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

SOME PRELIMINARY EXPERIMENTS UPON THE CLINKERING OF PORTLAND CEMENT.

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AS THE work which was begun in this laboratory about three years ago on the constitution of hydraulic cements progressed, it became more and more evident that if real progress was to be made in our knowledge of cements, the various factors entering into the problem must be considered separately. The experiments described in the present paper were performed by Messrs. C. A. Burck, A. G. Smith and W. B. Cady, and I wish here to acknowledge my indebtedness to them for the care with which they have carried on the work. The object of these preliminary experiments was to furnish a basis on which a complete series of experiments could be based which should show the exact relation between the chemical composition of a slurry and the temperature required for burning. When the exact influence of each constituent upon the property of a clinker produced at a given temperature has been determined, we may then begin to study systematically the influence of variations in mechanical treatment, subsequent to the formation of the clinker, on the properties of the finished cement.

The influence of the many factors such as fineness of grinding, ageing, per cent. of gypsum used, and the method of mixing and working, which come into play after the clinkering is completed, has been studied by others much more carefully than has the influence of each factor which determines the constitution of the clinker. Of these latter factors those which must be considered are: silica free or combined, alumina, ferric oxide, calcium oxide, magnesium oxide, the fineness of division and physical state of the raw material, the temperature, the atmosphere within the furnace whether oxidizing or reducing, and the time during which the material is under treatment. So far as we are aware the only experimental work which has been done to determine the relation of the chemical composition of the material under treatment and the temperature employed in burning, is that of A. Meyer, *Thonindustrie Zeitung*, 73, 1201, abstracted by S. B. Newberry in

Cement, **2**, 350. Meyer's results, which were obtained by most careful and painstaking experiments, illustrate better the conditions found in fixed kilns than in the rotary furnaces so generally used in this country. Meyer made three mixtures and burned each mixture nominally at four different temperatures. The material for each burning was placed in a stationary furnace and raised by means of a gas burner to a specified temperature which was indicated by means of a Seger cone. No statement is made as to the length of time during which the material was heated or whether any means were employed to show variations, especially lowering of the temperature below the maximum indicated by the cones during the burning. In heating a considerable mass of material in a stationary furnace it would be extremely difficult if not impossible to have all the material obtain the same temperature for the same length of time. Possibly Meyer's results would represent those obtained from clinker, part of which had not attained the temperature indicated. It was on account of this difficulty, amounting almost to impossibility of heating a mixture in a stationary furnace uniformly and for the same length of time, that the fixed form of furnace was abandoned in this laboratory and a rotary kiln devised. A detailed description of the rotary kiln employed in the work described in this paper, will be found in this Journal, **24**, 248.

In the experiments herein described we have tried to pay close attention to all the factors which might enter into the formation of the clinker. All raw material was carefully dried and ground fine enough to pass a 100-mesh sieve, the thoroughly dried finely ground material was analyzed, and from materials thus prepared the various mixtures used in the different experiments were made and the composition of the resulting clinker calculated. The composition of the dried materials used is given in the following table:

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Loss on ignition.
Art. clay	67.95	15.76	5.64	1.19	2.02	5.22
Pen. clay.........	64.90	18.06	3.47	2.34	1.34	9.06
Syn. clay.........	55.32	11.78	21.53	2.43	1.82	6.72
No. 3 shale	53.05	26.59	5.87	1.84	1.51	9.87
Kaolin	47.35	36.66	1.85	0.40	0.25	12.50
L. W. marl.......	1.21	0.25	0.25	52.89	0.89	44.58

The slurries for burning were all prepared in as nearly the same way as possible, following the method given in the description of the rotary kiln referred to above. The marl required for 100 grams of clay or shale was calculated in each case and sufficient of each taken to make from 4 to 5 kilograms of dried slurry. The clay or shale was disintegrated with an amount of water equal to that of the dry materials and the marl then stirred in. This slurry was then evaporated with frequent stirring to the proper consistency for rolling out and cutting into cubes for drying.

In order to control the temperature the pressure in the gasoline tank was maintained steadily throughout the work between 48 and 50 pounds. When the pyrometer indicated that the furnace was at the lowest temperature at which it was desired to begin to collect clinker, feeding was begun. A number of experiments having shown that with 50 pounds' pressure in the gasoline tank the maximum temperature was about 35° C. higher than that recorded by the stationary couple used in controlling the temperature, the temperatures given in the following tables are all those of this hottest zone, that is, 35° C. higher than was actually measured by the stationary couple. The thermocouple used in this work was calibrated by direct comparison with a similar couple whose electromotive force was certified by the physikalische-technische Reichsanstalt. From time to time the couple was tested for constancy of electromotive force. The electromotive force of the couple did not change until after Experiment 98, when a temperature of 1618° C. actual having been attained, the wires became somewhat roughened and the electromotive force lowered but remained constant during the next three experiments. When it became necessary after Experiment 101 to replace the porcelain insulating tubing, an entire new couple was made with an electromotive force practically equal to that of the original couple.

When the rotary is making a single revolution in about one minute and twenty-five seconds and has a pitch of 6 per cent., the first pieces of clinker usually come through the furnace in from twenty-five to thirty minutes. This is not, however, the real time of passage, for these first pieces have nothing to impede their progress and pass through the furnace more quickly than when the furnace is fully charged. The real time of passage was determined by making a very basic slurry with pure kaolin an introducing single pieces of this slurry at intervals of about fifteen minutes during the burning of one of the slurries containing considerable ferric oxide. The clinker resulting from the kaolin being different in color from the rest was readily recognized and the average time of passage of these pieces was found to be about one hour and fifteen minutes. When the speed of the rotary was reduced so that a single revolution required two minutes and forty-five seconds, the time of passage was increased to an average of two hours and nineteen minutes. In the following experiments those which were made with the higher speed and shorter time of passage are marked only with a number, while those made with the slower speed and longer time of passage are indicated by a letter, A, following the number; thus Experiment 94A was made with the same slurry, etc., as Experiment 94, but with longer time of burning.

When from 80 to 100 grams of clinker had been collected at a given temperature, kept constant within 5° or less, the temperature was raised from 22° to 30° C. and kept constant for ten minutes before commencing to collect another sample. In this way a series of samples was collected at gradually increasing temperatures until the "overburning" temperature was attained. By the term "overburning temperature" is here meant that temperature at which the individual pieces of clinker begin to stick together or ball-up. This is the highest temperature at which samples can be collected. Experiment 98 was the only one of this series in which this overburning temperature was not reached. The progressive changes of appearance of the clinkers with increase of temperature are quite marked even for the comparatively small intervals of temperature. All the pieces produced at the same temperature are practically identical in appearance but in most cases the successive samples are readily distinguished from each other. With increasing temperature the material passes gradually from white or nearly white to deep brown or nearly black in color with marked contraction in volume as the sintering becomes more and more complete until the clinker produced at the highest temperature has a more or less glazed appearance as distinguished from the dull color of the preceding sample.

It was noticed during some of the experiments that if the per cent. of carbon monoxide in the escaping gases was allowed to exceed 0.3 per cent., the clinker assumed a yellowish brown color instead of the familiar deep brown or black of properly burned clinker, and the cement produced from it was off color instead of the normal color of good cement. The extent to which the chemical composition of the clinker is altered by carbon monoxide has not been thoroughly investigated as yet but we hope to do some more work on this question at a later date.

It was thought that a measure of the volume occupied by 1 gram of the clinker would be a much better indication of the shrinkage due to the sintering of the material than a determination of the specific gravity of the powdered material; this "volume per gram" of the clinker was measured in the following way and is given in the table under the various experiments. About ten grams of unbroken pieces of clinker were placed in a small flask containing sufficient glycerine to cover the pieces and the flask was then attached to an aspirator and exhausted until the pores of the clinker were filled with glycerine. A burette was filled with glycerine to within 10 cc. of the zero point. The pieces of clinker were then removed from the flask and wiped lightly on the outside with a cloth saturated with glycerine, and these pieces of clinker with the pores filled with glycerine were then dropped into the burette and the volume of glycerine displaced read off and calculated to the "volume per gram" of the clinker. As soon as the volume displaced by the first sample has been determined, enough glycerine may be drawn off to again bring the level of the glycerine to the starting-point and the volume of the second sample determined without removing the first and so on until the burette is full. This method of determining the volume per gram, and hence the shrinkage, gives rapid and much more satisfactory results than are obtained by determining the specific gravity of the powder.

All samples of clinker after collecting were kept in tightly stoppered bottles until ready for grinding and making pat tests which was usually done within two or three days from the time of burning. A portion of the crushed clinker was mixed in most cases with 2 per cent. of plaster of Paris, although in a few instances 3 per cent. had to be used. The amount employed is given under each experiment. After mixing with the plaster of Paris the clinker was ground until all of it would pass a 100-mesh sieve. The per cent. of water required for normal consistency was determined by adding water to a weighed amount of the cement with thorough mixing until a ball of the material about one-half inch in diameter when dropped from a distance of about 12 inches would flatten slightly but would not crack. The time of setting was determined upon pats made with the required amounts of water using needles of $^1/_{12}$ and $^1/_{24}$ inch in diameter weighted with $^1/_4$ and 1 pound respectively for initial and final sets. The time of the initial and final set was taken as that when the above needles just failed to make an impression on the pat. Unless care is used to have the glass on which pats are made strictly clean a pat will often come loose which would otherwise adhere and give a perfect boiling test. The boiling test was made on pats which had stood twenty-four hours in a damp atmosphere. They were placed in a frame supported in a continuous water-bath; the bath was then lighted and the water brought to the boiling-point and kept boiling for twenty-four hours when the pats were removed and, after cooling, examined. The details of the influence of temperature upon shrinkage, amount of water required,time of setting and boiling tests upon various mixtures are given in the following tables under the various experiment numbers. The proportion of clay or shale, and marl used in each mixture and the molecular formula of the clinker reduced to a basis of 100 molecules of silica in each case is also given.

TABLE I.—EXPERIMENT 103.

	Grams.
Art. clay	100
L. W. Marl	275

Composition of clinker: SiO_2, 28.83; Al_2O_3, 6.65; Fe_2O_3, 2.15; CaO, 59.61; MgO, 1.80.

Molecular formula: $100(1.868\,CaO, 0.091\,MgO, SiO_2) + 13.4(2\,CaO.Al_2O_3) + 2.8(2\,CaO.Fe_2O_3)$.

Eight samples of clinker collected and ground with 3 per cent. plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Per cent. water.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1395	0.78	27	14	310	Badly warped, one crack, weak.
2	1419	0.76	27	11	276	Badly warped, large cracks, weak.
3	1443	0.74	25	10	208	Slightly warped, no cracks, strong.
4	1467	0.64	24	9	14	Perfect.
5	1493	0.60	24	5	12	Perfect.
6	1515	0.55	24	10	25	Perfect.
7	1537	0.46	24	7	35	Perfect.
8	1549	0.38	24	6	25	Perfect.

TABLE II.—EXPERIMENT 98.

	Grams.
Art. clay	100
L. W. marl	339.3

Composition of clinker : SiO_2, 25.48; Al_2O_3, 5.87; Fe_2O_3, 2.29; CaO, 63.87; MgO, 1.79.

Molecular formula: $100(2.347\ CaO, 0.105\ MgO, SiO_2) + 13.5(2CaO.Al_2O_3) + 3.4(2\ CaO.Fe_2O_3)$.

Fourteen samples of clinker collected and ground with 2 per cent. plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1353	0.65	30	165	193	Disintegrated.
2	1381	0.65	30	110	260	Expanded over edge of glass, easily rubbed to sand.
3	1405	0.65	29	91	246	Not warped, expanded, rather weak.
4	1427	0.61	29	100	290	Slightly warped, moderately expanded, rather weak.
5	1456	0.60	28	97	300	Moderately warped, no cracks, strong.
6	1475	0.59	27	80	300	Moderately warped, no cracks, strong.
7	1498	0.56	27	90	300	Slightly warped, no cracks, very strong.
8	1521	0.55	25	91	306	Loose from glass, free from cracks, very strong.
9	1545	0.54	25	84	330	Perfect.
10	1567	0.53	25	60	240	Off color due to carbon monoxide.
11	1589	0.55	25	58	264	Perfect.
12	1611	0.50	25	57	359	Perfect.
13	1633	0.50	25	65	356	Perfect.
14	1653	0.45	25	59	361	Perfect.

TABLE III.—EXPERIMENT 87.

	Grams.
Pen. clay	100
L. W. marl	271.3

Composition of clinker: SiO_2, 28.26; Al_2O_3, 7.77; Fe_2O_3, 1.72; CaO, 60.44; MgO, 1.51.

Molecular formula: 100(1.90 CaO, 0.079 MgO,SiO_2) + 16(2 CaO.Al_2O_3) + 2.3(2 CaO.Fe_2O_3).

Seven samples of clinker collected and ground with 3 per cent. plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1337	...	36	12	31	No cracks, quite strong.
2	1365	...	34	24	355	Fine cracks, quite weak.
3	1389	...	27	18	276	Disintegrated.
4	1417	...	25	152	187	Very badly warped, cracked, easily rubbed to sand.
5	1441	...	24	214	259	Warped, deep cracks, but very strong.
6	1467	...	24	204	254	Perfect.
7	1491	...	24	35	65	Perfect.

Nos. 1 and 2 were loose from glass six hours after making.

Made a set of pats with 2 per cent. of plaster of Paris as follows:

Sample num	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1337	...	34	10	45	Fine hair cracks, moderately strong.
2	1365	...	31	10	35	Fine hair cracks, not quite as strong as No. 1.
3	1389	...	25	10	27	Disintegrated.
4	1417	...	24	8	23	Disintegrated.
5	1441	...	24	5	6	Loose from glass, badly warped.
6	1467	...	24	5	10	Perfect.
7	1491	...	24	5	11	Perfect.

Nos. 1 and 2 were loose from glass eight hours after making.

TABLE IV.—EXPERIMENT 88.

	Grams.
Pen. clay	100
L. W. marl	301.85

Composition of clinker: SiO_2, 26.51; Al_2O_3, 7.28; Fe_2O_3, 1.63; CaO, 62.73; MgO, 1.56.

Molecular formula: 100(2.137 CaO, 0.088 MgO,SiO_2) + 16.1(2 $CaO.Al_2O_3$) + 2.3(2 $CaO.Fe_2O_3$).

Nine samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1343	0.83	34	9	13	Somewhat warped, fine cracks, rather weak.
2	1363	0.77	30	10	12	Disintegrated.
3	1407	0.66	26	8	15	Disintegrated.
4	1431	0.61	25	60	100	Badly warped, easily rubbed to sand.
5	1453	0.51	24	89	189	Badly warped, fine cracks, moderately strong.
6	1463	0.44	24	94	229	Loose from glass, slightly warped, no cracks, very strong.
7	1507	0.41	24	100	240	Loose from glass, not warped, no cracks, very strong.
8	1533	0.41	23	102	312	Perfect.
9	1553	0.39	23	137	250	Perfect.

Nos. 1 and 2 were loose from glass six hours after making.

TABLE V.—EXPERIMENT 97.

	Grams.
Syn. clay	100
L. W. marl	298.7

Composition of clinker: SiO_2, 22.76; Al_2O_3, 4.80; Fe_2O_3, 8.61; CaO, 61.97; MgO, 1.73.

Molecular formula: 100(2.393 CaO, 0.113 MgO, SiO_2) + 12.4(2 $CaO.Al_2O_3$) + 13.7(2 $CaO.Fe_2O_3$).

Twelve samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1285	0.93	56	4	63	Slightly warped away from glass, fine cracks, weak.
2	1309	0.92	45	5	66	Slightly warped away from glass, quite strong.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
3	1335	0.75	35	4	9	Slightly warped away from glass, cracked, very weak.
4	1359	0.75	30	5	10	Badly disintegrated.
5	1383	0.70	30	34	122	Very badly disintegrated.
6	1407	0.68	28	56	440	Somewhat warped, badly scaled, weak.
7	1431	0.60	25	40	436	Moderately warped, numerous cracks, strong.
8	1455	0.52	24	120	434	Perfect.
9	1479	0.50	23	32	375	Perfect.
10	1505	0.47	21	105	315	Perfect.
11	1526	0.41	21	95	345	Perfect.
12	1549	0.38	21	81	341	Perfect.

TABLE VI.—EXPERIMENT 102A.

	Grams.
No. 3 shale..........	100
L. W. marl..............................	124.7
MgO.......	82.8, added in

the form of pure magnesium carbonate.

Composition of clinker: SiO_2, 22.53; Al_2O_3, 11.11; Fe_2O_3, 2.55; CaO, 28.00; MgO, 35.28.

Molecular formula: $100(CaO, 2MgO,SiO_2) + 29(CaO.MgO.Al_2O_3) + 4.2(CaO.MgO.Fe_2O_3)$.

Six samples of clinker collected and ground with 3 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1321	0.86	40	20	55	Loose, free from cracks, moderately strong.
2	1347	0.84	39	26	..	Loose, free from cracks, weak.
3	1373	0.82	33	22	..	Loose, free from cracks, rather weak.
4	1395	0.80	34	33	..	Loose, free from cracks, rather weak.
5	1423	0.68	32	1232	..	Loose, free from cracks, rather weak.
6	1445	0.44	29	120	..	Loose, free from cracks, rather weak.

Nos. 2, 3, 4, 5, and 6 were not set after nine hours; No. 2 was set after eighteen hours; Nos. 3, 4, and 6 set after twenty-two hours; No. 5 was not set after twenty-four hours.

This cement even after long setting appeared to crumble more or less under the fine needle, instead of becoming firm as with most hydraulic cements.

TABLE VII.—EXPERIMENT 92.

	Grams.
No. 3 shale	100
L. W. marl	250.1

Composition of clinker: SiO_2, 24.51; Al_2O_3, 11.90; Fe_2O_3, 2.84; CaO, 58.63; MgO, 1.64.

Molecular formula: $100(1.905\ CaO, 0.10\ MgO, SiO_2) + 28.5(2CaO.Al_2O_3) + 4.3(2CaO.Fe_2O_3)$.

Six samples of clinker collected and ground with 3 per cent. plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1336	0.84	40	15	25	Rather weak.
2	1361	0.835	35	20	105	Loose from glass, rather weak.
3	1391	0.75	30	57	107	Loose from glass, badly warped, cracked, very weak.
4	1415	0.55	24	100	145	Very badly warped, cracked, easily rubbed to sand.
5	1427	0.41	24	118	148	Very badly warped, cracked, rather weak.
6	1438	0.39	25	2	6	Loose from glass, free from cracks, strong.

No. 1 was loose from glass three hours after making.

TABLE VIII.—EXPERIMENT 92A.

Composition identical with Experiment 92, the only difference being increased time of passage of material through the furnace.

Four samples of clinker were collected and ground with 3 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1359	0.69	30	50	225	Very badly warped, cracked, rather easily rubbed to sand.
2	1383	0.65	27	145	220	Very badly warped, cracked, easily rubbed to sand.
3	1407	0.44	25	145	165	Very badly warped, cracked, rather weak.
4	1431	0.40	24	155	205	Loose from glass, free from cracks, strong.

TABLE IX.—EXPERIMENT 95A.

	Grams.
No. 3 shale	100
L. W. marl	250.1
MgO	18.45, added as

pure magnesium carbonate.

Composition of clinker: SiO_2, 22.77; Al_2O_3, 11.05; Fe_2O_3, 2.64: CaO, 54.47; MgO, 9.01.

Molecular formula: $100(1.907\ CaO, 0.589\ MgO, SiO_2) + 28.5(2CaO.Al_2O_3) + 4.3(2CaO.Fe_2O_3)$.

Six samples of clinker collected and ground with 3 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1335	0.89	38	6	19	Cracked, rather weak.
2	1359	0.72	34	12	230	Very badly warped, cracked, very weak.
3	1383	0.69	32	38	292	Very badly warped, easily rubbed to sand.
4	1405	0.52	30	148	313	Very badly warped, very easily rubbed to sand.
5	1431	0.47	25	45	195	Free from cracks, slightly warped, quite weak.
6	1455	0.39	25	6	10	Firmly adherent to glass, but rather weak.

No. 1 was loose from glass before submitting to boiling test.

TABLE X.—EXPERIMENT 93.

	Grams.
No. 3 shale	100
L. W. marl	275.3

Composition of clinker: SiO_2, 23.19; Al_2O_3, 11.24; Fe_2O_3, 2.70; CaO, 60.75; MgO, 1.63.

Molecular formula: $100(2.148\ CaO, 0.105\ MgO, SiO_2) + 28.4(2CaO.Al_2O_3) + 4.4(2CaO.Fe_2O_3)$.

Eight samples of clinker collected and ground with 3 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1331	0.94	55	10	13	Not cracked, very weak.
2	1357	0.93	50	8	21	Not cracked, very weak.
3	1383	0.87	40	7	8	Loose from glass, no cracks, stronger than No. 2.
4	1407	0.82	35	8	23	Warped, moderately cracked, very weak.
5	1431	0.72	32	18	192	Disintegrated.
6	1455	0.58	28	20	192	Disintegrated.
7	1481	0.51	24	85	205	Loose from glass, free from cracks, very strong.
8	1503	0.41	24	75	205	Perfect.

Nos. 1 and 2 were loose from glass before submitting to boiling test.

TABLE XI.—EXPERIMENT 101.

	Grams.
No. 3 shale	100
L. W. marl	294.4

Composition of clinker : SiO_2, 22.35; Al_2O_3, 10.79; Fe_2O_3, 2.60; CaO, 62.22; MgO, 1.63.

Molecular formula: $100(2.328\,CaO, 0.109\,MgO,SiO_2) + 28.3(2CaO.Al_2O_3) + 4.4(2CaO.Fe_2O_3)$.

Five samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1463	0.60	28	105	134	Disintegrated.
2	1487	0.57	28	80	140	Disintegrated.
3	1511	0.55	25	138	156	Perfect.
4	1535	0.51	24	76	139	Perfect.
5	1557	0.42	24	135	240	Off color, loose from glass, warped, cracked.

No. 1 was loose from glass before submitting to boiling test.

TABLE XII.—EXPERIMENT 94.

	Grams.
No. 3 shale	100
L. W. marl	300.8

Composition of clinker: SiO_2, 22.07; Al_2O_3, 10.64; Fe_2O_3, 2.57; CaO, 62.64; MgO, 1.59.

Molecular formula: $100(2.385\ CaO, 0.107\ MgO, SiO_2) + 28.3(2CaO.Al_2O_3) + 4.4(2CaO.Fe_2O_3)$.

Ten samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1359	0.89	60	38	360	Loose from glass, fine cracks, rather weak.
2	1383	0.87	55	10	65	Loose from glass, fine cracks, rather weak.
3	1407	0.80	47	5	33	Badly warped, cracked, difficultly rubbed to sand.
4	1431	0.71	40	5	33	Disintegrated.
5	1455	0.66	30	65	80	Disintegrated.
6	1478	0.54	25	87	105	Warped from glass, cracked, very weak.
7	1501	0.50	24	94	100	Loose from glass, sound, very strong.
8	1525	0.496	23	85	101	Loose from glass, sound, very strong.
9	1549	0.42	23	105	165	Perfect.
10	1573	0.40	23	140	255	Perfect.

Nos. 4 and 5 were loose from glass before submitting to boiling test.

TABLE XIII.—EXPERIMENT 94A.

Composition identical with Experiment 94, the only difference being due to increased time of passage of material through the furnace.

Nine samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1359	0.78	35	5	8	Very badly cracked, easily rubbed to sand.
2	1383	0.67	34	15	20	Very soft, almost completely disintegrated.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
3	1407	0.66	30	52	62	Very soft, almost completely disintegrated.
4	1431	0.60	26	66	81	Very badly warped, cracked, easily rubbed to sand.
5	1455	0.50	25	86	116	Warped away from glass, free from cracks, very strong.
6	1478	0.49	24	109	154	Perfect.
7	1501	0.45	24	146	284	Perfect.
8	1525	0.44	23	120	260	Perfect.
9	1545	0.40	23	108	240	Perfect.

No. 1 was loose from glass before submitting to boiling test.

TABLE XIV.—EXPERIMENT 96A.

	Grams.
No. 3 shale	100
L. W. marl	300.8
MgO	18.45, added as

pure magnesium carbonate.

Composition of clinker: SiO_2, 20.59; Al_2O_3, 9.94; Fe_2O_3, 2.40; CaO, 58.45; MgO, 8.22.

Molecular formula: $100(2.387\ CaO, 0.594\ MgO, SiO_2) + 28.3(2CaO.Al_2O_3) + 4.4(2CaO.Fe_2O_3)$.

Ten samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1361	0.73	36	3	5	Very badly broken, almost disintegrated.
2	1389	0.69	34	4	10	Disintegrated.
3	1411	0.61	29	65	79	Disintegrated.
4	1437	0.59	26	94	154	Very badly warped, large cracks, quite weak.
5	1463	0.52	25	116	216	Warped, fine radical cracks, strong.
6	1487	0.44	25	125	260	Perfect.
7	1509	0.44	24	140	294	Perfect.
8	1535	0.44	23	105	269	Perfect.
9	1557	0.41	23	92	212	Perfect.
7A	1519	0.41	23	92	240	Perfect.

During the collection of sample 7A an excess of gasoline was admitted into the furnace, the products of combustion showing carbon dioxide, 9 per cent., oxygen, 0.20 per cent., and carbon monoxide, 9.3 per cent. The cement produced was yellowish in color instead of the usual color of good cement.

TABLE XV.—EXPERIMENT 99.

	Grams.
No. 3 shale	100
L. W. marl	318.14

Composition of clinker: SiO_2, 21.34; Al_2O_3, 10.28; Fe_2O_3, 2.50; CaO, 63.83; MgO, 1.62.

Molecular formula: 100(2.54 CaO, 0.113 MgO, SiO_2) + 28.3($2CaO.Al_2O_3$) + 4.4(2 $CaO.Fe_2O_3$).

Eight samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1447	0.67	43	3	5	Completely disintegrated.
2	1473	0.63	37	13	15	Completely disintegrated.
3	1497	0.55	29	13	14	Completely disintegrated.
4	1523	0.52	25	100	204	Cracked, expanded, slightly warped, very weak.
5	1545	0.50	25	96	201	Expanded, badly warped, very weak.
6	1587	0.49	24	120	265	Warped, free from cracks, very strong.
7	1593	0.43	24	96	219	Loose from glass, very strong.
8	1613	0.40	23	94	304	Loose from glass, very strong.

TABLE XVI.—EXPERIMENT 100.

	Grams.
No. 3 shale	100
L. W. marl	353.6

Composition of clinker: SiO_2, 20.07; Al_2O_3, 9.61; Fe_2O_3, 2.36; CaO, 66.12; MgO, 1.63.

Molecular formula: 100(2.881 CaO, 0.121 MgO, SiO_2) + 28.1($2CaO.Al_2O_3$) + 4.4($2CaO.Fe_2O_3$).

Eight samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sa	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1461	0.60	28	120	198	Completely disintegrated.
2	1485	0.55	28	128	218	Almost disintegrated.
3	1509	0.51	25	105	205	Very badly broken.
4	1529	0.50	25	122	242	Badly warped, much expanded, very weak.
5	1555	0.49	25	129	240	Badly warped, much expanded, very weak.
6	1581	0.46	25	167	247	Badly warped, much expanded, very weak.
7	1599	0.44	25	153	243	Moderately warped, free from cracks, very strong.
8	1625	0.41	24	140	245	Warped, free from cracks, very strong.

No. 1 was loose from glass before submitting to boiling test.

TABLE XVII.—EXPERIMENT 86.

	Grams.
Kaolin	100
L. W. marl	387.24

Composition of clinker: SiO_2, 17.27; Al_2O_3, 12.45; Fe_2O_3, 0.93; CaO, 67.92; MgO, 1.23.

Molecular formula: $100(2.884\ CaO, 0.106\ MgO, SiO_2) + 42.3(3CaO.Al_2O_3) + 2(3CaO.Fe_2O_3)$.

The separate samples were not collected in this case, but the over-burning temperature was found to be 1571° C. After determining the overburning point the temperature was dropped to 1549° C. and a single large sample collected. This sample ground with 1.5 per cent. of plaster of Paris required 30 per cent. of water, gave an initial set of five minutes and a final set of nine minutes. On submitting the pat to the boiling test, it warped loose from glass, cracked, and was easily rubbed to sand.

The phenomena connected with the time of setting of these cements will not be discussed in this paper but will be reserved for further study. The amount of plaster of Paris was in all cases 2 per cent. except where the small amount of calcium oxide in the cement made 3 per cent. necessary in order to retard the setting sufficiently to obtain measurements. The contraction of the material during burning, as shown in the tables under volume per

Table XVIII.

Exp.	Calculated percentage composition of clinker.					Molecular ratios calculated to basis of 100 molecules SiO_2.					Molecular ratio of RO bases to 100 molecules $SiO_2 + Al_2O_3 + Fe_2O_3$.			
	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	$SiO_2 + Al_2O_3 + Fe_2O_3$.	CaO.	MgO.	CaO + MgO.
	Art clay													
103	28.83	6.65	2.15	59.61	1.80	100.0	13.4	2.8	219.2	9.1	100.0	188.6	7.8	196.4
98	25.48	5.87	2.29	63.87	1.79	100.0	13.5	3.4	268.5	10.5	100.0	229.7	8.9	238.6
	Pen clay													
87	28.26	7.77	1.72	60.44	1.51	100.0	16.0	2.3	226.6	7.9	100.0	191.6	6.7	198.3
88	26.51	7.28	1.63	62.73	1.56	100.0	16.1	2.3	253.5	8.8	100.0	214.1	7.4	221.5
	Syn. Clay A (Art Clay + $Fe(OH)_3$)													
97	22.76	4.80	8.61	61.97	1.73	100.0	12.4	13.7	291.5	11.3	100.0	231.2	8.9	240.1
	No. 3 Shale													
102A	22.53	11.11	2.55	28.00	35.28	100.0	29.0	4.2	133.1	232.9	100.0	100.0	174.7	274.7
92	24.51	11.90	2.84	58.63	1.64	100.0	28.5	4.3	256.1	10.0	100.0	192.8	7.5	200.3
92A	24.51	11.90	2.84	58.63	1.64	100.0	28.5	4.3	256.1	10.0	100.0	192.8	7.5	200.3
95A	22.77	11.05	2.64	54.47	9.01	100.0	28.5	4.3	256.3	58.9	100.0	192.9	44.3	237.2
93	23.19	11.24	2.70	60.75	1.63	100.0	28.4	4.4	280.4	10.5	100.0	211.1	7.9	219.0
101	22.35	10.79	2.60	62.22	1.63	100.0	28.3	4.4	298.2	10.9	100.0	224.7	8.2	232.9
94	22.07	10.64	2.57	62.64	1.59	100.0	28.3	4.4	303.9	10.7	100.0	228.8	8.1	236.9
94A	22.07	10.64	2.57	62.64	1.59	100.0	28.3	4.4	303.9	10.7	100.0	228.8	8.1	236.9
96A	20.59	9.94	2.40	58.45	8.22	100.0	28.3	4.4	304.1	59.4	100.0	229.1	44.7	273.8
99	21.39	10.28	2.50	63.83	1.62	100.0	28.3	4.4	319.4	11.3	100.0	240.8	8.5	249.3
100	20.07	9.61	2.36	66.12	1.63	100.0	28.1	4.4	353.1	12.1	100.0	266.4	9.1	275.5
	Kaolin													
86	17.27	12.75	0.93	67.92	1.25	100.0	42.3	2.0	421.3	10.6	100.0	291.7	7.3	299.0
	Results of Meyer's experiments													
M. 1	23.20	11.40	2.50	61.50	2.70	100.0	28.8	4.0	285.1	17.3	100.0	214.6	13.0	227.6
M. 2	22.10	9.70	2.40	63.30	2.40	100.0	26.1	4.1	310.8	16.4	100.0	238.7	12.5	251.2
M. 3	20.90	8.80	2.20	65.50	2.30	100.0	24.7	3.9	335.6	16.4	100.0	260.7	12.8	273.5

TABLE XVIII (*Continued*).

Exp.	Ratios of atoms of oxygen in RO bases to 100 atoms of oxygen in $SiO_2 + Al_2O_3 + Fe_2O_3$. $SiO_2 + Al_2O_3 + Fe_2O_3$.	CaO.	MgO.	CaO+MgO.	Temperatures. Degrees Centigrade. Maximum disintegration.[1]	First perfect boiling-test.[2]	Over-burning temperature.[3]	Percentage of water required for normal consistency. Maximum disintegration.[1]	First perfect boiling-test.[2]	Over-burning temperature.[3]
	Art clay									
103	100.0	88.1	3.5	91.6	1419	1467	1549	27	24	24
98	100.0	107.1	4.2	111.3	1353	1545	above 1653	30	25	25
	Pen clay									
87	100 0	88.8	3.1	91.9	1389	1467	1491	25	24	24
88	100.0	99.3	3.4	102.7	1363	1533	1553	30	23	23
	Syn. Clay A (Art Clay + $Fe(OH)_3$)									
97	100.0	104.7	4.1	108.8	1359	1455	1549	30	24	21
	No. 3 Shale									
102A	100.0	44.3	77.7	122.0	None[4]	None[4]	1445	..[4]	..[4]	29
92	100.0	85.8	3.3	89.1	1415	1438[5]	1438	24	25[5]	25
92A	100.0	85.8	3.3	89.1	1383	1431[5]	1431	27	24[5]	24
95A	100.0	85.8	19.7	105.5	1383	1455	1455	32	25	25
93	100.0	93.9	3.5	97.4	1431	1503	1503	32	24	24
101	100.0	100.0	3.9	103.9	....	1511	1557	..	25	24
94	100.0	101.9	3.6	104.5	1431	1549	1573	40	23	23
94A	100.0	101.9	3.6	104.5	1383	1478	1545	34	24	23
96A	100.0	102.0	19.9	121.9	1389	1487	1557	34	25	23
99	100.0	107.3	3.7	111.0	....	1593[5]	1613	..	24[5]	23
100	100.0	118.6	4.1	122.7	....	None	1625	..	..	24
	Kaolin									
86	100.0	126.5	3.2	129.7	....	None	1571	..	..	..
	Results of Meyer's experiments									
M. 1	100.0	95.5	4.3	99.7	1370?	1550?	....	..	..	..
M. 2	100.0	106.9	5.6	112.5	1370?	1490?	....	..	..	.
M. 3	100.0	117.8	5.7	123.5	1370	None	....	..	..	..

[1] By temperature of maximum disintegration is meant the temperature at which that clinker was produced which, when made into pats, showed the greatest disintegration in boiling water.

[2] By temperature of first perfect boiling-test is meant the lowest temperature at which clinker was produced which, when made into pats, remained strong, free from cracks, and firmly adherent to the glass after exposure to boiling water for twenty-four hours.

[3] By over-burning temperature is meant the lowest point during the burning at which the individual pieces of clinker commenced to stick badly to each other or to the inside of the furnace.

[4] These pats were all free from cracks but rather weak.

[5] These pats were strong, free from cracks, not warped, but loose from glass.

gram, increases in all cases with increasing temperature up to the highest temperature attained. At the overburning temperature the volume per gram for all ordinary cements lies within the narrow limits of 0.38-0.42 cc. per gram.

We desire to discuss more fully the phenomena connected with the clinkering as indicated by the soundness of the cement shown by the boiling test. For that purpose we have summarized the more important data in Table XVIII, and have included some results given by Meyer which we have recalculated to the same basis as our own. A comparative study of the soundness of the pats after having been subjected to the action of boiling water for twenty-four hours shows most clearly the relation existing between the chemical composition and temperature of burning. In any series the successive pats show differences in behavior in boiling water. If the collection be begun below about 1250° C. the first pats will come loose from the glass soon after making but will become quite strong and remain sound and free from cracks under the boiling test. As the temperature of burning rises, the pats begin to crack more and more, then go to pieces and finally nearly or quite completely disintegrate. With further increase of burning temperature the extent of disintegration diminishes until, if the cement is properly proportioned, the pats again become sound and strong, remaining firmly attached to the glass. Further increase of temperature does not affect the soundness of the pat unless carbon monoxide is present in the furnace gases. In this case the pat may come loose from the glass but will still remain sound and strong.

For purposes of study, three points have been selected as indicating important changes in clinker. Such changes in condition of clinker may indicate formation of definite chemical compounds or changes in the phases of a solid solution. The three points selected are: 1. *temperature of maximum disintegration* by which is meant the temperature at which that clinker was produced which, when made into pats, showed the greatest disintegration in boiling water; 2. *temperature of perfect boiling test,* by which is meant the lowest temperature at which clinker was produced which, when made into pats, remained strong, free from cracks and firmly adherent to the glass after exposure to boiling water for twenty-four hours; 3. *overburning temperature* by which is meant the lowest point during the burning at which the individual pieces of clinker commenced to stick badly to each other or to the inside of the furnace.

The influence of chemical composition will be discussed with reference to these three temperatures.

TEMPERATURE OF MAXIMUM DISINTEGRATION.

For a given clay the ratio CaO to $SiO_2 + Al_2O_3$ must reach a certain magnitude before the pats will completely disintegrate. Experiments 103, 102A, and 87 did not completely disintegrate for any temperature. Any increase in the calcium oxide over this minimum amount for any given clay does not increase the temperature of maximum disintegration.

Experiment	92	93	94
Temperature	1415°	1431°	1431°

The temperature of maximum disintegration is lowered by increasing the time of passage through the furnace.

Experiment	92	92A	94	94A
Temperature	1415°	1383°	1431°	1383°

When the ratio of CaO to $SiO_2 + Al_2O_3$ is enough for complete disintegration the addition of MgO does not change the temperature of maximum disintegration.

Experiment	92A	95A	94A	96A
Temperature	1383°	1383°	1383°	1389°

The substitution of R_2O_3 for SiO_2 materially raises the temperature of maximum disintegration.

Experiment	87	92	88	93	98	94
Temperature	1389°	1415°	1363°	1431°	1353°	1431°

For a given clay the amount of water required for normal consistency increases with increase of CaO provided the time of passage through the furnace is kept constant.

Experiment	92	93	94	92A	94A
Per cent. water	24	32	40	27	34

TEMPERATURE FOR FIRST PERFECT HOT TEST.

For a given clay the burning temperature necessary to obtain a perfect hot test increases with increase of CaO.

Experiment	103	98	87	88	92	93	101	94	99
Temperature	1467°	1545°	1467°	1533°	1438°	1503°	1511°	1549°	1593°

This temperature is lowered by increase of time of passage through the furnace.

Experiment........	92	92A	94	94A
Temperature.......	1438°	1431°	1549°	1478°

When the ratio of CaO to $SiO_2 + Al_2O_3$ is enough to ensure a perfect boiling test at some temperature, the addition of MgO does not materially raise the temperature necessary to obtain clinker giving a perfect boiling test.

Experiment........	92A[1]	95A	94A	96A
Temperature.......	1431°	1455°	1478°	1487°

The substitution of R_2O_3 for SiO_2 lowers the temperature for a perfect pat when the ratio of CaO to acidic oxides is low.

Experiment	87	92	88	93
Temperature............	1467°	1438°	1533°	1503°

With increasing amount of calcium oxide the temperature for perfect hot test is increased and the point is soon reached when a perfect hot test cannot be obtained at all.

Experiment	98	94	99	100
Temperature............	1545°	1549°	1593°	none

The amount of water required for normal consistency varies within slight limits but does not rise over 25 per cent. irrespective of the clay used and the composition of cement.

OVERBURNING TEMPERATURE.

For a given clay the overburning temperature increases with increase of CaO.

Experiment......	103	98	87	88
Temperature	1549°	above 1653°	1491°	1553°

Experiment ...	92	93	101	94	99	100
Temperature...	1438°	1503°	1557°	1573°	1613°	1625°

The overburning temperature is lowered by increasing the time of passage through the furnace.

Experiment..........	92	92A	94	94A
Temperature	1438°	1431°	1573°	1545°

MgO may replace CaO molecularly up to an empirical formula, $2RO.SiO_2,2RO.Al_2O_3,2RO.Fe_2O_3$, without much change in overburning temperature.

Experiment........	102A	92A
Temperature.......	1445°	1431°

[1] his pat was free from cracks but rather weak.

When the CaO is at least $2CaO.SiO_2$,$2CaO.Al_2O_3$,$2CaO.Fe_2O_3$, the addition of magnesium oxide raises the overburning temperature only slightly, not nearly so much as an equivalent amount of calcium oxide.

Experiment 92A, 1431°; Experiment 95A, 1455°. These have same ratio CaO to acidic oxides, but 95A has increased MgO.

Experiment 95A, 1455°; Experiment 94A, 1545°. These have same ratio RO to acidic oxides, but in 94A the RO is nearly all CaO.

Experiment 94A, 1545°; Experiment 96A, 1557°. These have same ratio CaO to acidic oxides but 96A has increased MgO.

Experiment 102A, 1445°; Experiment 96A, 1537°; Experiment 100, 1625°. These have same ratio RO to acidic oxides but 102A overburns at almost same temperature as 92A, 96A at almost same temperature as 94A which has same ratio CaO to acidic oxides, while 100 which has almost all CaO has highest overburning temperature of any.

The substitution of R_2O_3 for SiO_2, molecule for molecule, materially lowers the overburning temperature.

Experiment ..	87	92	88	93	98	94
Temperature..	1491°	1438°	1553°	1503°	above 1653°	1573°

The water required for normal consistency with overburned cements is only slightly less than that required for cements burned to give perfect boiling test.

SUMMARY.

Viewed from the standpoint of the influence of chemical composition upon the changes in temperature necessary to produce a sound cement and the temperature at which the clinker will give trouble by sticking in the rotary, we find that:

The minimum temperature necessary to produce Portland cement which will give a perfect pat test *from fresh clinker* is about 1450° C. This temperature is for a minimum amount of calcium oxide. It increases with increase of calcium oxide until in ordinary commercial cements it reaches 1550°. With the most heavily limed commercial cements this figure would be somewhat higher. It depends somewhat on the length of time required to pass through the rotary, slow driving tending to lower the temperature. The substitution of Al_2O_3, or Fe_2O_3 for SiO_2, that is, the use of a richer clay, lowers the overburning temperature but may *lower or raise* the temperature required for perfect boiling test. With mixtures low in calcium oxide, the burning temperature for perfect boiling test is lowered by this substitution, but with mixtures high in calcium oxide the burning temperature required for perfect boiling test is raised and may become coincident with the overburning temperature. Any attempt to raise the overburning temperature by increasing the proportion of lime will fail to give a perfect hot test even at the overburning temperature, as illustrated in Experiment 100. This is a confirmation of what manufacturing experience has shown—that with lean clays heavily limed there is a wide margin between the proper clinkering temperature and the overburning temperature, while with rich clays in order to prevent the clinker from balling-up, great care must be exercised to maintain the proper clinkering temperature. With the amount of calcium oxide found in ordinary cement the introduction of 8 or 9 per cent. of magnesium oxide has but little influence on the temperature for perfect boiling test or overburning temperature. So far as the clinkering is concerned, magnesia, as has been maintained by Newberry, acts as an inert substance.

While the conclusions above set forth seem to be fully warranted by our experiments, we realize that a much greater amount of experimental research must be performed, before the exact influence of each factor influencing the clinkering of cement can be determined with certainty. In the light of the knowledge gained by the present set of experiments, we are planning a much more complete series upon which we hope to report at some future date. In this new series we intend to include more cements whose basicity shall be equal to or greater than that found in the commercial cements. We have excluded from the present paper any discussion of phenomena connected with the setting of cement and its subsequent behavior aside from the amount of water required for normal consistency and the behavior under the boiling test. We have been studying this subject also for the past three years and hope later to present some results.

ANN ARBOR, MICHIGAN,
June, 1902.