

tion should be prepared by which to check the table for the individual using it.

TABLE II.—SHOWING PERCENTAGES OF SULPHUR.

Illinois coal.	Washings from Mahler bomb. (Per cent.)	Residues from Parr calorimeter in photometer. (Per cent.)
1 Odin, pea .....	2.30	2.17
2 St. John's lump .....	1.55	1.65
3 Pana, slack .....	4.03	4.04
4 Danville, lump.....	2.16	2.31
5 Ridgely, pea .....	4.00	4.01
6 Bloomington, lump.....	2.57	2.68
7 Spring Valley, washed.....	3.04	3.20
8 Elmwood .....	1.53	1.61

Results from use of this method, as above outlined, in comparison with those obtained under standard conditions, are shown in Table II.

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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

### FURTHER EXPERIMENTS ON THE CLINKERING OF PORTLAND CEMENT AND ON THE TEMPERATURE OF FORMATION OF SOME OF THE CONSTITUENTS.<sup>1</sup>

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THIS work is, in a way, a continuation of the results published by the author in this Journal (24, 248, 969; 25, 1103), and the experiments have been largely suggested by the results of the work previously reported.

In a paper entitled "An Experiment upon the Influence of the Fineness of Grinding upon the Clinkering of Portland Cement" (25, 1103), the author, with S. Ball, described the progress of linkering in a raw mixture used by a prominent eastern cement mill. This raw mixture was burned in the laboratory rotary cement kiln, employed for our previous experiments. Two experiments, 104 and 105, were made with this same raw material. In Experiment 104 the raw mixture was burned without

<sup>1</sup> The laboratory work in the experiments to be described in this paper has been done during the present year by Messrs. E. E. Ware, D. H. Clary, and M. G. Doll, to whom I wish here to acknowledge my indebtedness for the care with which the work has been done.

further grinding, while in Experiment 105 the material was ground before burning, so that 98 per cent. would pass a 200 mesh sieve. In Experiment 105 twenty-four samples of clinker were collected at approximately equal temperature intervals over a range from 1022° C. to 1627° C. The progress of clinkering was indicated, first, by the gradual change in color of the clinker from white through various shades of yellow and brown to nearly black when the temperature reached about 1475° C and above. These samples of clinker were ground with 1.5 per cent. of calcium sulphate (dehydrated gypsum) and from the resulting cement pats were made. The per cent. of water required for normal consistency, the initial and final sets were determined, and the behavior of the pats on submitting to the action of boiling water for twenty-four hours was noted. The extent to which silica had combined was shown in a number of cases by determining the proportion of silica soluble in hot dilute hydrochloric acid and in 10 per cent. sodium carbonate. In Experiment 105 the results showed that the combination of the silica progressed with increasing temperature until about 1352° C. was reached when the amount of "undecomposed silicates" was a minimum. This temperature, 1352° C., was that of maximum disintegration of the pats by boiling water. By the time the temperature has reached 1475° C. the constituents of the clinker had become rearranged that the pats stood a perfect boiling test.

In the raw mixtures usually used in the production of Portland cement, the silica, alumina and ferric oxide almost always occur chemically combined in the form of clay, shale or other silicates. In the theories now usually held in regard to the progress of clinkering, the calcium oxide is supposed at one stage of the process to combine directly with the clay substance, that is, the silicates as a whole; and the double silicates thus formed are supposed to split up and form the final tricalcium silicate characteristic of a perfectly formed Portland cement. So far we have but little data to show at what temperatures such double silicates may be formed, or at what temperature they may be split up and tricalcium silicate be formed. If a comparison of the behavior during clinkering of a purely mechanical mixture of various oxides, acidic and basic, could be made with that of a natural rock mixture in which the silica, alumina and fer

oxide are chemically combined, we might observe differences in behavior which would give some knowledge as to the probable temperatures of formation and rearrangement of the various constituents.

*Experiment 110.*—This experiment was undertaken for the purpose of comparing the behavior during clinkering of a purely mechanical mixture of the oxides entering in the formation of cement, with that of a natural rock mixture of the same ultimate composition, such as that used in Experiments 104 and 105.

The raw materials used for Experiment 110 consisted of pure glass sand, a comparatively pure marl, chemically pure hydrated ferric oxide, chemically pure hydrated aluminum oxide, and chemically pure magnesium oxide, obtained by ignition of the carbonate.

The composition of the materials used is given in Table I.

TABLE I.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Loss on ignition.
L. W. marl. . . . .	1.21	0.25	0.25	52.89	0.89	44.58
Glass sand. . . . .	99.60	0.25	....	....	....	....
Al(OH) <sub>3</sub> . . . . .	....	74.15	....	....	....	25.85
Fe(OH) <sub>3</sub> . . . . .	....	....	86.13	....	....	13.87
MgO . . . . .	....	....	....	....	100.00	....

These materials were first finely ground separately. The molecular ratio of the clinker in Experiment 105, calculated on the basis of 100 molecules of silica, was as follows: SiO<sub>2</sub>, 100; Al<sub>2</sub>O<sub>3</sub>, 24.9; Fe<sub>2</sub>O<sub>3</sub>, 4.5; CaO, 315.2; MgO, 19.1. In order to attain the same molecular ratio from materials of the composition given as in the above table, we should have to use them in the following proportions: Sand, 566 grams; Al(OH)<sub>3</sub>, 329 grams; Fe(OH)<sub>3</sub>, 74 grams; L. W. marl, 3343 grams; MgO, 47 grams. The above amounts of the various materials were carefully mixed dry and subjected to a second grinding of six hours in the porcelain-lined mill used in Experiment 105. The finely ground material was then moistened with sufficient water to enable it to be rolled out and cut into cubes for burning, as in former practice.

The furnace employed was that used in previous experiments, and the method of measuring the temperature attained by the clinker was the same as that used in Experiment 105. The thermocouples employed were carefully checked, from time to time,

to detect and correct for any change in electromotive force due to long heating in an atmosphere rich in carbon dioxide, with occasionally traces of carbon monoxide.

From the prepared mixture of oxide eleven samples of clinker were collected from 1257° C. to 1571° C. On comparing the color of these various clinkers with those from Experiment 105, made at corresponding temperatures, it was found that the colors agreed, as closely as could be detected, with each other in practically all cases. The samples of clinker were ground with 1.5 per cent. calcium sulphate (dehydrated gypsum) and from the resulting cement pats were made; the amount of water required for normal consistency, the initial and final sets, and the behavior under the boiling tests, were noted. The results of these tests are summarized in Table II, together with those obtained from the clinkers in Experiment 105, produced at temperatures corresponding most closely with those of the present experiment.

The completeness of chemical combination of the silica was determined as in Experiment 105, in the two samples produced at 1348° C. and 1480° C., by dissolving in dilute hydrochloric acid and treating the undissolved residue with 10 per cent. sodium carbonate, thus obtaining a final insoluble residue of "undecomposed silicates." The residue of "undecomposed silicates" on sample No. 9 was fused with sodium carbonate and thus resolved into its constituents, which were determined in the usual manner. The amount of undecomposed silicates from sample No. 4 was only 0.41 per cent., while that of sample No. 9 was 1.45 per cent., made up of 1.08 per cent.  $\text{SiO}_2$ , 0.15 per cent.  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , 0.08 per cent.  $\text{CaO}$ , and 0.14 per cent.  $\text{MgO}$ . The complete analysis of sample No. 9 gave the following results: Total  $\text{SiO}_2$ , 20.74 per cent.;  $\text{Al}_2\text{O}_3$ , 10.44 per cent.;  $\text{Fe}_2\text{O}_3$ , 2.56 per cent.;  $\text{CaO}$ , 63.79 per cent.;  $\text{MgO}$ , 2.29 per cent.; total, 99.82 per cent.

The physical tests on the cement from Experiment 110 compared with that of Experiment 105, made at the nearest corresponding temperature, are summarized in Table II. As the experiments were performed by different men, and it was found by subsequent weighing that the average weight of clinker from Experiment 110 was about twice that in 105 we must expect that the reactions in 110 will apparently lag somewhat behind those of 105. This is best illustrated in the temperature at

which the first perfect pat is obtained, the difference in this case being  $35^{\circ}$  C.

TABLE II.

Expt. number.	Sample number.	Clinker temperature, $^{\circ}$ C.	Per cent. water.	Initial set. Hours.	Initial set. Minutes.	Final set. Hours.	Final set. Minutes.	Hot test.
110	1	1257	80	..	29	..	..	Very soft, mushy, loose from glass.
105	10	1247	62	..	$\frac{1}{2}$	3	40	Badly cracked, warped, very weak.
110	2	1273	74	..	16	2	52	Expanded, not warped, easily rubbed to sand.
105	11	1281	54	..	1	5	..	Badly warped and broken.
110	3	1318	59	..	11	..	51	Very easily rubbed to sand, cracked.
105	13	1327	44	..	1	..	29	Very badly warped, cracked, almost disintegrated.
110	4	1348	47	..	5	1	5	Disintegrated.
105	14	1352	40	..	3	..	21	"
110	5	1374	37	..	5	1	..	"
105	15	1378	37	..	$3\frac{1}{2}$	..	27	"
110	6	1400	27	..	18	2	26	"
105	16	1401	$33\frac{1}{2}$	..	18	3	15	"
110	7	1432	25	..	6	4	58	Badly warped, easily rubbed to sand.
105	17	1425	32	..	10	2	22	Badly warped and cracked, almost disintegrated.
110	8	1457	26	..	11	5	..	Badly warped and weak.
105	18	1451	30	..	14	4	45	Slightly warped, cracked, loose from glass, but quite strong.
110	9	1480	26	..	12	5	..	Badly warped, quite strong.
105	19	1475	28	1	5	4	40	Perfect pat.
110	10	1510	26	..	5	1	52	"
105	20	1501	27	..	32	4	22	"
110	11	1571	26	..	5	2	37	"
105	23	1582	24	..	21	4	..	"

The data obtained from Experiment 110, together with all the results from Experiment 105, as reported in our previous article, are represented graphically in Plate I. In this plate the abscissae represent the temperature at which the various samples of clinker were collected, and the ordinates the per cent. of water required for normal consistency, and the time for initial and final sets. Sample No. 21, Experiment 105, has been omitted from this curve, because, as was explained in the paper describing this work

in detail, at the time when this particular sample was collected, carbon monoxide was found in the products of combustion, which caused the clinker produced to give abnormal results.

The rate of cooling and the conditions under which clinker cools has a marked influence on the time of both initial and final set. In both these experiments the hot clinkers falling from the rotary were caught in small metal trays so that they cooled comparatively quickly in the air, probably quicker than in most cases in commercial practice. This more rapid cooling tends to make the cement have a much quicker initial and final set, although the quantitative influence of this variable has not yet been determined.

The present experiment would have been more satisfactory had the collection of clinkers begun at as low a temperature as that employed in Experiment 105, because, in Experiment 110 the heavy lining of the furnace, with which the clinker is constantly in contact, would probably not have had time to attain the same temperature as the thermocouple and would probably exert a more or less cooling effect on the clinker collected in the first hour or so. The result of this is to throw some doubt on the similarity of the behavior of a mechanical mixture of the oxides and that of a cement mixture when heated to temperatures below  $1350^{\circ}\text{C}$ . However, by the time the temperature has reached about  $1350^{\circ}\text{C}$ . we have the most nearly complete combination of the silica at least, no matter in what form the constituents existed in the original mixture: that is, if the material is finely enough divided, the same compounds or solid solutions will be formed at about  $1350^{\circ}\text{C}$ . in all cases, irrespective of the condition in which the constituents existed in the original mixture. As the temperature is raised above that at which maximum disintegration takes place, the basic silicates, probably tricalcium silicate, begin to separate out, leaving a more acid magma, as is shown by the larger proportion of "undecomposed silicates" found in clinker burned at very high temperatures than in that burned at the temperature of maximum disintegration. The results found in Experiment 110 confirm on this point those described under Experiment 105. The complete separation of the basic silicate, characteristic of Portland cement, which apparently was complete in Experiment 105 at  $1475^{\circ}\text{C}$ ., did not take place in the present instance until  $1510^{\circ}\text{C}$ . was reached, probably on account of the larger pieces of clinker in Experiment 110; but, as has also been shown in our pre-

liminary experiments, this reaction, indicated by the formation of a pat capable of standing a perfect boiling test, may vary between  $1400^{\circ}$  C. and  $1575^{\circ}$  C. In case an excessive amount of calcium oxide is employed, no perfect boiling test will be obtained at all.

*Experiment 107.*—This experiment was undertaken to show the behavior of dicalcium ferrite in clinkering. The raw materials used were chemically pure ferric hydroxide and L. W. marl, previously described, as used in Experiment 110. The finely divided material was first mixed and then subjected to prolonged grinding to insure fineness and a perfect mixture. The materials were carefully proportioned so as to give the molecular ratio  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ . The material thus prepared was moistened with sufficient water to enable it to be rolled out and cut into cubes for burning, as in the previously described experiments. From this material eleven samples were collected, from  $976^{\circ}$  C. to  $1307^{\circ}$  C., at which temperature the material began to fuse and stick to the sides of the rotary, showing that the overburning temperature had been reached.

These clinkers varied in color from dull brown to nearly black as the temperature at which they were made increased. The various samples were ground with 1.5 per cent. of calcium sulphate (dehydrated gypsum), and from the resulting material pats were made to determine the amount of water required for normal consistency, the initial and final sets and the behavior under the boiling test. The results obtained on these samples are summarized in Table III.

TABLE III.

Sample No.	Clinker temperature.	Per cent. $\text{H}_2\text{O}$ .	Initial set. Hours.	Initial set. Minutes.	Final set. Hours.	Final set. Minutes.	Hot test.
1	976	51	..	7	3	27	Slightly warped, weak.
2	1017	45	..	6	2	8	Warped badly, stronger.
3	1042	43	..	8	2	16	Warped slightly, fairly strong.
4	1069	42	..	10	2	6	Warped considerably, quite strong.
5	1103	37	..	14	2	48	Warped a little, quite strong.
6	1135	32	..	11	1	23	Warped very little, stronger.
7	1163	28	..	9	1	7	Same as No. 6.
8	1192	23	..	11	..	23	Same as No. 6.
9	1215	22	..	8	..	32	Not warped, very strong.
10	1258	22	..	8	..	35	Same as No. 9.
11	1307	21	..	3	..	31	Warped, very strong.

*Experiment 108.*—This was undertaken to study the behavior of dicalcium aluminate in clinkering. The materials used were finely ground, chemically pure aluminum hydroxide and L. W. marl. These were mixed in proportion to give the molecular ratio  $2\text{CaO}.\text{Al}_2\text{O}_3$ , and after mixing, were subjected to thorough grinding, as in the preparation of dicalcium ferrite, in order to insure fineness and perfect mixture.

Fourteen samples of clinker were collected between  $871^\circ\text{C}$ . and  $1305^\circ\text{C}$ ., which latter was the overburning temperature, as was indicated by the clinkers beginning to fuse and stick to the sides of the rotary. All the clinkers from this experiment were very light, almost white in color. The tests obtained from the clinkers after grinding with 1.5 per cent. calcium sulphate (dehydrated gypsum) are summarized in Table IV.

TABLE IV.

Sample number.	Clinker temperature.	Per cent. $\text{H}_2\text{O}$ .	Initial set. Hours.	Initial set. Minutes.	Final set. Hours.	Final set. Minutes.	Hot test.
1	871	78	1	14	None		Pats 1 to 7 inclusive were very soft after boiling.
2	905	98	..	47	"		
3	942	121	over 6	..	"		
4	976	125	4	52	"		
5	1013	127	4	37	"		
6	1038	118	..	47	"		
7	1065	113	2	41	"		
8	1107	104	..	27	over 8	..	Perfect pat.
9	1132	98	..	40	6	57	"
10	1161	95	..	26	2	18	Free from glass, not warped.
11	1191	..	..	6	2	5	Warped very slightly, some cracks.
12	1222	72	..	4	1	10	Warped considerably, cracked badly.
13	1256	69	..	12	2	1	Warped, cracked and broken.
14	1305	60	..	3	2	19	Disintegrated.

*Experiment 109.*—This was intended to show the behavior of monocalcium aluminate on clinkering. The materials used were the same as those in Experiment 108. It was intended to proportion the aluminum hydroxide and marl so that the mixture should have the molecular ratio  $\text{CaO}.\text{Al}_2\text{O}_3$ . The check analysis made on a sample of the clinker to verify the accu-



rary of the mixture showed that the ratio of CaO to  $Al_2O_3$  was 0.85 to 1.00 instead of 1.00 to 1.00, as originally intended. On reviewing the figures it was found that an arithmetical mistake had caused this error. The analysis of a number of samples of clinker, however, revealed an interesting point, due to this very error.

Nine samples of clinker were collected between  $1156^\circ C.$  and the overburning temperature, which did not occur until  $1505^\circ C.$ , or  $200^\circ$  above that of the dicalcium aluminate. The clinkers obtained were ground without addition of calcium sulphate and made into pats, which were tested in the usual way. The results of these tests are summarized in Table V.

TABLE V.

Sample No.	Clinker temperature.	Per cent. $H_2O$ .	Initial set. Hours.	Initial set. Minutes.	Final set. Hours.	Final set. Minutes.	Hot test.
1	1156	135	..	18	over 24	..	Nos. 1, 2, and 3 very soft, disintegrated, getting harder in order of numbers.
2	1215	125	1	13	1	56	
3	1254	124	1	4	1	41	
4	1280	109	..	58	1	45	Harder than No. 3, easily pulverized with fingers.
5	1315	91	..	51	1	53	Harder than No. 4, less easily pulverized, weak.
6	1349	80	..	54	2	12	Difficultly pulverized with fingers, stronger than No. 5.
7	1367	73	1	41	2	40	Could not pulverize with fingers, quite strong and hard.
8	1407	54	1	47	3	49	Stronger than No. 7, harder and quite brittle.
9	1505	45	2	00	2	30	Very strong, hard and brittle, warped.

Analyses of samples Nos. 1, 5 and 8 were made to determine the proportion of calcium and aluminum oxides, readily soluble in hot, dilute hydrochloric acid. This was done by first boiling a 0.5 gram sample of the finely ground material with 50 cc. of water and then adding 5 cc. of hydrochloric acid (sp. gr. 1.20), stirring for two or three minutes and then filtering to determine the amount of insoluble residue. The calcium and aluminum oxides in the filtrate were determined in the usual manner, and the molecular

proportions in which they were found were calculated. The results of these analyses are given in Table VI.

TABLE VI.

Sample No.	Temperature.	Insoluble residue.	CaO in solution.	Al <sub>2</sub> O <sub>3</sub> in solution.	Molecular ratio.	
					CaO.	Al <sub>2</sub> O <sub>3</sub> .
1	1156	42.48	29.81	22.71	1	0.418
5	1315	28.75	29.25	39.10	1	0.736
8	1407	16.98	28.94	52.76	1	1.006

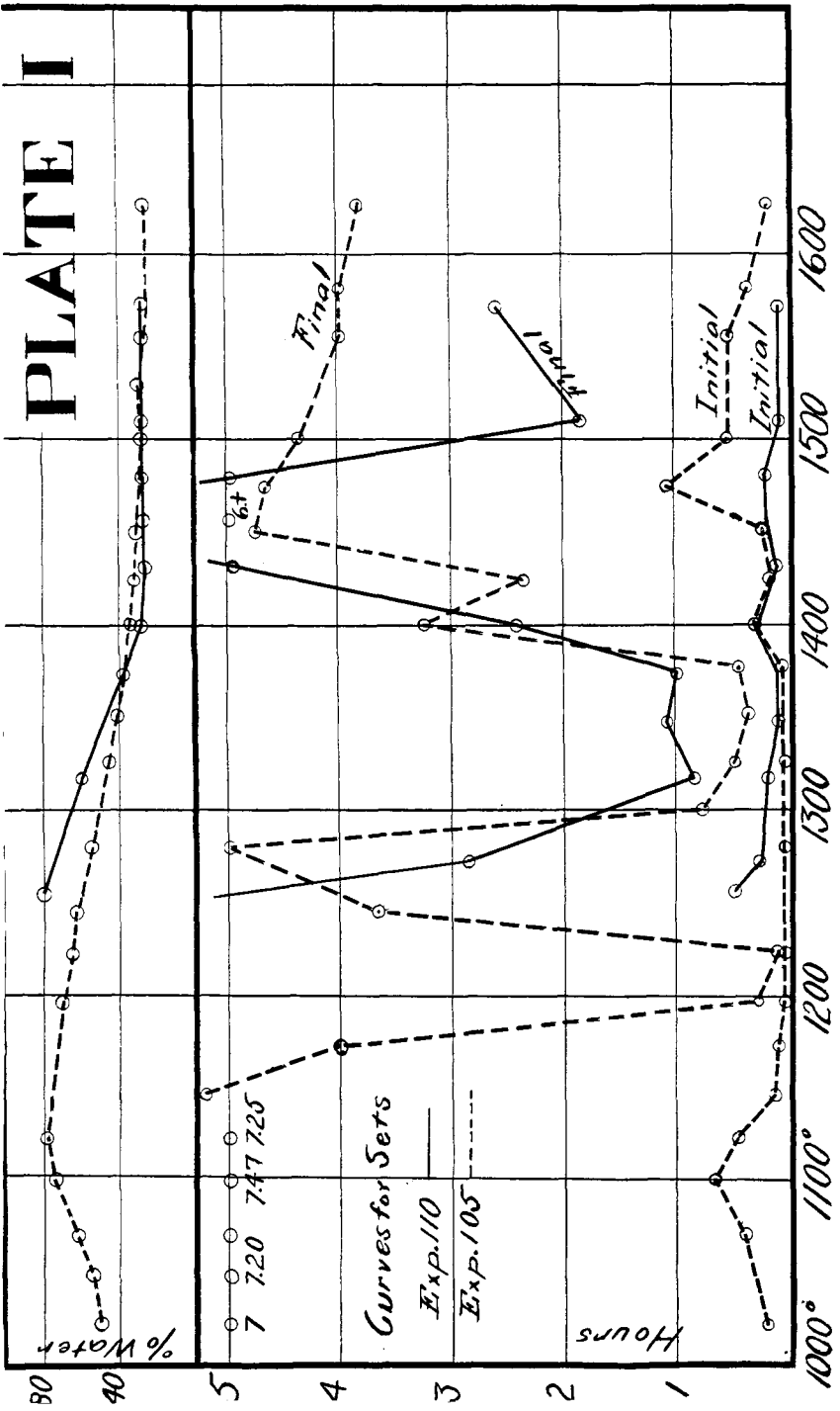
A study of the figures given in the last two columns of Table VI brings out the significant fact that when CaO is heated with Al<sub>2</sub>O<sub>3</sub>, probably the dicalcium aluminate is first formed, this formation being completed at about 1200° C. Further, that dicalcium aluminate, which may be completely formed a little above 1200° C., then begins to combine with more alumina, if present, as the temperature increases until the monocalcium aluminate has been formed at about 1400° C.

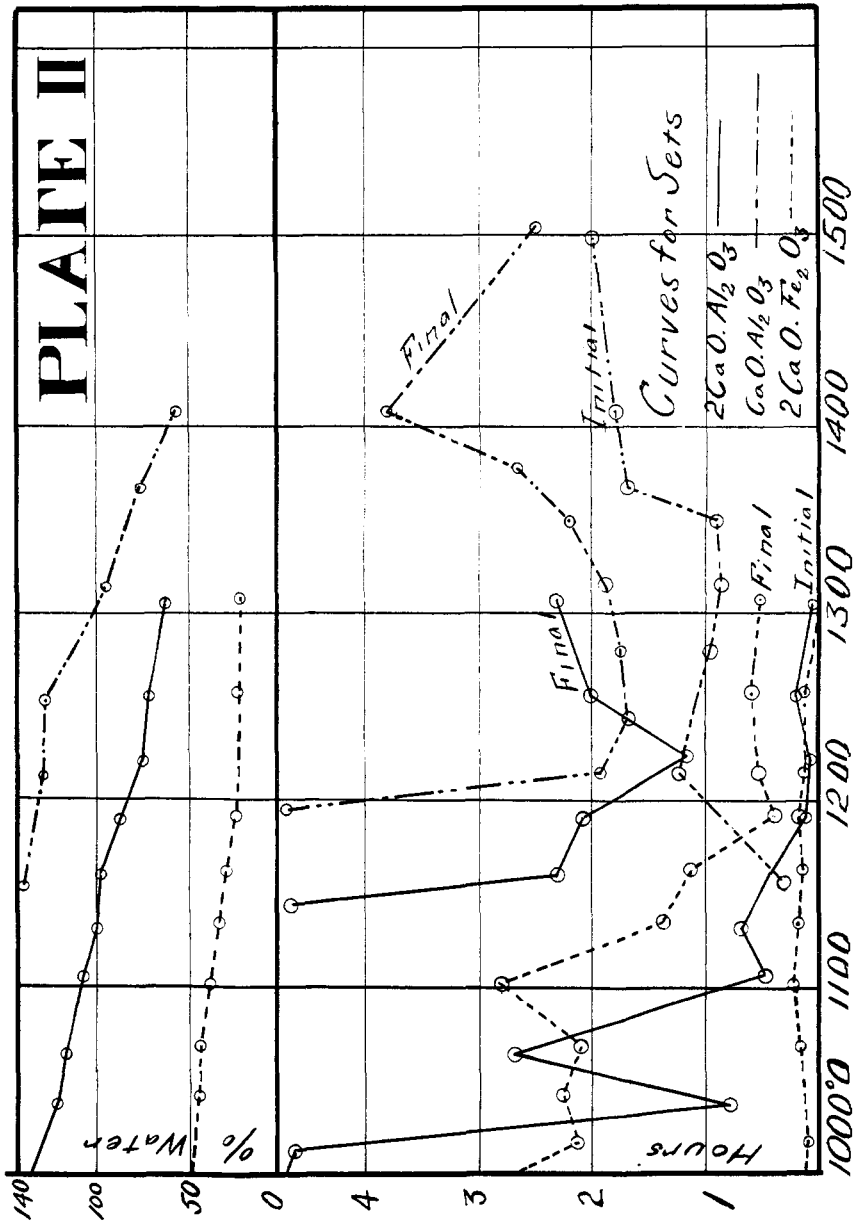
The dicalcium aluminate when completely formed, as is shown in sample No. 12, Experiment 108, has a quick initial and a comparatively quick final set, while the monocalcium aluminate has a slow initial and comparatively slow final set, even when the material has been partially fused, as is shown in sample No. 9, Experiment 109.

The results found in Experiments 107, 108 and 109 are shown graphically in Plate II in which, as in Plate I for Experiments 105 and 110, the ordinates represent the per cents. of water required for normal consistency, the initial and final sets and the abscissae show the temperatures at which the various samples were collected.

All the results so far obtained in this laboratory must, in a way, be considered as fragmentary, nevertheless they seem to point to a number of clearly marked changes which, taken together with a tentative hypothesis, may serve as a foundation for a complete series of experiments, which will demonstrate all the reactions which take place in the clinkering of Portland cement.

In natural rock cements which are burned at temperatures below most of those with which we have been dealing, it is generally supposed that the hydraulic properties are due to some compound of calcium oxide with the clay substance as a whole, and not to a number of new bodies resulting from the splitting up of these double compounds, and rearrangement at the high





temperature employed in the manufacture of Portland cement. It is the temperature of formation and behavior of these latter compounds which we will consider in the present discussion. In order to form a reliable judgment as to the equilibrium, which will exist in any mixture at a given temperature, and hence the properties of clinker produced from a given mixture burned at a definite temperature, we should know the properties of all the separate constituents which may be present; that is, if we regard clinker as a more or less complete solid solution containing a number of constituents, we must know the properties of all the constituents separately before we can judge the properties of the mixture or solid solution as a whole.

Although we have no data in regard to the behavior of pure tricalcium silicate, made at carefully controlled temperatures, we know from the experiments of Newberry and others that the tricalcium silicate is generally considered slow-setting. We have no data, either, in regard to the behavior of pure dicalcium silicate produced at definite temperatures. From the behavior of certain slags, however, and from the data given under Experiment 103 of our previously published work,<sup>1</sup> it would appear that dicalcium silicate formed above 1450° C. has probably a rather quick initial, as well as final set.

In regard to the aluminates of calcium, Experiments 108 and 109 probably give the first data in regard to the initial and final sets of these compounds from clinker produced at carefully controlled temperatures. A study of the curves in Plate II, Experiment 108, on the dicalcium aluminate shows that the amount of water required for normal consistency increased with increasing dissociation of calcium carbonate until it reached its maximum of 125 per cent. when a temperature a little over 1000° C. had been reached. From this temperature the amount of water required for normal consistency decreases with almost perfect uniformity, reaching its minimum of 60 per cent. for that sample produced at the overburning temperature. A study of the curves for initial and final sets would apparently indicate the increasing combination of aluminum oxide with calcium oxide as the temperature increased until by the time 1222° had been reached nearly all of the oxides were combined as dicalcium aluminate,

<sup>1</sup> This Journal, 24, 969.

as indicated by the initial and final sets reaching their minimum at this point. As the temperature rises above this point,  $1222^{\circ}\text{C}.$ , the slight slowing up of the initial set, together with the marked slowing up of the final set, would indicate probably more or less dissociation of dicalcium aluminate into the more slow-setting monocalcium aluminate and free calcium oxide.

The curves for Experiment 109, monocalcium aluminate, show a steady decrease in the amount of water required for normal consistency with increase of temperature. This decrease, however, apparently takes place more rapidly after about  $1255^{\circ}\text{C}.$  is reached. A word here may account possibly, or very probably, for the somewhat abrupt change in the water requirement, as well as some of the other properties. In this experiment the first clinker was collected within about an hour after lighting the furnace and it is not improbable that in this comparatively short time the heavy furnace lining had not become thoroughly heated through so that the pieces of clinker in contact with the furnace lining had not reached quite as high a temperature as would be indicated by the readings observed at the thermocouple. The curves for the initial and final sets of Experiment 109, however, studied in conjunction with the analyses obtained upon the three samples of clinker, would apparently indicate pretty clearly that dicalcium aluminate was first formed until nearly all of the calcium oxide had taken this form and then as the temperature increased the dicalcium aluminate began to dissociate into monocalcium aluminate and calcium oxide, which calcium oxide, however, would at once combine with the excess of alumina present, until at about  $1400^{\circ}\text{C}.$  nothing but monocalcium aluminate is found, together with the excess of uncombined alumina. The proportion of dicalcium aluminate and monocalcium aluminate, existing at any given temperature, will, of course, be largely influenced by the relative masses of the two oxides. From the curve for the final set, however, in Experiment 109 it would seem as though the dissociation of dicalcium aluminate began to take place rapidly, soon after  $1300^{\circ}\text{C}.$  has been passed. Monocalcium aluminate has apparently quite a slow initial and final set. Had samples been collected in Experiment 109 in the interval between  $1407^{\circ}\text{C}.$  and  $1506^{\circ}\text{C}.$  it is probable the curve would have had a somewhat different form, the final set especially slowing up for a longer

period before dropping off, thus approximating more nearly the curves for the final sets of Experiments 110 and 105.

The curves for the dicalcium ferrite, Experiment 107, show, as for the dicalcium aluminate, a regular diminution in the amount of water required for normal consistency with increase of temperature. The quick initial sets at  $1000^{\circ}$  C., or below, show that some dicalcium ferrite is probably formed even at this temperature; but the fact that the final set does not reach its minimum until nearly  $1200^{\circ}$  C., or about the same temperature as that for the same condition as for dicalcium aluminate, would indicate that ferric oxide behaves almost like aluminum oxide, which would be further confirmed by the fact that the overburning temperatures of dicalcium ferrite and dicalcium aluminate practically coincide. Again, this distinct, although somewhat slight, slowing up of the final set of dicalcium aluminate above  $1200^{\circ}$  C. would be suggestive at least of dissociation of part of the dicalcium into more slow-setting monocalcium ferrite; however, we have at present no data in regard to monocalcium ferrite. This last must be taken as merely suggested by the analogous behavior of the aluminates.

A study of the curves for Experiment 105 shows that the amount of water required for normal consistency falls off regularly with increase of temperature after the point necessary for complete dissociation for calcium carbonate has been passed, in this case about  $1125^{\circ}$  C. If we compare the curve for the initial and final sets in Experiment 105 with those from dicalcium aluminate and dicalcium ferrite, we will note that in all three cases we find the final sets reaching a minimum at a temperature very near  $1200^{\circ}$  C. and that the initial set is rapid in all three cases at this same temperature. This would indicate that in cement mixtures dicalcium aluminate and dicalcium ferrite were probably the most reactive constituents formed at this temperature. The very marked slowing up of the final set in Experiment 105, between  $1200^{\circ}$  C. and  $1300^{\circ}$  C., is probably due to some silicate formation, since this marked rise in the curve is absent from the curves for pure aluminates and ferrites. The samples of clinker collected at  $1352^{\circ}$  C. showed, as has been previously explained, maximum disintegration under the boiling test, together with a minimum amount of undecomposed silicates. Thus we would find this second valley,

so to speak, in the curve of final set representing that period in the process of clinkering where we have most complete combination of the silica, but where the tricalcium silicate, characteristic of Portland cement, has not as yet formed, or, at least, separated from solid solution. The rise in the curve between  $1352^{\circ}$  C. and  $1475^{\circ}$  C. is not improbably due to the gradual separation or formation of tricalcium silicate, perhaps accompanied by progressive dissociation of dicalcium aluminate and ferrite.  $1475^{\circ}$  C. is that temperature at which the first perfect boiling test is obtained. Whether the gradual falling off in the time of final set with rise of temperature above  $1475^{\circ}$  C. is due to dissociation of tricalcium silicate and formation of the more quick-setting dicalcium silicate we are not prepared at this time to venture an opinion, since our work has not as yet reached a point which would justify a positive opinion in regard to the behavior of the silicates themselves.

Experiment 110 would have been much more satisfactory had the collection of samples begun at as low a temperature as was employed in Experiment 105. Nevertheless, if correct allowance is made for the first few samples of clinker probably not being quite as hot as is indicated by the thermocouple, we find that the curves are of very much the same nature and indicate that probably the same reactions took place in both cases. In forming this judgment due allowance must be made for the fact that in Experiment 110 the individual pieces of clinker weighed twice as much as those in Experiment 105, and that the furnace lining during the collection of the first two or three samples had probably not had time to approach the temperature of the thermocouple as in Experiment 105.

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### MAGNESIUM AMALGAM AS A REDUCING AGENT.

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WHILE magnesium amalgam has been known for some time, having been prepared by Wanklyn and Chapman in 1866, its use as a reducing agent in organic chemistry has hitherto been neglected.