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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.]

**AN EXPERIMENT UPON THE INFLUENCE OF THE FINE-  
NESS OF GRINDING UPON THE CLINKERING OF  
PORTLAND CEMENT.**

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IN A paper entitled "Some Preliminary Experiments upon the Clinkering of Portland Cement,"<sup>1</sup> one of the authors has reported some results obtained in a laboratory rotary cement kiln. The calcium carbonate used in all the preliminary experiments was in the form of a very light marl, so that when clinkering took place it was accompanied by very marked contraction in volume. It was suggested that a burning on raw material, such as is used in the cement mills of Eastern Pennsylvania, might give somewhat different results from those obtained from the light marl mixed with clay, and so it was decided to make a couple of experiments with rock-cement mixtures. The material employed in the two experiments, to be later described, was a ground raw mixture just as it is fed into the rotary for the dry process. This raw mixture is that used by one of the best Lehigh Valley mills and was furnished for these experiments through the courtesy of the management.

<sup>1</sup> This Journal, 24, 959.

Before detailing the experiments made upon the cement-rock mixture, we wish to describe the method now employed in this laboratory for determining the actual temperature attained by the pieces of clinker in passing through the rotary. In the first papers published by one of us on "A Rotary Cement Kiln for use in the Laboratory,"<sup>1</sup> the method of measuring the temperature of the furnace is described. In this method, the temperature attained by a Le Chatelier thermocouple, insulated with porcelain tubing and protected with sheet platinum, is observed. But this temperature was supposed to be  $35^{\circ}$  to  $40^{\circ}$  C. lower than that attained by the clinker. The temperatures given in the paper, first quoted in this article as representing the temperatures attained by the clinker, are based on the assumption that the clinker becomes  $35^{\circ}$  hotter than the protected thermocouple. It is true that if the bare couple be placed in the rotary, it will reach a higher temperature than that shown by the protected couple. This does not, however, warrant the assumption that pieces of clinker in contact with the rotary lining will attain as high a temperature as the bare couple. It was because of the feeling that the relation between the temperature of the clinker and that of the fixed couple was not what we have assumed in our previous work, that a series of experiments was made to determine the relation of these temperatures. A calibration of the fixed thermocouple was made, as in our previous work, by careful comparison of the electromotive force with that of a couple standardized by the physikalische-technische Reichsanstalt. The electromotive force at the melting-point of strictly pure platinum was also determined, and used in the calibration. Although an entirely new set of thermocouples and galvanometer were used in the present experiments, the temperatures recorded for the fixed thermocouple agreed within the limits of experimental error with those of our previous work. In order to determine the relation between the temperature attained by pieces of clinker and that observed at the fixed thermocouple, the following method was used: About 2 kg. of magnesite brick were crushed, and, after mixing with one-ninth its weight of a rather fusible clay, was ground to a fine powder. This mixture was moistened with enough water to enable it to be rolled out and cut into cubes, of about three-eighths inch, which were then dried. These cubes were passed through

<sup>1</sup> This Journal. 24, 248.

the rotary at a full heat, the result being hard, well-sintered, but infusible "magnesite clinkers." A Seger cone of the standard size was placed in an assay muffle, the temperature of which was then raised until the top of the cone bent over enough to touch the bottom—the method usually employed for standardizing these cones. The extent to which this cone had rounded at the corners, etc., gave a standard with which to compare pieces of cone which had passed through the rotary. In testing the temperatures attained by the clinker in the rotary, a cone of low fusing-point ( $990^{\circ}\text{C}.$ ) was first employed. Cones of this softening-point were broken into pieces of as nearly as possible the same size as the "magnesite clinker." When the rotary was filled with the magnesite, a piece of the cone was fed with the magnesite every four or five minutes. The temperature was gradually raised until the pieces coming out showed an extent of softening or fritting equal to that of the standard cone. This point was usually quite sharply defined, as when the pieces of cone attained this condition they would begin to stick either to each other or to adjacent pieces of magnesite. In this way our experiments were made with a number of cones of a higher softening-point, up to between  $1500^{\circ}$  and  $1600^{\circ}\text{C}.$  These experiments showed that at the lower temperature the clinker does not get as hot as the fixed couple, but that it approaches the temperature of the fixed couple as the heat is raised, until at about  $1270^{\circ}\text{C}.$  they are equal. At temperatures above  $1270^{\circ}\text{C}.$ , the clinker is hotter than the thermocouple, this difference amounting to very nearly  $19^{\circ}$  at  $1600^{\circ}\text{C}.$  The relation of the "clinker temperature" to that observed at the fixed couple is shown in the following table:

TABLE I.

Observed temperature. $^{\circ}\text{C}.$	Clinker temperature. $^{\circ}\text{C}.$	Difference.
1000	984	-16
1100	1090	-10
1200	1196	- 4
1300	1302	+ 2
1400	1407	+ 7
1500	1513	+13
1600	1619	+19

The "clinker temperatures," reported in experiments 104-105 to be described, were determined according to this table. The "clinker temperature," in our previously reported work, can be

easily derived by first subtracting  $35^{\circ}$ , thus obtaining the "observed temperature," and then applying the necessary correction according to the above table.

#### EXPERIMENT 104.


























The material used in this experiment was, as mentioned earlier in this paper, the ground raw mixture just as it is fed into the rotaries of one of the leading Eastern cement-mills employing the dry process. The chemical composition of this mixture will be described under Experiment 105. A mechanical analysis of the raw mixture gave the following figures:

	Per cent
Retained on 50-mesh sieve .....	3.1
"    "    100    "    " .....	11.3
"    "    200    "    " .....	13.2
Through 200-mesh sieve .....	77.4

This raw mixture was moistened with just enough water to allow it to be rolled out and cut into small cubes, as done in our previous work. The rotary furnace was fed with this prepared material, and samples of from 80 to 100 grams each were collected at twenty-five different temperatures ranging from  $993^{\circ}$  to  $1612^{\circ}$  C. When the desired amount of clinker had been collected at any given temperature, the temperature of the furnace was raised up to the next higher point desired, and the first 60 to 70 grams of clinker leaving the furnace rejected before the final sample was kept. The 60 to 70 grams of clinker, rejected between the sample saved, is the amount required to fill the furnace from the hot zone to the discharge end and, consequently, represents the clinker formed at heats intermediate between the desired temperatures. The change in appearance of the samples of clinker is shown in Plate I, made from a full-sized photograph.

Samples of these clinkers were ground with 1.5 per cent. calcium sulphate (dehydrated gypsum). The methods employed for determining the water required for normal consistency, the initial and final sets, and boiling tests were those employed in our previous experiments. The data obtained from Experiment 104 are summarized in the following table:

# Ex 104 PLATE I

1 993° 	2 1028° 	3 1058° 	4 1081° 	5 1110° 
6 1134° 	7 1165° 	8 1187° 	9 1216° 	10 1247° 
11 1270° 	12 1295° 	13 1318° 	14 1342° 	15 1369° 
16 1393° 	17 1418° 	18 1445° 	19 1469° 	20 1493° 
21 1520° 	22 1545° 	23 1570° 	24 1603° 	25 1612° 

Temp. in degrees Cent.



TABLE II, EXPERIMENT 104.

Sample number.	Clinker temperature.	Water. Per cent.	Initial set.		Final set.		Boiling test.
			Hours.	Minutes.	Hours.	Minutes.	
1	993	39	..	24	3	53	Perfect pat.
2	1028	48	..	30	3	58	" "
3	1058	54	..	30	4	20	" "
4	1081	66	..	35	4	33	" "
5	1110	76	..	41	5	38	Badly cracked.
6	1134	75	..	48	6	5	Badly cracked, broken up, loose from glass.
7	1165	76	..	17	1	45	{ Cracked after twenty-four hours. Boiling test, badly cracked and broken up.
8	1187	60	..	1	..	16	Slightly cracked and warped, loose from glass, quite strong.
9	1216	55	..	½	..	19	Loose from glass, moderately strong.
10	1247	47	..	1	..	6	Badly cracked, disintegrated, very weak.
11	1270	43	..	1	..	4	Warped, cracked, almost completely disintegrated.
12	1295	38	..	2	..	4½	" " " " " "
13	1318	37	..	3	..	11	Completely disintegrated.
14	1342	32	..	7	1	38	" "
15	1369	31½	..	12	1	26	" "
16	1393	30½	..	23	4	8	Completely disintegrated, coarse-grained.
17	1418	28½	..	33	4	..	Almost completely disintegrated.
18	1445	26	..	21	3	48	" " "
19	1469	26	..	33	3	50	Slightly warped, badly cracked, very weak.
20	1493	26½	..	13	2	53	Slightly warped, cracked, very weak.
21	1520	25½	..	34	4	9	Badly warped, cracked, very weak.
22	1545	25	1	..	5	..	Slightly warped, cracked, quite strong.
23	1570	24	..	50	4	6	" " " " "
24	1603	23	..	32	3	50	{ Badly warped, cracked very weak. (This sample was ground too coarsely.)
25	1612	23½	..	17	3	48	Very slightly warped, cracked, very strong.

The appearance of the pats from Experiment 104 is shown in Plates II, III, IV and V.

#### EXPERIMENT 105.

The material used in this experiment was the same raw material as that used in Experiment 104. Before adding water and molding into cubes for burning, the dry mixture was ground in a pebble mill for five hours. The jar in which the grinding was done had a special lining made for this purpose of the best Berlin porcelain. The pebbles used were carefully selected, smooth flints. A mechanical analysis of the mixture after five hours' grinding gave the following results:

	Per cent.
Retained on 100-mesh sieve.....	0
"    "    200    "    "    .....	2
Through 200-mesh sieve.....	98

That material ground in this porcelain-lined jar mill does not take up sufficient impurities to seriously alter the composition was determined in two ways: First, 2 kilograms of crushed crystalline calcite were ground for three hours. The combined per cent. of silica, alumina, and ferric oxide before grinding was 0.71; after grinding three hours, the material showed 0.75 per cent. Second, the clinker from Experiment 104 gave total silica and undecomposed silicates, 22.02 per cent., while that from Experiment 105 gave 22.06 per cent.

The raw mixture used had the following composition:  $\text{SiO}_2$ , 14.09;  $\text{Al}_2\text{O}_3$ , 5.94;  $\text{Fe}_2\text{O}_3$ , 1.67;  $\text{CaO}$ , 41.21;  $\text{MgO}$ , 1.76;  $\text{SO}_3$ , 0.39; loss on ignition, 34.60. The finely ground, raw material was mixed as in the previous experiment with enough water to allow it to be rolled out and cut into cubes for burning. From this prepared material, twenty-four samples of the clinker were collected at temperatures ranging from  $1022^\circ$  to  $1627^\circ$  C.

The composition of the clinker produced at some of the higher temperatures was as follows: Total  $\text{SiO}_2$ , 21.55; total  $\text{Al}_2\text{O}_3$ , 9.09;  $\text{Fe}_2\text{O}_3$ , 2.56;  $\text{CaO}$ , 63.01;  $\text{MgO}$ , 2.73;  $\text{SO}_3$ , 0.60; total 99.56 per cent.

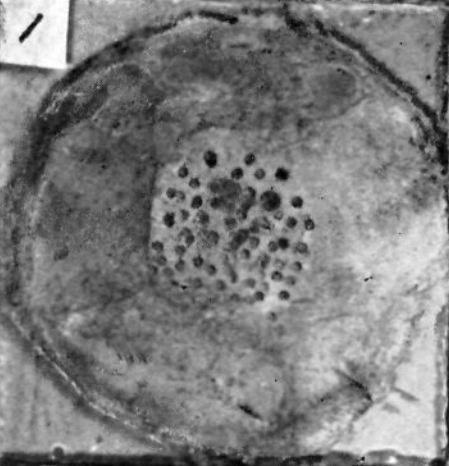
The molecular ratios in the clinker calculated to the basis of 100 molecules of silica are as follows:  $\text{SiO}_2$ , 100;  $\text{Al}_2\text{O}_3$ , 24.9;  $\text{Fe}_2\text{O}_3$ , 4.5;  $\text{CaO}$ , 315.2;  $\text{MgO}$ , 19.1. The appearance of the clinkers is shown in Plate VI.



Exp. 104

PLATE II

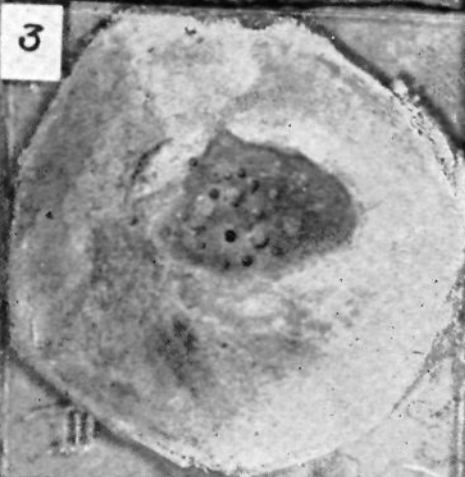
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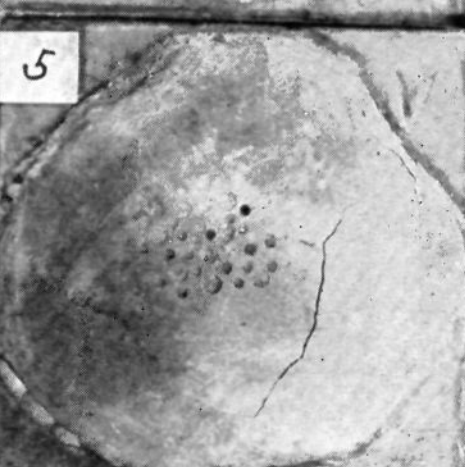
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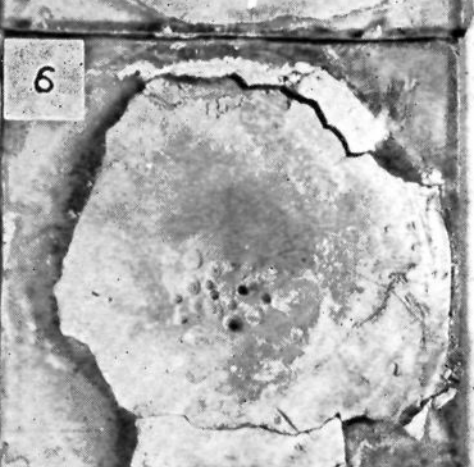
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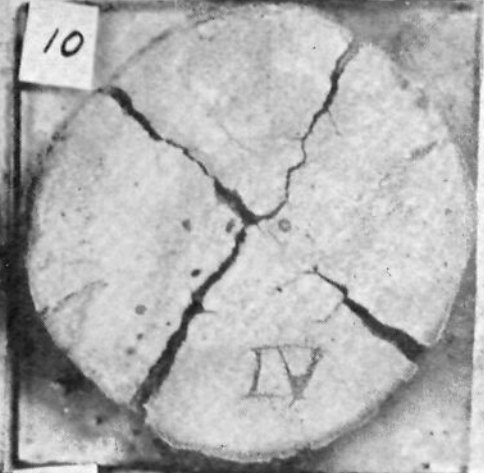
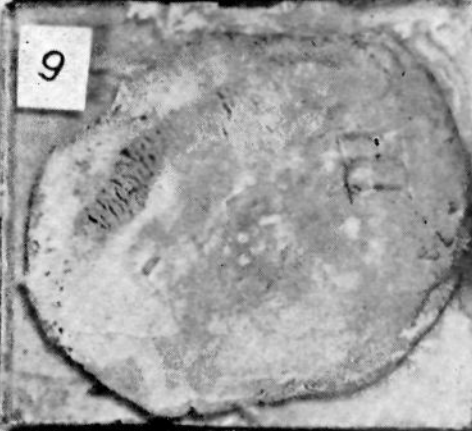
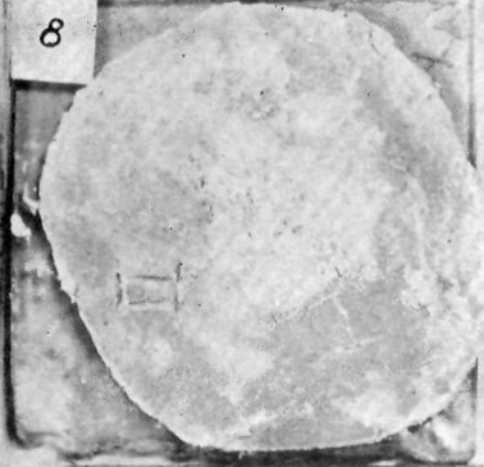
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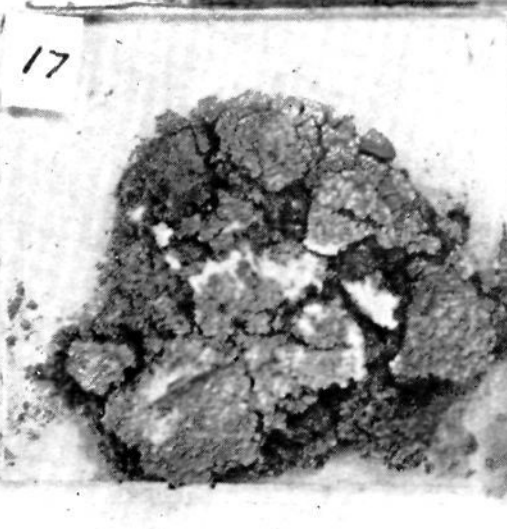
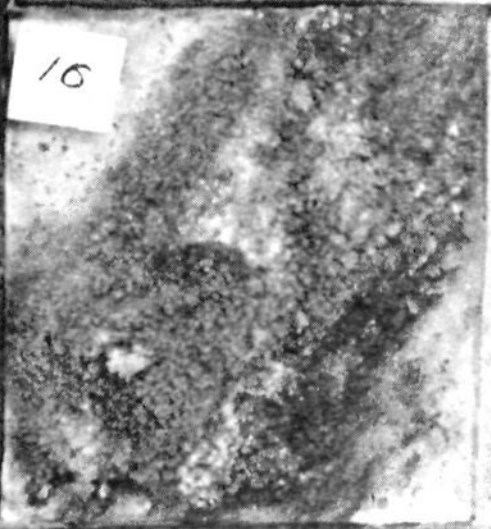
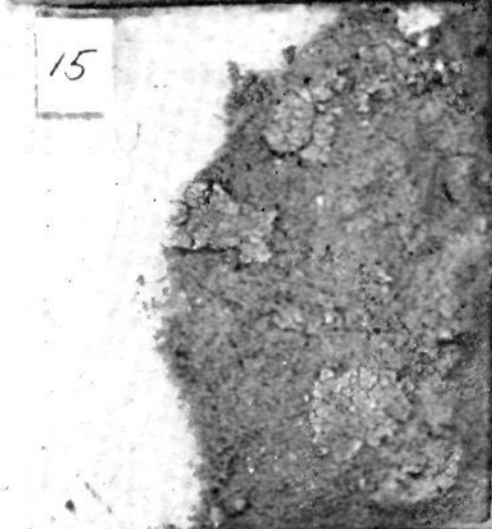
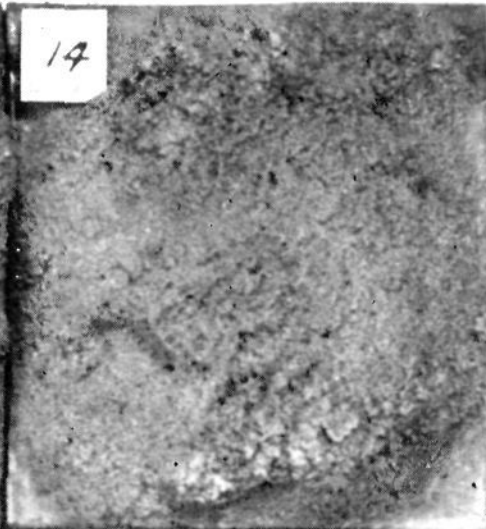
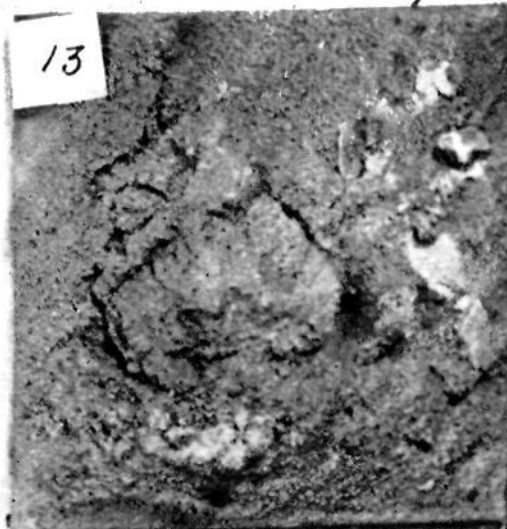
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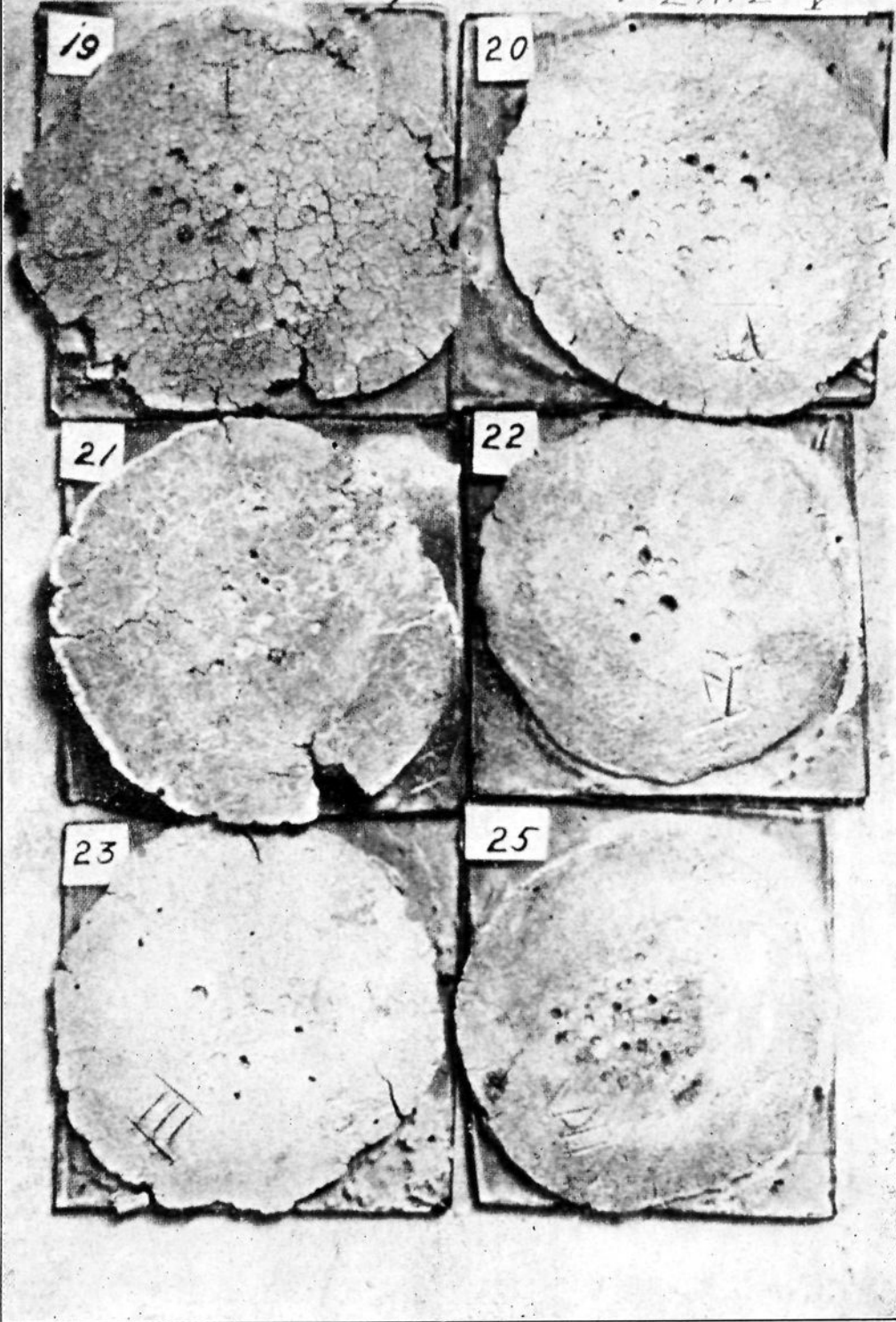
Exp. 104 PLATE III



Exp. 104 PLATE IV
















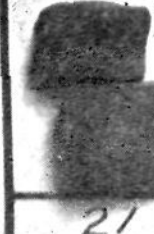


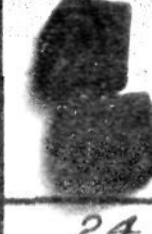







Exp. 104 PLATE V





# Exp. 105 PLATE VI

1 1022° 	2 1049° 	3 1071° 	4 1101° 	5 1124° 
6 1148° 	7 1174° 	8 1198° 	9 1224° 	10 1247° 
11 1281° 	12 1301° 	13 1327° 	14 1352° 	15 1378° 
16 1401° 	17 1425° 	18 1451° 	19 1475° 	20 1501° 
21 1530° 	22 1556° 	23 1582° 	24 1627° 	

Temp. in degrees Cent.



TABLE III, EXPERIMENT 105.

Sample number.	Clinker temperature.	Water. Per cent.	Initial set.		Final set.		Boiling test.
			Hours.	Minutes.	Hours.	Minutes.	
1	1022	49	..	11	5	10	Perfect pat, quite strong.
2	1049	53	..	18	7	..	" " " "
3	1071	61	..	23	7	20	" " " "
4	1101	73	..	39	7	47	Loose from glass, slightly cracked, quite strong.
5	1124	77	..	27	7	25	Slightly warped, cracked, quite weak.
6	1148	78	..	7	5	13	Badly warped, cracked, very weak.
7	1174	77	..	5	4	..	Badly cracked, very weak.
8	1198	69	..	½	..	16	Badly cracked, warped, very weak.
9	1224	64	..	½	..	4	" " " " "
10	1247	62	..	½	3	40	" " " " "
11	1281	54	..	1	5	..	Badly warped and disintegrated.
12	1301	46	..	1	..	46	Very badly warped and disintegrated.
13	1327	44	..	1	..	29	Very badly warped, cracked, almost completely disintegrated.
14	1352	40	..	3	..	21	Completely disintegrated.
15	1378	37	..	3½	..	27	" "
16	1401	33½	..	18	3	15	" "
17	1425	32	..	10	2	22	Badly warped and cracked, almost completely disintegrated.
18	1451	30	..	14	4	45	Slightly warped, cracked, loose from glass, but quite strong.
19	1475	28	1	5	4	40	Perfect pat.
20	1501	27	..	32	4	22	" "
21	1530	28½	..	1	3	53	Perfect pat, sample slightly off color.
22	1556	26½	..	32	4	..	Perfect pat.
23	1582	24	..	21	4	..	" "
24	1627	24½	..	10	3	50	" "

Samples of these clinkers were ground with 1.5 per cent. calcium sulphate (dehydrated gypsum), and determinations of water required for normal consistency, initial and final sets, and boiling tests were made as in the previous experiment. The data obtained from Experiment 105 are summarized in Table III.

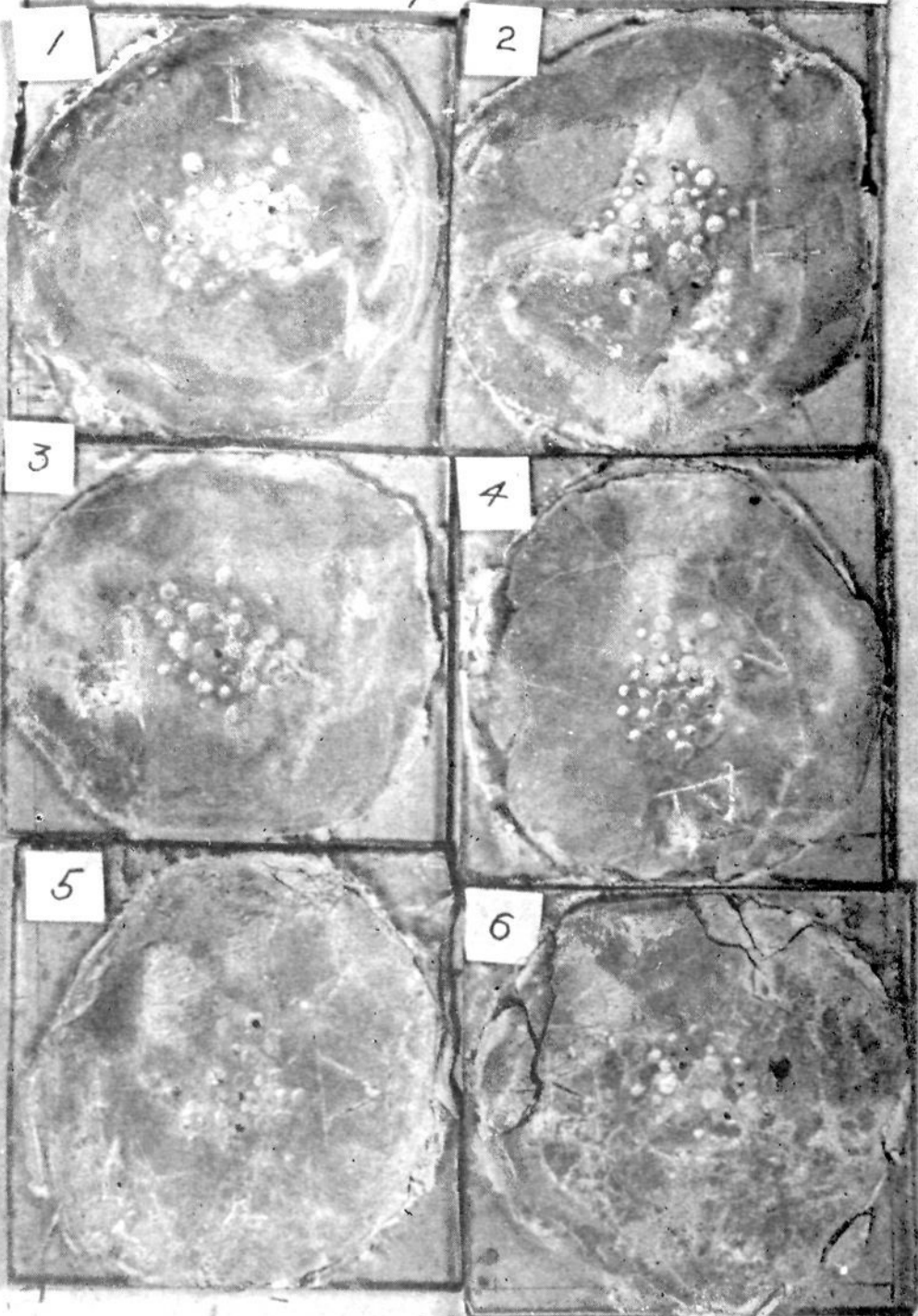
The appearance of the pats from Experiment 105 is shown in Plates VII, VIII, IX and X.

In considering the samples of Experiment 105, the conditions of formation of sample No. 21 should be taken into account. Up to sample No. 20 inclusive, the color of the clinker darkened progressively with increase of temperature. Owing to some difficulty with the hydrocarbon burner, the gasoline jet would not draw in sufficient air for complete combustion above  $1501^{\circ}$  C., at which temperature No. 20 was burned. When the valve was opened a little wider in order to raise the temperature, a small amount of carbon monoxide was produced in the gas with the result that the clinker became a little lighter rather than darker in color. Oxygen was introduced from the time No. 21 was collected with the result that Nos. 22, 23 and 24 all had the deep blackish brown color characteristic of properly burned clinker. Whether the quick initial set of No. 21 was due to the slight reducing conditions in the furnace at the time of burning, we are not prepared to state positively. It will be noticed that with the exception of No. 21, the time of the initial set, after a perfect hot test was obtained, decreased with increased temperature, but the time between the initial and the final set for these same samples was nearly constant. The influence of the atmosphere within the furnace upon the time of setting as well as upon the other properties of cement, we hope to investigate more closely at a later date.

It was thought that some light might be thrown upon the reactions of clinkering by dissolving, in dilute hydrochloric acid, some of the clinkers produced at temperatures at which there were marked changes in the physical properties of the cement. The first method employed was that usually recommended; that is, three successive boilings for five minutes each with 10 per cent. hydrochloric acid. A number of experiments, however, proved that more complete decomposition could be effected by digestion with hot hydrochloric acid than with successive boilings. If the



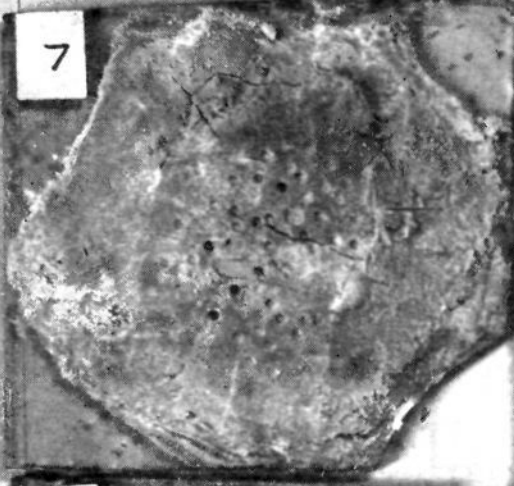
EXP. 105 PLATE VII



Exp. 105

PLATE VIII

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8



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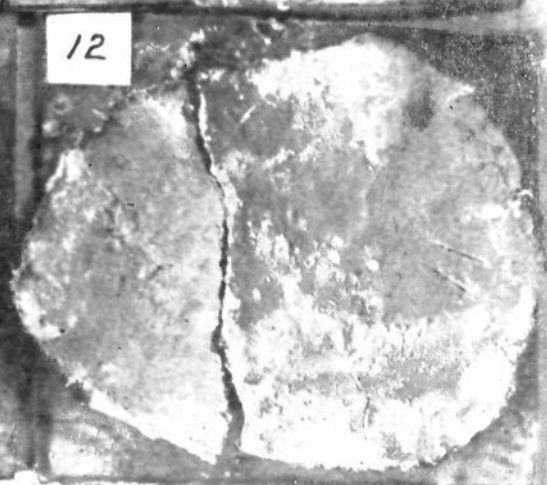
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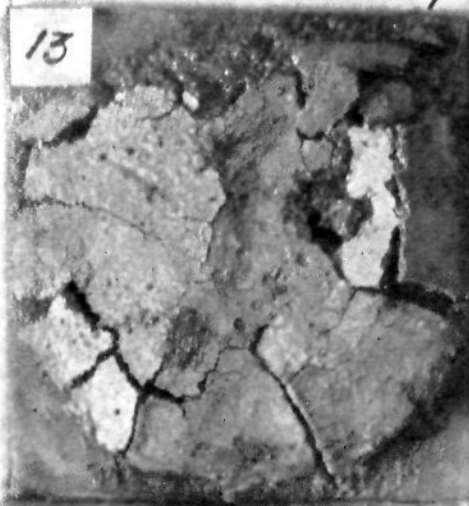


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EXP. 105 PLATE IX

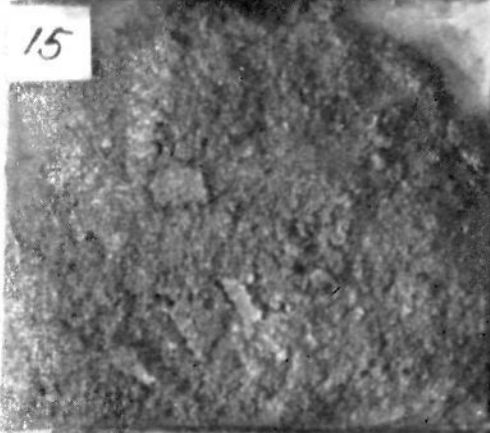
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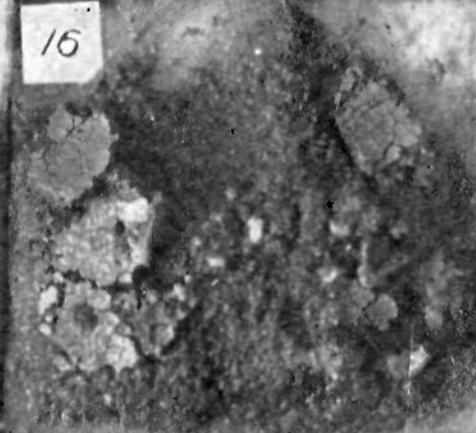
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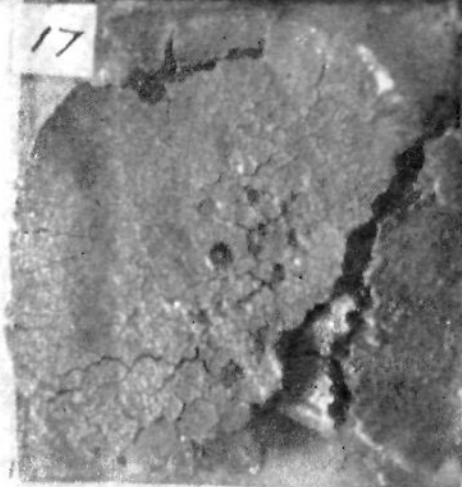
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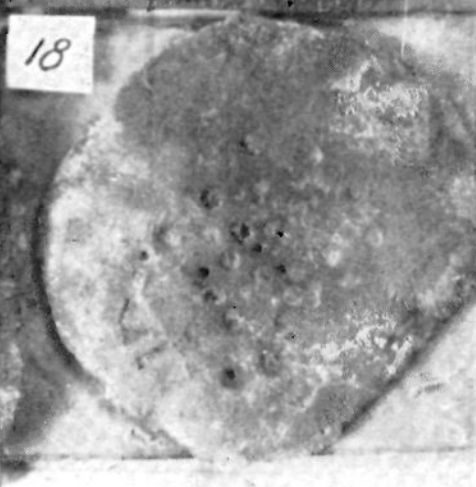
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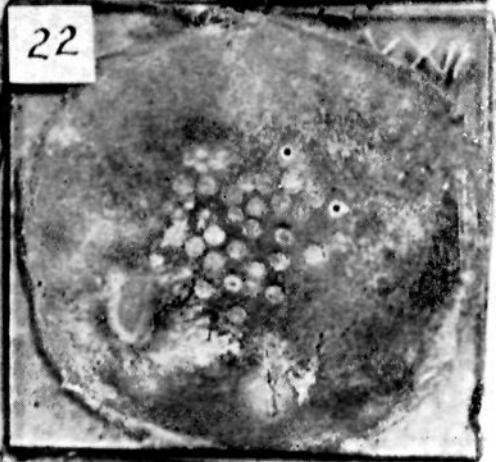
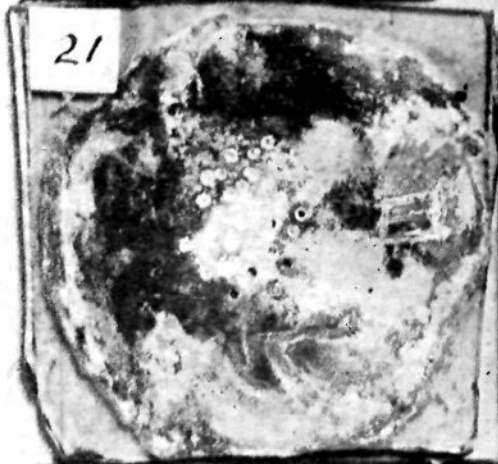
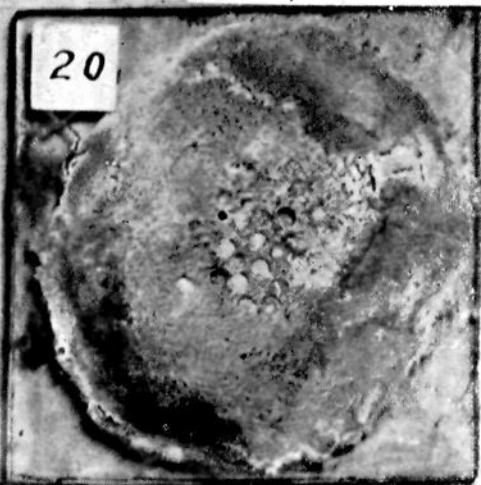
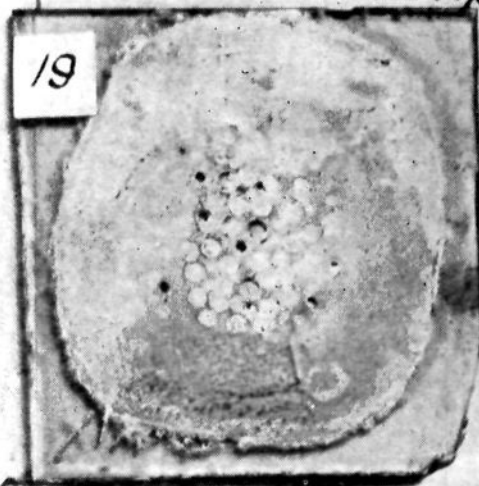
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18



EXP. 105 PLATE X



acid solution containing the cement in suspension is boiled, gelatinous silicic acid seems to deposit on some of the larger particles of cement, thus preventing the acid from effecting complete decomposition. It was found that if 0.5 gram of the cement is placed in 50 cc. of water and this boiled for from two to three minutes, then removed from the hot plate and 5 cc. hydrochloric acid (sp. gr. 1.20) added, and the solution stirred for about five minutes without further heating, the silicic acid set free nearly all remains in solution and a more perfect decomposition is apparently effected than by boiling.

Accordingly, six of the samples were treated in this way. The total silica having been determined, samples of the various clinkers examined were first boiled with water, to which was then added the hydrochloric acid, and after a few minutes' stirring the solution was filtered. The residue, after washing with acidified water until free from soluble salts, was gently ignited and weighed. The difference in weight between this residue and that obtained by the usual method of decomposition, evaporation to dryness, etc., for total insoluble residue, was taken as "SiO<sub>2</sub> soluble in HCl." The residue insoluble in hydrochloric acid was boiled in a platinum dish with 10 per cent. sodium carbonate, filtered, washed, and weighed. The loss thus obtained was reported as "SiO<sub>2</sub> soluble in Na<sub>2</sub>CO<sub>3</sub>." The residue from the digestion with sodium carbonate was treated with hydrofluoric acid, the loss giving the "SiO<sub>2</sub> by HF." The final residue was reported as "Residue from HF." With the exception of No. 1, which gave a loss on ignition of 21.03 per cent., the decomposition of the calcium carbonate of the samples examined was complete. The action of hydrochloric acid, etc., upon the six samples examined is summarized in the following table:

TABLE IV.

Sample number.	Clinker temperature.	SiO <sub>2</sub>			Residue from HF.
		sol. in HCl.	sol. in Na <sub>2</sub> CO <sub>3</sub> .	by HF.	
1	1022	5.67	1.18	10.67	4.54
6	1148	8.77	0.86	8.34	4.09
9	1224	13.92	1.19	4.09	2.86
14	1352	17.91	3.61	0.28	0.26
19	1475	19.99	1.23	0.42	0.42
24	1625	20.03	1.07	0.50	0.46

Although the results given in Table IV cannot be considered as final and will need confirmation, they indicate one or two rather interesting points.

It will be noticed that the silica, soluble in hydrochloric acid, increases with the increase in the temperature at which the clinker is produced. The silica, soluble in sodium carbonate, however, reaches a maximum in sample No. 14, burned at 1352°. The total insoluble residue after treatment with sodium carbonate, usually reported as "undecomposed silicate," is smallest (0.54 per cent.) in this same sample. The amount of undecomposed silicates seems to increase with rise in temperature above 1352°, and the proportion of silica given off on treating these undecomposed silicates with hydrofluoric acid, is about one-half their weight.

These results would go to indicate that probably all of the original silicates were converted into readily decomposable basic silicates by the time a temperature of 1352° was reached, and that the increased amount of undecomposed silicates found in the high numbers may be due to the more acid silicates left in the magma, from which the tricalcium silicate or other true cement-forming material has separated.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

### THE THEORIES OF INDICATORS.<sup>1</sup>

BY JULIUS STIEGLITZ.

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IN CONNECTION with the use of indicators in the titration of acids and alkalis there are two main questions of theoretical interest: First, what chemical change does the indicator undergo which causes it to change color, and, second, what is the cause of the characteristic differences in sensitiveness shown by such indicators as phenolphthaleïn and methyl orange towards the various acids and bases—differences which are of the greatest importance in laboratory practice.

Considering first the more interesting question as to the change of color, we find two distinct views held; but only one, the theory of Ostwald, has become generally known and has found a place

<sup>1</sup> See Stieglitz, *this Journal*, 24, 588 (1902).