

AZBE AWARD NO. 1

**A STUDY OF THE REACTION BETWEEN
CALCIUM OXIDE AND WATER**

By

**T. C. MILLER, TECHNICAL DIRECTOR
INDUSTRIAL SALES DIVISION
NATIONAL GYPSUM COMPANY
BUFFALO, NEW YORK**

**(1960 Winner of the Victor J. Azbe Lime Award for the
Best Technical Paper on Lime)**

Published by

NATIONAL LIME ASSOCIATION

WASHINGTON 5, D. C.

FOREWORD

In 1960 Victor J. Azbe, President of the Azbe Engineering Corp., Clayton, Missouri, generously established through an irrevocable trust an annual award of \$1000 for the best technical paper on lime. Mr. Azbe, who has dedicated 40 years of his life as an international lime plant engineering consultant, hopes that this award will help stimulate greater interest in research on lime.

The National Lime Association -- administrator of this annual contest -- is pleased to publish the first award paper by T. C. Miller of the National Gypsum Company, which deals with the fundamental reaction between quicklime and water. If succeeding winning papers attain the high quality of Mr. Miller's, the lime industry will be the benefactor, and Mr. Azbe's generosity will be more than justified.

The Victor J. Azbe Lime Contest covers all aspects of lime manufacturing, including limestone processing, calcination, hydration, etc.; research on lime's physical and chemical properties; and methods of tests for evaluating lime's properties and quality. Further details of this contest can be obtained from the National Lime Association.

Robert S. Boynton, General Manager
National Lime Association
Washington 5, D.C.

A STUDY OF THE REACTION BETWEEN CALCIUM OXIDE AND WATER

By T. C. Miller
National Gypsum Co.

TABLE OF CONTENTS

I	Introduction	5
II	Methods of Evaluation of the Physical Properties of Calcium Hydroxide	6
	A Settling Time and Rate	6
	B Specific Surface	7
III	Methods of Hydration	8
	A Dry Hydration	8
	1 Conventional Dry Hydrate	10
	2 Special Dry Hydrate	11
	B Wet Slaking	12
IV	Heat Distribution Calculations	13
	A Dry Hydration.	13
	B Wet Slaking.	16
V	Method of Wet Slaking.	19
	A Procedure	19
	B Method of Testing.	20
	1 Specific Surface	20
	2 Settling Time	20
	3 Viscosity	21
VI	Results	22
	A Slaking Temperature and Slaking Time	22
	B Settling Time.	25
	C Specific Surface	42
	D Viscosity	47
VII	Conclusions	50

I - INTRODUCTION

The reaction between calcium oxide (CaO) and water (H₂O) is an interesting and complex process. A great deal of confusion has existed in the use of calcium oxide by the chemical industry when it is required that the calcium oxide be converted to calcium hydroxide with water only, and oftentimes has resulted in unexpected results because of the unusual characteristics of such a calcium hydroxide. Commercial dry calcium hydroxide also has been criticized because of the varying degree of characteristics of a product from one producer. A study has been made of the reaction between calcium oxide and water for a wide range of variation in temperature to understand more fully the results to be expected when the reaction is carried out under specified conditions, from producing a dry product to that of producing suspensions with a large excess of water.

The physical analysis of products resulting from the dry hydration of calcium oxide under a variety of conditions indicates wide variations in settling time and specific surface or mean particle diameter. A similar study of aqueous suspensions of calcium hydroxide resulting from the wet slaking of calcium oxide in an excess of water under various conditions of temperature and concentration indicate that by this process of converting calcium oxide to calcium hydroxide a wide variation of settling times and specific surfaces is being obtained. Requests for the study of the process of a large number of chemical industries indicate the need for more technical knowledge of the hydration or slaking process and the resulting products. Results compiled from the study of industrial processes indicate the need for a search for a better understanding of conditions controlling the physical properties of calcium hydroxide and for better test methods which would more clearly define these physical properties.

It has been known for many years that the physical properties of settling rate and specific surface may vary over a relatively wide range with slight variations in a hydration process but these variations have never been studied in the effort to establish laws by which these variations take place. The data from industrial processes indicated that some law may exist by which these characteristics could be controlled and maintained. This paper deals with the results of such a study in slaking calcium oxide in an excess of water to produce aqueous suspensions of calcium hydroxide. It is not the intention at this time to include the results from a study of the dry hydration process.

It has been established during recent years that the specific surface of calcium hydroxide could be changed within certain limits by a change of either the concentration or the temperature of the water used for hydrating.

It is also known that there is correlation between specific surface and settling time of calcium hydroxide, but this correlation is not always in as close agreement as would be desired.

The cause for this disagreement has been studied with the result that physical limits have been established for standardizing the hydration of calcium hydroxide to produce the most desirable product available to increase the efficiency of a chemical process.

The single important fact to come from this study is the discovery of conditions that have given a clue to certain laws governing the control of particle diameter of calcium hydroxide resulting from the reaction of calcium oxide and water.

II METHODS OF EVALUATING THE PHYSICAL PROPERTIES OF CALCIUM HYDROXIDE

A Settling Time and Rate

The lack of understanding the physical properties of dry, as well as aqueous suspensions of calcium hydroxide has been primarily the result of the limited means of test methods. Since the introduction of commercial dry calcium hydroxide powder in 1904 the only test methods have been the settling time or rate determination and the sieve test. Although in use for an indeterminate number of years, the settling test did not become a standard test method until recently (A.S.T.M. C110-58). It is certainly a reliable and reproducible method of evaluation, but two major disadvantages make it difficult to become a popular test.

First, the time required to determine the settling time or rate on many types of calcium hydroxide, especially aqueous suspensions prepared by using an excess of water resulting in a slow settling product, make the test unsatisfactory as a control test. Second, when slight changes in the hydrating or slaking procedure are permitted, these changes influence a change in the viscosity of the suspension and consequently influence the settling time or rate. This gives the impression that changes in the quality of the calcium oxide are responsible for the differences in settling time or rate. Therefore, it appears that settling time tests of aqueous suspensions may require the determination of some other characteristic or characteristics to fully define the settling rate.

A sieve test is meaningless as far as defining a physical characteristic of calcium hydroxide is concerned. This test merely indicates the maximum size particle to which the calcium oxide has been slaked or the calcium hydroxide sieved or air separated. A sieve test gives no information on the size or distribution of particles finer than the finest sieve used.

A test method which would give more positive information in a short length of time has been desirable and is even in greater demand in present-day chemical processes where more definite physical characteristics are required. A study of various test methods has been undertaken over the years and very few have shown promise of becoming accepted methods for process control. Liquid elutriation methods employing water, methanol, ethanol and various other organic suspending mediums have been ruled out for the same reason that has made the settling time test so unpopular as a process-control test - - its time-consuming aspects.

Gas absorption methods are the most precise even for research work, but the cost of equipment and the high skill required for operation will undoubtedly prevent the method of being accepted as a control test.

B Specific Surface

During the past 15 years the Blaine air permeability method for specific surface has been employed as a method for studying the characteristics of calcium hydroxide. The results have been very encouraging. The method has been used throughout the present work and it is concluded that it is the most economical and rapid method for process control. The inexpensive apparatus makes it possible to provide more than one instrument for plant control where constant control must be maintained throughout more than one department. It is encouraging to cite that several of these testing instruments have been installed by industry for process-control testing. Approximately twenty to thirty minutes are required for testing a dry calcium hydroxide and approximately one and one-half hours for testing aqueous suspensions of calcium hydroxide.

The Blaine specific surface results are not influenced by viscosity or other physical properties. It is a test for the area exposed by one gram of calcium hydroxide which can be employed to calculate the theoretical mean particle diameter. The reader is referred to National Gypsum Company's Industrial Sales Department Technical Bulletin 2 BC for details of this method.

III METHODS OF HYDRATION

A Dry Hydration

The reaction between calcium oxide and water is not a simple one from any point of view. Calcium oxide is practically insoluble in water. Theoretically, 0.131 g dissolves in 100 ml water at 0° C and 0.07 g dissolves in 100 ml water at 100° C. Calcium oxide reacts with water to form calcium hydroxide. Calcium oxide is a member of a group of chemicals which liberates a considerable quantity of heat when reacting with water. This is known as an exothermic reaction. It is a remarkable property found in but a few materials which lime producers and consumers have failed to recognize to its fullest.

The reaction between calcium oxide and water takes place according to the equation



That is, 56.08 pounds of calcium oxide will react with 18.016 pounds of water to produce 74.096 pounds of calcium hydroxide. Each pound of calcium oxide will produce 1.3213 pounds of calcium hydroxide by combining with 0.3213 pound of water. The calcium hydroxide produced contains theoretically 75.7% calcium oxide and 24.3% water. Calcium hydroxide also is practically insoluble in water. The solubility at 0° C is 0.185 g per 100 ml of water and at 100° C is 0.077 g per 100 ml of water.

One significant property of this reaction is the liberation of 27,500 Btu of heat for each lb-mol (56.08 lbs) of calcium oxide. An idea of this amount of heat is illustrated by the fact that it is sufficient to raise the temperature of 194 pounds of water from 70° F to 212° F (boiling). Considering that only 18.016 pounds of water are theoretically required for each lb-mol of calcium oxide, a greater amount of heat is liberated than can be utilized with this amount of water simply to heat the product to 212° F and therefore the mass will become heated above 212° F unless a larger amount of water is used.

The extent of this exothermic reaction offers an opportunity to utilize the heat in three distinct methods of hydration according to the type of calcium hydroxide desired as determined by the utilization of this heat. These methods are outlined in Figure 1. The most familiar method of hydration used by commercial lime producers is the conventional one producing a dry powder at temperatures not exceeding 214° F. A second method produces

THE PRODUCTION OF CALCIUM HYDROXIDE FROM ROTARY KILN QUICKLIME

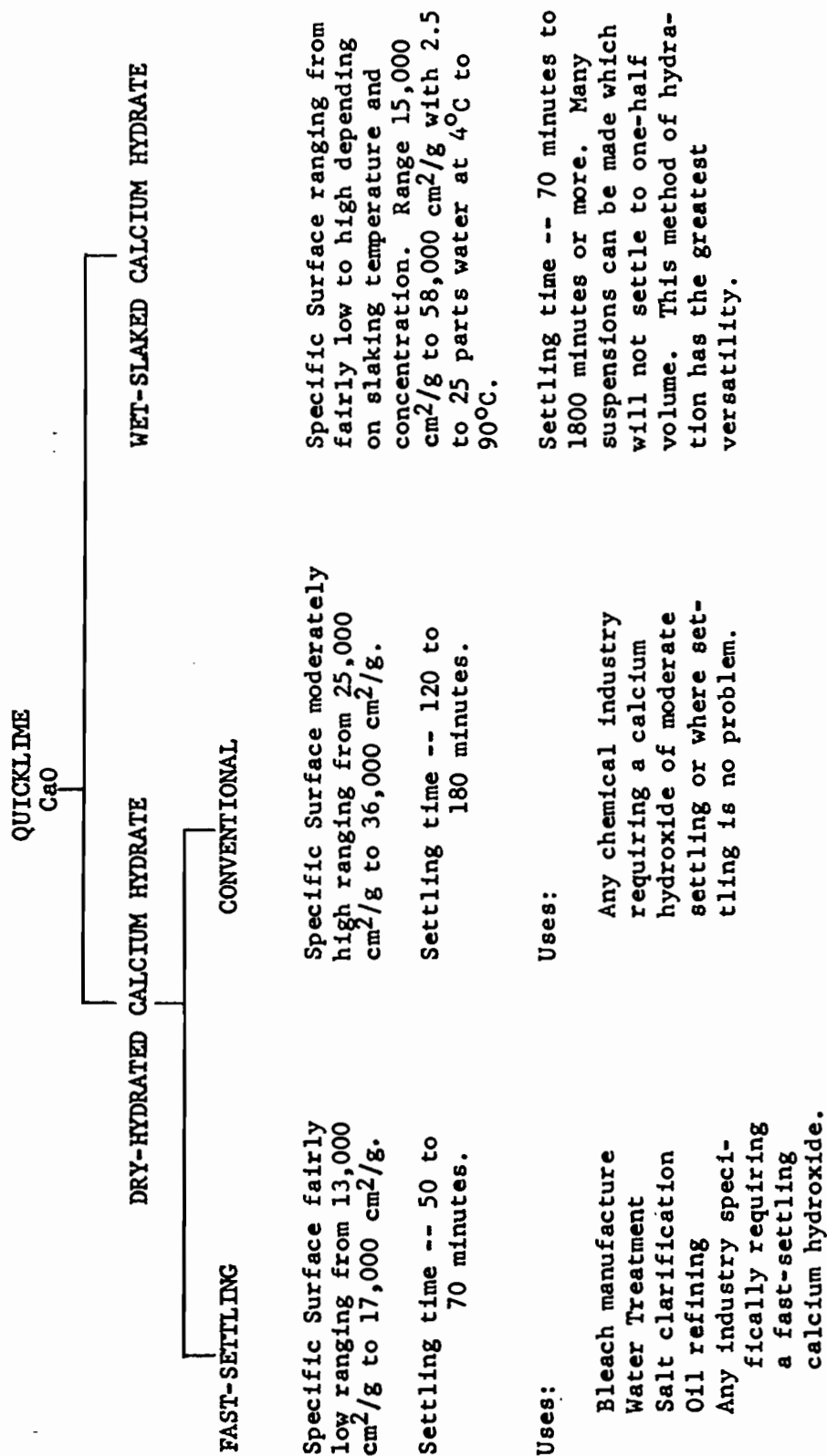


FIG. 1

a dry product at temperatures above 212° F by taking advantage of the liberated heat to control the size of calcium hydroxide particles. The third method of hydration, known more commonly as slaking, employs an excess of water to produce an aqueous suspension of calcium hydroxide. The chemical industry employs this method of producing calcium hydroxide principally because more economical equipment can be used and a greater latitude of variation is permissible with less skill. But recent studies of this method of producing calcium hydroxide indicate that closer controls are necessary to maintain constant physical properties of the calcium hydroxide.

1. Conventional Dry Hydrate

Commercial dry calcium hydroxide is normally produced by reacting approximately one pound of calcium oxide with 0.75 to 1.0 pound of water in a continuously agitated machine or hydrator. The mixture of CaO and H₂O, in the very early stages of hydration, produces a wet or "soupy" mass just prior to the beginning of the heat reaction. This mass reaches the temperature of boiling water within a few minutes when the excess water begins to be evaporated. The temperature cannot exceed the boiling point of water (212° F) at atmospheric pressure as long as liquid water (not water vapor alone) is present. The process is regulated with sufficient water to be assured that liquid water is present until the hydration reaction is practically complete. Then the last trace of liquid water is evaporated to produce a finely divided dry powder practically free of excess moisture.

The degree of burning a limestone to produce a quicklime influences to a great extent the type of calcium hydroxide which can be produced. A soft-burned quicklime reacts very readily with water as indicated by the temperature rise test involving a small amount of lime in a comparatively large amount of water. On the other hand, an overburned lime reacts much slower with water to give a low temperature rise by this test. Rotary kiln or other similar quicklimes generally have a high temperature rise which indicates a soft burned product capable of producing a finely-divided calcium hydroxide. Shaft kiln quicklimes generally have a low temperature rise indicating their inability of producing as finely divided calcium hydroxide as rotary kiln quicklime. Both types of dry calcium hydroxide may have the same percentage passing a 325 mesh sieve, which might indicate equal quality as far as fineness is concerned, but this is not true. The real difference in the products is the size of the particles or distribution of sizes smaller than 325 mesh. Two evaluations may be used to denote this difference. One of these is the settling rate of a ten per cent suspension to one-half volume in a 100 ml graduated cylinder. Calcium hydroxide containing particles of large diameter will settle at a faster rate than a calcium hydroxide containing particles of small diameter.

Another method of evaluation is the determination of the specific surface or the mean particle diameter. This may be determined with the Blaine air permeability apparatus,

The difference between shaft kiln and rotary kiln quicklimes is illustrated by the results of Table I.

TABLE I
Settling Time, Specific Surface and Mean Particle Diameter of Calcium Hydroxides from Shaft Kiln and Rotary Kiln Quicklimes

Lime	Settling Time to 1/2 Volume Minutes	Specific Surface cm ² /g	Mean Diameter u
Shaft Kiln "A"	50	14,451	1.8
Shaft Kiln "B"	40	13,624	2.0
Rotary Kiln "A"	133	30,238	0.9
Rotary Kiln "B"	150	29,379	0.9

A great many chemical processes were established on calcium hydroxide produced from shaft kiln quicklime before the widespread production of rotary kiln quicklime. These industries may be able to use a hydrated lime produced from a rotary kiln quicklime, but most generally it means the investment in additional equipment or an alteration in the process to compensate for the differences in physical properties. A great many industries can use this finer product without disadvantage. Also, a great many industries can and do use a much finer calcium hydroxide than is obtainable commercially in a dry form from either shaft kiln or rotary kiln quicklimes. These industries must produce their calcium hydroxide from quicklime slaked in an excess of water.

2. Special Dry Hydrate

A study of the dry hydration of calcium oxide at temperatures greater than 212° F indicated that the diameter of the particles could be increased as denoted by a decrease in specific surface or an increase in mean particle diameter.

A decrease in specific surface or increase in mean particle diameter decreases the settling time of the dry product. This increase of particle diameter is proportional to the increase in temperature of hydration above 212° F. The increase in temperature of hydration is accomplished by regulating amount and rate of water addition to produce a high temperature that will maintain all the water as liquid and vapor, or vapor alone at atmospheric pressure until hydration is complete. This method of hydration can be used to reduce the settling time of dry calcium hydroxide to approximately one-third that of commercial dry rotary kiln calcium hydroxide produced by conventional methods and is comparable to calcium hydroxide produced from shaft kiln calcium hydroxide.

The reaction of calcium oxide in an excess of water, which we choose to call wet slaking, offers a great magnitude of variation of particle diameter control by a single method. Because the chemical industry uses this method exclusively in processing calcium oxide it offers great opportunity to standardize calcium hydroxide suspensions with constant physical properties.

B Wet Slaking

It is indeed interesting that the exothermic reaction of calcium oxide and water offers such control of particle diameter by slaking the calcium oxide in an excess of water. When a particle of soft burned calcium oxide is dropped in water, the lime immediately absorbs the water into the interstices left by the escaping carbon dioxide during the calcination process, and wets every part of the particle. Hydration begins immediately. When the lime is over-burned or when shaft kiln calcium oxide is used, the reaction rate is considerably slower. If the particle of calcium oxide is considered to be made up of many smaller particles, these very small particles will disintegrate during the hydration to produce even smaller particles of calcium hydroxide. The rate of reaction or the degree of hydration should then offer some means of controlling the size of the resulting calcium hydroxide particles. The process involving only sufficient water to produce a dry calcium hydroxide has been known as hydration, while the reaction utilizing an excess of water has been known as slaking. The two chemical reactions are identical as far as producing a calcium hydroxide is concerned, the only difference being that hydrating produces a dry product and slaking is spoken of as producing a suspension.

Realizing that the liberation of 27,500 Btu of heat per lb-mol of calcium oxide could have considerable influence on the development of the particle diameter of calcium hydroxide, the reactions were carried out not only with water at various temperatures from 4° C (39° F) to 90° C (194° F), but also at concentrations from 2.5 pounds of water per pound of calcium oxide to 25 pounds of water per pound of calcium oxide. This range in temperature would give us all practical values between the freezing and boiling points of water. The range of concentration would likewise be from the most concentrated suspension to a diluted suspension which would be feasible in any chemical process.

IV HEAT DISTRIBUTION CALCULATIONS

The liberation of a large amount of heat from the reaction between calcium oxide and water makes it desirable to study the effect of this heat on the hydrating mass. It is desirable to determine the distribution of heat in dry hydrating as well as wet slaking to better understand the possibilities of particle size control. The amount of heat developed and its distribution or dissipation controls the particle size and the particle size distribution of a calcium hydroxide and these calculations may be helpful in better understanding its effect.

A Dry Hydration

1 Conventional Dry Hydrates

Nearly every lime producer operates a hydrating plant for the production of a dry commercial calcium hydroxide. These plants are normally operated by the conventional process of adding sufficient water to convert the calcium oxide to calcium hydroxide at temperatures not exceeding 214° F (elevation of the boiling point of water by about 2° F by the presence of the solid calcium hydroxide).

Theoretical calculations for the use of 0.75 pound water per pound of calcium oxide, without heat loss from radiation, are shown in Table II. These calculations show that theoretically 94.3% of the water is used for hydrating and dissipating the heat, leaving 5.7% in the finished product. This amount of water constitutes 3.14% of the finished product.

This calculation is not exactly true, because no corrections were made for radiation losses. Neither were allowances made for the amount of recovered water from escaping steam normally captured by one of the sprays in the system. The efficiency of the hydrating machine or the amount of heat losses will determine whether this amount of water is sufficient to completely convert the calcium oxide to calcium hydroxide. Practical operation of the process in a hydrator with low radiation losses produces a finished product with 0.5% or less free moisture.

2 Special Dry Hydration

It has been found that the development of higher temperatures in the production of a dry calcium hydroxide has a desirable effect on increasing the particle size. Calculations illustrating the temperatures possible by this process have been made.

Theoretical calculations for the operation of such a process above 212° F are shown in Table III. When 0.40 pound water per pound calcium oxide

(Cont - pg. 16)

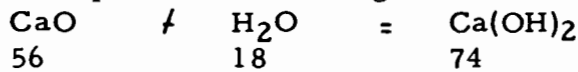
TABLE II

Basis: Normal Hydration

56 lbs. CaO (1 lb-mol)
 42 lbs. H₂O (0.75 lbs. H₂O per lb. CaO)

42 lbs. H₂O added to CaO at one time.

56 lbs. CaO will require the following amount of H₂O for theoretical hydration:



Therefore 18 lbs. of water will be used for converting CaO to Ca(OH)₂
 Excess H₂O will be 42 - 18 = 24 lbs.

Total heat evolved in combining 56 lbs. CaO ≠ 18 lbs. H₂O = 27,500 Btu

Amount of heat required to raise the temperature of 24 lbs. H₂O from
 70° F to 214° F = (24)(144) = 3452 Btu

Amount of heat required to raise the temperature of 74 lbs. Ca(OH)₂ from
 70° F to 214° F = (74)(0.29)(144) = 3089 Btu

Therefore, the heat required to heat both Ca(OH)₂ and H₂O from
 70° F to 212° F = 3452 ≠ 3089 = 6541 Btu

Remaining Btu's available for heating 24 lbs. excess H₂O above 214° F is
 27,500 Btu - 6541 Btu = 20,959 Btu

Quantity of water which can be evaporated at 212° F with this quantity of
 heat will be:

$$\frac{20,959}{970} = 21.6 \text{ lbs.}$$

Water as liquid at 212° F remaining in 74 lbs. Ca(OH)₂ will be
 24.0 - 21.6 = 2.4 lbs. or

The composition of the finished product will be, therefore 74.0 lbs.
 Ca(OH)₂ ≠ 2.3 lbs. excess water or a total weight of 76.3 lbs.

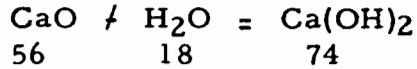
Water	2.4 lbs.	3.14%
Ca(OH) ₂	74.0 lbs.	96.86%
<hr/>		<hr/>
Total	76.5 lbs.	100.00%

TABLE III

Basis: Special Hydration for size control

56 lbs. (1 lb-mol)
 22.4 lbs. (0.40 lbs. H₂O per lb. CaO)

22.4 lbs. H₂O added under controlled conditions
 56 lbs. CaO will require the following amount of H₂O for theoretical hydration



Therefore, 18 lbs. of H₂O will be used in converting CaO to Ca(OH)₂
 Excess H₂O will be 22.4 - 18 = 4.4 lbs. H₂O per 56 lbs. CaO

Total heat evolved in combining 56 lbs. CaO + 18 lbs. H₂O = 27,500 Btu

Amount of heat required to raise the temperature of 4.4 lbs. H₂O from
 70° F to 212° F = (4.4) (142) = 625 Btu

Amount of heat required to raise the temperature of 74 lbs. Ca(OH)₂ from
 70° F to 212° F = (74) (0.29) (142) = 3057 Btu

Therefore, the heat required to heat both Ca(OH)₂ and H₂O from
 70° F to 212° F = 625 Btu + 3057 Btu = 3682 Btu

Remaining Btu's available for heating 4.4 lbs. excess H₂O above 212° F is
 27,500 Btu - 3682 Btu = 23,818 Btu

Quantity of water which can be evaporated at 212° F with this quantity of
 heat will be:

$$\frac{23,818}{970} = 24.6 \text{ lbs.}$$

Since there is less water than this in the mass, a different method calculation
 must be made. The amount of heat necessary to evaporate 4.4 lbs. of H₂O
 at 212° F is:

$$(4.4) (970) = 4268 \text{ Btu}$$

Excess heat still available is 23,818 - 4268 = 19,550 Btu

Heat required for 74 lbs. Ca(OH)₂ from 212° F to 575° F will be
 (74) (0.29) (363) = 7790 Btu

Heat available for heating water vapor only = 19,550 - 7790 = 11,760
 Temperature attainable = (4.4) (0.48) (x - 212) = 15,516

$$\text{or } x = \frac{12,207}{2.11} = \underline{\underline{578^\circ \text{ F}}}$$

is used and added at such a rate that evaporation is maintained throughout the process to provide vapor for hydration, it is shown that theoretically temperatures of 578° F can be maintained.

Greater quantities of water, to a maximum of 0.75 pound water per pound calcium oxide, will decrease the final temperatures to that for conventional hydration as shown in Table II. A decrease in final temperature results in a decrease in mean particle diameter or an increase in specific surface. An increase in specific surface is accompanied by an increase in settling time of the calcium hydroxide.

B WET SLAKING

The theoretical temperatures expected from the reaction of calcium oxide and water were calculated for water temperatures from 4°C (39° F) to 90° C (194° F) and for water-to-calcium oxide ratios from 2.5 pounds to 25 pounds. The calculations are based upon a constant weight to give 0.503 pound pure calcium oxide. Water ratios of 2.5, 7.5, 10.5, 13.5, 18.5 and 25 corresponding to excess weight of water of 1.16, 3.81, 5.39, 6.98, 9.36 and 13.06 pounds respectively were used.

Calcium oxide in the amount of 0.503 pound will produce 0.665 pound calcium hydroxide. The theoretical heat evolved by 0.503 pound calcium oxide during hydration is 246.9 Btu.

The amount of heat required to raise the temperature of water to any temperature up to and including 212°F (boiling), where

- H = the heat in Btu
- W = the weight of water
- h = the heat capacity of water = 1
- T₁ = the initial temperature of the water, and
- T₂ = the final temperature of water

is calculated from the equation

$$H = (W) (h) (T_2 - T_1) \text{ or } (W) (T_2 - T_1) \quad (2)$$

The amount of heat required to raise the temperature of calcium hydroxide where

- H' = the heat in Btu
- W' = the weight of calcium hydroxide
- h' = the heat capacity of calcium hydroxide = 0.29
- T'₁ = the initial temperature
- T'₂ = the final temperature

is calculated from the equation

$$H' = (W')(h')(T'_2 - T'_1) \text{ or } (W')(0.29)(T'_2 - T'_1) \quad (3)$$

When a constant weight of 0.503 pound calcium oxide is used with a value for H of 246.9 Btu and a weight for calcium hydroxide of 0.665 pound the equations become

$$246.9 = (W)(T_2 - T_1) \quad (4)$$

and

$$H = (0.665)(0.29)(T'_2 - T'_1) = (0.193)(T'_2 - T'_1) \quad (5)$$

respectively.

The total heat derived from the hydration reaction is the distribution of the evolved heat from the calcium oxide between the water and the calcium hydroxide to the same temperature. It is the sum of the heat required to raise the temperature of the water and the heat required to raise the temperature of the calcium hydroxide to the same temperature.

The combined equation then becomes Equations (4) + (5) or

$$H = W(T_2 - T_1) + W'h'(T'_2 - T'_1) \quad (6)$$

or

$$H = (W)(T_2 - T_1) + 0.193(T'_2 - T'_1) \quad (7)$$

The final temperature of hydration can be calculated from this equation by solving for T_2 since $H = 246.9$ Btu. The equation then becomes

$$T_2 = \frac{H + (0.193 + W) T_1}{0.193 + W} \quad (8)$$

When it becomes desirable to calculate the temperature necessary to start a reaction with a given weight of calcium oxide to theoretically result in a final temperature of 212° F the equation becomes

$$T_1 = \frac{(0.193 + W) T_2 - 246.9}{0.193 + W} \quad (9)$$

The theoretical final temperatures expected from the same weight of pure calcium oxide (0.503 lb.) with various ratios of water at several temperatures as calculated by equation (7) are shown in Table IV.

TABLE IV

(following page)

TABLE IV

Theoretical Slaking Temperature ($^{\circ}\text{F}$) of calcium oxide with water at various temperatures and proportions.

Ratio $\text{H}_2\text{O}/\text{CaO}$	Excess H_2O lbs.	Temperatures of Slaking Water					
		4°C 39°F	10°C 50°F	20°C 68°F	40°C 104°F	60°C 140°F	90°C 194°F
2.5	1.16	221.4	232.5	250.3	286.3	322.5	376.4
7.5	3.81	100.7	111.8	129.7	165.7	201.7	255.7
10.5	5.39	83.2	94.2	112.2	148.2	184.2	238.2
13.5	6.98	73.4	84.4	102.4	138.4	174.4	228.3
18.0	9.36	64.8	75.9	93.9	129.8	165.7	210.7
25.0	13.06	57.6	68.6	86.6	122.6	158.6	212.6

Temperatures in excess of 212°F are shown above and to the right of a dotted line, indicating that insufficient water is present to absorb the liberated heat and therefore part of the water will be evaporated during the slaking cycle. Temperatures of calcium hydroxide suspensions less than boiling (212°F) can be expected from the reacting between calcium oxide and water for ratios greater than 7.5 and for all temperatures from 39°F (4°C) to 140°F (60°C).

The initial temperature of water for the reaction of all ratios of water to calcium oxide to give a final temperature of 212°F were calculated by equation (8). These initial temperatures are shown in Table V.

TABLE V

THEORETICAL INITIAL TEMPERATURE (T_1) ($^{\circ}\text{F}$) OF SLAKING WATER TO GIVE A FINAL SLAKING TEMPERATURE (T_2) OF 212°F .

Ratio $\text{H}_2\text{O}/\text{CaO}$	Excess Water Lbs.	T_1		T_1 corrected for radiation loss	
		$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$
2.5	1.16	29.6	-1.4	54.6	12.6
7.5	3.81	150.3	65.6	166.8	74.9
10.5	5.39	167.7	75.4	180.1	82.3
13.5	6.98	177.5	80.8	185.8	85.4
18.0	9.36	186.1	85.6	196.5	91.4
25.0	13.06	193.4	89.6	205.0	96.0

All of these calculations have been made to illustrate the wide temperature variations expected in using a variation of ratios and temperatures of water to effect the development of particle diameters of calcium hydroxide in aqueous suspension and to compare the theoretical values with the actual values. It should be emphasized that the degree of rotary kiln calcination of a limestone may affect the rate of slaking and therefore all calcium oxides may not reach these expected temperatures. Only soft-burned calcium oxide will check the values.

V METHOD OF WET SLAKING

A very reactive rotary kiln pebble calcium oxide was used for this study. The reactivity was measured by testing the temperature of 180 grams of the pebble calcium oxide in 900 ml of water at 24° C in an insulated stainless steel beaker. The temperature rise in 30 seconds was 33° C. The quality of the calcium oxide was determined by the sugar method for calcium oxide. It was found to contain 95% calcium oxide.

A Procedure

The procedure for preparing suspensions of calcium hydroxide employed 240 g of pebble calcium oxide for each sample. The amount of water for the preparation of the suspensions ranged from a ratio (R) of 2.5 to 25 times the weight of calcium oxide. A tabulation of the weight of calcium oxide and the volume of water are shown in Table VI.

TABLE VI

Weight of CaO and Volume of H₂O used for
Preparing Ca(OH)₂ Suspensions

R	Rotary Kiln Pebble CaO g	Total Water ml	Excess Water	
			g	lbs.
2.5	240	600	527	1.16
7.5	240	1800	1727	3.81
10.5	240	2500	2447	5.39
13.5	240	3240	3167	6.98
18.0	240	4320	4247	9.36
25.0	240	6000	5927	13.06

The water for each slaking test was heated to the required temperature. The weighed amount of rotary kiln pebble calcium oxide was added to the water at one time. The mixture was mechanically stirred and the reaction temperature measured with a thermometer calibrated to 0.1°C. Agitation was continued until the temperature reached a maximum and began to recede.

The proper agitation of a mixture of calcium oxide and water during the hydration cycle is of the utmost importance. Agitation must be provided to prevent local overheating of the calcium oxide, especially in large quantities of water, and to assure that each particle of lime is supplied constantly with a fresh supply of necessary water to carry out the entire hydration reaction. The most satisfactory method of agitation was found to be supplied by a stirrer having two arms perpendicular to each other and of sufficient length to extend almost to the periphery of the reaction vessel. The agitator speed was controlled during the hydration cycle to provide maximum agitation without overflowing the vessel.

The suspensions of very high solids concentration were very difficult to agitate to a homogeneous mass. The evaporation of water was so rapid that it was difficult to prevent local drying before the temperature decreased below the boiling point. This condition may introduce errors of accurate temperature determination of the slaking reaction.

B Method of Testing

1. Specific Surface

A sample of each suspension was taken immediately after hydration was complete for a specific surface determination. Approximately 100 - 250 ml of the suspension were filtered on a 3-inch Buechner funnel under vacuum, washed with five portions of alcohol to remove the water and then washed with five portions of ether to remove most of the alcohol. The evacuated sample was then dried under infra-red heat until all of the ether and most of the alcohol had been evaporated. The sample was finally dried for approximately 30 minutes in an oven at 105 to 110°C.

A weight of 1.30 g of dried powder was used for determining the specific surface of each sample.

2. Settling Time

Each suspension was then stored in a 1/2 gallon sealed mason jar to allow cooling to room temperature. Then each well mixed suspension was analyzed by the sugar method to determine the concentration of calcium hydroxide in grams per liter. The suspension was then diluted with water or decanted of clear supernatant liquid to give 100 grams per liter of calcium hydroxide and rechecked by the sugar method. This concentration is equivalent to 10 grams of dry calcium hydroxide in 100 ml of suspension for the settling time test. Settling rate was then determined on 100 ml each of suspension by noting the time-rate required to settle to 50 ml (1/2 volume) for those samples which would settle to this point, or to determine the minimum volume each suspension of calcium hydroxide would assume when

no settling value could be obtained. The latter condition existed for those samples having a high specific surface, indicating a bulkiness for the extremely fine particles.

3. Viscosity

It is known that the viscosity of calcium hydroxide suspensions can be increased by dispersing the particles more completely in the liquid vehicle. It is also known that the increase in viscosity in a given suspension is accompanied by an increase in specific surface when there is no change in the water ratio of the suspension. The increase in specific surface increases the settling time of the particles in the suspension. The degree of dispersion of particles during wet slaking is proportional to the degree of calcination of the limestone and the temperature and ratio of the slaking water.

It is not the intention to go into details of the viscosity of calcium hydroxide suspensions in this report, but to briefly touch on the subject to show that some relation exists between the quality of the calcium oxide, the method of slaking and the characteristics of the resulting calcium hydroxide.

All types of calcium oxide will not produce aqueous suspensions of calcium hydroxide of equal viscosity at the same concentration by the same procedure of slaking. For example, one type of calcium oxide slaked in six parts water at 20° C (68° F) and stirred for five minutes produces a calcium hydroxide suspension with a viscosity of 46 centipoises while another type of calcium oxide slaked under exactly the same conditions of stirring and water temperature and ratio produced an aqueous suspension of calcium hydroxide with a viscosity of 273 centipoises. These same calcium oxides slaked in exactly the same manner but using water at a temperature of 60°C (140°F) produced suspensions of calcium hydroxide having viscosities of 716 centipoises and 395 centipoises respectively. Further agitation of these suspensions produced some surprising results. The suspensions produced with slaking water at 20°C and stirred for twenty-five minutes after slaking was complete yielded viscosities of 200 centipoises and 288 centipoises respectively. The suspensions produced with slaking water at 60°C and stirred for twenty-five minutes after slaking was complete had viscosities of 3875 centipoises and 390 centipoises respectively.

Far too little study has been made on the viscosity of calcium hydroxide suspensions from various types of calcium oxide to understand the mechanics of viscosity control. The viscosity of suspensions produced for this report was determined for various concentrations. The determinations were made with a standard Brookfield viscometer.

VI RESULTS

A Slaking Temperatures and Slaking Time

The slaking temperatures of samples for all concentrations and initial water temperatures are shown in Table VII.

TABLE VII

Maximum Slaking Temperatures of CaO with Various Amounts of Water at Various Temperatures

R	<u>Initial Water Temperature</u>											
	4		10		20		40		60		90	
	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$
	85	185	90	194	100	212	100	212	100	212	100	212
2.5	85	185	90	194	100	212	100	212	100	212	100	212
7.5	32.2	90	36.5	98.7	43.6	110.5	63	145.4	82	179.6	100	212
10.5	24.6	76.3	29	84.2	38	100.4	58	136.4	77	170.6	100	212
13.5	21.2	70.2	25.5	77.9	34.8	94.7	54	129.2	69	156.2	100	212
18.0	16.0	60.8	21.6	70.9	30.6	87.1	50	122.0	69	156.2	100	212
25.0	12.2	52	19.0	66.2	27.8	82.0	48	118.4	65	149.0	100	212

These values are also shown graphically in Figure 2.

Temperatures less than 100°C (212°F) are shown to the left and below a dotted line.

A comparison of these actual slaking temperatures with the theoretical expected temperatures indicated quite a variation. The percentage differences between these two values, based upon the theoretical, are shown in Table VII-A. No values are shown for tests with R at 2.5 or a temperature of 194°F.

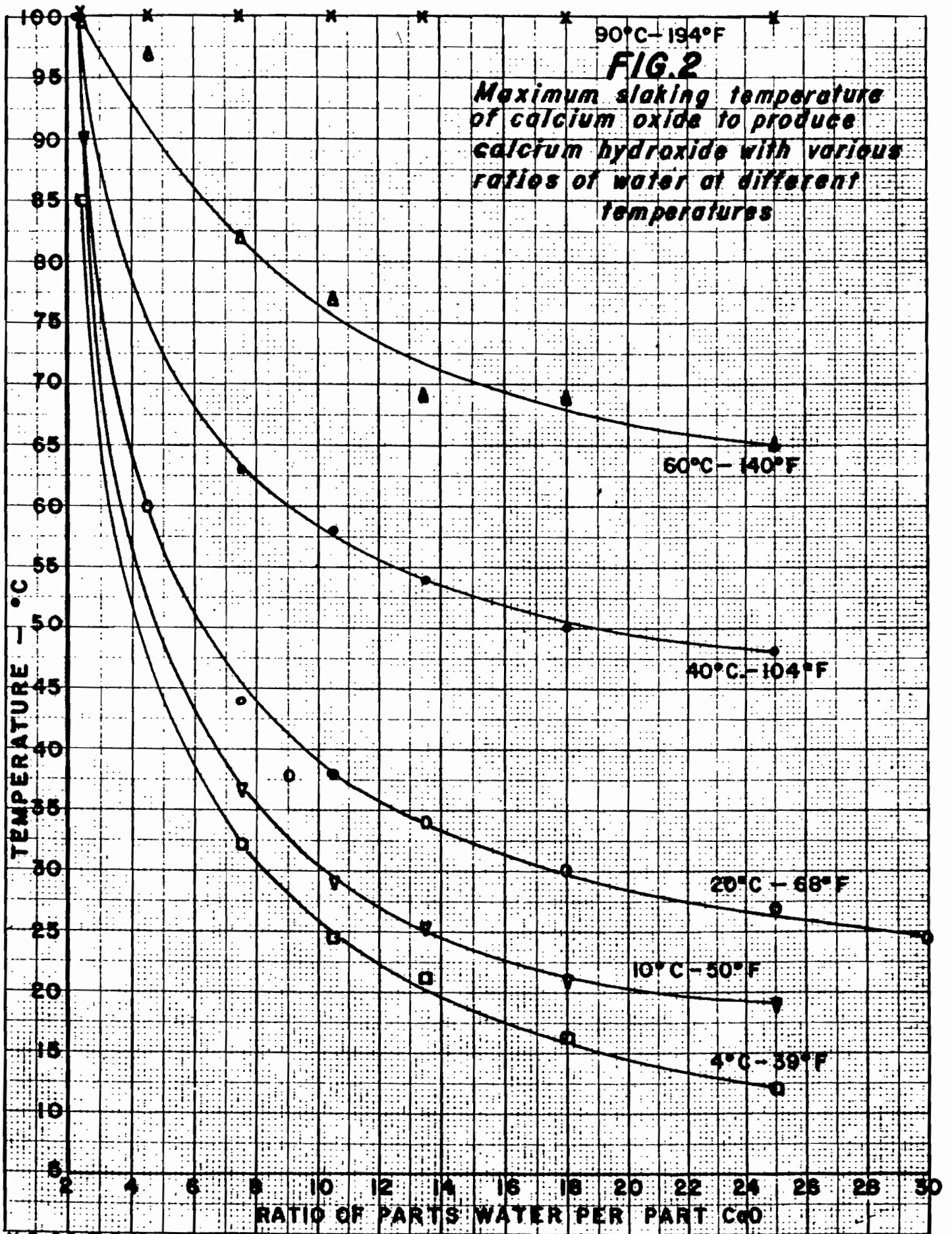


TABLE VII-A

Percentage Difference between Theoretical and Actual Slaking
Temperature

<u>R</u>	<u>Initial Water Temperature °F</u>				
	<u>39</u>	<u>50</u>	<u>68</u>	<u>104</u>	<u>140</u>
7.5	10.6	11.7	14.8	12.3	11.0
10.5	8.3	10.6	10.5	7.97	7.4
13.5	5.5	7.7	7.5	6.6	4.7
18.0	6.2	6.6	7.2	6.0	5.7
25.0	9.7	3.5	5.3	3.4	6.0

No correction was made in the theoretical calculations for heat loss in the steel container or for the radiation loss. A correction for heat loss in the steel slaking vessel would have been constant to give a uniform lower percentage difference between the theoretical and actual results. Radiation losses would be expected to be greatest at the higher temperatures which would result in a greater temperature difference. This, however, is not exactly true. Greatest losses were found to be at the lower values of R. The initial temperature of the slaking water appears to have little influence in increasing these losses. For example, at initial temperature of 60°C (140°F) the final slaking temperature was approximately 150°F or greater with percentage difference between theoretical and actual less than many other tests at lower initial water temperature. There is a general trend for lower percentage differences between theoretical and actual slaking temperatures with an increase in the value of R.

All rotary kiln calcium oxides will not produce slaking temperatures corresponding exactly to these values. The activity or slaking rate of the calcium oxide (V-1, p. 19) and the viscosity of the calcium hydroxide suspension will affect the final slaking temperature. Regardless of the activity of the calcium oxide the slaking temperature will be proportionate to the values shown as changes in R and water temperature are made. These data indicate anticipated temperatures to be expected for changes in R and T₁.

The time for the reaction between calcium oxide and water to be completed is dependent upon both the solids concentration and the initial temperature of the water. An increase in the ratio of water at a given temperature increases the slaking time, but an increase in the initial water temperature at a given concentration decreases the slaking time.

The approximate slaking time for each sample prepared is shown in Table VIII. The values give the slaking time to the nearest minute for the temperature to reach a maximum.

TABLE VIII

Slaking Time (Minutes) of CaO with Various Amounts of Water at Various Temperatures

		<u>Initial Water Temperature</u>					
		10	20	40	60	90	
<u>°C</u>	<u>°F</u>	<u>50</u>	<u>68</u>	<u>104</u>	<u>140</u>	<u>194</u>	
2.5	4	3	6	1	2	1	
7.5	8	16	7	3	2	1	
10.5	18	20	7	4	2	1	
13.5	13	23	8	4	2	1	
18.0	14	20	7	4	2	1	
25.0	18	12	8	4	2	1	

These values are shown graphically in Figure 3.

B Settling Time

The settling rate of each suspension, adjusted to 100 gpl Ca(OH)_2 , prepared at all concentrations and at temperatures of 4°, 10°, 20°, 40°, 60° and 90°C are shown in Tables IX, X, XI, XII, XIII and XIV respectively. The data is also shown graphically in Figures 4, 5, 6, 7, 8 and 9. A summary of the settling time to one-half volume (50 ml) for each sample is shown in Table XV and graphically in Figure 10. The volume occupied by the settled calcium hydroxide after 24 hours for each suspension is shown in Table XVI and shown graphically in Figure 11.

The settling time of a series of calcium hydroxide suspensions prepared with water of the same initial starting temperature increases as the ratio of water decreases for final temperatures less than 212°F. For example, using water at 4°C (39°F), the settling time is 80 minutes when the ratio is 25 pounds of water per pound of CaO and 480 minutes when the ratio of water has been decreased to 7.5 pounds water per pound CaO. Also, using water with an initial temperature of 60°C (140°F) the settling time is 835 minutes when the ratio is 25 pounds water per pound calcium oxide and 1800 minutes when the ratio is decreased to 7.5 pounds water per pound calcium oxide.

FIG. 3

Approximate Slaking Time (in minutes),
required to produce Calcium Hydroxide
from Calcium Oxide and various ratios
of water at 4°C, 10°C, 20°C, 40°C,
60°C & 90°C.

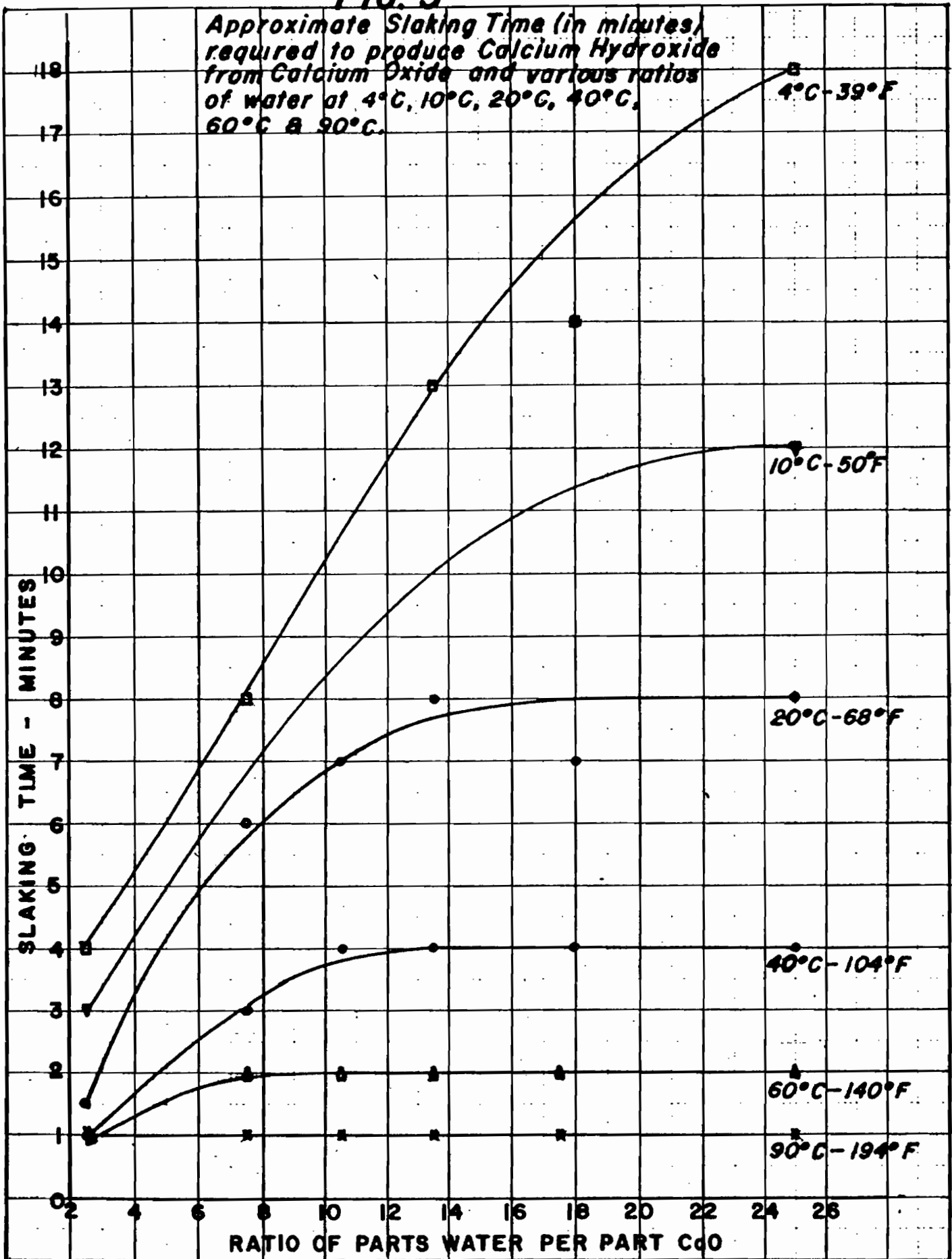


TABLE IX

SETTLING RATES OF HYDRATES

Temp. ° C	4	4	4	4	4	4
° F	39	39	39	39	39	39
R	2.5	7.5	10.5	13.5	18	25
Min. (hr.)						
0	0	0	0	0	0	0
5	1	1.5	1.5	1.5	3	1.5
10	2	2.5	4.0	5	5.5	7.5
15	2.5	4.5	7.0	9	8.5	14.5
20	3	6.5	10.5	13.0	11	22.5
25	3.5	9.5	15.0	18.5	14	32.0
30	4	11.5	18.0	22.5	16	37.0
35	5	13.5	21.5	26.5	18.5	40.0
40	6	16.5	25.5	32.5	21	42.0
45	7	18.5	30.5	37.0	23.5	43.0
50	9	21.0	34.0	39.0	26	44.5
55	11	24.5	36.0	41.0	28.5	45.5
60 (1)	13	28.5	37.0	42.0	31	46.5
70	15	31.5	39.0	44.0	37.5	48.5
80	-	33.5	40.5	45.0	-	50.0
90	18	35.0	42.0	46.5	46.5	51.0
100	-	36	43.0	47.5	-	52.0
110	20.0	37	43.5	48.5	49.0	53
120 (2)	20.5	38	44.5	49.0	50.0	54
135	21.5	39	45.5	50.0	51	55
150	22.5	40	46.5	51.0	52	56
165	23.5	41	47.5	52	53	57
180 (3)	24.0	41.75	48.25	52.75	54	58
195	25.0	42.5	49.0	53.5	55	58.5
210	-	43.25	49.75	54.0	-	59 7
225	27.0	43.75	50.00	54.75	57	59.75
240 (4)	-	44.25	50.5	55 7	-	60 7
270	28.0	45.5	52	56.5	57.5	61.5
300 (5)	29.0	46 7	52.75	57	58.5	62
330	30	47.0	53.5	58	59	62.5
360 (6)	31	48.0	54.25	58.75	59.5	63
390	31.5	48.5	55.0	59.25	59.75	63.5
420 (7)	32.25	49.25	55.5	59.75	60	64.0
480 (8)	33.5	50.0	56.0	60 7	60	64.0
540	-	50.5	56.5	60.5	-	64.5
1440 (24)	44	57	61	63.4	61	66

TABLE X
SETTLING RATES OF HYDRATES

Temp. °C	10	10	10	10	10	10
° F	50	50	50	50	50	50
R	2.5	7.5	10.5	13.5	18	25
Min. (hr)						
0	0	0	0	0	0	0
5	0.5	1	1	0.5	1	1.5
10	1.5	3	3.5	2.5	3	8.5
15	2.5	4.5	5.5	5.0	6	15.0
20	4	7.0	8.5	8.0	10.5	21.5
25	6	10.0	12.0	12.0	15.5	30.0
30	8	12.0	14.0	14.5	20	37.0
35	9	14.0	17.0	17.5	25.5	41.5
40	10	16.0	19.5	20.5	32	43.5
45	11	19.0	23.0	24.0	37	45.0
50	12.5	22.0	26.0	27.0	39	46.0
55	13.5	25.0	30.0	32.0	40.5	47.5
60	(1) 14.25	29.5	34.5	36.5	41.5	48.5
70	15.5	33.0	38.0	40.0	43.75	50.0
80	16.5	35.0	40.0	42.0	45	51.0
90	17.5	36.5	41.5	44.0	46.5	52.5
100	-	37.5	43.0	45.0	-	53.0
110	19.5	38.5	43.5	46.0	48.5	54.0
120	(2) 20	39.5	44.5	47.0	49.5	55.0
135	21	40.5	45.5	48.0	50.75	56.0
150	22	41.5	46.5	49.0	51.75	56.75
165	23	42.5	47.5	50.0	52.75	57.5
180	(3) 23.75	43.25	48.5	51.0	53.5	58.25
195	24.5	44.0	49.0	51.75	54.25	59
210	25.7	45.0	50.0	52.50	55	59.5
225	-	45.25	50.5	53.0	-	60.0
240	(4) 26.5	46.0	51.0	53.75	56	60.5
270	-	47.25	52.5	55	-	61.5
300	(5) 28.5	48.0	53.25	56	-	62
330	-	49.0	54.25	57	-	62.75
360	(6) -	49.75	55.0	57.5	-	63.25
390	-	50.5	56.0	58.5	-	63.75
420	(7) -	51.7	56.5	59.0	-	64.0
480	(8) -	51.75	57.0	59.5	-	64.25
540	-	52.5	57.75	60.0	-	64.5
1440	(24) 43	58	61.5	63	60	66

TABLE XI
SETTLING RATES OF HYDRATES

Temp. ° C	20	20	20	20	20	20
° F	68	68	68	68	68	68
R	2.5	7.5	10.5	13.5	18	25
Min. (hr)						
0	0	0	0	0	0	0
5	0.5	1.0	1.0	2.0	2.0	2.0
10	1.0	2.5	2.5	4.5	4.5	6.0
15	1.5	4.5	4.0	7.0	8.0	10.5
20	2.0	7.0	6.0	10.0	12.0	15.0
25	2.75	9.0	8.0	13.0	15.5	19.5
30	3.25	11.0	10.0	15.5	19.0	24.0
35	3.75	13.5	12.25	18.75	23.0	28.5
40	4.25	15.5	14.5	21.75	26.75	34.0
45	4.75	17.5	16.0	24.0	30.0	39
50	5.0	20.0	18.5	27.5	34.5	42.5
55	5.5	23.0	21.25	31.0	39.5	44.5
60 (1)	6.0	25.75	24.5	35.0	42.5	45.75
70	6.75	31.5	31.0	42.0	44.75	47.5
80	7.5	37.5	34.5	43.0	46.5	49.0
90	8.0	39.5	36.5	45.5	47.75	50.0
100	8.75	41.0	38.0	46.75	49.0	51.5
110	9.0	42.0	39.0	47.5	50.0	52
120 (2)	10.0	43.0	40.0	48.5	50.5	53.0
135	10.5	44.5	41.0	49.75	51.75	54.0
150	11.25	45.5	42.0	50.75	52.5	55.0
165	12.00	46.5	43.0	51.75	53.25	56.0
180 (3)	12.75	47.5	44.0	52.5	54.0	57.0
195	13.5	48.0	45.0	53.5	55.0	57.5
210	13.75	48.5	45.0	54.0	55.5	58.0
225	14.5	49.5	46.0	54.5	56.0	58.5
240 (4)	15.0	49.75	46.5	55.0	56.5	59.0
270	16.0	51.0	47.5	56.0	57.75	60.0
300 (5)	17.0	52.0	48.75	57.0	58.75	61.0
330	18.0	53.0	49.75	58.5	59.75	62.0
360 (6)	18.75	54.0	50.5	59.0	60.0	62.5
390	19.5	54.75	51.0	59.5	61.0	63.0
420 (7)	20.5	55.5	52.0	60.25	61.5	63.25
480 (8)	22.0	56.5	53.0	61.0	62.50	64.0
540	23.0	57.5	54.0	62.0	63.0	64.5
600 (10)	24.5	58.5	55.0	62.5	63.5	65.0
660	26.0	59.0	55.75	63.0	64.0	65.0
960 (16)	31.75	60.75	58.5	64.0	65.0	65.75
1200 (20)	34.25	61.25	59.0	64.25	65.0	65.75
1440 (24)	37	61.5	59.0	64.25	65.0	66.0

TABLE XII

SETTLING RATES OF HYDRATES

Temp. °C	40	40	40	40	40	40
	°F	104	104	104	104	104
	R	2.5	7.5	10.5	13.5	18
Min. (hr)						
0	0	0	0	0	0	0
5	5	1.0	1.0	1.0	2.0	2.0
10	1.0	2.5	1.5	1.5	2.0	3.0
15	2.0	2.5	3.0	3.0	4.0	5.5
20	2.5	4.0	4.0	5.0	6.0	7.75
25	3.0	4.75	5.25	6.5	7.75	10.0
30	4.0	6.0	7.0	8.25	9.75	12.0
35	4.75	7.0	8.0	10.0	11.5	14.5
40	6.0	8.5	9.75	12.0	13.5	17.0
45	7.0	10.0	11.0	13.5	15.5	19.0
50	8.5	11.0	12.25	15.5	17.5	21.25
55	10.0	12.5	14.0	17.5	20.0	23.0
60 (1)	12.0	14.0	15.5	20.0	22.0	27.0
70	15.0	17.0	18.5	24.0	27.0	33.0
80	16.0	20.0	22.0	28.5	32.0	39.5
90	17.25	23.5	26.0	34.0	38.0	42.0
100	18.5	28.0	30.5	37.75	40.25	43.50
110	19.0	31.5	34.5	39.0	41.5	44.5
120 (2)	20.0	33.0	36.5	40.0	42.5	45.5
135	21.0	35.0	38.0	41.75	44.0	47.0
150	21.75	36.0	39.75	43.0	45.0	48.0
165	22.75	37.0	41.0	44.0	46.0	49.0
180 (3)	23.5	38.0	42.0	45.0	47.0	50.0
195	24.0	39.0	42.5	45.5	47.75	50.5
210	24.5	39.5	43.0	46.0	48.0	51.0
225	25.0	40.0	44.0	47.0	49.0	51.5
240 (4)	25.75	40.75	44.5	47.5	49.5	52.5
270	27.0	42.0	45.5	48.5	50.5	53.5
300 (5)	28.0	43.0	46.75	49.75	52.0	54.5
330	29.0	44.0	48.0	50.5	53.0	55.5
360 (6)	29.5	44.5	48.5	51.5	53.75	56.25
390	30.0	45.5	49.5	52.0	54.5	57.0
420 (7)	31.0	46.0	50.0	53.0	55.0	57.5
480 (8)	32.25	47.25	51.5	54.25	56.5	58.75
540	33.5	48.5	52.5	55.25	57.5	59.5
600 (10)	34.5	49.5	53.5	56.0	58.5	60.5
660	35.5	50.5	55.0	57.0	59.0	60.75
960 (16)	40.0	54.0	58.0	59.5	61.0	62.25
1200 (20)	41.0	54.5	58.25	60.0	61.0	62.5
1320 (22)	42.0	54.75	58.5	60.0	61.0	62.5
1440 (24)	43.0	55.0	58.75	60.0	61.0	62.5

TABLE XIII

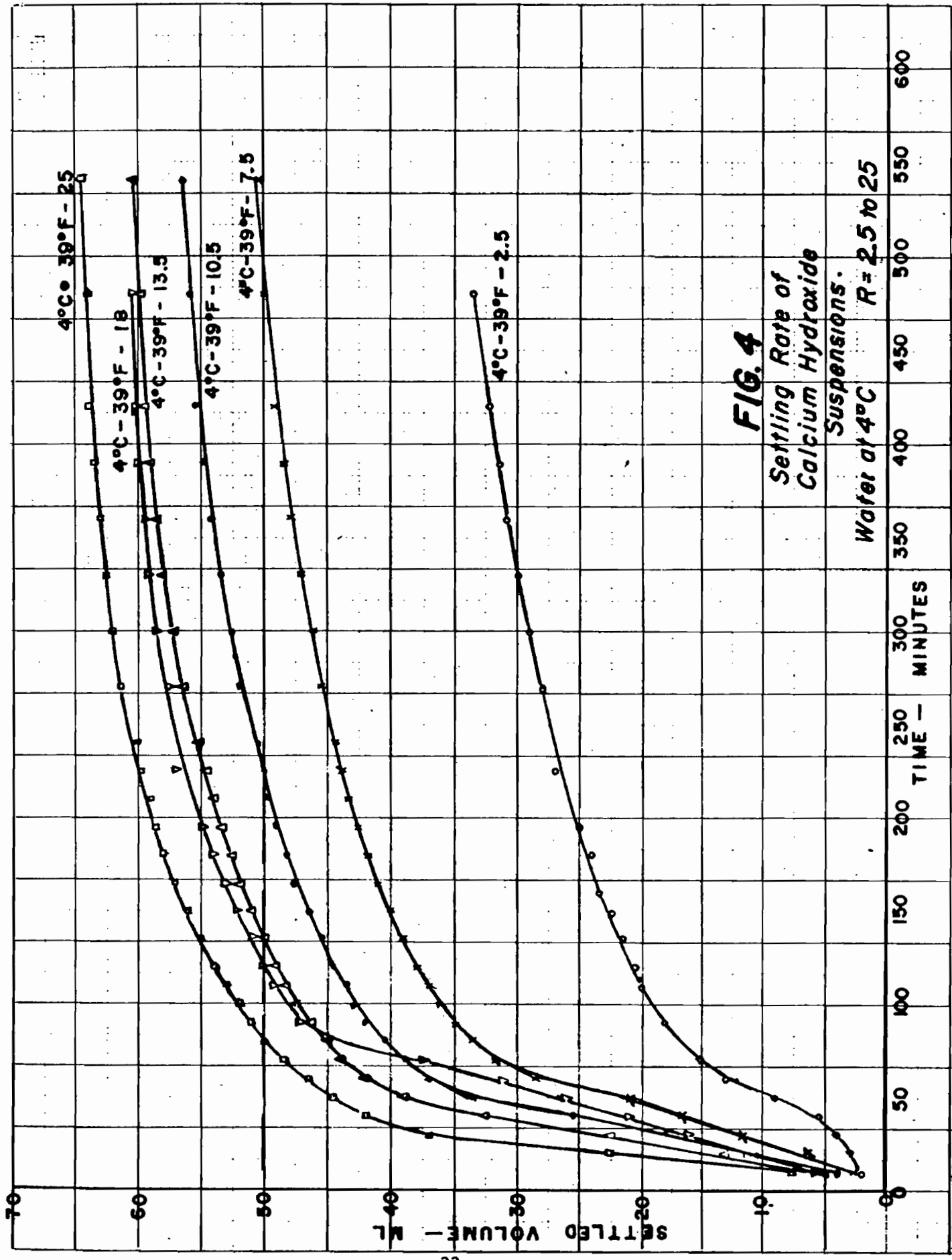
SETTLING RATES OF HYDRATES

Temp. °C	60	60	60	60	60	60
°F	140	140	140	140	140	140
R	2.5	7.5	10.5	13.5	18	25
Min. (hr)						
0	0	0	0	0	0	0
5	1	1	1	1	1	2
10	2	2	2	2	2	2.5
15	2.5	2.5	2.1	2.1	2.5	4.0
20	3.0	3.2	3.2	3.2	3.5	5.0
25	4.0	4.0	4.0	4.3	4.5	6.0
30	5.0	5.1	5.0	5.5	5.5	7.5
-	-	-	-	-	-	-
60 (1)	10.1	10.5	10.0	12.0	12.0	16.0
90	14	18.0	18.0	21.0	21.0	27.1
105	15	22.8	20.8	26.0	27.0	29.0
120 (2)	16	26.0	26.0	30	29.2	31
135	17	27.8	27.0	32	31.0	32.5
150	17.5	29.0	29.8	33	32.0	33.5
240 (4)	21	34	34.8	38	38	38.5
300 (5)	22.8	36	36.9	40	39.0	40.5
330	23.5	37	37.8	41	40.0	41.7
360 (6)	24.0	37.9	38.8	41.9	40.9	42.5
370	25.0	38.5	39.1	42.5	41.4	43.2
420 (7)	25.6	39.0	40.0	43.0	42.0	44.0
480 (8)	26.9	40.2	41.0	44.1	43.1	45.1
600 (10)	29.0	42.3	43.1	46.4	45.2	47.2
660 (11)	29.9	43.1	44.0	47.3	46.1	48.1
720 (12)	30.6	44.0	45.0	48.0	47.0	49.0
780 (13)	31.6	44.9	45.9	48.9	48.0	49.8
840 (14)	32.1	45.3	46.3	49.6	48.4	50.1
900 (15)	33.0	46.0	47.0	50.0	49.0	50.9
960 (16)	33.8	46.6	47.7	50.7	49.6	51.2
1230	36.3	48.3	49.2	51.9	51.1	52.9
1380 (23)	37.6	49.0	50.0	52.5	51.5	53.2
1440 (24)	38.0	49.2	50.0	52.5	51.7	53.5

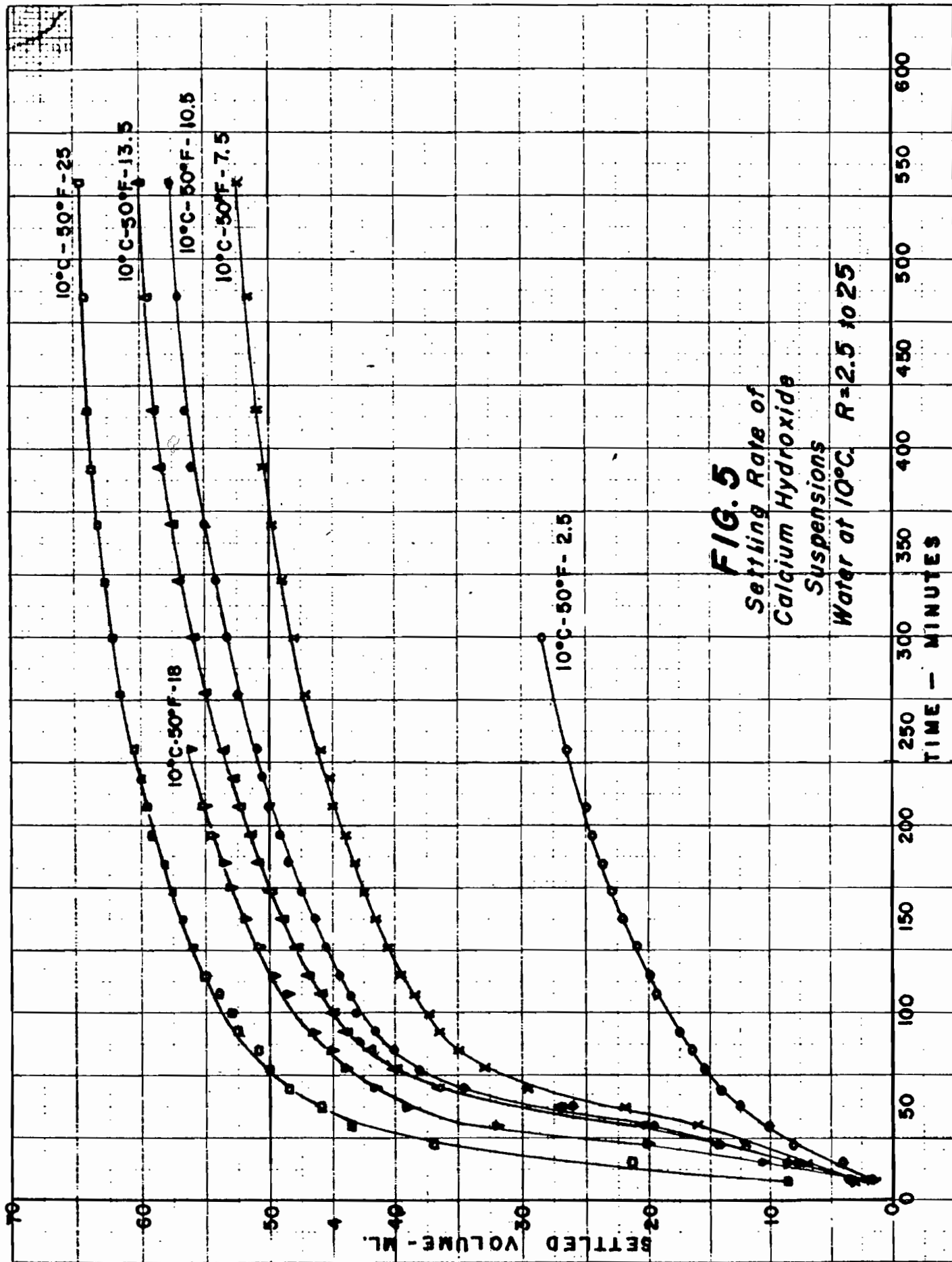
TABLE XIV

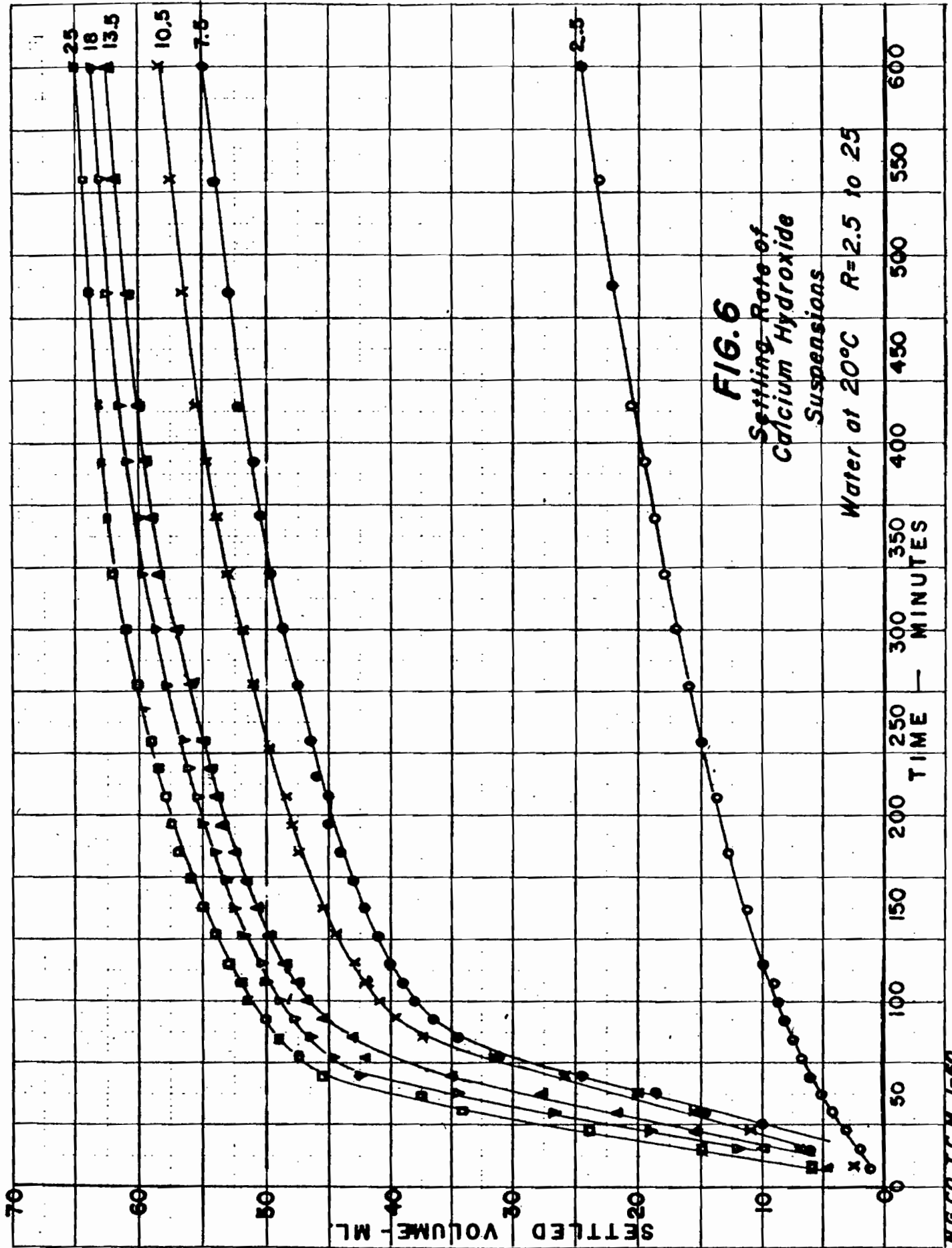
SETTLING RATES OF HYDRATES

Temp. ^o C	90	90	90	90	90
^o F	194	194	194	194	194
R	4.5	7.5	10.5	13.5	18.0
Min (hr)					
0	0	0	0	0	0
5	1.0	1.0	1.0	0.5	0.5
10	1.0	1.0	1.0	0.5	1.0
15	1.8	2.0	2.0	1.0	1.4
20	2.6	2.6	3.0	2.0	2.1
25	3.4	4.0	3.8	2.4	3.1
30	4.5	5.0	4.9	3.5	4.0
35	5.0	5.8	5.6	4.2	4.8
40	6.0	7.0	6.8	5.0	5.2
45	7.1	8.0	7.5	6.0	6.0
50	8.0	9.0	8.0	6.6	7.2
55	9.0	10.0	9.0	7.2	7.9
60	(1) 10.0	10.9	10.0	8.2	9.2
70	11.1	12.8	12.8	10.0	11.8
80	13.0	15.1	13.8	11.9	14.9
100	17.5	20.8	17.8	15.8	22.0
110	20	24.1	20.0	18.1	24.0
120	(2) 23	27.2	22.9	21.1	25.1
150	29.6	30.4	31.0	29.9	28.1
165	31	31.6	32.1	31.2	29.1
180	(3) 32	32.8	33.8	32.8	30.0
210	33.8	34.1	35.0	34.3	32.0
240	(4) 34.1	35.8	36.8	36.0	33.2
300	(5) 37.4	37.7	38.8	38.1	35.3
330	38.1	38.5	39.8	39.1	36.6
360	(6) 39.1	39.1	40.5	40.0	37.1
390	40.0	40.0	41.1	40.9	38.0
420	(7) 40.6	40.6	41.9	41.7	38.9
480	(8) 42.0	41.9	43.1	43.0	39.9
540	(9) 43.0	43.0	44.2	44.0	41.1
660	(11) 44.8	44.8	46.2	46.0	43.0
780	(13) 46.2	46.1	48.0	47.8	44.5
900	(15) 47.8	47.4	49.4	49.0	45.9
1020	(17) 48.9	48.7	50.3	49.8	46.9
1080	(18) 49.2	49.0	50.9	50.0	47.1
1200	(20) 50.1	50.0	51.6	50.1	48.0
1260	(21) 50.6	50.1	51.9	50.4	48.2
1320	(22) 51.0	50.8	52.0	50.5	48.7
1380	(23) 51.2	51.0	52.1	50.8	48.9
1440	(24) 51.9	51.1	52.2	50.8	49.0

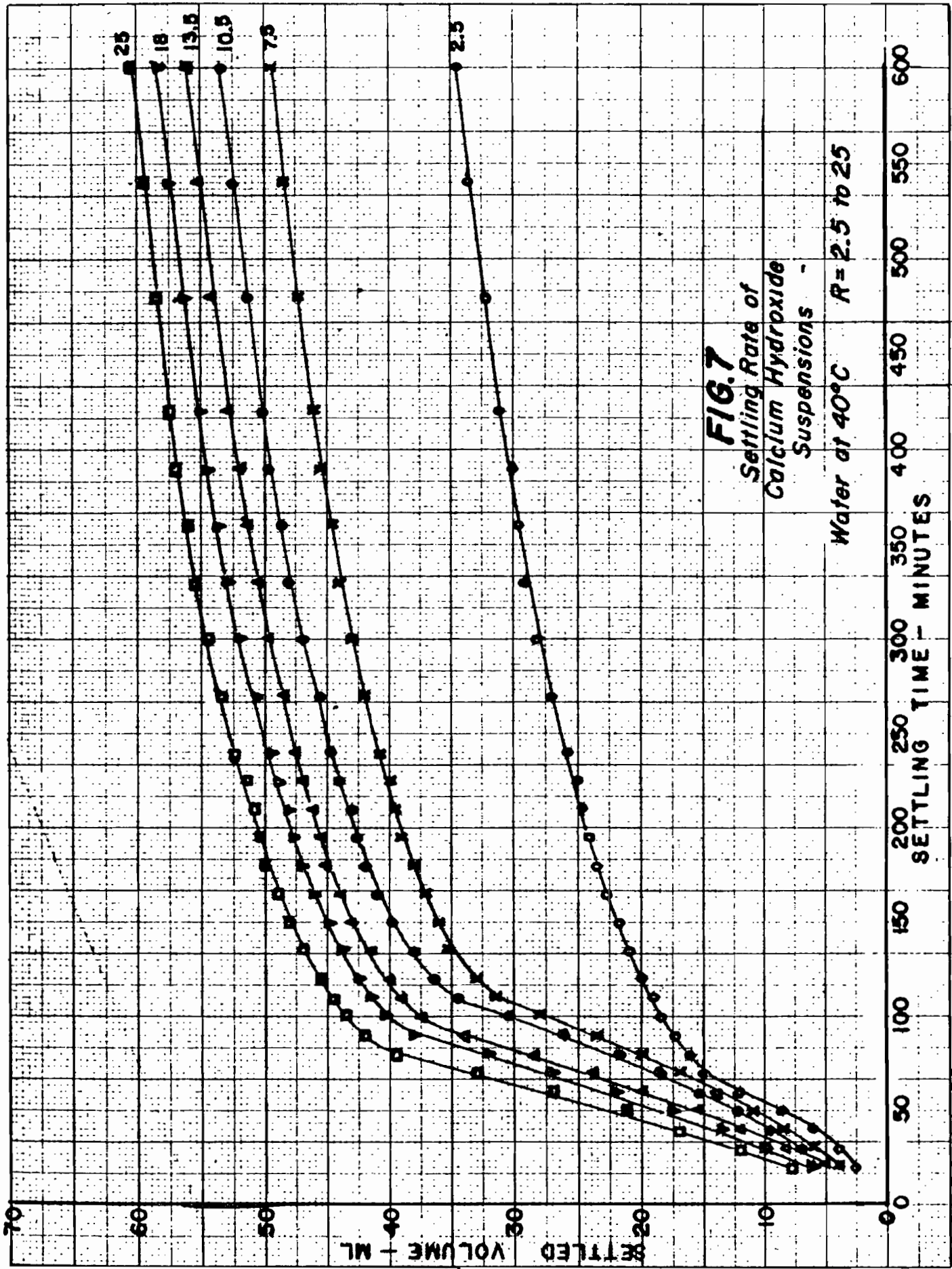


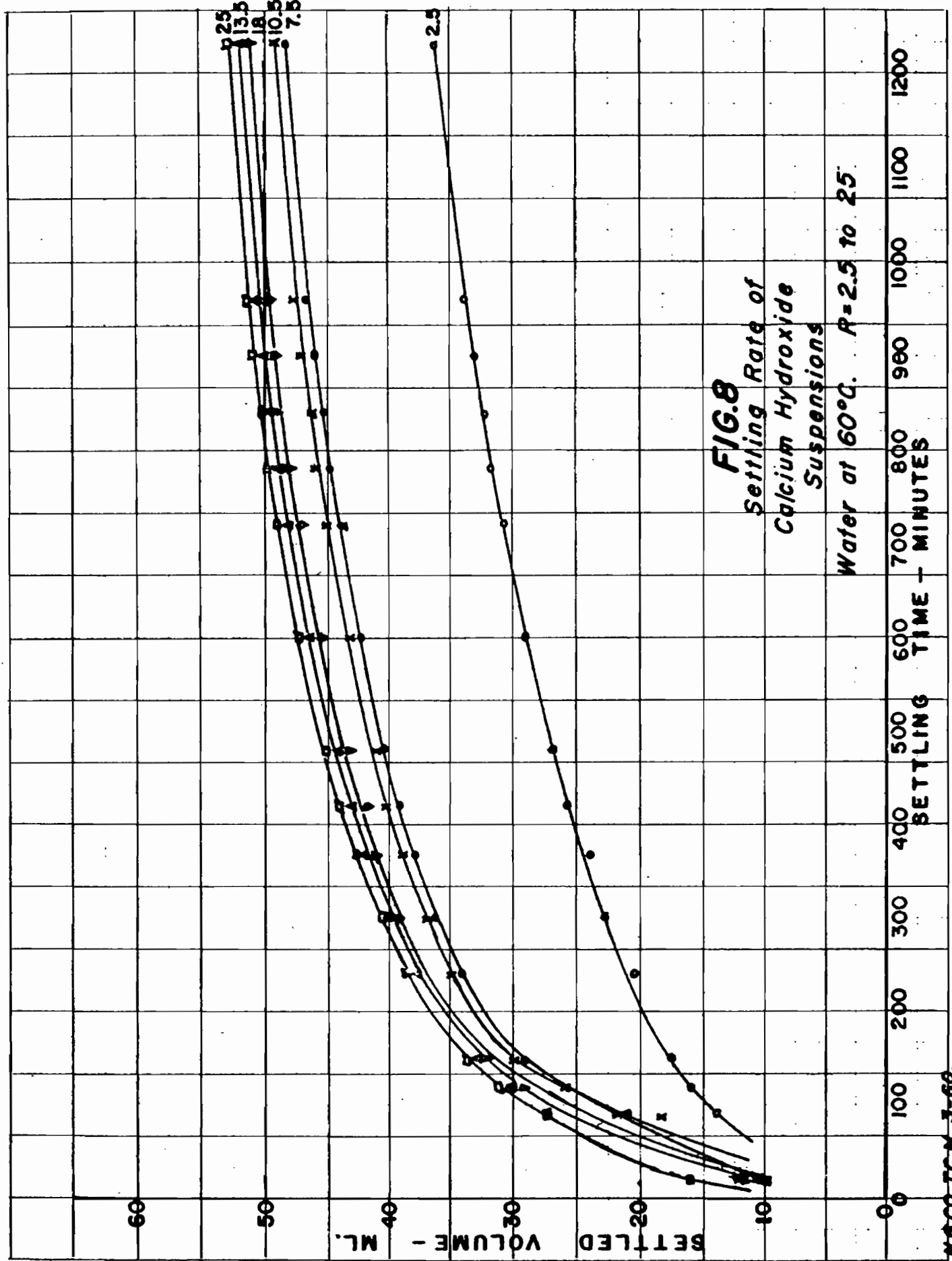
N.G.CO., T.C.M., 12-59.





N.G.CO., T.C.M., 7-60





M.C.O., I.C.N., 3-60.

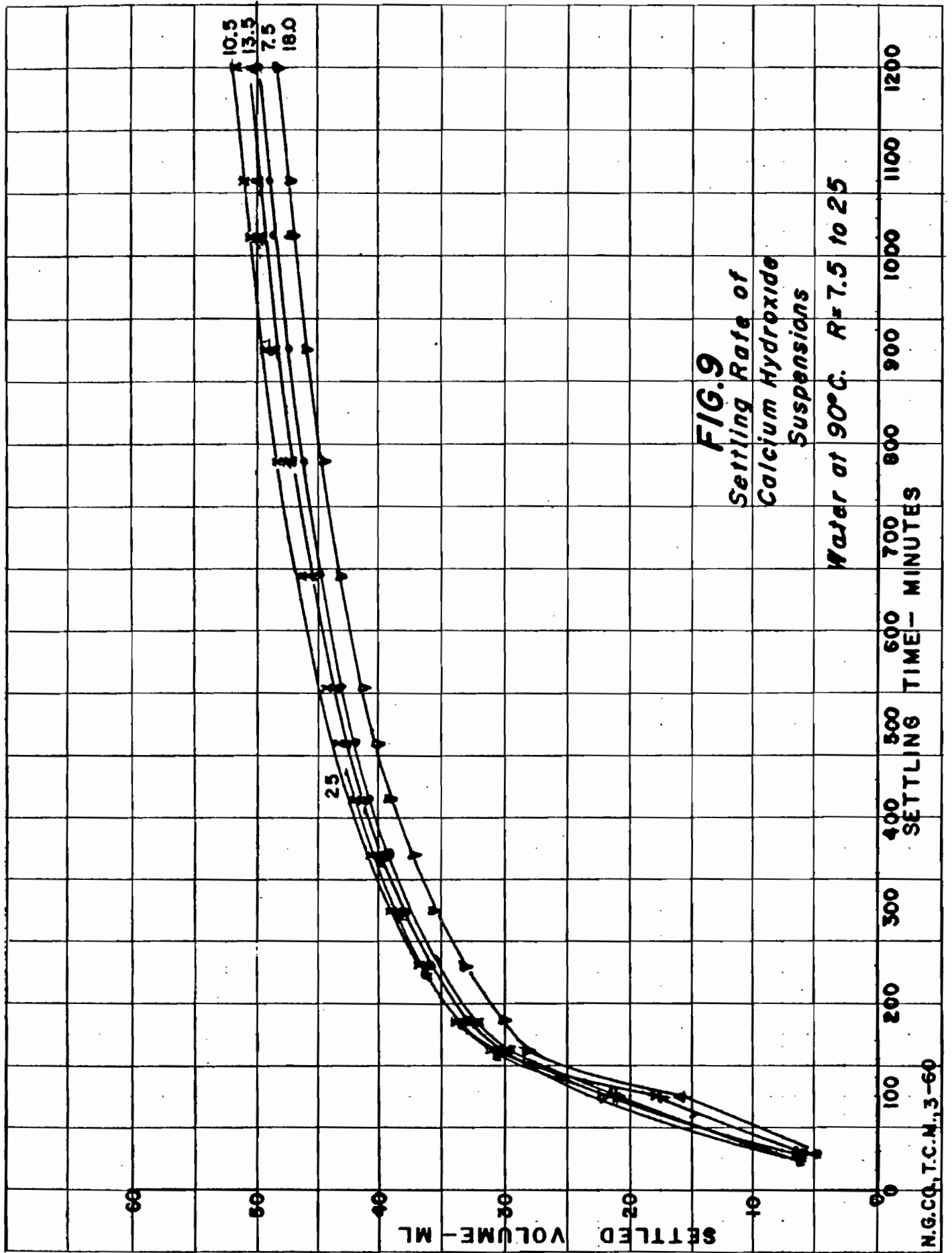


TABLE XV

SETTLING TIME OF CALCIUM HYDROXIDE

PRODUCED WITH VARIOUS RATIOS OF WATER OF DIFFERENT TEMPERATURE

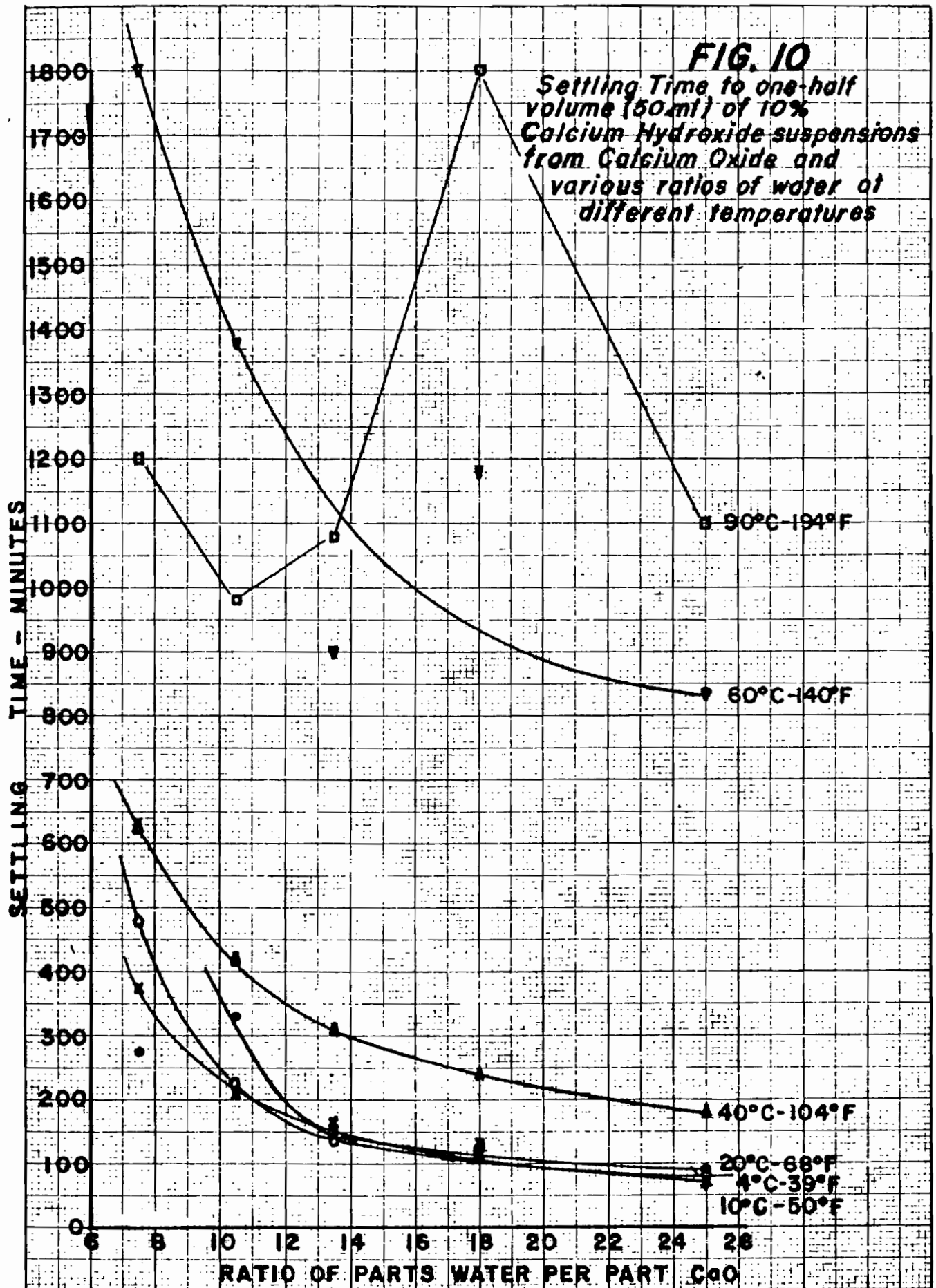
Temp. °C	4	10	20	40	60	90
°F	39	50	68	104	140	194
R(H ₂ O/CaO)	—	—	—	—	—	—
2.5						
7.5	480	375	275	630	1800	1200
10.5	225	210	330	420	1380	980
13.5	135	165	140	310	900	1080
18.0	120	126	110	240	1180	1800
25.0	80	70	90	180	835	1100

TABLE XVI

VOLUME OCCUPIED BY CALCIUM HYDROXIDE

AFTER SETTLING 10% SUSPENSION FOR 24 HOURS

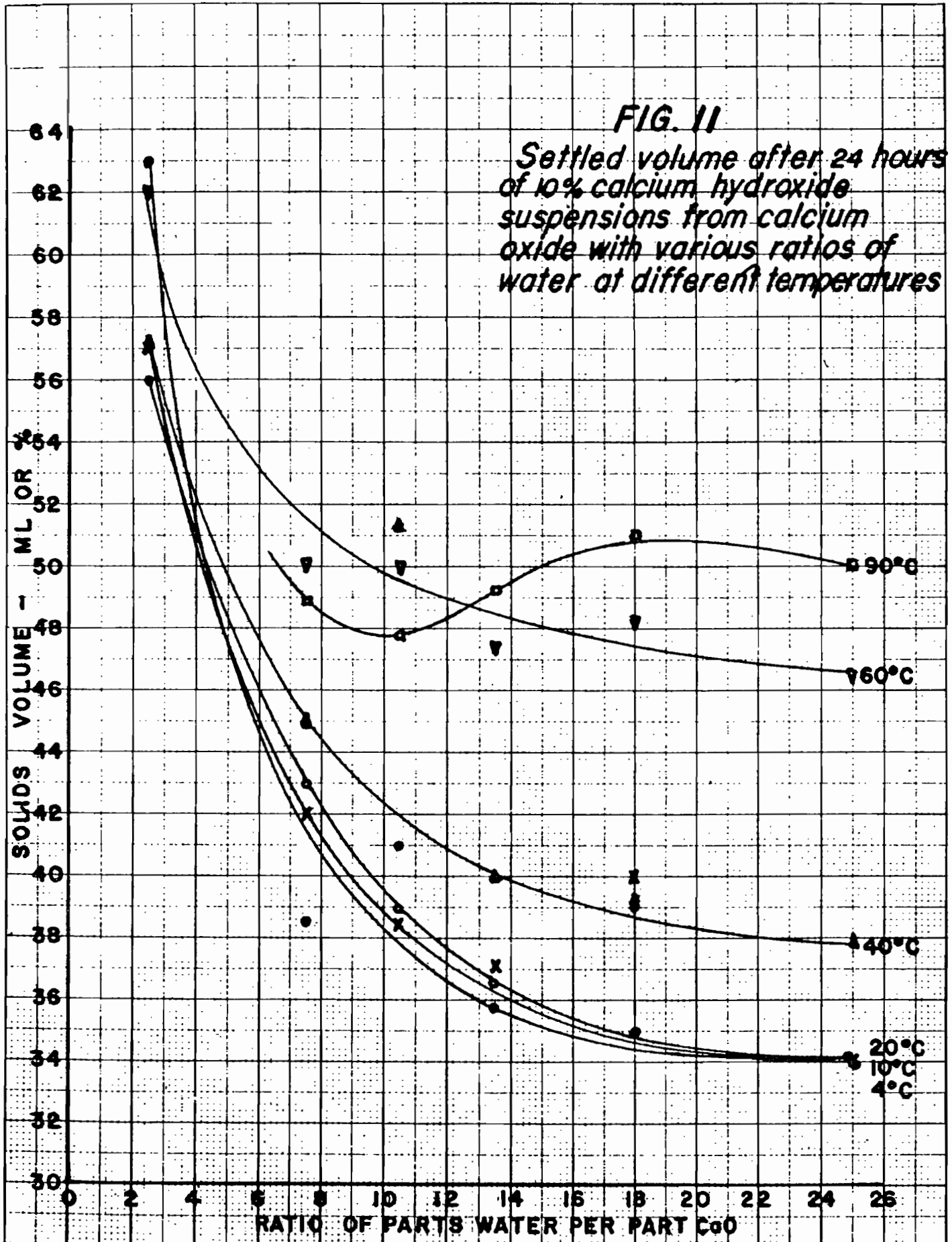
Temp. °C	4	10	20	40	60	90
°F	39	50	68	104	140	194
R(H ₂ O/CaO)	—	—	—	—	—	—
2.5	56	57	63	57	62	--
4.5	--	--	--	--	--	--
7.5	43	42	38.5	45	50.8	48.9
10.5	39	38.5	41	51.25	50	47.8
13.5	36.6	37	35.75	40	47.5	49.2
18.0	39	40	35	39	48.3	51
25.0	34	34	34	37.5	46.5	50



NG.CO.,T.C.M.3-60

FIG. II

*Settled volume after 24 hours
of 10% calcium hydroxide
suspensions from calcium
oxide with various ratios of
water at different temperatures*



None of the calcium hydroxides prepared with a ratio of 2.5 pounds water per pound calcium oxide settled to one-half volume even after one week (10,000 minutes). The settling time values for suspensions prepared with water between 4°C and 60°C fall between those values shown for 4°C and 60°C and are of the same increasing values with decrease in R.

The settling times for suspensions prepared with water at 90°C (194°F) are more constant for all values R than any of the suspensions prepared with water at lower temperatures. Some irregularity exists with changes in R, but this difference has not been fully explained. A decrease in settling time with an increase in the value of R does not occur at this temperature. The slaking temperatures for all values of R at this temperature theoretically exceeds 212°F (Table IV) and actually evaporated some of the slaking water during the reaction. This boiling temperature undoubtedly produced crystal growth of calcium hydroxide to increase both the settling time and the viscosity.

These data indicate that the settling time of calcium hydroxide can be controlled by choosing a combination of initial water temperature between 4°C and a temperature producing a final temperature less than 212°F, and ratio of water to calcium oxide to give the desired characteristic.

C Specific Surface

The time required to adjust the suspensions to the required 100 gpl calcium hydroxide and to determine the settling time was enormous, and would be unjustified as a control test in an industrial plant requiring several periodic checks per day. A shorter and more convenient method of testing involves the determination of specific surface. The specific surface of each sample is tabulated in Table XVII and shown graphically in Figure 12. The specific surface values range from a low of 15,314 cm²/g produced with hydrating water at 4°C at R = 25 to a high of 58,300 cm²/g produced with water at 90°C at R = 2.5. These specific surface values represent a mean particle diameter range from 1.74 microns (u) to 0.46 u respectively. The calculated mean particle diameters for the calcium hydroxide produced in all samples are shown in Table XVIII.

TABLE XVII

SPECIFIC SURFACE OF CALCIUM HYDROXIDE

PRODUCED WITH VARIOUS RATIOS OF WATER OF DIFFERENT TEMPERATURES

Temp. °C	4	10	20	40	60	90
°F	39	50	68	104	140	194
<u>R(H₂O/CaO)</u>	—	—	—	—	—	—
2.5	50,736	54,293	52,790	56,606	57,355	58,300
4.5	--	--	48,307	--	52,260	55,255
7.5	35,246	34,534	--	47,035	49,183	53,070
10.5	29,133	29,840	--	45,203	48,920	51,126
13.5	23,166	24,419	36,520	41,080	45,967	52,658
18.0	17,833	18,968	31,556	37,620	48,307	53,925
25.0	15,314	18,597	29,405	40,910	48,244	53,295

TABLE XVIII

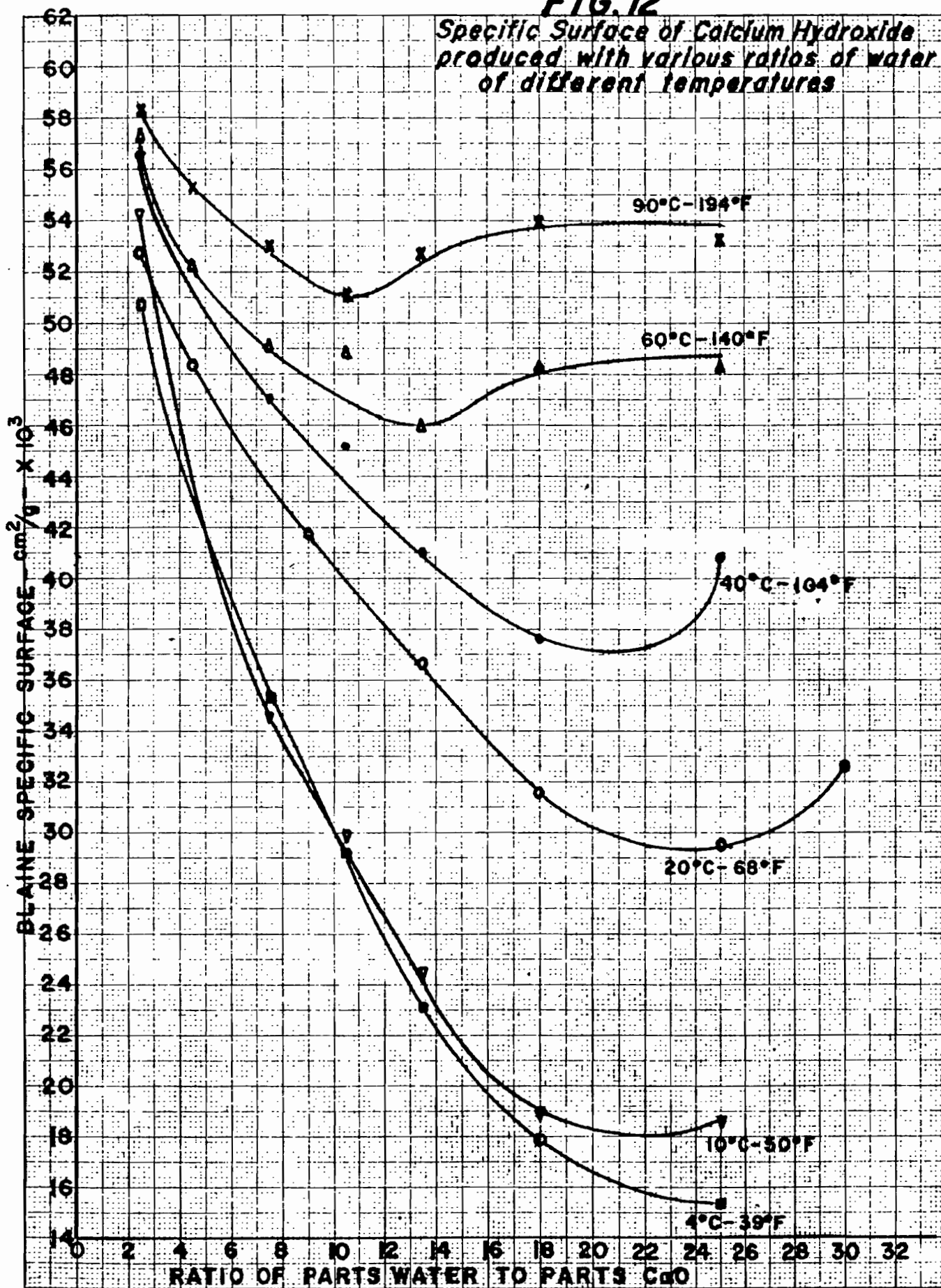
CALCULATED PARTICLE DIAMETER (MICRONS) OF CALCIUM HYDROXIDE

PRODUCED WITH VARIOUS RATIOS OF WATER OF DIFFERENT TEMPERATURES

Temp. °C	4	10	20	40	60	90
°F	39	50	68	104	140	194
<u>R(H₂O/CaO)</u>	—	—	—	—	—	—
2.5	0.53	0.49	0.50	0.47	0.46	0.46
4.5	--	--	0.55	--	0.51	0.48
7.5	0.76	0.77	--	0.57	0.54	0.50
10.5	0.91	0.89	--	0.59	0.54	0.52
13.5	1.15	1.09	0.73	0.65	0.58	0.51
18.0	1.49	1.40	0.84	0.71	0.55	0.49
25.0	1.74	1.43	0.90	0.65	0.55	0.50

FIG. 12

Specific Surface of Calcium Hydroxide produced with various ratios of water of different temperatures



An initial water temperature of 4°C (39°F) and a change in R from 2.5 to 25 pounds water to pounds calcium oxide produces calcium hydroxide with specific surfaces from 50,736 cm²/g to 15,314 cm²/g with corresponding mean particle diameters from 0.53 to 1.74 u. Settling times represented by particles of this size, according to Table IV, range from 480 minutes to 80 minutes respectively. A constant water temperature of 10°C (50°F) and R from 2.5 to 25 likewise produces calcium hydroxide of decreasing specific surfaces from 54,293 cm²/g to 18,597 cm²/g with corresponding mean particle diameter from 0.49 u to 1.43 u with increase in R. Particles of this range have settling times from 375 minutes to 70 minutes respectively. Water temperature of 20°C (68°F) follows a similar pattern with the usual change in R, but the change of a much smaller magnitude than either 4°C or 10°C.

The range of the calcium hydroxide at a water temperature of 20°C is from 52,790 cm²/g to 32,610 cm²/g specific surface with corresponding mean particle diameters of 0.50 u to 0.90 u, indicating that the higher temperature slaking water gives changes of less magnitude than at the two previous temperatures. Settling times of these samples more or less correlate this data by showing less variation of settling values from 235 minutes to 90 minutes. Water temperatures of 40°C (104°F) and 60°C (140°F) both show less mean particle size variation than the previous temperatures. At 40°C the change will be seen to be from 56,606 cm²/g to 40,910 cm²/g specific surface corresponding to mean particle diameters of 0.47 u to 0.65 u, while at 60°C the variation is from 57,355 cm²/g to 48,244 cm²/g specific surface with mean particle diameters of 0.46 u to 0.55 u. This narrow range of mean particle diameters would be expected to show longer settling time than previous series for all values of R.

Slaking water at 90°C (194°F) produces from 58,300 cm²/g to 53,295 cm²/g specific surfaces for all values of R with a mean particle diameter range of only 0.46 u to 0.50 u. Very long settling times would be expected from these suspensions. Table XIV and Figure 9 show active settling times from 980 minutes to 1200 minutes.

The specific surface decreases (mean particle diameter increases) for all initial water temperatures to 60°C as the ratio (R) of water increases from 2.5 to 25. Also, the specific surface increases (mean particle diameter decreases) for each value of R as the initial water temperature increases.

The highest specific surface calcium hydroxides were obtained from those tests producing final temperatures of or greater than 212°F. These temperatures were obtained with R at 2.5 for all initial slaking water temperatures investigated and for an initial slaking water temperature of 90°C at all values of R. The development of specific surface of a calcium hydroxide is therefore a function of the final slaking temperature. Final slaking temperatures less than 100°C (212°F) develop the specific surface of calcium hydroxide in proportion to the final temperature, which is another way of defining the ratio; R, of water. Higher ratios of water resulting in lower final temperatures produce the lower specific surfaces, and low ratios of water resulting in higher final temperatures produce higher specific surfaces. Investigating this condition further, the amount of water required for several ratios was heated to the calculated initial temperature (T₁) to result in a final temperature (T₂) approaching 100°C or 212°F (Table V), and used for slaking tests. The tabulation of data for the tests and the results of final temperature of the suspension and specific surface of the calcium hydroxide are shown in Table XIX.

TABLE XIX

Results from Volume and Temperature of H₂O (T₁) to Produce a Final Temperature (T₂) of approximately 212°F

R	Temperature °F		Specific Surface cm ² /g
	T ₁	T ₂	
2.5	57.2	210.9	55,100
7.5	167	211.1	52,300
13.5	190	211.6	51,600
25.0	205	212.7	53,200

The final temperature of each test approached the expected value of 212°F. The specific surface values are of the same magnitude. Therefore, these data offer further proof that to produce extremely high specific surface or small particle-diameter calcium hydroxide requires a high slaking temperature approaching 100°C (212°F). It is a matter of choice for the ratio of water to be used so long as the temperature calculated for this value of R will produce a final temperature approaching, but not exceeding, 212°F.

It is important that the calcium oxide have a high degree of activity to produce a high specific surface calcium hydroxide in a short slaking cycle. Otherwise, a low activity calcium oxide will increase radiation losses to reduce the slaking temperature below the necessary limit.

Very low values of R will produce high specific surface calcium hydroxide. However, at these concentrations, especially above an initial starting temperature 50°F (10°C) the final slaking temperature (T_2) will theoretically be above 212°F resulting in the evaporation of a large proportion of the water. Also, values of R at temperatures approaching 90°C (194°F) produce high specific surface calcium hydroxide. Final temperatures of these combinations will be theoretically above 212°F, so that a large amount of the slaking water will be evaporated.

Aqueous suspensions of calcium hydroxide exposed to heated bodies above 214°F have been shown to produce hexagonal crystals of fairly large size (Wire and Wire Products, October 1955). The specific surface of these suspensions increases as the crystallization increases because of the colloidal characteristics of aqueous suspensions of crystalline calcium hydroxide.

It has also been found optically that calcium hydroxide produced by the slaking of calcium oxide in water at values of R and T_1 to result in a final slaking temperature T_2 of 212°F or calculated theoretically to exceed 212°F also produces crystalline calcium hydroxide. The specific surface, settling time and viscosity of these suspensions are greatly increased because of this crystallization.

Suspensions produced at all values of R with T_1 at 194°F (90°C) contained large amounts of crystalline calcium hydroxide which account in part to the very high specific surfaces. Crystallization also increases the settling time as shown in Table XIV.

The initial slaking temperature (T_1) should be chosen to assure a final slaking temperature (T_2) of 212°F or less to prevent or reduce to a minimum the opportunity for crystal growth.

D VISCOSITY

The viscosity was determined on calcium hydroxide suspensions slaked with several ratios of water and temperatures then cooled to 70°F. Two of the suspensions were prepared at R of 7.5 and T_1 of 4°C (39°F) and 60°C (140°F). One suspension was prepared at R of 2.5 and T_1 of 14°C but was too viscous for a test. Three suspensions were prepared at R of 7.5, 13.5 and 25 and T_1 of 75°C (166.8°F), 88°C (190°F) and 96°C (205°F) respectively calculated to produce final temperatures (T_2) of 212°F. The values for T_2 and the viscosities, with the exception of the one prepared at R of 2.5, are shown in Table XX.

TABLE XX

Slaking Temperature and Viscosity (Centipoises) of Calcium Hydroxide Suspensions

Sample	R	°C Temperatures		Viscosity
		T ₁	T ₂	
1	7.5	4	33.8	38
2	7.5	60	88.3	163
3	2.5	14	99.4	--- *
4	7.5	75	99.5	241
5	13.5	88	99.8	28
6	25.0	96	100.4	10

* Suspensions prepared at this value of R are highly viscous and a viscosity test is meaningless.

The viscosity increased with an increase in temperature for a constant water ratio. When the water ratio was increased and the initial temperature of the water increased to produce a final temperature approaching 212°F the viscosity decreased at a very rapid rate.

The theoretical concentration of a suspension at R of 7.5 is approximately 162 gpl. The concentration at R of 13.5 and 25.0 are 91.4 gpl and 49.7 gpl respectively. The concentration at R of 2.5 is theoretically 456 gpl. Therefore it would be expected to find very low viscosities of suspension prepared with R of 13 and 25 as shown in samples 5 and 6. Samples 5 and 6 were allowed to settle and the calculated amount of supernatant water decanted to give a concentration equivalent to R of 7.5. Sample 3 required diluting with water to reduce the concentration from 456 to 162 gpl. The viscosities of these corrected suspensions are shown in Table XXI.

TABLE XXI

Viscosity (Centipoises) of Calcium Hydroxide Suspensions at approximately 177 gpl

Sample	R of Original Suspension	Viscosity of Suspension corrected to 162 gpl
3	2.5	131
4	7.5	241
5	13.5	360
6	25.0	291

The amount of water employed for slaking and its initial temperature has a decided effect on the viscosity of a calcium hydroxide during the slaking of calcium oxide. A ratio of water of 7.5 at a temperature of 75°C (167°F) produces a suspension of higher viscosity than a suspension prepared with a ratio of 13.5 even though the same final slaking temperature is reached. However, when both suspensions are made to the same concentration, the one prepared with the greater ratio of water has the higher viscosity. A suspension of calcium hydroxide prepared at a ratio of 25 and an initial temperature of 96°C does not produce the same viscosity when corrected to 162 gpl.

The viscosity of the calcium hydroxide suspensions at a concentration of 100 gpl were determined. It was anticipated the values would be relatively low at this low concentration, but it was thought that values for any differences, however slight, may help to explain some of the differences in the settling rates. The values for most of the samples produced are shown in Table XXII.

TABLE XXII

Viscosity (Centipoises) of Calcium Hydroxide Suspensions
at Concentration of 100 gpl (CaOH)₂

R	°C °F	Initial Water Temperature					
		4 39	10 50	20 68	40 104	60 140	90 194
2.5	--	--	--	72	42	63	--
7.5	35	27	21	25	32	28	
10.5	28	24	24	22	32	27	
13.5	--	23	22	20	29	26	
18.0	--	--	21	19	33	--	
25.0	--	--	20	19	--	--	

The viscosities of suspensions of this low concentration will be very low. The viscosities are higher at the lowest water ratio of 2.5. These samples are undoubtedly influenced by the presence of crystalline calcium hydroxide produced at this low water ratio. The viscosity decreases with an increase in the water ratio between 39°F and 104°F. The viscosity appears constant at ratios from 7.5 to 18 for initial water temperatures of 60°C (140°F) and 90°C (194°F).

The higher viscosities of suspensions prepared with water ratios of 2.5 indicate a change in physical properties which will decrease the settling time. Therefore, the settling time is not dependent upon mean particle diameter (or specific surface) of the suspended calcium hydroxide alone.

VII CONCLUSIONS

This preliminary study of the reaction between calcium oxide and water reveals the complexity of the reaction in producing results regarding settling time, specific surface and viscosity of calcium hydroxide suspension prepared with an excess of water.

Advantage can be taken of the thermodynamics of the reaction by altering the ratio and temperature of water per pound of calcium oxide to produce calcium hydroxide varying in particle diameter from fairly large to extremely small as determined by the Blaine air permeability method. Low ratios of water produce higher reaction temperatures and calcium hydroxide of high specific surfaces. Specific surfaces vary less with changes in water temperatures at low water ratios. Specific surfaces also vary less with water at high temperatures for all ratios. The specific surface of the calcium hydroxides vary over a very wide range at ratios of 7.5 to 25 and at temperatures from 4°C (39°F) to approximately 60°C (140°F).

Settling times of calcium hydroxide suspensions corrected to 100 gpl do not correlate changes in ratios and temperature of water as well as specific surface measurements. This may be caused by the influence of the viscosity of a suspension on the settling rate of the particles of calcium hydroxide. A considerable change in viscosity was found which has not been fully explained.

This study, although presenting encouraging data on specific surface control, indicates the need for more information on the factors influencing the difference in the rate of settling and a more thorough knowledge of particle size distribution with changes in the process.

Data on the control of specific surface or mean particle diameter by either a change in the ratio of water to calcium hydroxide or a change in the temperature of water at any given ratio of water to calcium hydroxide is presented which, to our knowledge, has not been previously available to the chemical industry. A better understanding of this principle offers the industry a new method of more consistent control at higher efficiency.