HYDRATION OF LIME AS A FUNCTION OF OXIDE HISTORY

BY
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ENTITLED **"HYDRATION OF LIME AS A FUNCTION OF OXIDE HISTORY"**

BE ACCEPTED* AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF **MASTER OF SCIENCE IN CHEMISTRY**

George L. Clark
In Charge of Thesis

Roger Adams
Head of Department

Recommendation concurred in†

Committee
on
Final Examination†

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*Subject to successful final examination in the case of the doctorate.
†Required for doctor's degree but not for master's.

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I. INTRODUCTION

Lime making is seldom thought of as an important industry. It is an industry so old as to be taken for granted. A casual inspection will be quite revealing. Among the many important uses, lime is essential to mortar used in stone and brick construction; to plaster, the predominant interior finish of homes; to industry as the cheapest industrial base; to agriculture as a fertilizer. From the days of the first settlers in this country, lime making has been of major, if fundamental, importance.

Within the past few years the chemist and engineer have been called upon to suggest better methods, to solve the apparent anomaly of poor product from good material and good product from poorer material. The methods of production are undergoing gradual change for the better. But not all problems have been solved. The fundamental cause for variation in properties of the product is not too well understood. It is the purpose of this thesis to investigate the relationship of the decomposition temperature of hydrates as a function of oxide history. This is a part of a much larger investigation which includes X-ray diffraction studies, electron microscope pictures, and the reverse of this procedure, studies of hydration rates as a function of oxide history.

II. HISTORICAL AND THEORETICAL

The age old process of production of the calcium and magnesium oxides, "quicklime", consists of heating raw limestone or dolomite at such a temperature that the following reactions occur:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$MgCO_3 \rightarrow MgO + CO_2$$

These reactions are fundamental and well known. However, these reactions do not proceed in one direction only. Equilibria exist between the products and reactants such that:

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

Temperature and time are therefore vitally important factors in the production of quicklime. At ordinary pressure calcination of two inch stone goes to completion in about twelve hours, at 800° C. If the temperature is raised to 1100° C., stone of the same size calcinates in about two hours.

Limestone is of quite indefinite composition. From practically pure calcium carbonate, percentages as high as 50% of magnesium carbonate may be encountered. Seemingly, there are as many different varieties as there are veins of stone, and the methods of production vary depending on the character of the raw material.

The limestone or dolomite when quarried is in the form of rather large pieces with an accompanying amount of small waste stone. In order to get stone of such a size that it may be burnt under optimum conditions, crushing is necessary. This is a factor in the expense of manufacture of a product which must sell at a very low margin of profit. As a result, the distribution of sizes of stone charged into a kiln often varies from two to twelve inches. Quicklimes produced in this manner are heterogeneous in character because the distribution of heat through a large lump is very uneven. The outer portions reach a much higher temperature and become less active or "hardburned" and, therefore, less desirable quicklime.

Besides the large difference in composition and size of the raw material, kiln construction and operation are seldom quite the same in any two cases. There are two major variations in kiln construction, vertical shaft kilns and rotary kilns. The vertical kiln is charged with fairly large sized stone, while the rotary kiln is best used for small size and waste stone. Quicklime from the rotary type kiln is usually softer burned and more homogeneous in response to hydrating. Minor variations as to fuel and control of temperature are frequent.

In the general trend toward a more uniform and softer burned product one type of kiln deserves special mention.[1] It is the center fired automatic draw kiln. In operation this kiln is charged and drawn every two hours. This is quite a different picture from the older practice of drawing and charging every other day.

The cheapest and oldest method of hydrating quicklime is in an open vessel. The quicklime reacts with an excess of water and the material is then dried, graded and sold. Steam and pressure hydration are more recent techniques. The latest procedure suggests initial hydration in low temperature water vapor, followed by steam at 100 °C.[2] This method avoids excessive temperatures producing hydrate which is very finely divided, and very plastic.

The general properties of the product vary considerably depending on the manner of production. The degree of hydration is largely a function of the time and temperature of calcination. A wide variation in plasticity and sand-carrying capacity makes it important to know the reason for the variation in a seemingly simple reaction.

The behavior of magnesium carbonate in dolomitic lime has been investigated and was found to have profound influence on the quality of dolomitic lime.[3] The rates of calcination as a function of time, temperature and stone size, as well as the percent hydration as a function of calcination temperature, have been determined.

The study of the relative strength with which hydrates of various plasticities hold water such as encountered in plaster is important in the determination of the actual basic property which is the basis of the plasticity of hydrates.

The extent to which the manner of calcination of limestone effects the properties of the hydrate is questionable. The decomposition rates of hydrates when subjected to high temperature is a method of determining the influence of the history of the oxide.

III. EXPERIMENTAL

In the determination of the rate of loss of water from a sample of hydrate mixed with water, a new Brabender Moisture Tester was used. This instrument consists of a thermostated oven and a balance mechanism to weigh the material in the oven itself. The oven has a rotary plate which is made to hold ten samples for simultaneous determination of moisture loss. The balance mechanism reads directly in percent moisture lost on the basis of ten grams of starting material in an eleven and one-half gram sample dish.

The sample dishes are made of aluminum. It was found necessary to protect the dishes from corrosion by the strong base. The dishes were therefore coated with Bakelite varnish and recalibrated to eleven and one-half grams in weight. This protection was found to be satisfactory both from point of protection of the metal and also from point of constant weight.

The rates of drying of six samples of commercial hydrate of known relative plasticity were determined. Five grams of water were mixed with five grams of hydrate in the sample dish. Weight loss readings were taken every five minutes at an oven temperature of 95 °C. Cf. Table I.

Samples used in order of decreasing plasticity were Peerless Finishing, U.S. Gypsum Finish, Corson Miracle, Corson Regular, and Riverton hydrates.

The study of the decomposition of the hydrate to the oxide made necessary an apparatus to determine temperature and weight loss simultaneously as a function of time. The temperatures re-

TABLE I

% Moisture Loss of Putty (5 g. hydrate + 5 g. water) at 95°C.

Minutes	Peerless	U.S. Gypsum	Corson Miracle	Corson Regular	Marble Cliff	Riverton
0	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
5	3.4	3.4	3.2	3.6	3.8	1.0 (2 min.)
10	5.8	5.2	5.2	5.7	6.1	3.1(7)
20	13.2	10.7	10.9	11.9	13.0	9.6(17)
30	21.8	17.7	17.5	18.7	20.4	16.4(27)
40	31.1	25.0	24.6	25.9	27.9	29.9(37)
50	39.7	33.0	31.6	33.2	35.4	30.5(47)
60	47.1	40.1	38.6	39.3	42.4	37.4(57)
70	49.9	46.1	44.8	45.0	48.3	44.7(67)
80	49.9	49.6	48.4	48.5	49.8	49.3(77)
90	50.0	49.8	49.7	49.7	49.8	50.2(87)
100	50.0	49.8	49.7	49.7	49.8	50.2(97)
110	50.0	49.8	49.7	49.7	49.9	50.2(107)

quired were from room temperature to about 600° C. Accordingly, an apparatus (cf. Fig. I) was constructed, using a small electric furnace of the type used for carbon analysis in steel. The furnace was mounted in a vertical position and a brass sample basket, suspended by thermocouple leads from the arm of an analytical balance, hung in it. The thermocouple junction was in the sample itself so that the temperatures read were the temperatures of the sample. The junction was lead off the balance arm by a flexible coil of very fine copper wire. The sensitivity of the balance was adjusted to ±.01 gram. Temperature was read by a Leeds and Northrup Potentiometer, model 8657-C. The assembled apparatus allowed convenient and accurate determination of temperature and weight of sample simultaneously.

In the determination of the decomposition rates of the hydrates, the current was adjusted so that the furnace heated from room temperature to 524° C. in twenty minutes. The sample in the basket was placed in the cold furnace. As the furnace heated, temperature and weight were taken at timed intervals. Where no decomposition occurred, readings were made at two to five minute intervals. At the points of decomposition readings were made at each minute.

Two different stones were used in this study, Lewisburg and Gibsonburg. The first, Lewisburg, is a high calcium stone, while the second is dolomitic. The Lewisburg stone was burned at 816° C. and 1066° C. Samples of the Gibsonburg stone were burned at 871° C. and 1188° C. These oxides were hydrated in water and dried at 120° C. for four and one-half hours. Tables II and III contain the

Figure 1

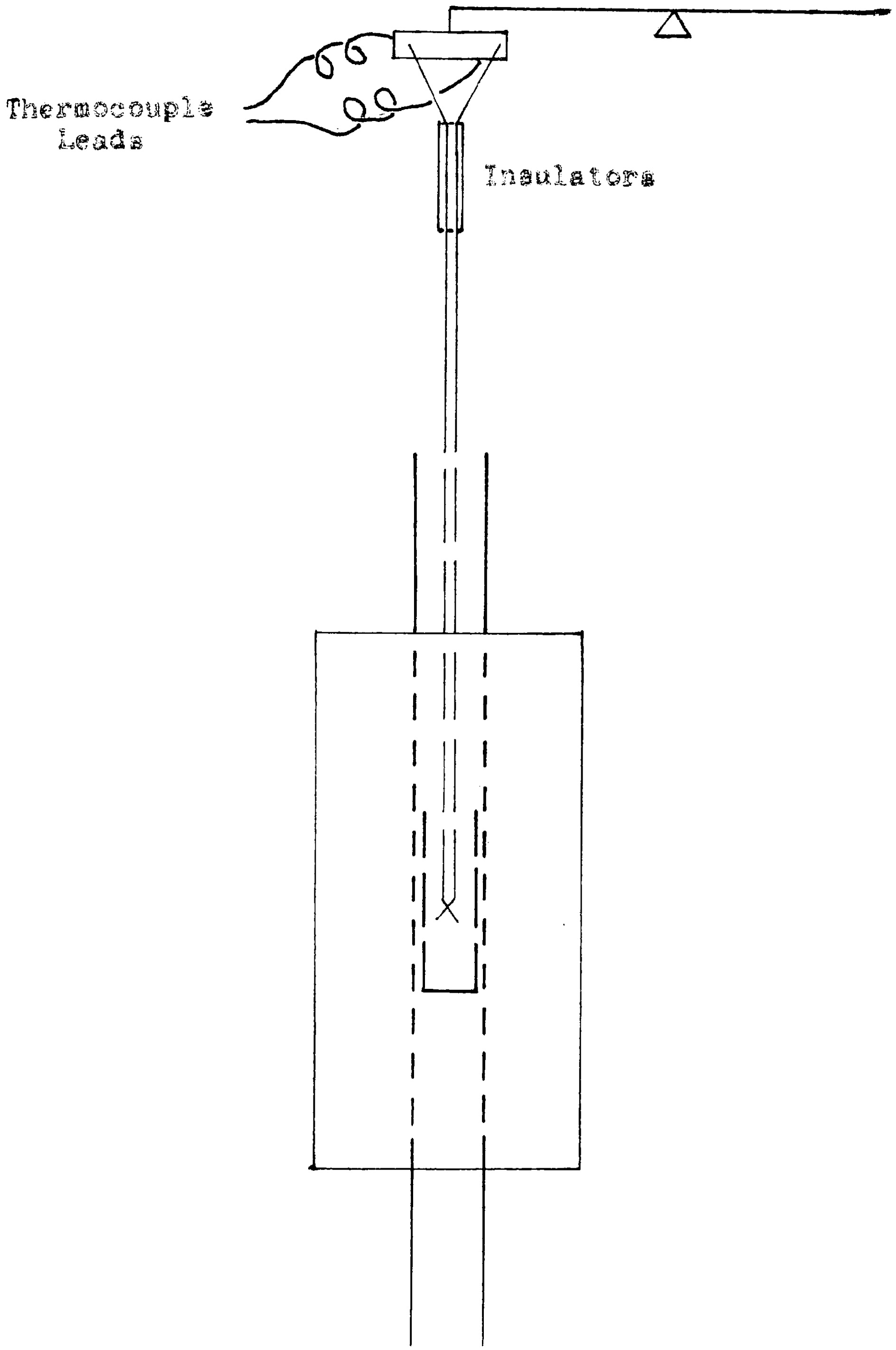


TABLE II

Marble Cliff High Calcium

Sample A.	Sample B.
Calcination - 788 °C.	Calcination - 1066 °C.
Hydration - water	Hydration - water
Dried 4-1/2 hrs. at 120 °C.	Dried 4-1/2 hrs. at 120 °C
Dehydration:	Dehydration:

Time	%Weight Loss	Temp.	Time	%Weight Loss	Temp.
0 min.	0.0	27 °C.	0 min.	0.0	22 °C.
5	0.8	96	5	1.7	124
10	2.6	316	10	3.3	349
12	3.0	427	15	7.3	524
13	3.4	463	17	11.9	524
15	5.6	521	18.5	15.4	524
16	8.0	521	20	19.4	524
17	11.0	524	22	23.2	524
19	15.8	524	23.5	24.8	527
20	17.9	524	25	26.2	560
22	21.4	524	30	26.5	799
23	23.6	530	35	26.6	843
25	25.1	613	40	26.6	899
27	25.1	741			
30	25.2	785			
35	26.1	835			

TABLE III

Gibsonburg Dolomite

Sample C

Calcination - 871° C.
Hydration - water
Dried 4-1/2 hrs. at 120° C.
Dehydration:

Sample D

Calcination - 1013° C.
Hydration - water
Dried 4-1/2 hrs. at 120° C.
Dehydration:

Time	%Weight Loss	Temp.	Time	%Weight Loss	Temp.
0 min.	0.0	29° C.	0 min.	0.0	28° C.
5	0.3	66	2	0.0	28
8	0.9	174	5	0.4	85
10	1.2	249	8	0.9	193
12	1.4	335	10	1.2	274
13	2.6	360	11	1.4	310
14	5.2	371	12	1.7	349
15	7.8	370	13	3.3	371
16	9.8	370	14	4.5	371
17	11.6	371	15	6.8	371
18	13.1	377	16	8.7	374
19	13.7	391	17	10.1	374
20	14.1	463	18	11.4	380
21	15.0	504	19	13.5	396
22	16.3	521	20	14.1	449
23	18.5	521	22	15.3	524
25	21.6	521	23	18.5	524
26	21.7	521	24	19.0	524
27	24.6	522	25	20.2	524
28	25.8	524	26	22.1	524

Time	%Weight Loss	Temp.	Time	%Weight Loss	Temp.
29	26.2	527	27	24.5	524
30	27.0	538	28	25.6	530
32	27.4	657	29	26.5	538
34	27.4	699	30	26.9	560
			31	27.3	610
			33	27.4	682
			35	27.4	707

time, weight temperature data on these samples.

IV. DISCUSSION OF RESULTS

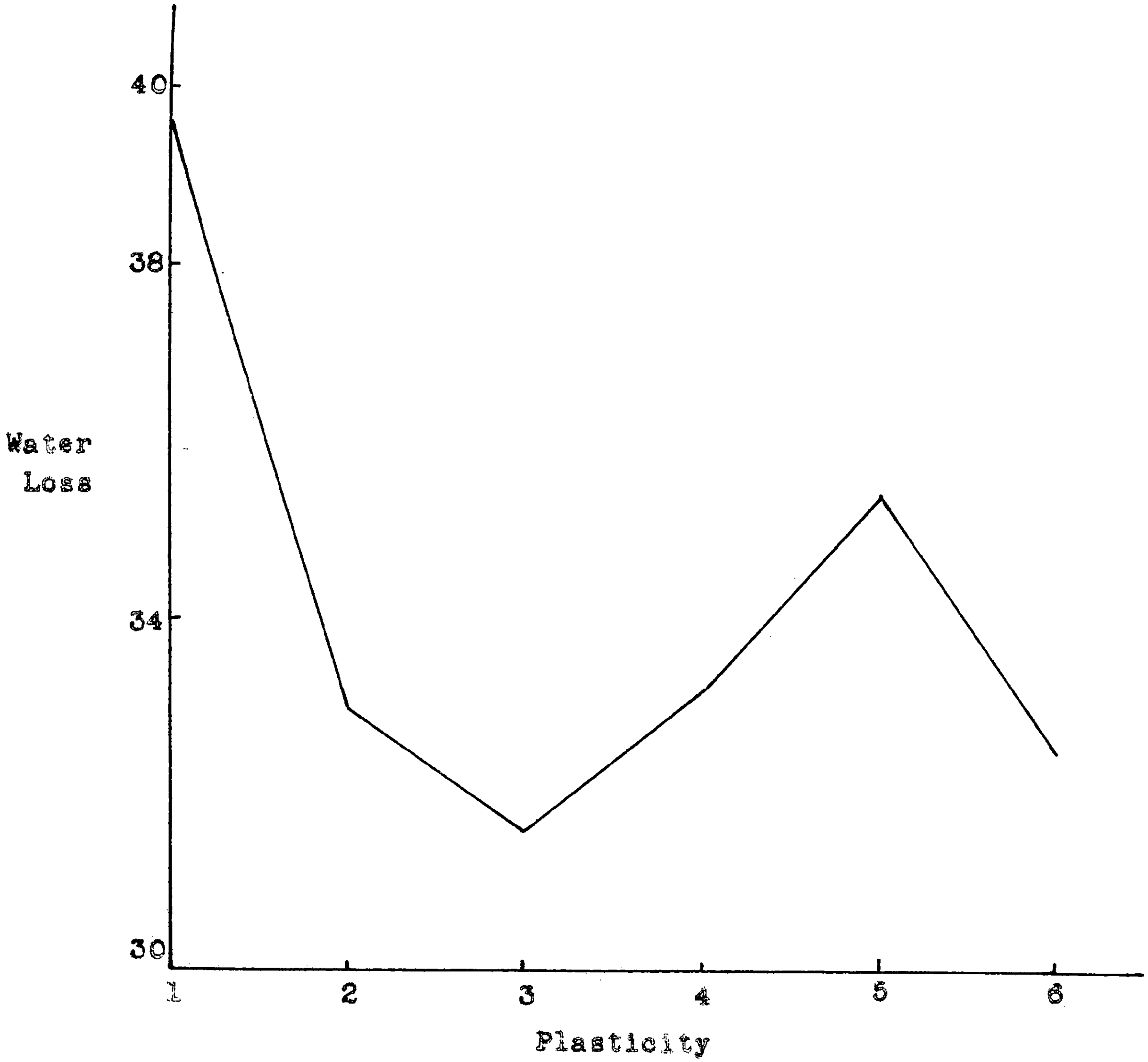
A. The rate of drying of the putties of the six samples of varying plasticities showed no correlation between plasticity and rate of drying. Actually there is little variation in these rates except in the case of Peerless finishing hydrate. The water evaporated more rapidly in this sample than in the others. Peerless is first in order of plasticity, but a graph of percent weight loss after fifty minutes at 95 °C. against the numerical order of plasticity shows that this high loss in weight is not a function of plasticity. Cf. Graph I.

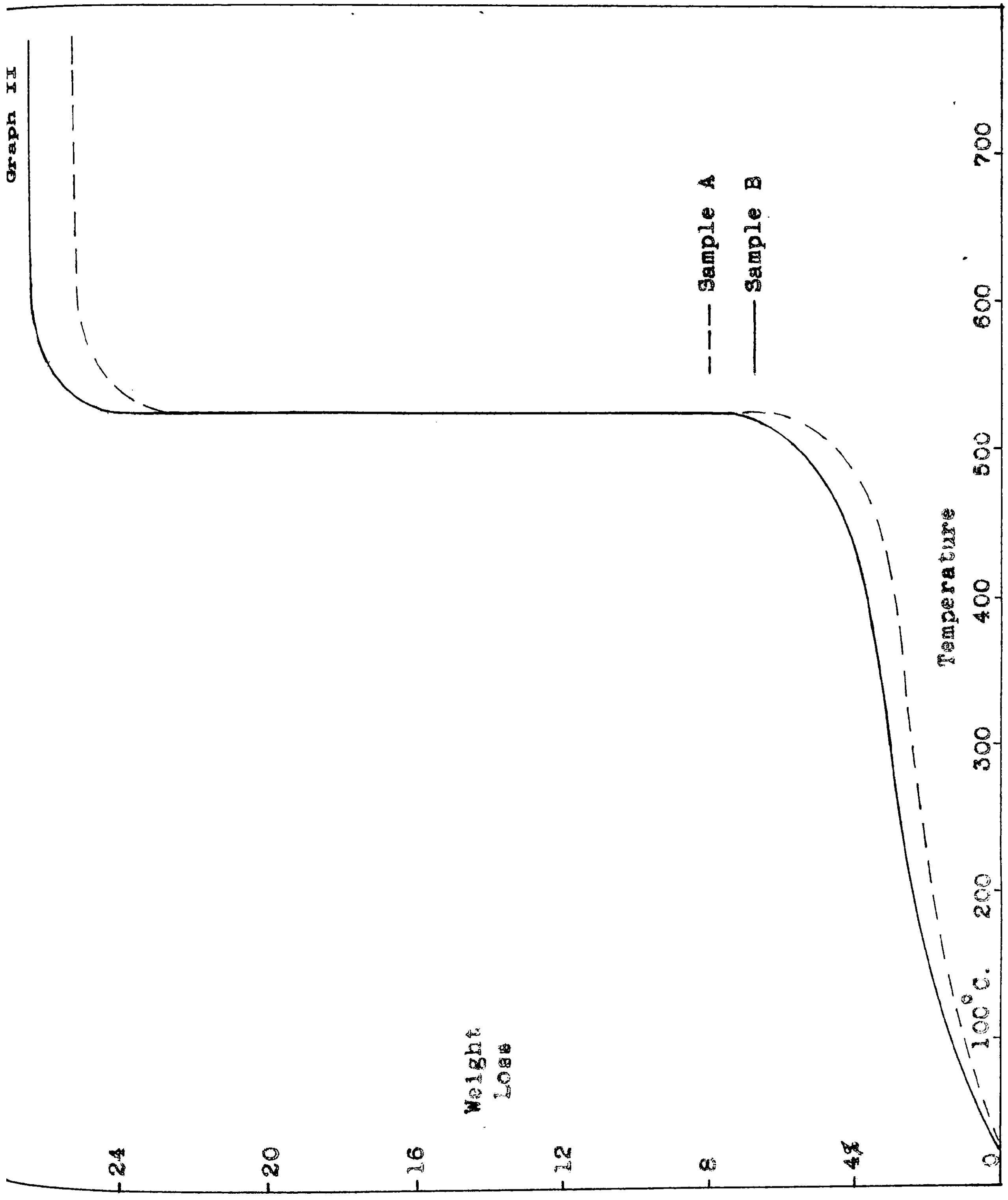
B. The data on the dehydration of the laboratory prepared hydrates at high temperature includes three variables. On Graphs II and IV temperature of sample is plotted against weight loss. Graphs III and V show temperature as a function of time.

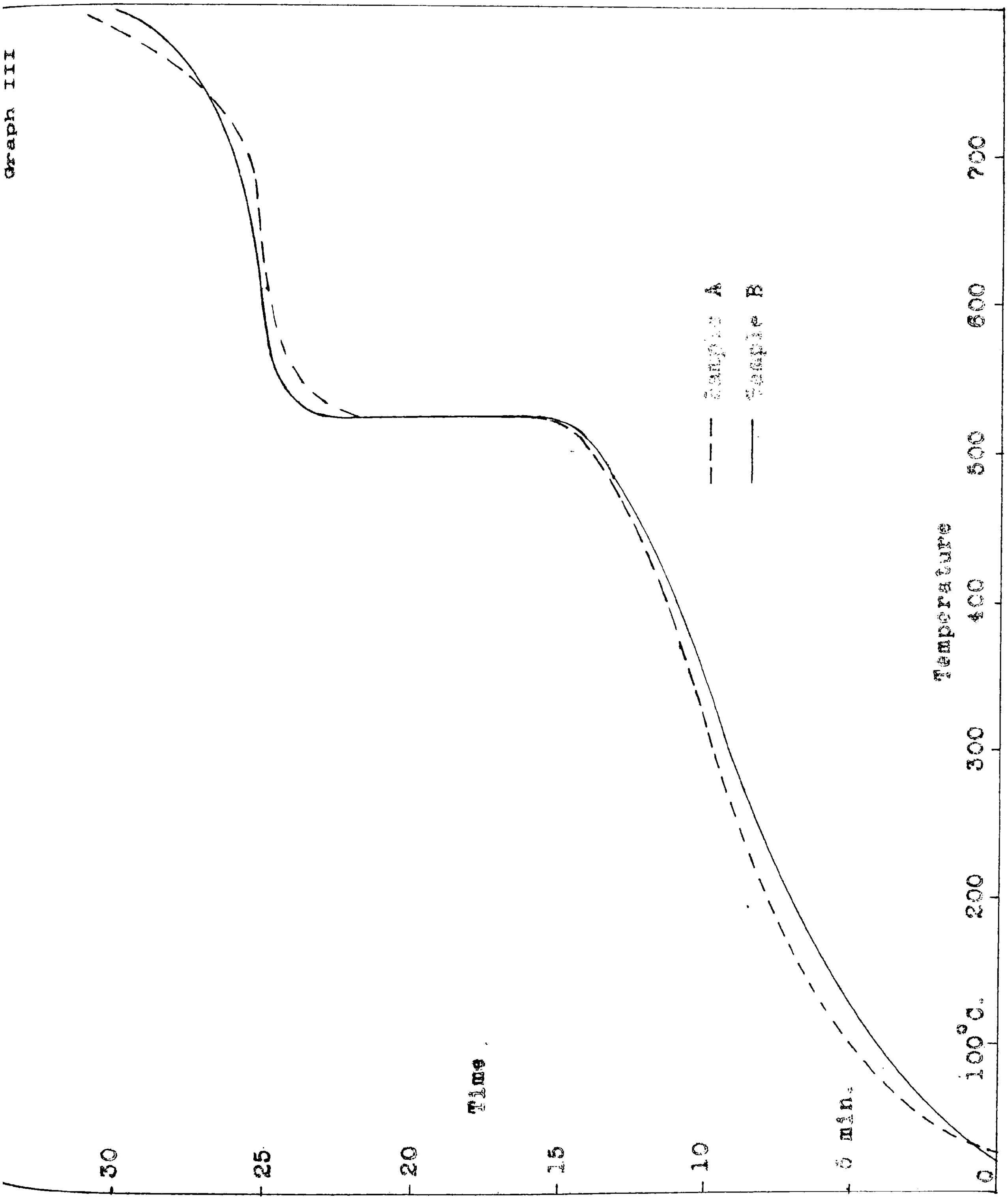
Data on Lewisburg high calcium lime from Table II is plotted on graphs II and III. The shapes of both the weight loss-temperature and temperature-time curves are very similar. No effect of difference of calcination temperature is noted between the two samples. Dehydration of calcium hydroxide occurred at 524 °C.

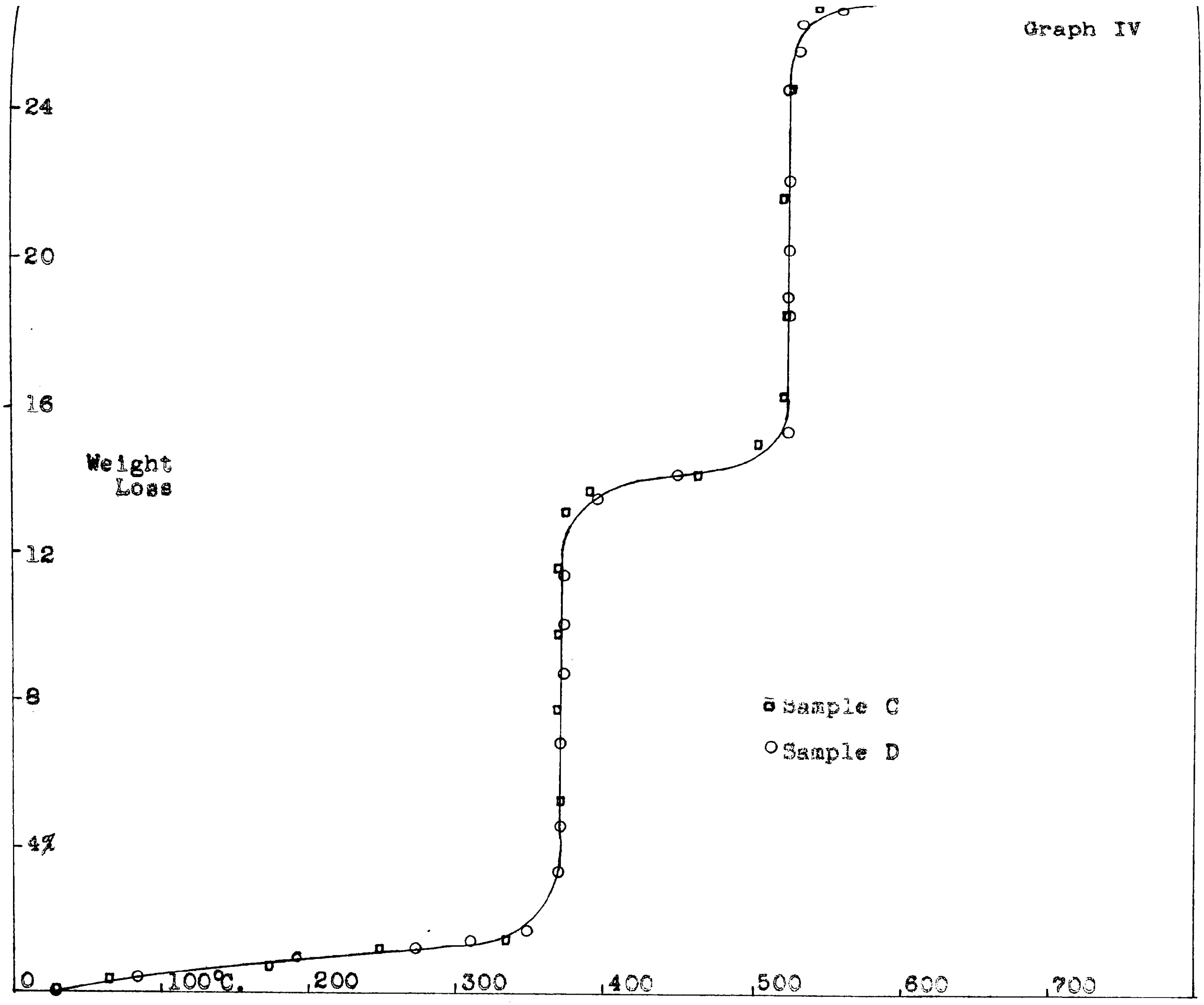
On Graphs III and IV data from the dehydration of Gibsonburg dolomite is plotted similarly. These curves are almost coincident so that a single curve is drawn for both sets of points. Magnesium hydroxide decomposed at 371 °C. Regardless of the difference in temperature of calcination, the hydrates are identical so far as dehydration rates are concerned.

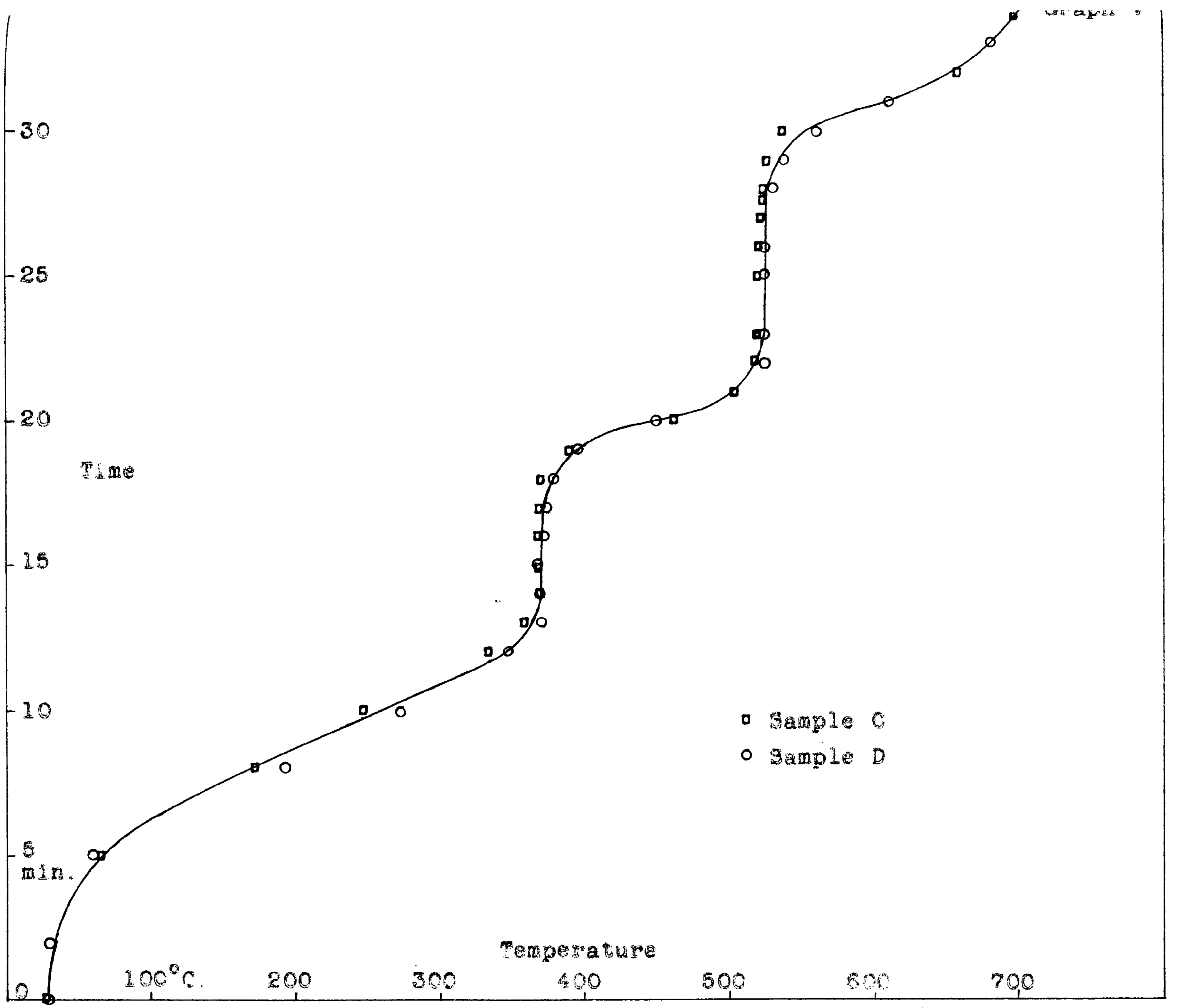
Graph I




Graph II
Sample A
Sample B
Weight Loss
0
4%
8
12
16
20
24
Temperature
100°C.
200
300
400
500
600
700


Graph III
Time
5 min.
10
15
20
25
30
Temperature
0
100°C.
200
300
400
500
600
700
Sample A
Sample B


Graph IV
Weight Loss
24
20
16
12
8
4%
0
100°C.
200
300
400
500
600
700
□ Sample C
○ Sample D


30
25
20
15
10
5
min.
0
Time
100°C.
200
300
400
500
600
700
Temperature
□ Sample C
○ Sample D

V. CONCLUSIONS

In the investigation of the plasticity of the samples of known plasticity it was shown that no correlation is possible on the basis of the rate of loss of moisture from a putty. Rate of loss of water is independent of the plasticity of the sample.

Study of the large variations in properties of hydrates manufactured in various ways through dehydration of various laboratory prepared hydrates proved that the dehydration rates are very similar. Consequently the wide difference in properties of commercial products cannot be ascribed to the difference in stability of the hydrates. This property is independent of oxide history.

X-ray diffraction studies have indicated that hydrate properties are definitely a function of oxide history. This work was done as a part of a larger study to determine the fundamental cause for variation. Continuation of this work by the author will include study of hydration rates and temperatures, the reverse of this procedure of this thesis, X-ray diffraction, and electron microscope research.

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