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DEHYDRATION OF CLAYS

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By G. H. Brown and E. T. Montgomery

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I. INTRODUCTION

1. STATEMENT OF THE PROBLEM

Upon ignition the hydrous silicates of alumina, of the general type $Al_2O_3.2SiO_2.2H_2O$, which form a greater or smaller part of the pure and impure clays, lose their combined water within a certain temperature range. With this dissociation the character of the clays changes in an important manner. The property of plasticity is greatly diminished and may even be completely destroyed and deep-seated molecular transformations occur which are indicated by a decrease in specific gravity, increased solubility in acids and alkalies, and other decided alterations.

2. EARLIER INVESTIGATIONS

Until recently the dehydration temperatures of clay were not known with any degree of exactness. Le Chatelier[1] assumed a series of ranges which depended upon the structure of the substance, varying from 150 to 770° C. Kaolin he supposed to

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[1] Zs. physik. Chemie, **1**, p. 396; 1887. Comptes Rendu, **104**, pp. 1443, 1517.

dehydrate at 770°, a value considerably too high in the light of later measurements. Depending upon the dehydration ranges, Le Chatelier attempted a classification of clay like hydrous minerals, distinguishing five classes of substances, but examination of his lag curves would seem to indicate that this procedure is based upon very slender evidence.

An American investigator, Ellis Lovejoy,[2] determined the ignition loss of a No. 2 fire clay at the melting points of different metals and found the dissociation temperature to be near the fusion point of antimony, about 630°. Another American, A. E. Barnes,[3] as the result of similar work, reported the decomposition as taking place at about 565°. W. M. Kennedy,[4] under the direction of Edward Orton, jr., carried on a series of weighings of brickettes made from Florida kaolin, 30 grams in weight, at temperatures up to 1000° C. Here loss of combined water was clearly shown to have taken place at 475°. The chemical study of dehydrated kaolin received attention by Hillebrand,[5] F. W. Clarke,[6] McNeil,[7] Knote,[8] and others. Hillebrand described a sample of pure crystalline kaolinite and stated that none of the water escapes at 330° C. The water was considered by this investigator to be probably basic water.

Clarke mentions that "after dehydration at low redness kaolin is completely decomposable by hydrochloric acid, but the ignited mass contains no silica soluble in sodium carbonate solution." The complete decomposition of dehydrated kaolin was confirmed by McNeil. Knote, upon treating Kentucky flint clay heated to 600° C and 1000° with hydrochloric acid, found that the material ignited to the lower temperature yielded an extraction of 44 per cent, while the more highly calcined clay resulted only in the solution of 5 per cent. The relation between calcination temperature and solubility was studied more closely by Sokoloff, to whose work reference will be made later.

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[2] The Clay Worker; 1888.

[3] The Clay Worker, **23**, p. 705; June, 1895.

[4] Trans. Am. Ceram. Soc., **4**, p. 152; 1902.

[5] U. S. Geol. Survey, Bull. **20**, p. 98; 1885.

[6] Ibid., Bull. **125**, p. 32.

[7] J. Am. Chem. Soc., **28**, p. 590.

[8] Trans. Am. Ceram. Soc., **12**, p. 226; 1910.

3. RECENT INVESTIGATIONS

Knote,[8] in a research on fire clays, showed by means of specific-gravity curves that a sudden increase in volume occurs between 450° and 500° which reaches a minimum at 550° in the case of a plastic clay and at 600° with a Kentucky flint clay. For most clays, however, the point was found to be located at 550°. Beyond this temperature the density increased gradually up to 900°, when, between this temperature and 950°, a more or less rapid decrease in specific volume occurred. As regards the density drop at 550°, Knote suggests that the $Al_2O_32SiO_22H_2O$ breaks up to form $Al_2O_3SiO_2+Al_2O_33SiO_2+4H_2O$, a reaction which is not very probable. The rise in density at 950°, accompanying an exothermic transformation, was noted by Le Chatelier and by him ascribed to the polymerization of alumina.

The increase in volume coincident with dehydration has been noted by several earlier investigators. Lovejoy[9] noted that during this stage a decided expansion took place in bricks which he measured.

H. E. Ashley[10] summarized the facts known with reference to dehydration and reported some determinations of the dehydration range of a number of clays made in the clay products laboratory of the Bureau of Standards at Pittsburgh.

In heating clay an initial slow rate of heating was noted, due to the water held by the colloidal clay up to 300°. A retardation was then observed from 500° to 575°, due to the expulsion of the combined water. Following this stage a second retardation from about 825° to 925° and an acceleration occurring at about 925° were detected. The acceleration is the same which was previously found by Le Chatelier.[11]

An investigation dealing with this subject has been reported by J. W. Mellor and A. D. Holdcroft.[12] The temperature range of the decomposition of kaolin was determined, and it was found that dehydration begins at no fixed temperature, but that the decomposition is appreciable at 500°. A marked lag appeared only

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[9] Trans. Am. Ceram. Soc., **7**.

[10] J. Ind. and Eng. Chem., **3**, pp. 91–95; February, 1910.

[11] See footnote 1.

[12] Trans. Engl. Ceram. Soc., **10**, pp. 94–120.

between 600° and 700°. At about 900° the exothermic reaction was noted. The specific gravity of kaolin was reduced from 2.615 at 110° to 2.489 at 700°. Kaolin heated to 700° was found to be more soluble in hydrochloric acid than the untreated material. The above investigators conclude from the evidence obtained that upon dehydration the molecule breaks up into free silica, free alumina, and water. The exothermal change, it is claimed, corresponds to a physical change of the free alumina whereby the latter becomes less soluble in acids, less hygroscopic, and more dense. A certain parallelism exists in the properties of alumina and calcined kaolin. (This does not agree with the results obtained by Sokoloff and his assistants.) On the basis of somewhat incomplete evidence Mellor and Holdcroft assume that the OH and Al groups are symmetrically placed in the molecule. Upon heating dehydrated kaolin under steam pressure these investigators succeeded in restoring 3 to 4 per cent water.

An extensive research upon the dehydration of clays was carried on by R. Rieke,[13] who sought to determine the differences in the dehydration temperatures of kaolins and clays, the possibility of definite dissociation temperatures and the loss of combined water at different temperatures. It was found by means of heating curves that heat absorption was observable at temperatures as low as 425° with some clays. The beginning of a pronounced halt, however, was never noted below 510° and for the average of 10 kaolins this point was about 538°. The lag extended to about 580° in most cases. Similar results were obtained with fire clays. The loss of weight increases rapidly with the temperature, since the velocity of the dissociation increases greatly as the temperature rises. Again, it was found that the decomposition was not completed at 700° after long continued heating, there remaining almost 0.5 per cent to be driven off at a still higher temperature. Rieke found that plasticity was not necessarily destroyed upon dehydration. No evidence was produced which tended to show an unsymmetrical arrangement of the OH groups.

This question was likewise studied by A. M. Sokoloff[14] with special reference to the readiness with which the kaolin molecule

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[13] Sprechsaal, **44**, pp. 637–641, 653–656.

[14] Tonindustrie Zeitung, **36**, 1107–1111.

is decomposed by a hot hydrochloric-acid solution. Upon heating kaolin for five hours at different temperatures the following results were obtained:

Temperature	Loss in heating	Per cent soluble Al_2O_3
°C	Per cent	
400	3.85	.....
500	11.70	28.99
600	.....	33.74
700	12.94	33.96
800	13.00	34.67

The molecular ratio $Al_2O_3:H_2O$ for all temperatures approaches 1:2 quite closely.

II. EXPERIMENTAL WORK

The present study was undertaken for the purpose of comparing a number of typical American clays as regards the following relations: (1) Dehydration temperature range; (2) loss of weight upon heating at constant temperatures; (3) specific gravity after heating to several temperatures; (4) loss of plasticity due to heating to several temperatures.

The clays examined in this work were as follows: No. 1, kaolin from North Carolina; No. 2, kaolin from Georgia; No. 3, ball clay No. 3 from Tennessee; No. 4, a second-grade fire clay from Union Furnace, Ohio; No. 5, a plastic fire clay of good grade from Mount Savage, Md.; No. 6, flint clay from Mount Savage, Md.; No. 7, a ferruginous shale from Cleveland, Ohio; No. 8, a paving-brick shale from Galesburg, Ill.; No. 9, highly plastic surface clay from Curtice, Ohio; No. 10, plastic surface clay from Columbus, Ohio.

1. DEHYDRATION TEMPERATURE RANGE

Owing to the fact that dehydration is an endothermic reaction, a more or less distinct lag is to be expected upon heating specimens of the clay. The determinations under consideration were made by comparing the heating curve of an electrically heated furnace with that obtained by measuring the temperature within a clay cylinder. The furnace temperature was read by means of a thermocouple, that of the interior of the clay cylinder by means of a resistance coil and a Leeds and Northrup bridge suitable for this work. The heating coil consisted of a chrome-nickel wire around the interior of the furnace, which was 5 inches long and 2 inches in diameter.

The test specimens, which weighed about 30 grams, were dried at 110° C, until constant in weight, when they were heated to 200° before being placed in the furnace. In Figs. 1 and 2 the heating curves of the clays are shown, together with the time-temperature curve of the furnace, which follows a straight line obtained by close regulation of the current. Taking up the clays in their order the following observations were made:

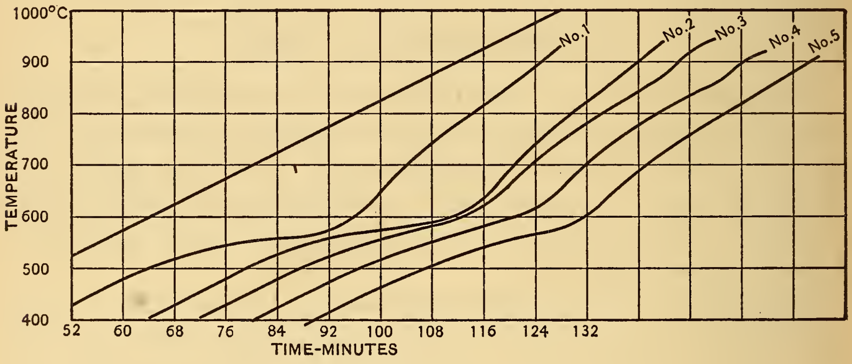

Fig. 1.—*Heating curves*

No. 1. North Carolina Kaolin.—This clay shows a marked retardation, first distinguished at about 480°, the main heat absorption being between 540° and 570°. The loss in weight of the clay at 650° was 13.20 per cent. The exothermic change below 850° is clearly marked.

No. 2. Georgia Kaolin.—The heat absorption becomes evident with this clay at 525° and the lag is prominent between this temperature and 590°, covering a period of 24 minutes. At 650° the loss in weight was 12.93 per cent. In this case also the heat evolution appears to start at 850°.

No. 3. Tennessee Ball Clay.—Retardation becomes manifest at 510° and the lag extends to 600°, with a period of about 20 minutes. Exothermic acceleration not so well marked as in preceding clays. Loss in weight, 10.67 per cent at 650°.

No. 4. Ohio Fire Clay.—Lag begins at 520° and is not as well defined as for the purer clays. It is most evident between 550° and 600°. The loss in weight at 650° is 6.69 per cent. The exothermic transformation is observed more faintly than in the preceding materials.

No. 5. Maryland Fire Clay.—Lag begins at 480° and extends over a considerable period of time and temperature range. The retardation is most pronounced at 580°. The loss in weight at 650° is 5.68 per cent. The acceleration between 850° and 900° is decidedly faint.

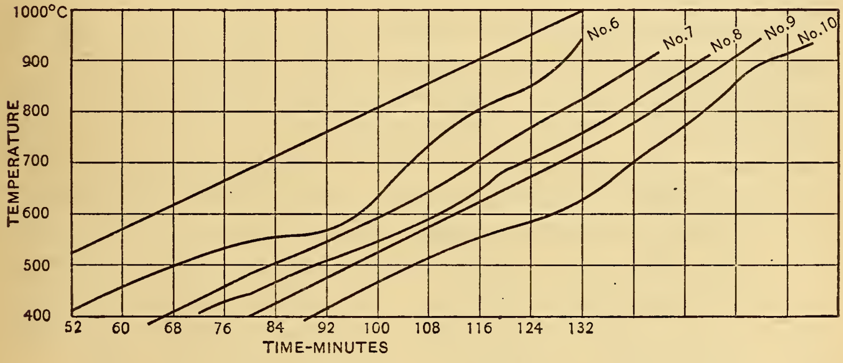

Fig. 2.—*Heating curves*

No. 6. Maryland Flint Clay.—A pronounced retardation is shown by this material already recognizable at 450° and most evident between 550° and 575°. The loss in weight was 10.45 per cent at 650°. The exothermic reaction is particularly well shown between 870° and the final temperature.

No. 7. Ohio Shale.—A slight lag is observed which is first recognized at 485°. The loss in weight at 650° is 3.98 per cent. Owing to the various factors affecting the weight of the clay, such as the oxidation of the carbon and ferrous oxide, dissociation of pyrites, etc., the weight after heating can not be considered a reliable expression of the combined water loss. At 880° the acceleration of the curve is distinctly noticeable.

No. 8. Illinois Shale.—Lag not well defined, though extending over a considerable period of time. It is distinctly recognized at 480° and may be traced up to 670°. An acceleration is noticed beyond 850°. In impure clays of this type it is difficult to determine whether changes of this kind are to be ascribed to the exothermic reaction of Le Chatelier or to the combustion of the small quantities of carbon. The loss of weight at 650° was found to be 4.88 per cent.

No. 9. Ohio Surface Clay.—No lag is shown in this curve, but the acceleration is observed. The loss in weight was 5.63 per cent.

No. 10. Georgia Surface Clay.—The lag is first observed at 490° and becomes quite noticeable at 600°. The loss in weight was 10.09 per cent.

Comparison of the diagrams brings out clearly the fact that the combined water of the clay substance is expelled at no definite temperature but leaves throughout a fairly long continued temperature range. We are dealing, therefore, not with compounds analogous to pure hydrates, but rather with substances in which the water is held only in part as water of hydration. The distinctness of the lag, as is to be expected, affords a criterion of the purity of the clay. Water is expelled before a lag in the heating curves is shown, though at a slow rate. The acceleration in the heating curve at about 850° seems to be most pronounced in the clays higher in combined water; that is, clays of the purer types.

2. LOSS OF WEIGHT UPON HEATING

In the study of the quantitative course of dehydration it was decided to use the loss in weight as the measure of decomposition. From the exact standpoint, of course, it would be far more desirable to determine the residual combined water directly by the standard methods employed for this purpose. Since, however, the main object of the work was to ascertain the rates of loss and the critical temperature range, the direct estimation of the fixed water was not considered necessary.

In this part of the work specimens of clay, weighing about 10 grams, were used. They were dried at 110° to constant weight and then heated to 200°, 400°, 450°, 500°, 550°, 600°, 650°, and 700°, until practically constant in weight; i. e., when the loss in

TABLE 1

Loss of Weight in Per Cent After Heating for 4 to 6 Hours at Indicated Temperatures

Clay	200°	400°	450°	500°	550°	600°	650°	700°	800°	1000°
1	0.42	1.76	2.20	11.50	12.45	12.65	13.20	13.37	13.99	14.00
2	0.21	0.77	2.16	11.64	12.42	12.52	12.93	13.18	13.42	13.46
3	1.44	1.86	4.88	9.90	10.35	10.53	10.67	11.02	11.20	11.20
4	0.10	1.59	3.60	5.35	6.25	6.58	6.69	6.88	6.99	7.25
5	0.30	1.30	2.37	5.01	5.23	5.49	5.68	5.81	5.84	6.00
6	0.30	1.09	4.28	9.36	9.84	10.15	10.45	10.68	10.77	10.95
7	0.32	1.20	1.74	3.00	3.51	3.72	3.98	4.13	4.27	4.57
8	0.24	1.26	2.50	3.80	4.14	4.86	4.88	5.06	5.27	5.47
9	1.33	2.83	3.54	4.31	5.13	5.36	5.63	5.65	5.76	6.07
10	1.25	3.13	5.98	9.14	9.57	9.86	10.09	10.04	10.62	10.64

a two-hour period did not exceed 0.2 per cent. The results of this work are compiled in Table 1 and are shown graphically in Figs. 3 and 4. From the diagram it appears at once that there

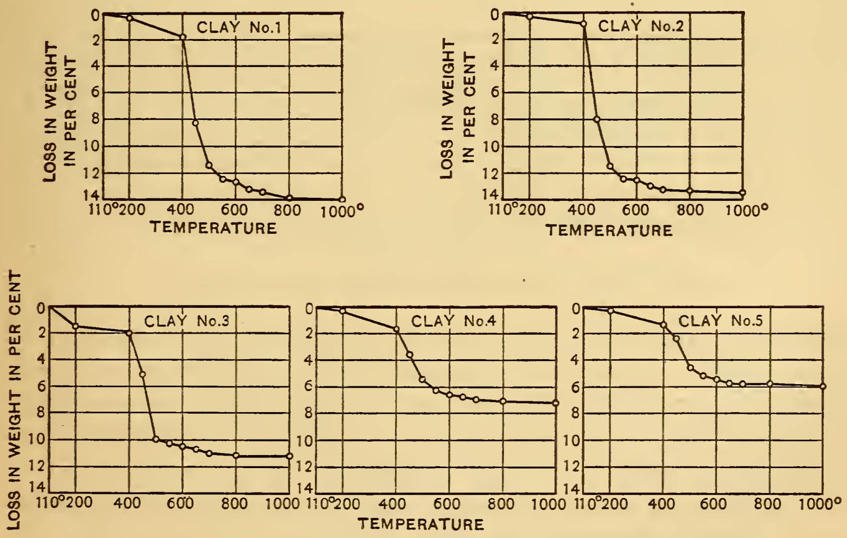

Fig. 3.—*Diagram showing loss in weight at different temperatures*

are, roughly, three stages in the evolution of the combined water. Some loss occurs at temperatures up to 400°, but at a comparatively slow rate. Between this temperature and 500° the rate of loss is greatly accelerated. Above 500° the loss of combined water is again retarded so that the expulsion of the last portions proceeds slowly. This diagram further affords a sharp classification of the various clays, according to their purity, based obviously on the contents of combined water. In this manner three groups of clays are differentiated—kaolin, fire clay, and impure clays. An interesting fact brought out is the presence of a surface clay in the middle group. This may be explained by the fact that this particular material is a Georgia clay of the ball clay type, rendered impure by the presence of an excessive amount of ferric oxide. Again, it is apparent that the kaolin and fire-clay groups possess clay substance very closely akin in mineralogical structure, since both show strong parallelism in regard to the temperature range at which maximum loss in weight occurs. The shales, the impure fire clay, and surface clay, on the other hand, differ decidedly, inasmuch as the loss curve covers a far wider range of temperature, and for this reason we are justified in assuming that the clay substance represents another type of material. The statement commonly made that the plastic sub-

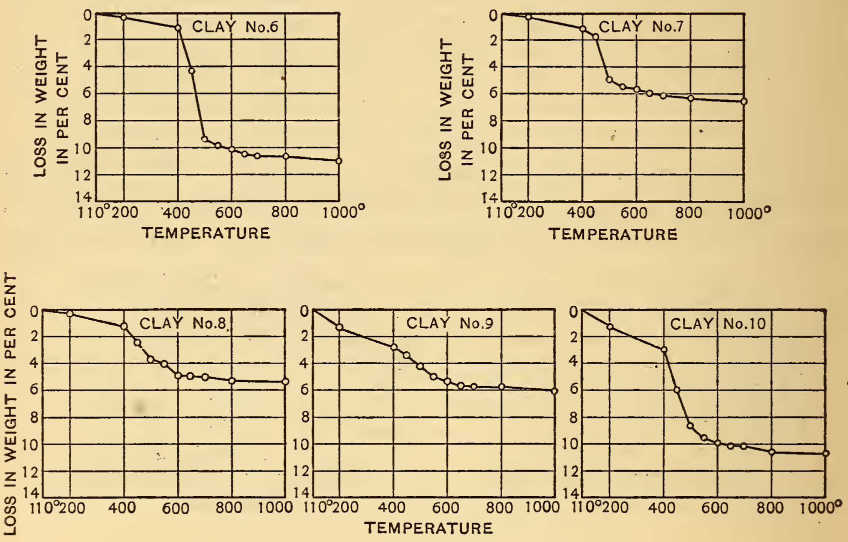

Fig. 4.—*Diagram showing loss in weight at different temperatures*

stance of all clays is of the same type, therefore, is in error. Attention must again be called to the fact that the loss in weight does not represent the true loss of combined water, owing to the changes occurring in connection with the combustion of the carbon, the oxidation of ferrous iron, the dissociation of pyrite, and the decomposition of calcium carbonate. These factors evidently are more pronounced in the impure clays than in the purer ones. However, the variations thus introduced are not sufficient to overthrow the general result as regards the essentially different rate of dissociation prevailing for the ferruginous clays and shales.

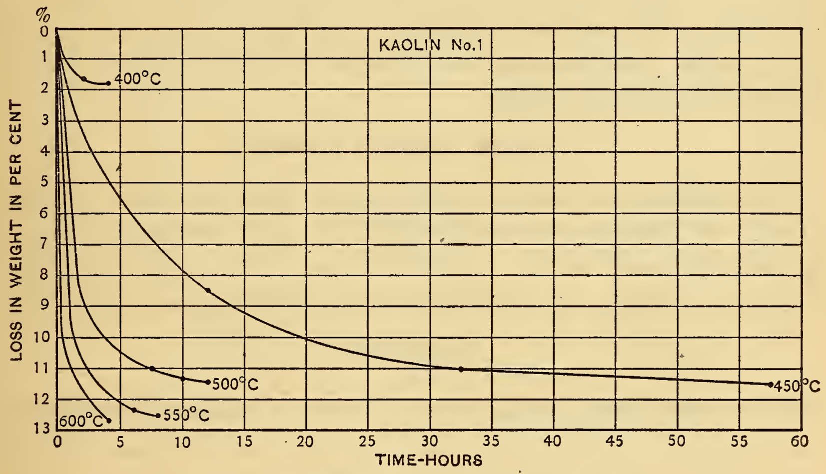

Fig. 5.—*Diagram illustrating rate of loss in weight*

An interesting feature of the dehydration process is the difficult elimination of the last portions of combined water. It is observed that at about 550° the rate of dehydration slows up very markedly. It is found, for instance, that with N. C. kaolin the chemical water expelled at 550° represents but 1.672 of the two molecules of H_2O, while for the Georgia kaolin and the Maryland flint clay these amounts are 1.73 and 1.795 molecules, respectively. This fact points out the necessity for thorough ignition to insure the complete dehydration of clay, and in addition seems to indicate a firmer union of the remaining portion of the water with the kaolin molecule than is shown by the part leaving between 450° and 550°. The rate of loss upon heating 10-gram pieces of kaolin is shown in the diagram of Fig. 5, from which it is seen that the velocity of the reaction increases rapidly with the temperature, but that it slows down as the curve approaches the amount of maximum loss. Thus, after four hours of heating the losses in weight were as follows: 1.75 per cent at 400°, 5 per cent at 450°, 10.1 per cent at 500°, 11.8 per cent at 550°, and 12.7 per cent at 600°. The run at 450° was carried on for 57½ hours and a loss of 11.5 per cent was reached. This shows that the bulk of the combined water can be expelled at the lower temperatures and it is possible that even all of it might be removed after a long-continued period of heating.

3. SPECIFIC GRAVITY CHANGES

This constant was carefully determined upon pulverized samples of eight of the clays heated under the usual precautions found necessary for such work. In order to point out more clearly the changes in density in correlation with the loss in weight, the curves showing the latter are replotted. The numerical results of the work are shown in Table 2 and are presented graphically in Figs. 6 and 7. As is to be anticipated, the purer clays show a much more marked decrease in density—i. e., increase in volume—

TABLE 2

Specific Gravity After Heating for 4 to 6 Hours at Indicated Temperatures

Clay	200°	400°	450°	500°	550°	600°	650°	700°
1	2. 600	2. 570	2. 480	2. 440	2. 480	2. 485	2. 490	2. 490
2	2. 600	2. 580	2. 520	2. 460	2. 485	2. 490	2. 500	2. 490
3	2. 650	2. 640	2. 630	2. 530	2. 590	2. 600	2. 590	2. 600
4	2. 720	2. 720	2. 710	2. 570	2. 580	2. 580	2. 580	2. 580
5	2. 690	2. 685	2. 650	2. 570	2. 610	2. 605	2. 615	2. 615
6	2. 620	2. 600	2. 550	2. 475	2. 500	2. 530	2. 560	2. 580
7	2. 790	2. 750	2. 730	2. 720	2. 710	2. 700	2. 710	2. 710
8	2. 740	2. 750	2. 750	2. 730	2. 715	2. 715	2. 700	2. 705
9	2.755	2.765	2. 730	2. 700	2. 690	2. 690	2. 670	2. 675
10	2. 625	2. 650	2. 565	2. 555	2. 595	2. 610	2. 615	2. 625

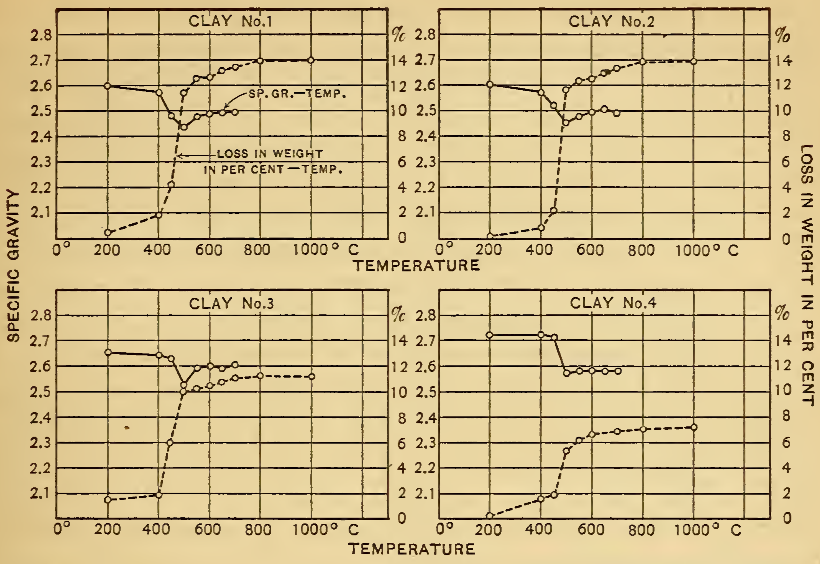

Fig. 6.—*Diagram showing specific gravity and loss in weight at different temperatures*

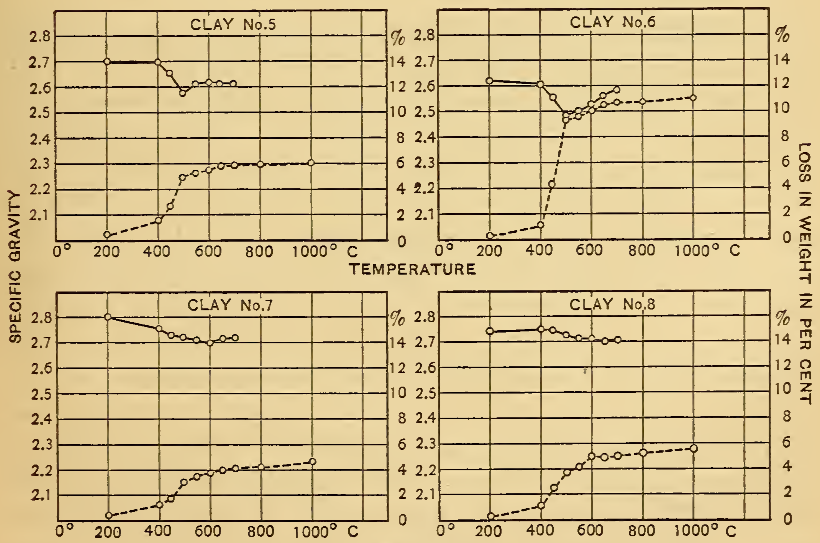

Fig. 7.—*Diagram showing specific gravity and loss in weight at different temperatures*

than the more impure ones. The interesting point in this connection is the sharp minimum shown at 500°, coincident with the greatest drop of the loss in weight curve. It would seem, then, from the specific gravity curve that the true dehydration temperature, the point at which the vapor tension is equal to the atmospheric pressure, might be located at approximately 500°. It is significant in this connection that the specific gravity curve shows such a decided reversal at the minimum point, which is rather unexpected. With the more impure clays the point of minimum density is recognized more difficultly or is not emphasized at all. According to Sokoloff, the maximum solubility of kaolin in hot hydrochloric acid is not reached before 700°. This condition is retained until 800°, when a sudden drop in solubility occurs between 800° and 900° and the clay becomes inert. It is quite evident that the exothermic reaction or transformation observed in the time-temperature curves is coincident with the sudden inert condition of the clay.

4. RESIDUAL PLASTICITY OF CLAYS

In this part of the work cylindrical specimens of clay, weighing from 80 to 90 grams, were prepared and dried at 110°. These were then heated to practically constant weight at several temperatures in an electric furnace. The pieces were then pulverized and made up again with water into cyclindrical shapes. The volume of these were at once determined in a volumenometer, using kerosene as the measuring liquid. The specimens were then dried and heated at 110°, upon which the volume was again determined. It was desired to show at what temperatures the clays lost their plasticity, using the working behavior and the drying shrinkage as a criterion of the plastic condition. In this connection the initial plastic state was subject to certain variations owing to the difficulty of establishing a uniform condition of consistency for all specimens. This condition became more difficult to control as the clays approached the granular nonplastic state. The numerical results are compiled in Tables 3 and 4.

TABLE 3

Drying Shrinkage, in Per Cent of Dry Volume, After Preheating to Indicated Temperatures

Clay	Air dry	110°	350°	400°	450°	500°	550°	600°	650°	700°	750°	800°
1	16.42	16.28	20.20	16.15	12.58	11.97	12.48	11.90	....	......	....	......
2	19.69	19.30	15.98	13.44	9.34	7.86	6.11	6.94	....	......	....	......
3	42.70	38.02	22.12	14.08	8.16	9.75	7.33	8.03	....	......	....	......
4	18.55	18.67	14.25	14.80	10.89	12.59	12.50	11.67	....	......	....	......
5	18.70	16.20	14.60	13.82	13.50	14.42	13.23	11.12	....	9.97	10.12	7.94
[15] 6	8.17	8.78	7.87	8.78	5.44	6.40	5.58	....	....	......	....	......
7	17.29	17.18	14.56	14.03	13.83	16.08	15.62	13.72	11.25	9.30	7.26	......
8	15.30	14.78	12.92	13.28	13.21	15.23	14.22	13.70	10.42	9.58	9.26	5.82
9	44.30	39.50	11.93	9.46	8.89	8.37	7.72	7.40	....	......	....	......
[16] 10	37.40	36.55	13.70	11.12	7.55	4.78	....	....	....	......	....	......

[15] At 600° test pieces crumbled.

[16] At 550° test pieces crumbled.

TABLE 4

Water of Plasticity, in Per Cent of the Dry Weight, After Preheating to Indicated Temperatures

Clay	Air dry	110°	350°	400°	450°	500°	550°	600°	650°	700°	750°	800°
1	32.32	32.03	38.48	37.90	42.39	46.83	46.66	48.67	....	....	....	......
2	32.33	32.22	32.56	31.60	34.83	36.85	37.30	38.65	....	....	....	......
3	47.40	44.50	38.50	36.65	40.30	44.20	42.70	46.70	....	....	....	......
4	21.35	21.40	19.65	21.38	22.35	24.70	26.45	26.92	....	....	....	......
5	22.65	22.20	21.40	22.18	24.56	25.97	26.80	27.10	26.42	25.30	26.55	28.58
6	15.30	15.28	16.78	17.43	19.70	22.00	22.18	23.80	....	....	....	......
7	20.99	21.25	21.67	22.08	24.55	25.20	25.92	25.65	26.20	25.73	28.80	......
8	24.65	23.45	23.50	23.85	24.23	28.25	28.95	30.15	29.00	28.92	30.70	32.20
9	35.48	34.68	28.25	28.80	28.45	30.83	31.75	33.55	....	....	....	......
10	39.55	36.85	32.20	34.80	37.20	38.55	42.40	39.52	....	....	....	......

The several clays showed peculiarities in behavior after preheating which are summarized as follows:

No. 1. North Carolina kaolin.—After preheating to 110° the plasticity was found to be the same as that of the air-dried sample. Upon heating to 350° a slight decrease in plasticity was observed which was apparently not diminished by carrying the temperature to 400°. At 450° a considerable decrease in the plastic behavior was observed, the clay becoming granular in structure.

This condition became more marked by heating to the higher temperatures.

No. 2. Georgia kaolin.—Preheating at 110° caused a slight decrease in plasticity. A quite noticeable decrease occurred at 350° which was slightly more marked at 400°. At 450° another decided change toward the nonplastic condition took place and the granular structure became apparent as in clay No. 1. At 650° and 700° there was no further change. A significant loss in plasticity was caused by heating at 750°, and at 800 the plasticity was entirely destroyed.

No. 3. Tennessee ball clay, No. 3.—This clay appeared to suffer a slight decrease in plasticity at 110° over that of the air-dried sample. At 350° a decided decrease in plasticity was observed, the clay being no longer "sticky," but having the working qualities of a No. 2 fire clay. At 400° there was a further large loss of the plastic quality, the clay assuming the granular structure observed in the two kaolins when heated to 450°. Heating at 450° developed a granular, sandy structure.

No. 4. Fire clay of second grade.—The plasticity of this clay was not materially decreased when heated to a temperature below 450°. At this point the material suffered a decided decrease in plasticity, although it still retained a fair working property. At 500° an additional loss on plastic behavior was noted, a condition not changed by heating to 550°. A somewhat granular structure was developed at 600°.

No. 5. Plastic fire clay.—Only a slight decrease in plasticity was noted upon heating to 350° with no further change caused by carrying the temperatures to 400° and 450°. The clay appears somewhat granular upon first adding water but the plastic state is rapidly developed. This condition persists at 500° and with practically no further change at 550°. At 600° an appreciable decrease is noted, although the material is still quite plastic. Smaller losses in plasticity are observed at 650° and 700°. At 750° the clay lost its ability to be molded.

No. 6. Flint clay.—The initial plasticity of the flint clay was small and decreased slightly with the temperature of heating. The test pieces could not be molded after heating to 600°.

No. 7. Shale.—At 110° there was no appreciable decrease in plasticity over that in the air-dried condition. At 350° there appeared to be a slight increase in plasticity as is shown by the improved molding properties. At 400° the working quality was bettered still more and no further change appeared to take place at 450°, 500°, and 550°. A very slight decrease in plasticity was observed at 600°, a condition somewhat emphasized at 650° and 700°. A large decrease in plasticity occurs at 750° and the working properties are destroyed.

No. 8. Shale.—The behavior of this shale is similar to that of No. 7, the plasticity being retained without decrease at temperatures below 650°.

No. 9. Surface clay.—This clay is exceedingly "sticky" and dries with difficulty. When preheated at 110° no decided change in plasticity was noted. At 250° the material loses its stickiness and has improved working qualities. At 300° there is a further reduction in plasticity and at 350° this property is entirely destroyed, the structure becoming granular. This condition is not changed by heating at the higher temperatures.

No. 10. Surface clay.—This clay also possesses excessive plasticity and is decidedly "sticky" in its nature. No reduction is caused by heating at 110°. At 250° the stickiness disappears and the working quality is improved. A further decrease in plasticity occurs at 300°. Heating at 350° develops a granular structure with poor working properties. At 400° and higher temperatures the plasticity is destroyed.

In the diagrams of Figs. 8 and 9 the volume shrinkage and water contents of the clays after preheating at the several temperatures are shown. It appears from the shrinkage curves that the plastic clays are far more sensitive to the heat treatment than are the less plastic ones, while the shales show surprising resistance and even seem to become more plastic at 350° to 400°. Excessively plastic clays become more workable at the latter temperatures and their rate of drying seems to be increased. The order in which the working plasticity of the several types of clays is destroyed is as follows: Surface clays, 400°; ball clay, 450°; kaolins, 600° and 500°, the more plastic one being affected more than the one less so; No. 2 fire clays, 600° and 750°; shales 750° and 800°. By comparing the shrinkage with the working behavior it is apparent that the former is by no means a criterion of the plasticity and does not express the effect of the granular structure caused by the agglomeration of the clay mass. Upon examining the water content of the clays after preheating, Fig. 9, it is shown that a more or less pronounced break occurs in the water content at 350° and 400°, with 9 of the 10 clays. Beyond this point the amount of water required to produce a mass which can be molded increases decidedly and may be equal to or greater than the weight contained in the natural plastic clay. Part of the water added penetrates more deeply into the clay structure to replace the so-called hygroscopic or absorbed water and even a portion of the combined water which has been expelled. In addition it would fill the space previously occupied by any organic matter which has been volatilized or oxidized, and a portion no doubt is used to occupy the larger pore space of the clay caused by agglom-

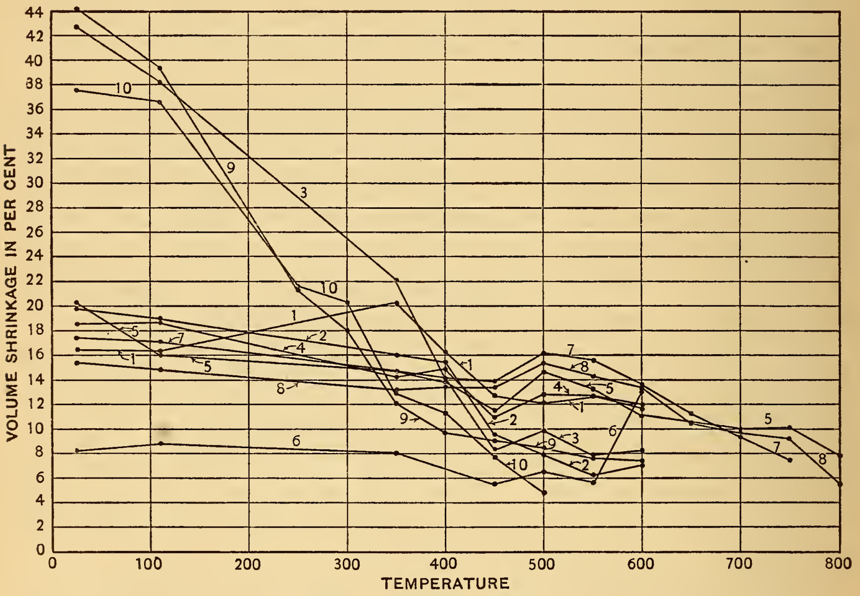

Fig. 8.—*Volume shrinkage of clays after preheating to different temperatures*

eration. A study of the distribution of the water as shrinkage, pore and residual water would undoubtedly be more valuable in correlating the loss in plasticity than the determination of volume shrinkage.

There can be no doubt but that the more or less pronounced break in the water content curve represents a critical temperature at which significant changes in the clay structure takes place. The production of a granular structure in the case of the plastic clays and the expulsion of the hygroscopic moisture are closely connected with this transformation. At 500°, at which temperature one should expect some significant changes, none are apparent except in the shrinkage curves where a number of the clays show a more or less marked maximum, to which, however, in the face of the possible variations in the water content, no special importance can be attached.

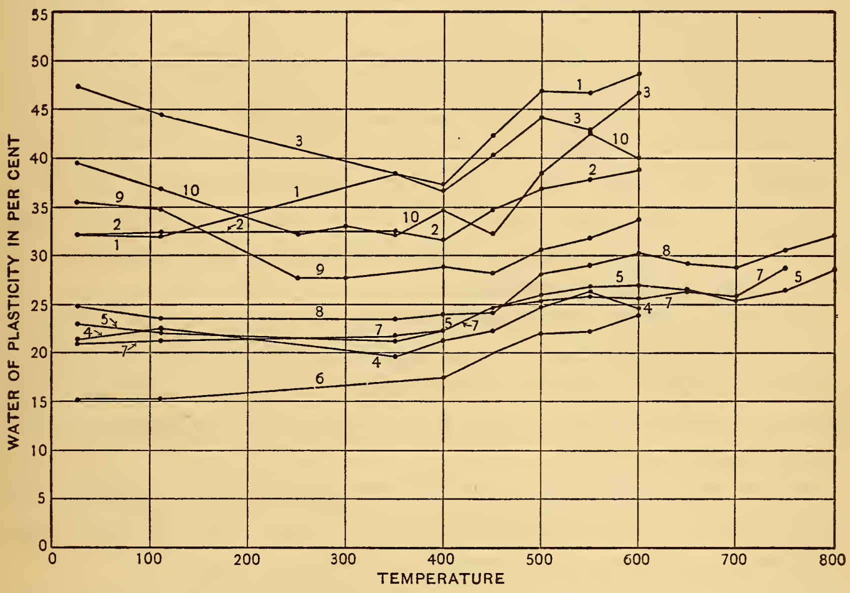

Fig. 9.—*Water required to produce plastic condition after preheating to different temperatures*

This work seems to prove also that the presence of organic compounds is not a primary factor in the property of plasticity since shales show good plastic qualities after heating to temperatures at which without question the carbon is completely burnt out. There can be no doubt that organic material has an important influence upon the plasticity of clays, but it is of a supplementary rather than a fundamental character.

III. SUMMARY

All of the combined water of clay is not part of the clay base in the sense of water of hydration. For this reason clay can not be said to possess a definite dehydration temperature. The combined water is expelled at comparatively low temperatures so that even at 450° C the bulk of it may be driven off. In heating clay to constancy in weight at different temperatures the velocity of the reaction is very slow at first and becomes suddenly rapid at 500°. The remaining portion of the water is removed more slowly, so that a temperature of not less than 800° is required to accomplish complete expulsion.

The distinctness of the endothermal lag as well as the total loss in weight upon ignition (excluding abnormal loss due to carbon, sulphur, etc.) are criteria of the purity of a clay. Likewise the thermal acceleration at about 850° is shown more clearly by the higher types of clay.

It has been shown that the clay substance of the impure clays represents a type essentially different from that of the purer materials, contrary to the generally accepted view.

A well-defined minimum is shown in the specific gravity curve of clays, located at approximately 500°.

Dehydration does not necessarily destroy the plasticity of clays, and hence the combined water appears to have no direct connection with the phenomenon of plasticity. Shales are least affected by heating within the dehydration temperature range, and in fact seem to be improved in plastic working behavior after preheating to about 500°. The surface clays examined lose their plasticity at the lowest temperatures, about 400°, followed by ball clay, at 450°, kaolin 500° to 600°, No. 2 fire clays 600° to 750°, and shales 750° to 800°.

It was likewise shown that the presence of organic compounds can not be a primary cause of plasticity, since these are oxidized in an atmosphere of pure air at about 500°. It was shown quite clearly that drying shrinkage is not a true criterion of plasticity, contrary to the statement of Rohland, who makes the claim that this contraction is the best measure of the property in question.

In connection with this work the writers wish to express their indebtedness to Mr. A. V. Bleininger for assistance in reviewing the results.

WASHINGTON, April 25, 1913.

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