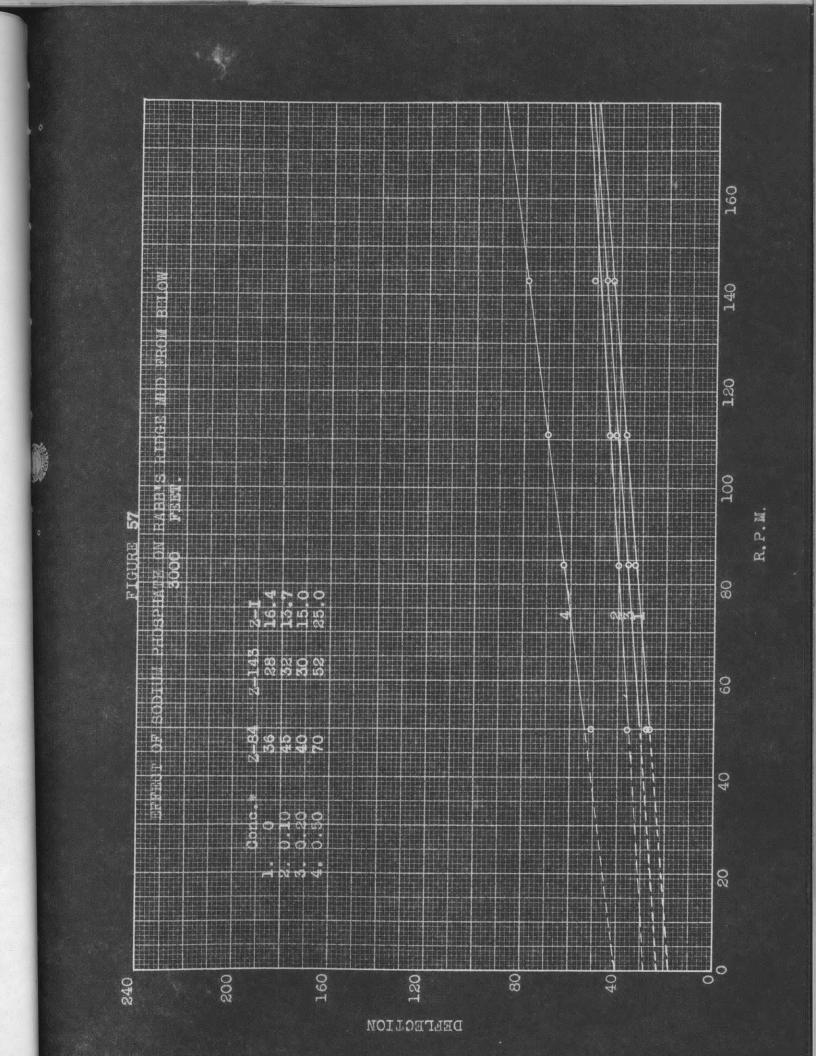


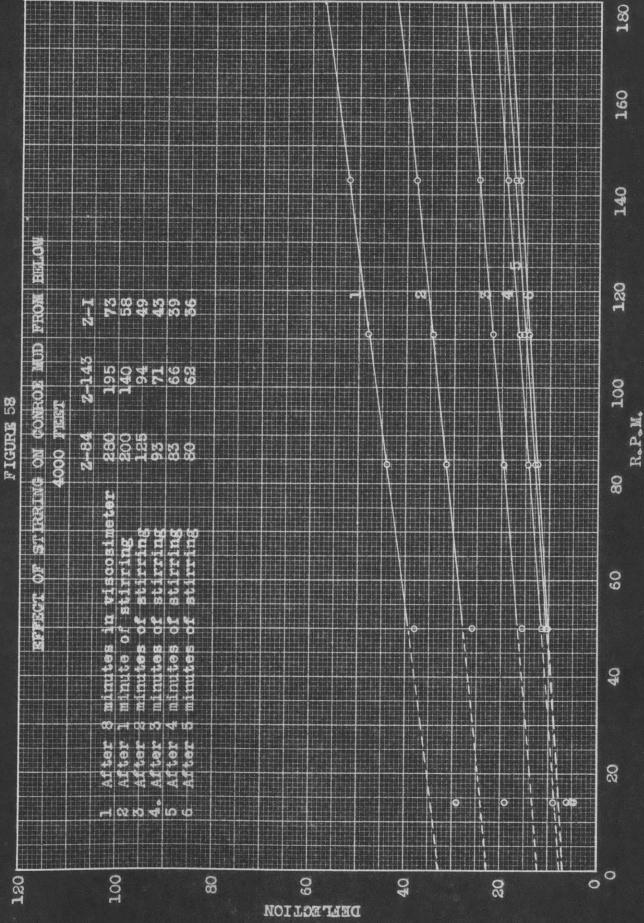


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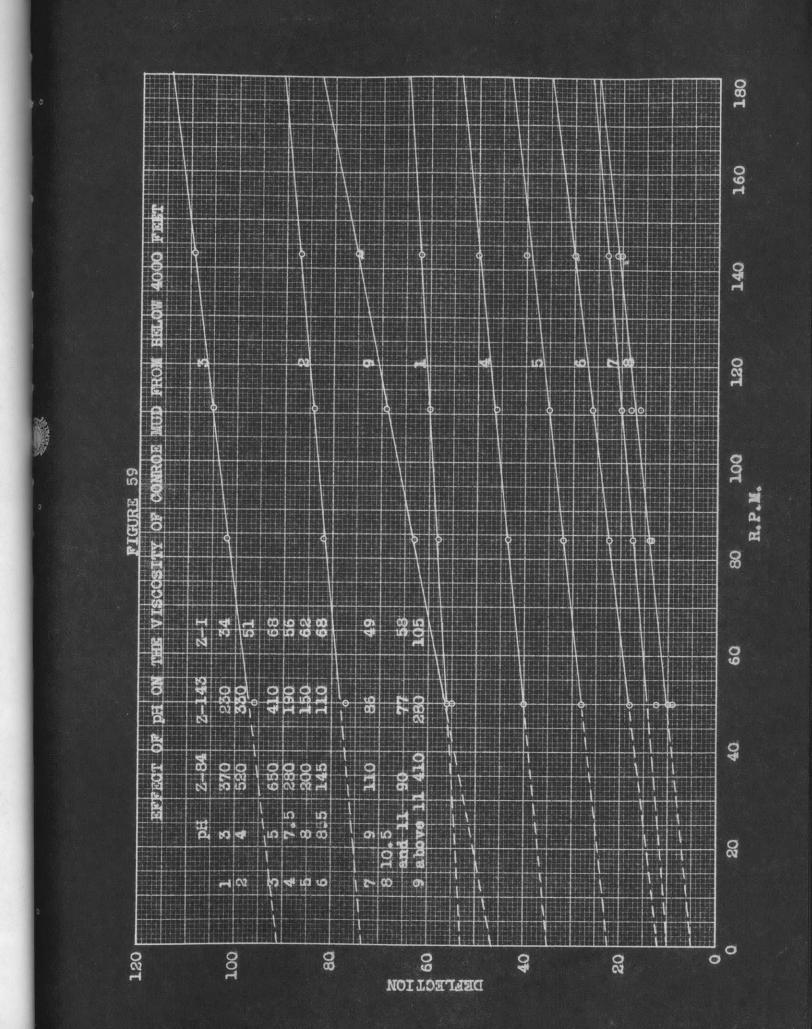


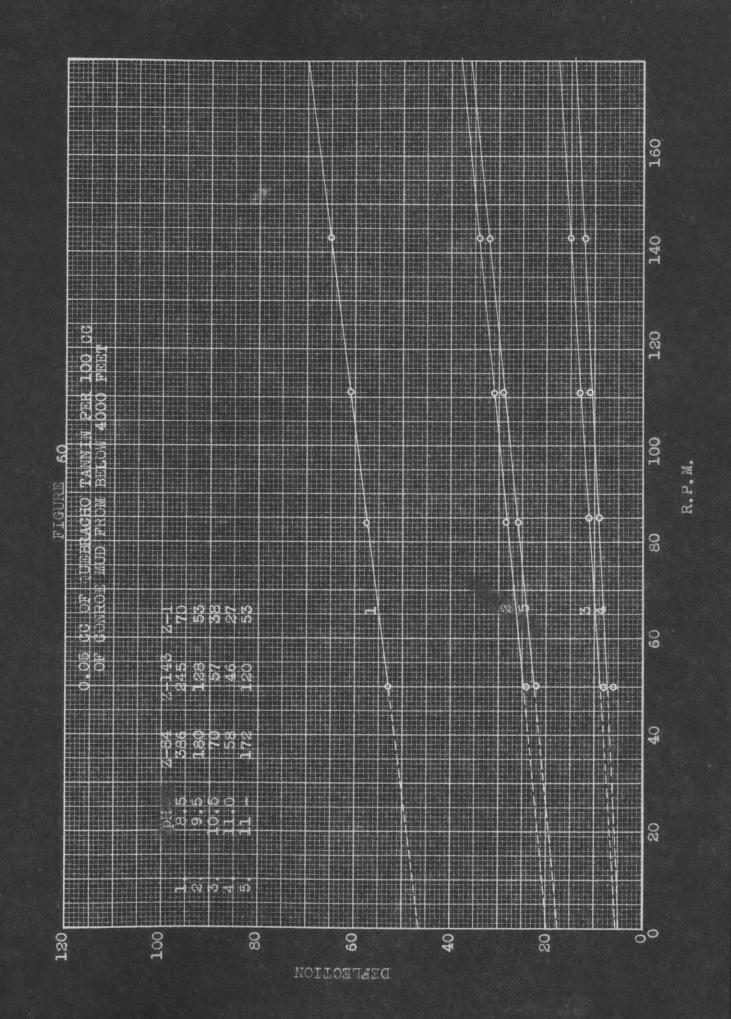




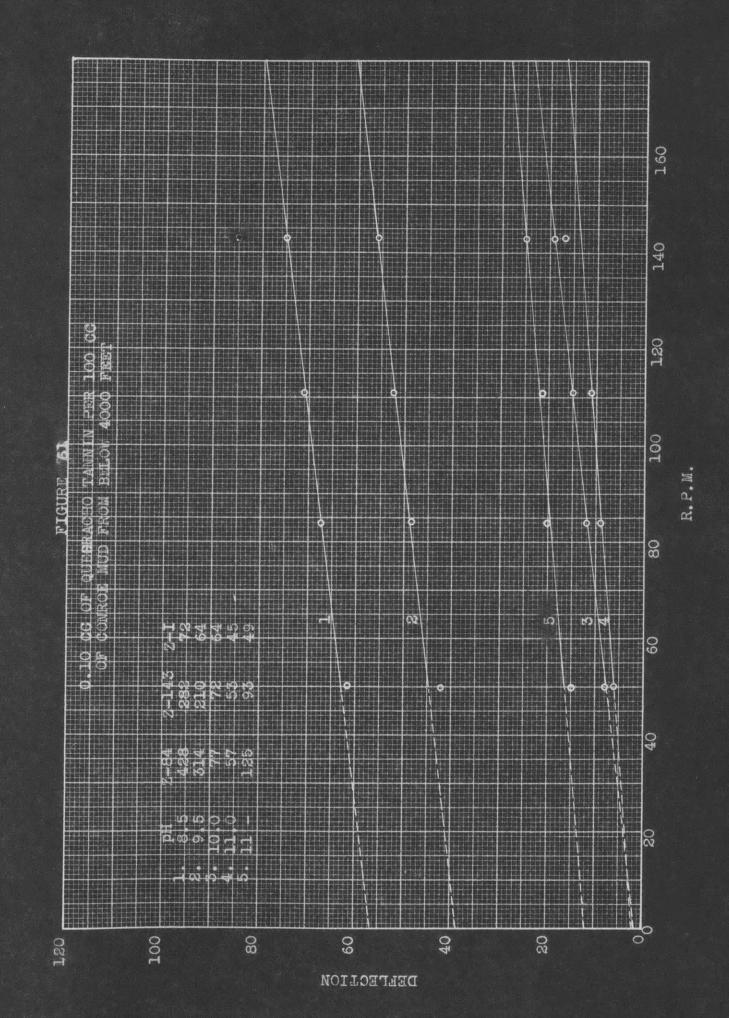


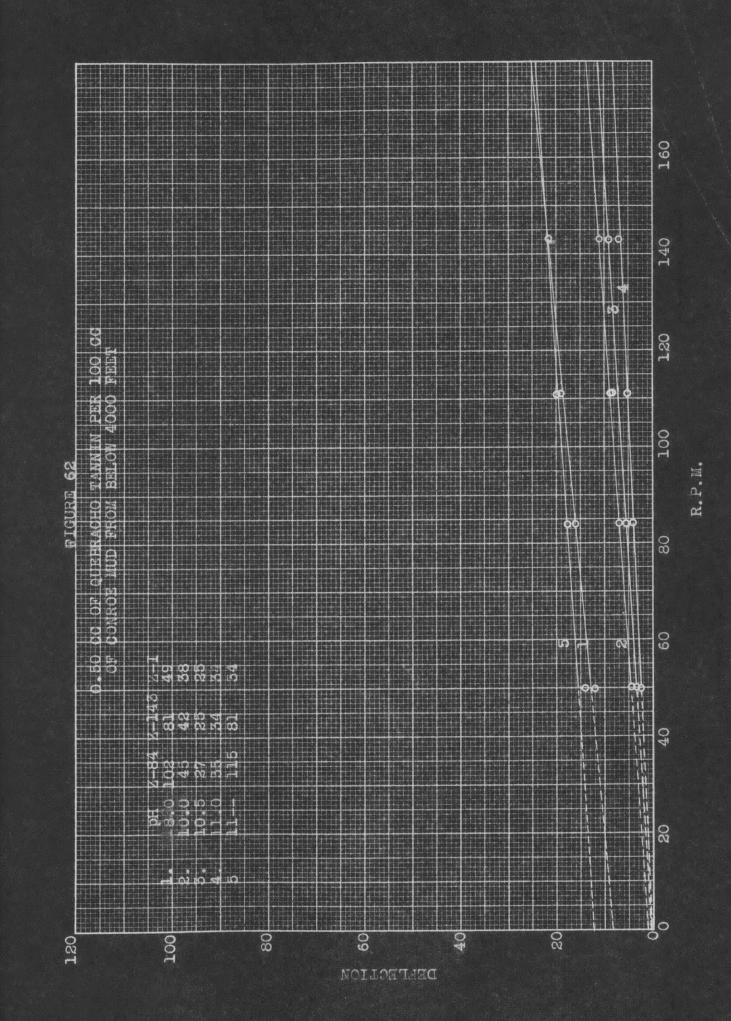
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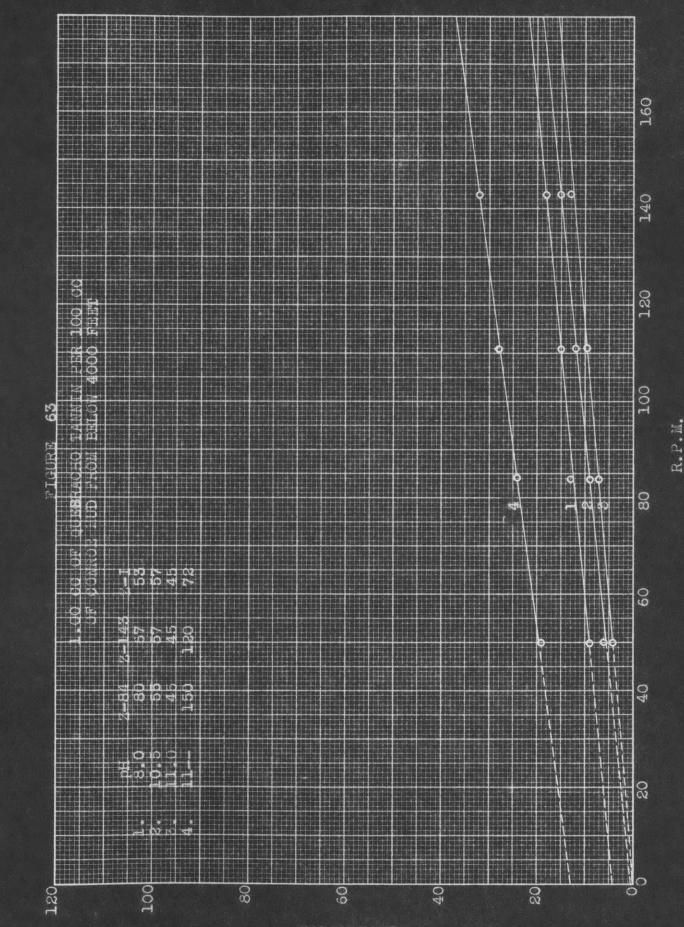


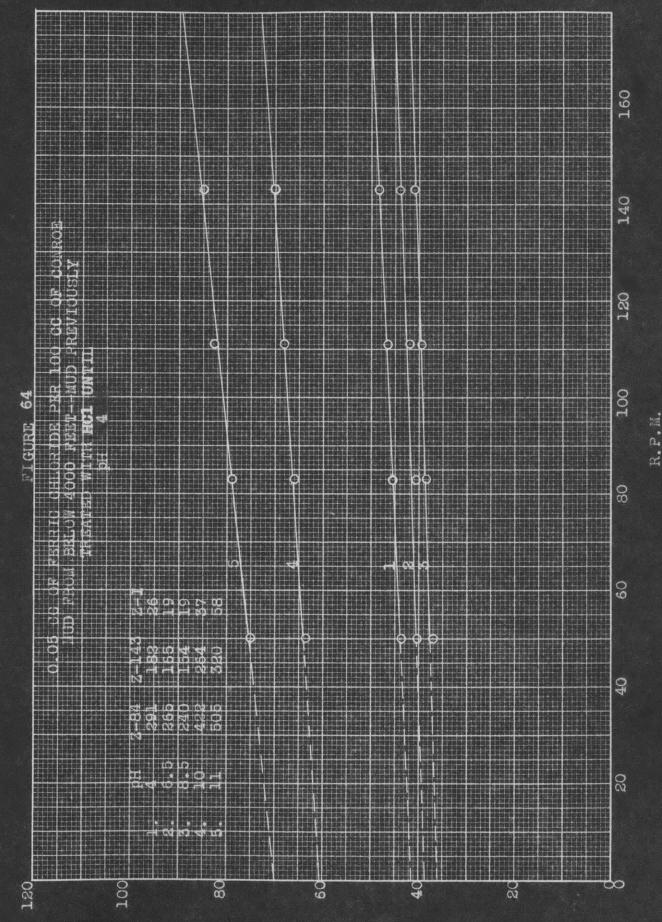


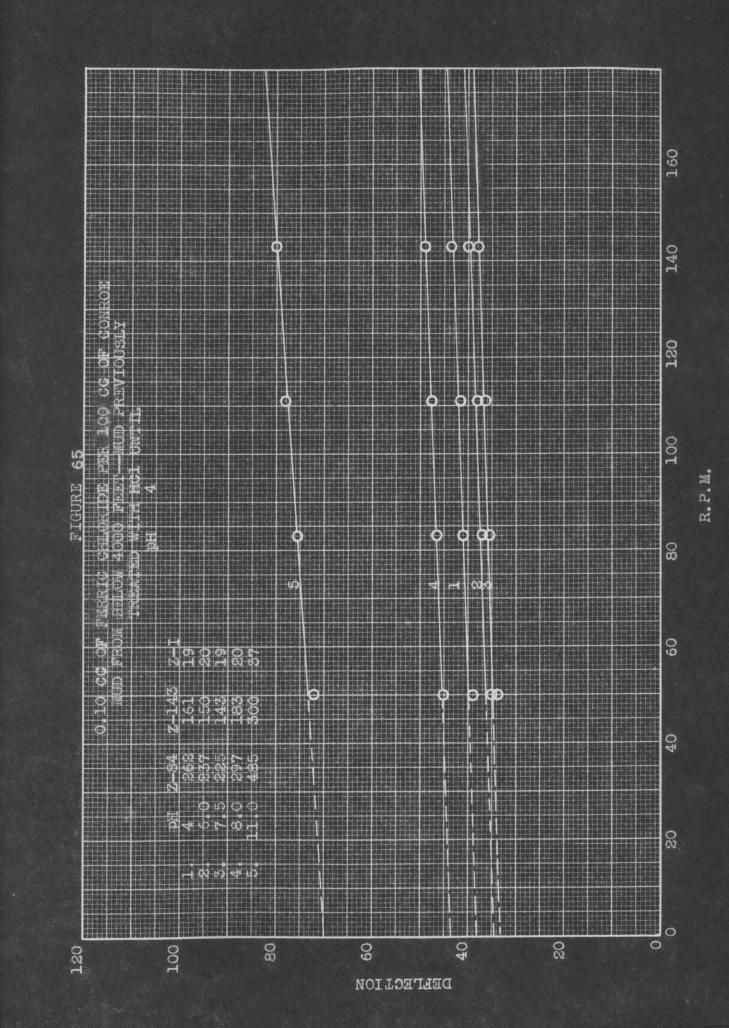
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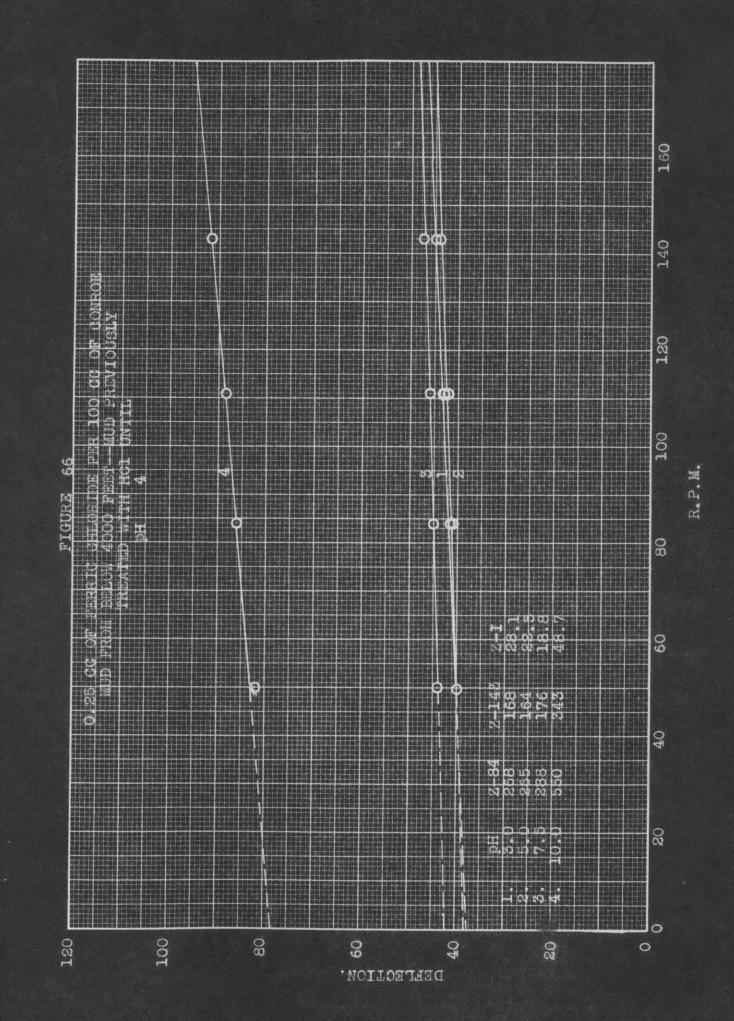


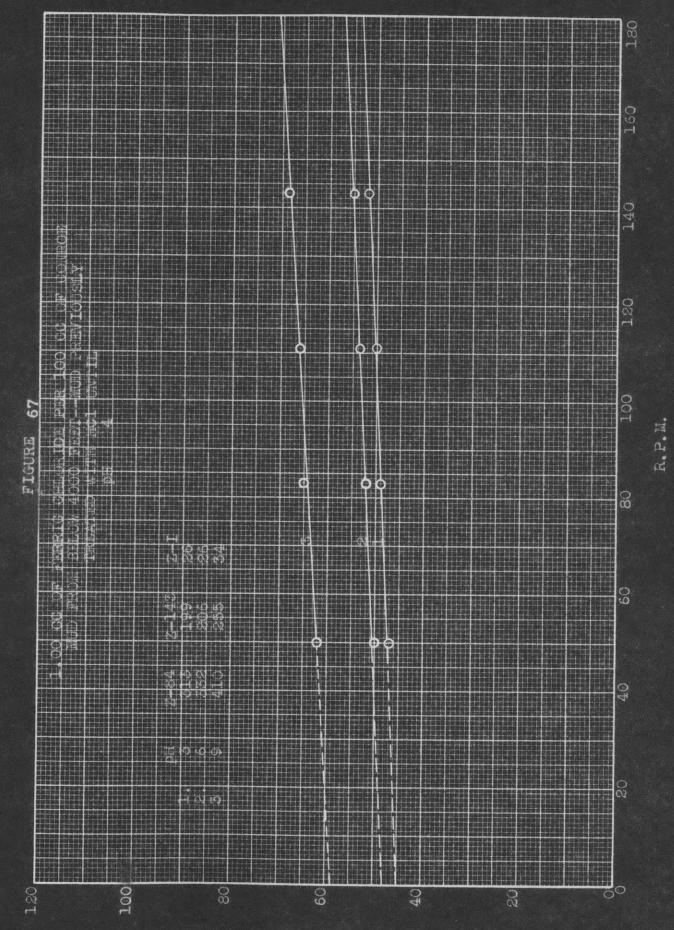




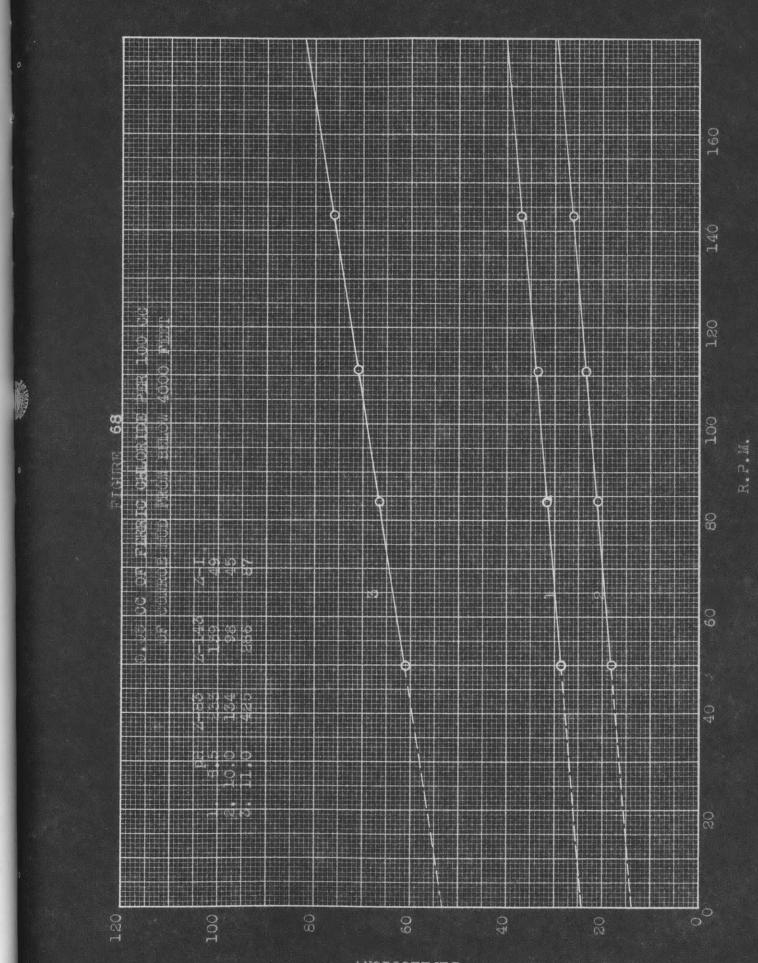


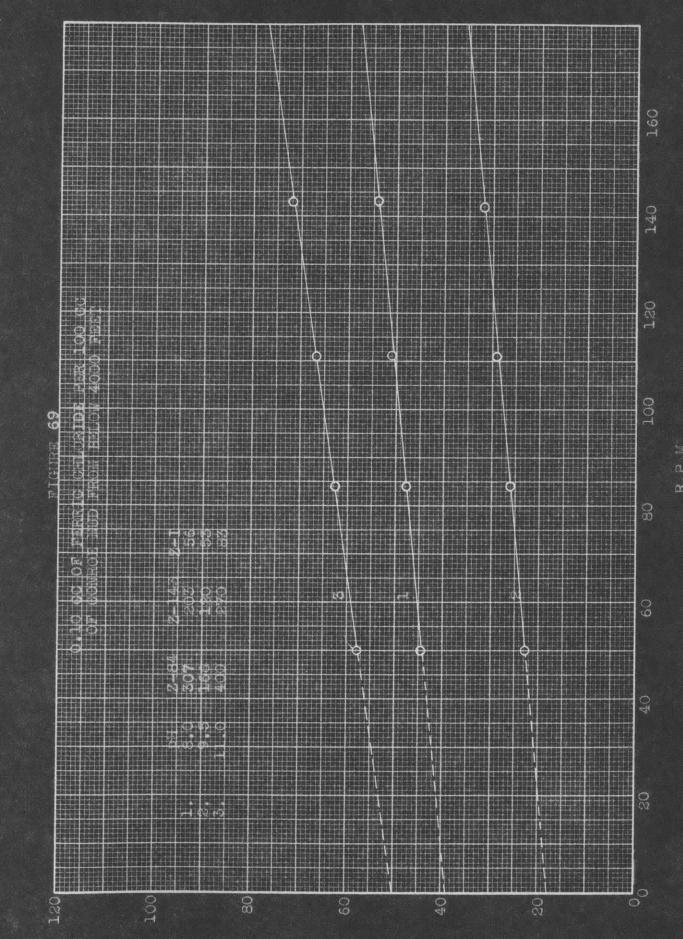
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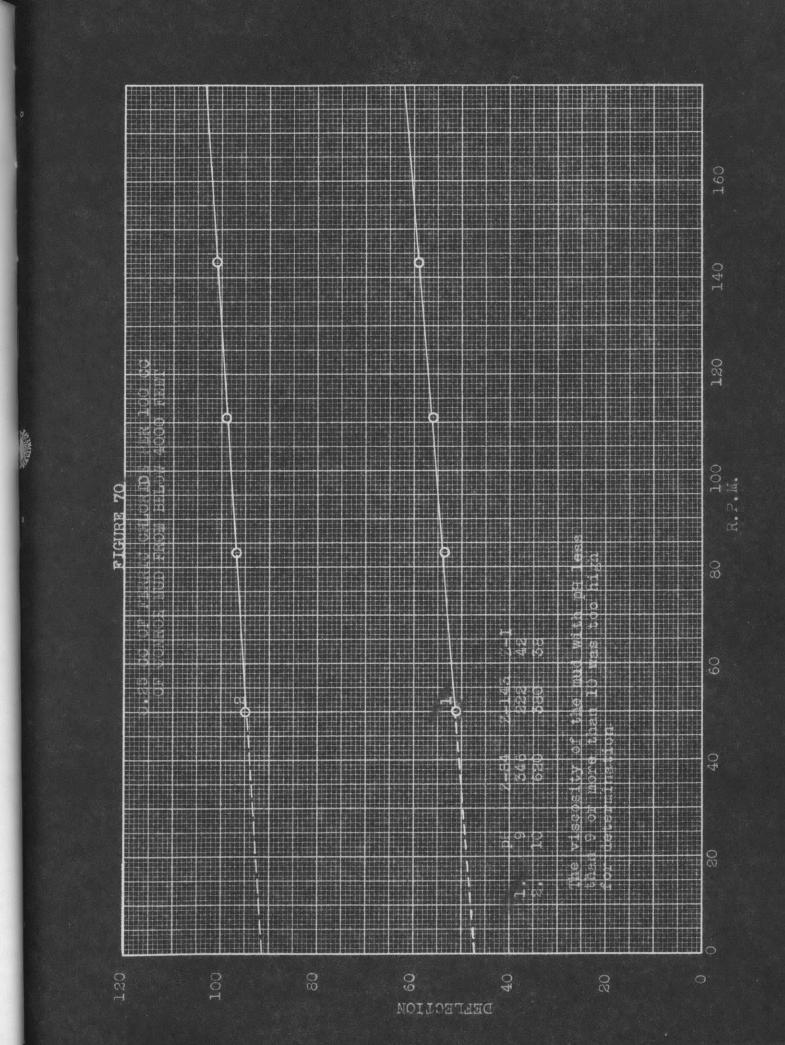


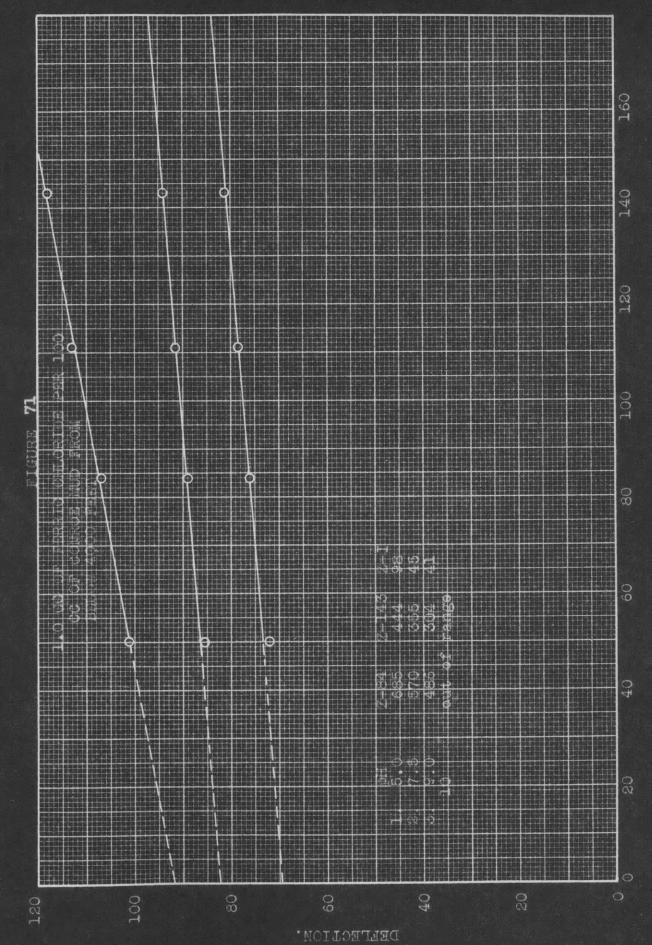
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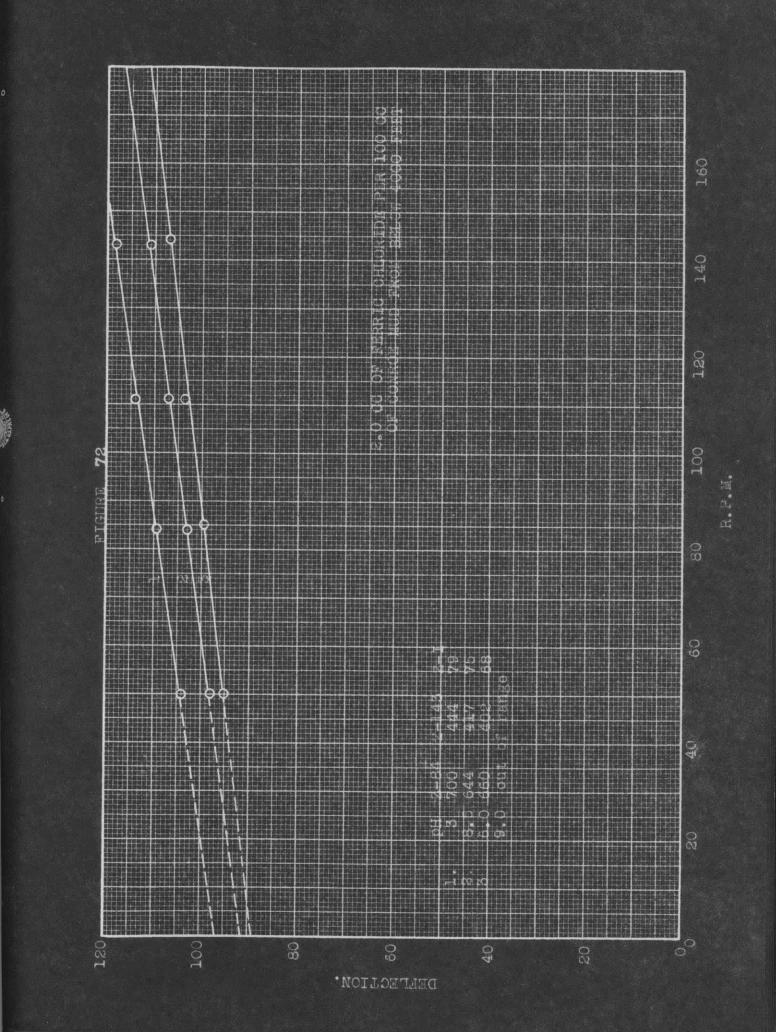
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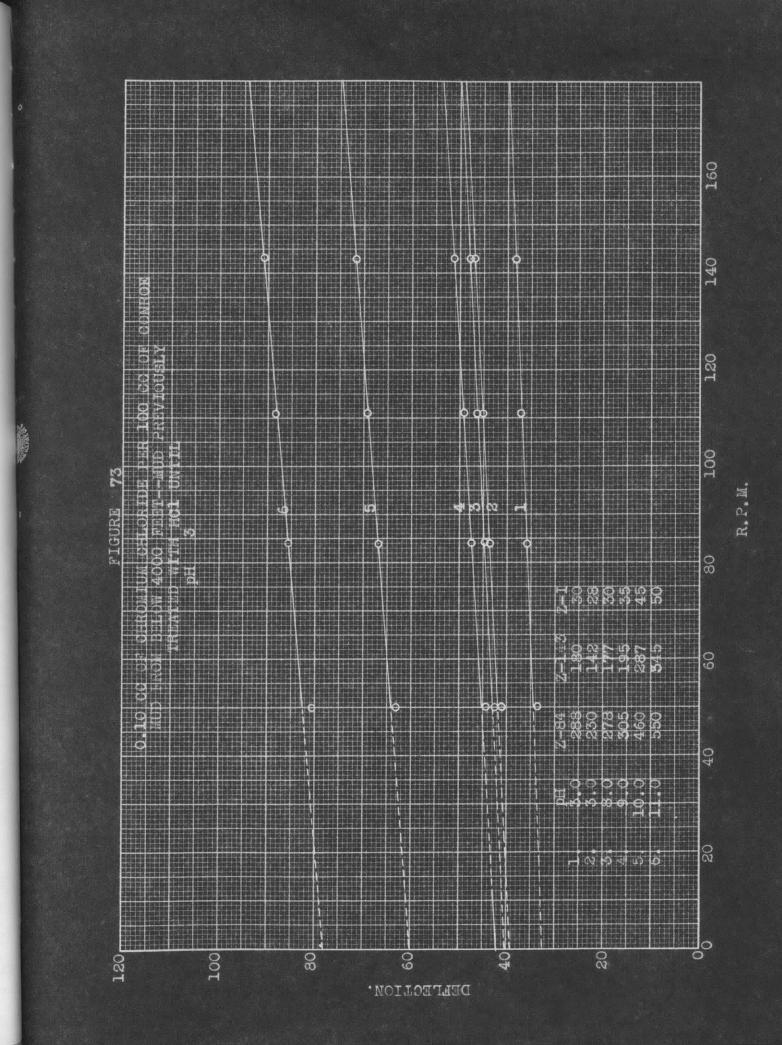


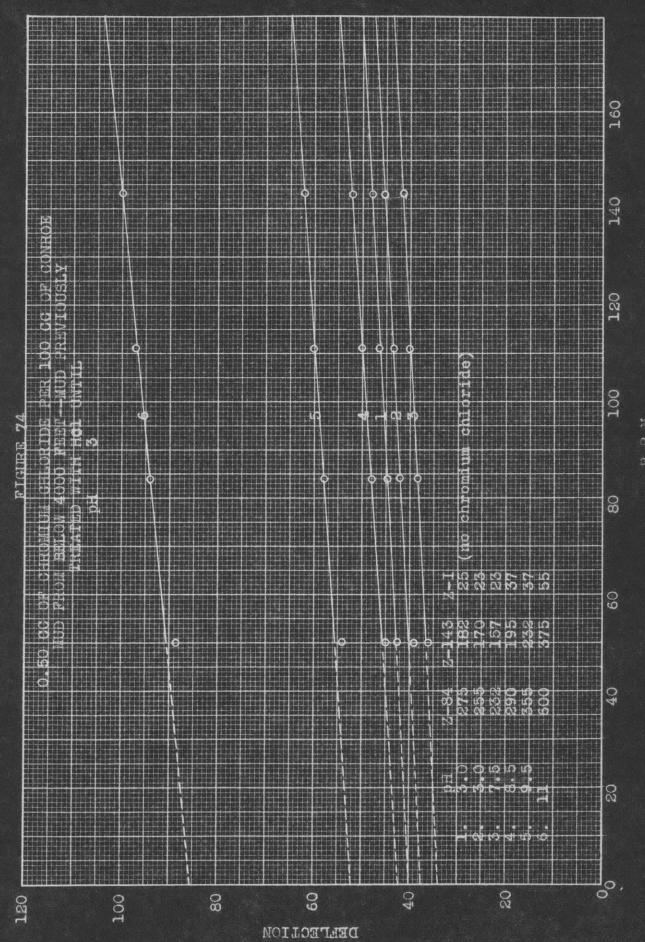


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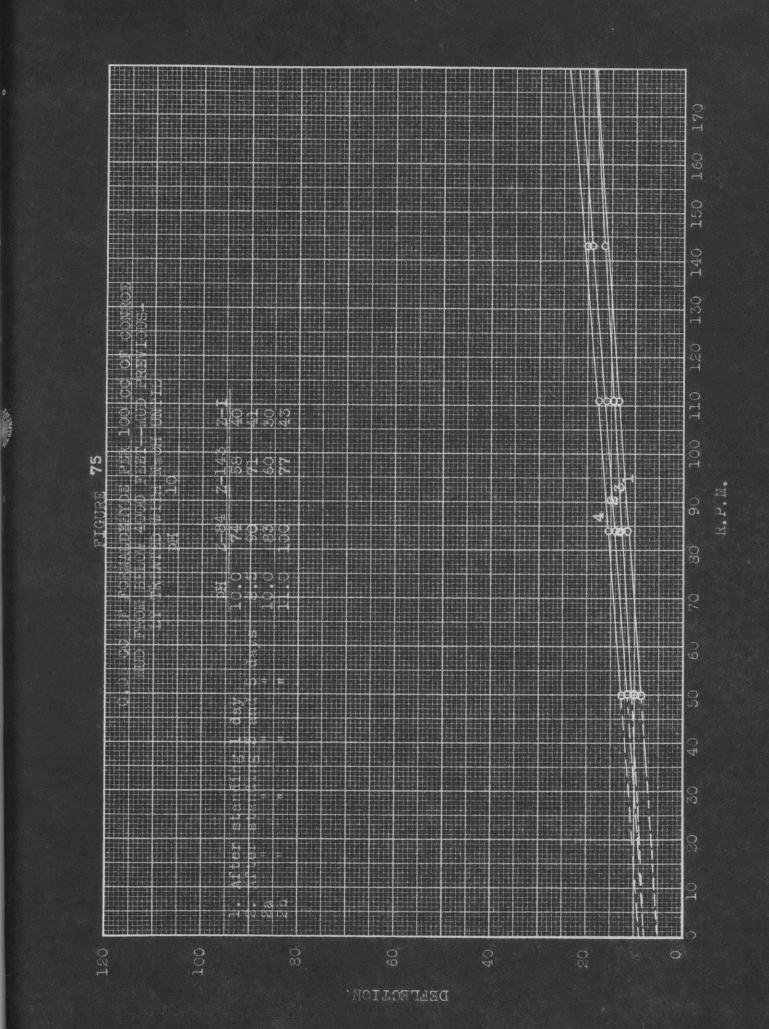


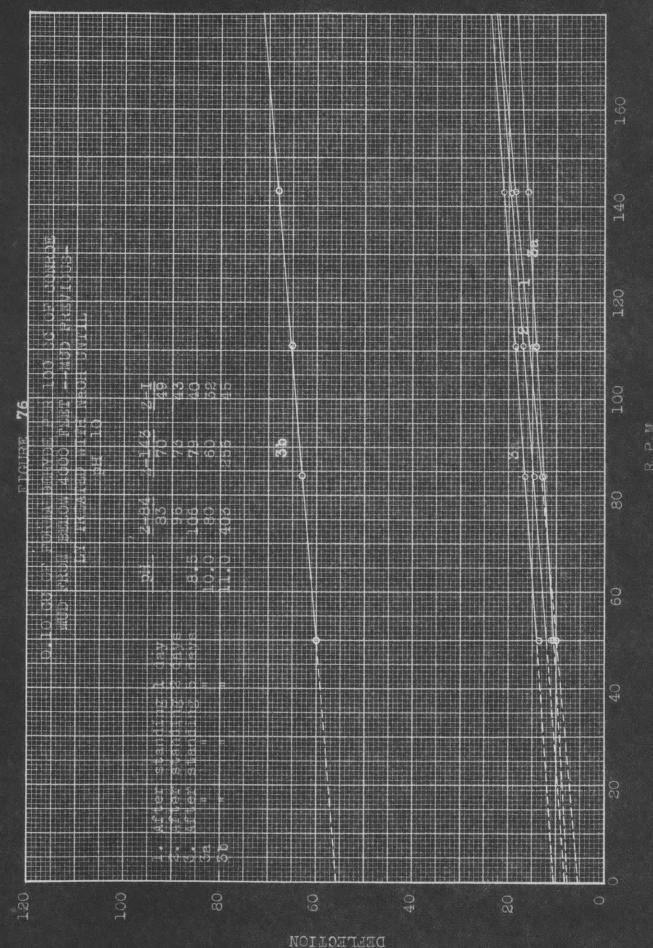




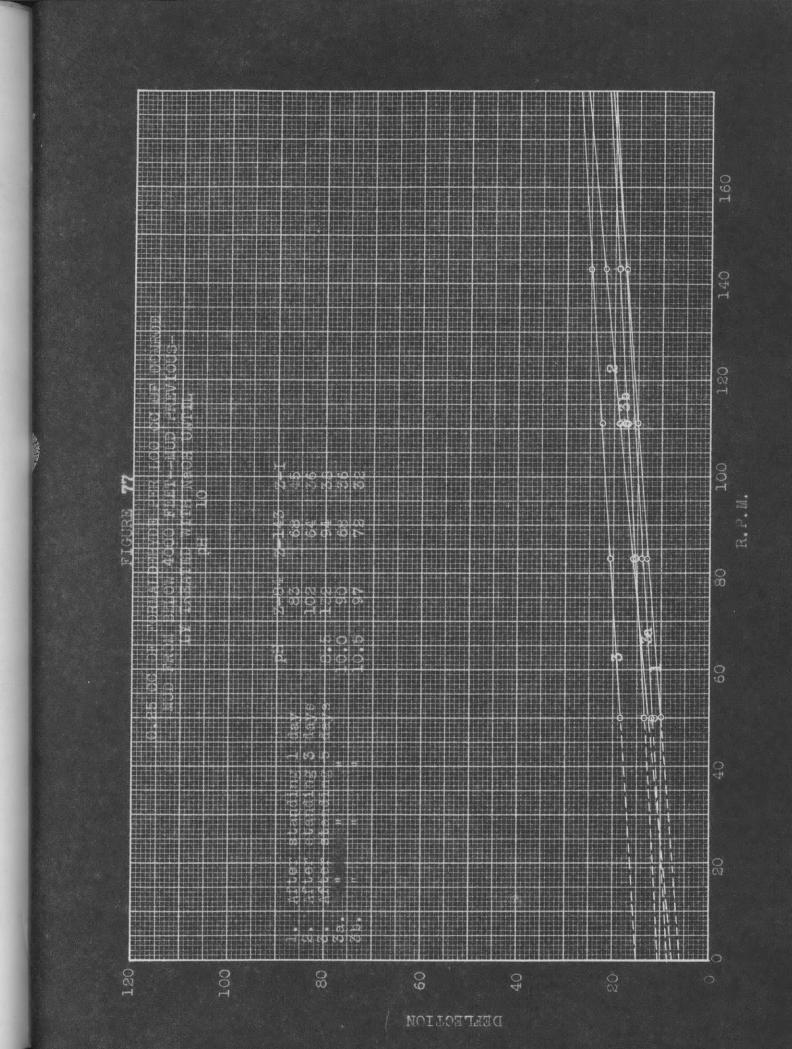
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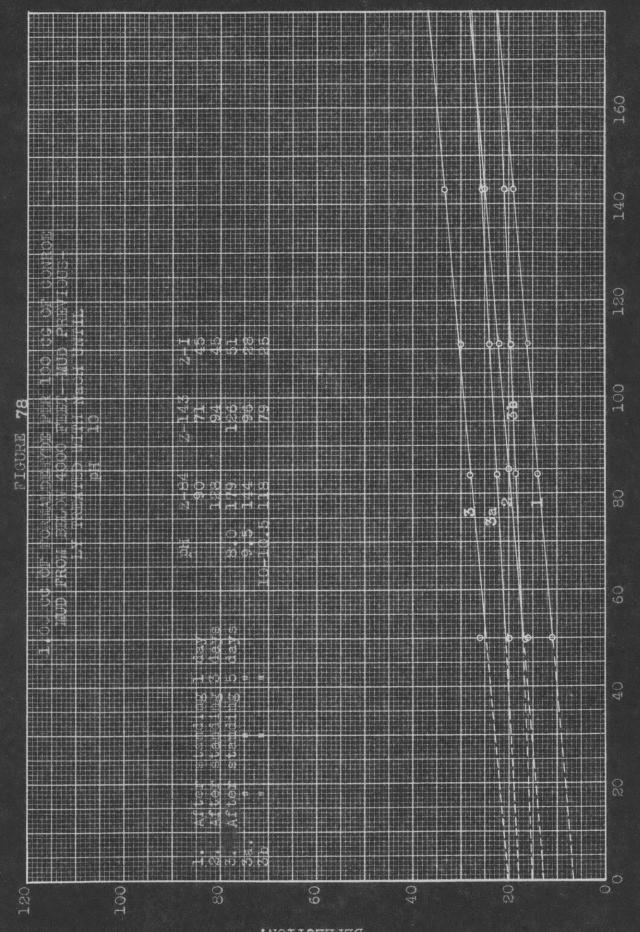
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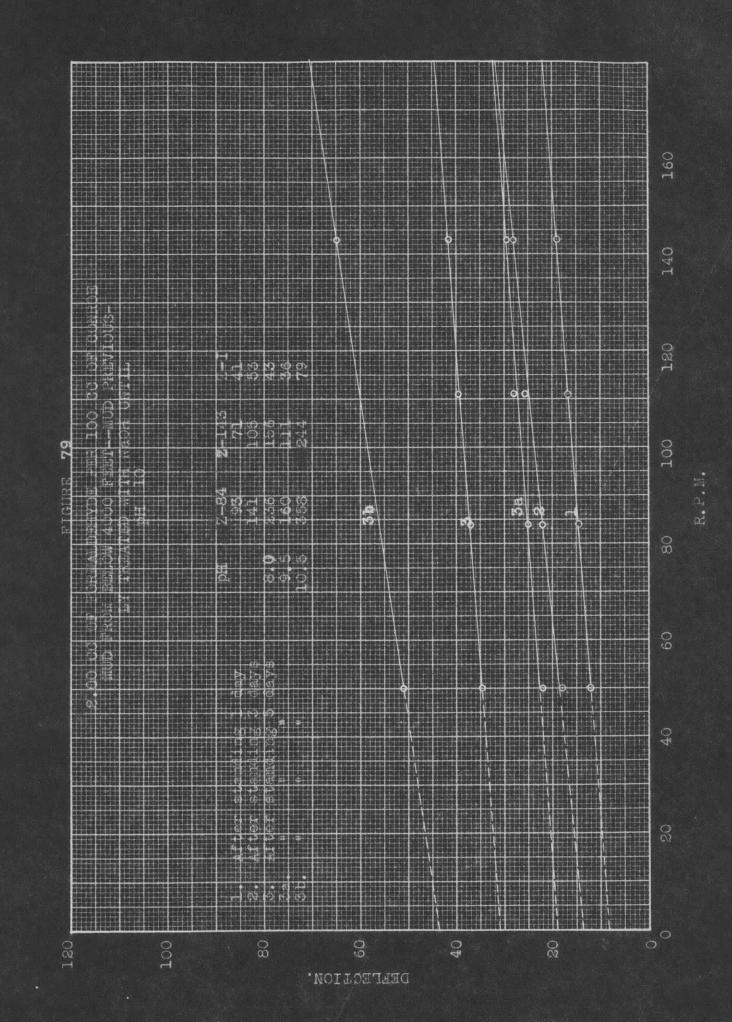
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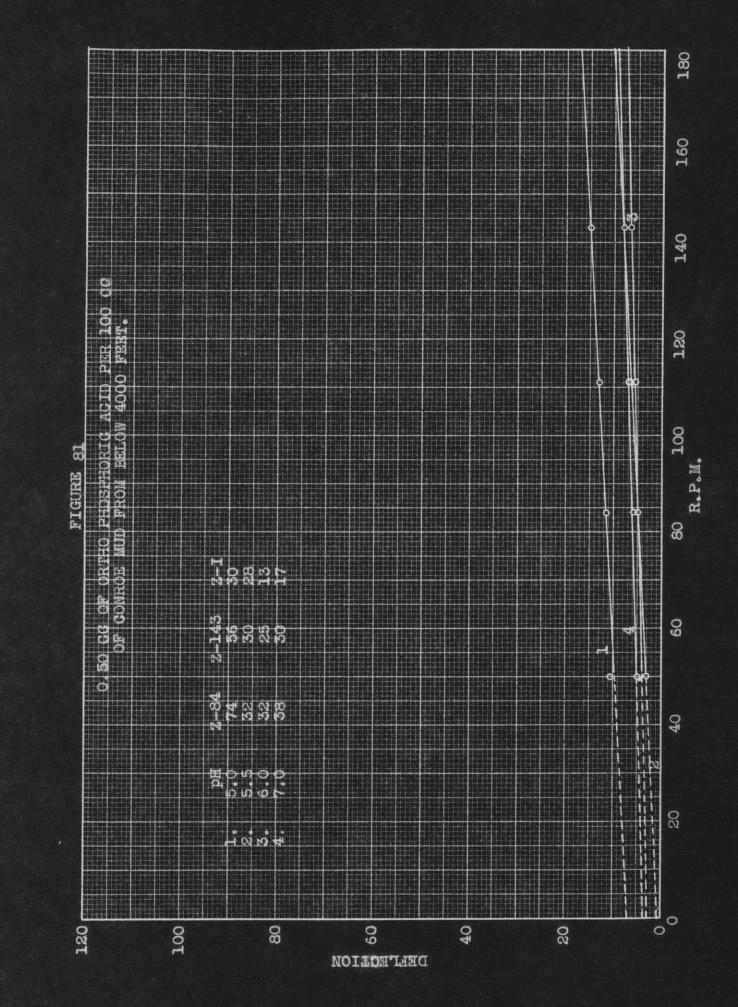


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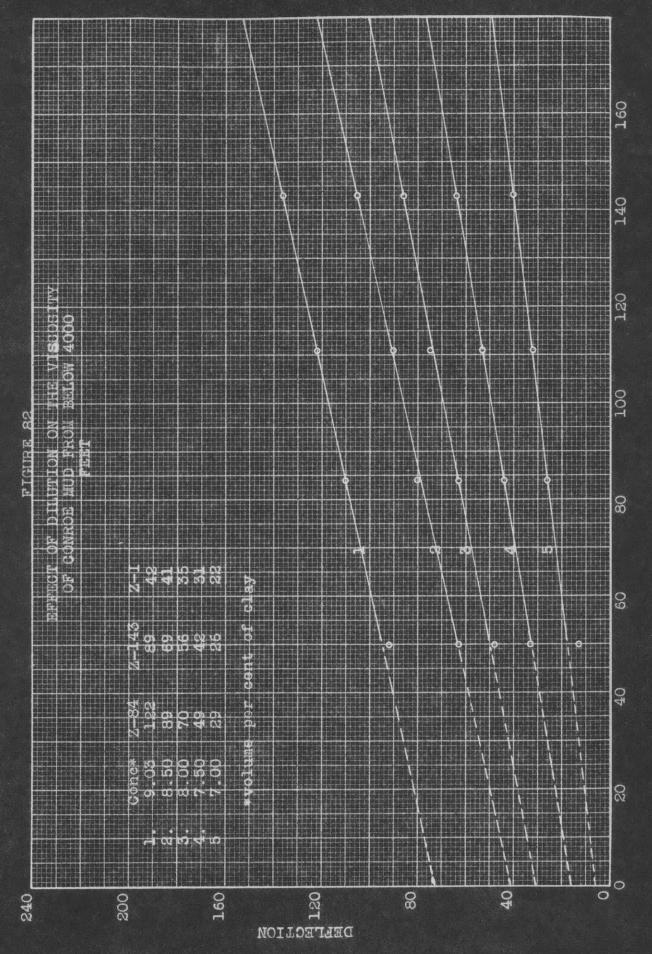
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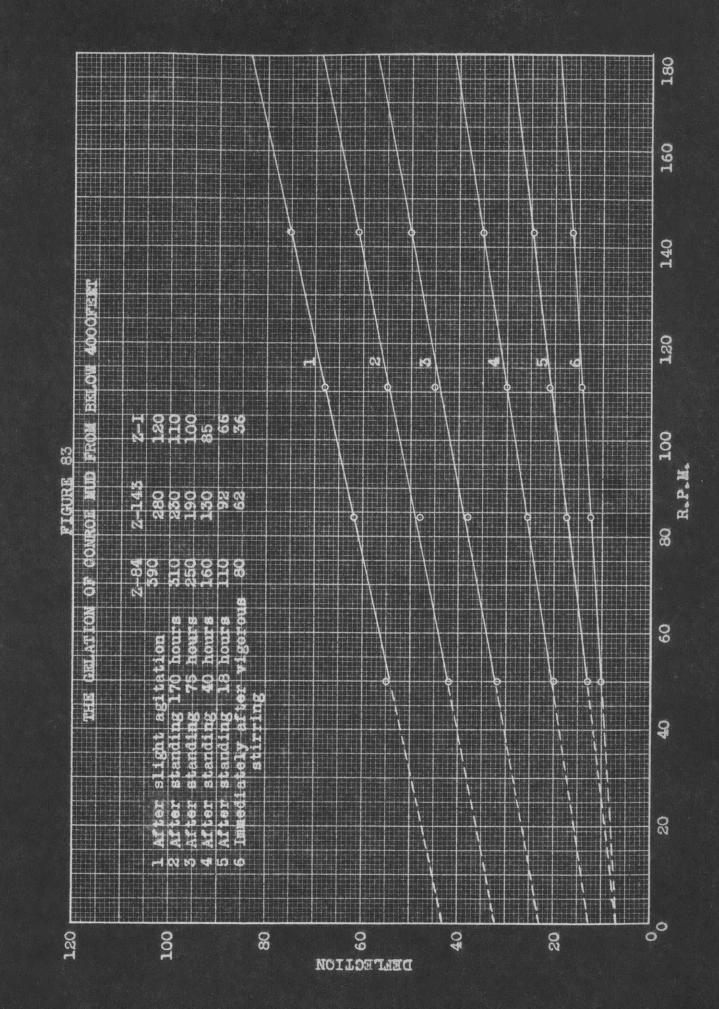


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