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SOME CONDITIONS INFLUENCING CONSTANCY OF VOLUME IN PORTLAND CEMENTS.

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WHATEVER other faults an engineer may forgive in Portland cement, he demands that it shall be reliable and perform its duty for an indefinitely long number of years without deterioration. He dare not use a cement which may change its volume after it forms part of an important structure and thus cause the development of enormous internal strains. Instances of how powerful these strains may be, can be seen by any one thoughtful enough to observe the cement sidewalks over which he passes. The experiments here described form part of a series made with the view of studying the effect of changes in chemical composition upon the properties of finished cement, and especially upon that most important one of constancy of volume. The portion presented in this paper considers a range of composition quite common in American practice where the cement is not very highly limed and the percentages of alumina and iron oxide are together less than half the silica.

These cements have nearly all been under observation for five years, so that we feel warranted in presenting conclusions drawn from a study of their behavior during this period. The chief evidence is supplied by direct micrometric measurements of changes of volume undergone by bars of neat cement either lying in water at room temperature or kept in air at room temperature.

Such measurements were first carried out by Professor Bauschinger, of Munich. many years ago in an apparatus devised by him which bears his name. Measurements have since been made by others and have, in spite of some conflicting evidence, shown quite clearly that good cements expand somewhat in water and contract in air. These measurements have, however, been nearly all made by engineers upon commercial cements concerning which exact knowledge was lacking as to details of method of manufacture, temperature of burning, composition, and age since burning. The present experiments have so far as possible taken account of all these factors and it is believed present a more nearly quantitative estimate of their value than has hitherto been attempted.

Our measurements of change in volume have all been made upon bars of neat cement, and not upon mixtures of cement and sand or crushed stone, such as are used in practice. This added material, so far as constancy of volume is concerned, acts simply as a diluent for the cement. The change of volume due to the cement will vary with the percentage of cement and the relative area of empty spaces, which will depend upon the coarseness of the crushed stone used and the firmness with which the concrete is tamped into place. The use of bars of neat cement eliminates these large variables and allows a close comparison of results between the different kinds of cement. When applying these measurements of change of volume to concrete, it will be necessary to apply an arbitrary factor which will vary with every local condition, and cannot be considered here.

The behavior of Portland cement in concrete kept constantly or usually wet is entirely different from that which is kept dry, and demands separate treatment. The more complicated case of cement bars stored in water is first considered, and afterwards the relatively simple behavior of cement kept in air is treated.

After a brief consideration of the methods and apparatus employed, the paper divides itself into:

I. The influence of free lime and the effect of aging such cements.

II. The influence of free magnesia and the effect of aging such cements.

III. Some considerations determining the form in which lime and magnesia exist in cement including a preliminary study of the probable equilibrium between free and combined lime, and free and combined magnesia in cements.

METHOD OF MANUFACTURING CEMENTS.

Where cements were to be burned in the laboratory each raw material was dried, thoroughly mixed and analyzed. The marls employed were ground to pass a 100-mesh sieve before using. All the cements described in this paper were made from a single clay which was not finely ground, but was disintegrated with water before mixing with the finely ground marl or other source of calcium carbonate. This method of disintegrating the clay left sand in suspension, and in calculating the proportion of basic material to be added, the assumption was made that silica in the form of quartz sand too coarse to pass a 100-mesh sieve was practically inert. The amount of coarse sand in the clay was determined and the necessary allowance made for it. Since one clay is used in all these experiments the results are strictly comparable with one another. The composition of the clinker as reported is calculated exclusive of this sand, which could average about $2^1/_2$ per cent. of the weight of the clinker.

TABLE I.—COMPOSITION OF RAW MATERIAL.

	No. 5 clay.	L. W. marl.	S. L. marl.	M. & W. marl.
SiO_2	46.91	1.21	0.90	1.36
Al_2O_3	15.89	0.25	0.20	0.55
Fe_2O_3	5.10	0.25	0.39	0.36
CaO	8.25	52.89	51.51	50.03
MgO	3.90	0.89	1.68	1.95

The raw materials were mixed with enough water to make a thin slurry, evaporated with frequent stirring to the proper consistency, moulded into cubes and burned in the laboratory rotary kiln as described in preceding papers from this laboratory.[1] Varying percentages of calcium sulphate in the form of plaster of Paris were added to the clinker, and the whole was ground till it practically all passed a 100-mesh sieve.

DESCRIPTION OF MICROMETER FOR MEASURING CHANGE OF VOLUME.

The change in volume was determined by measurement in a micrometer which possesses decided advantages in simplicity over the Bauschinger apparatus. As will be seen from the illustration, the rectangular bar is supported by two forks at an

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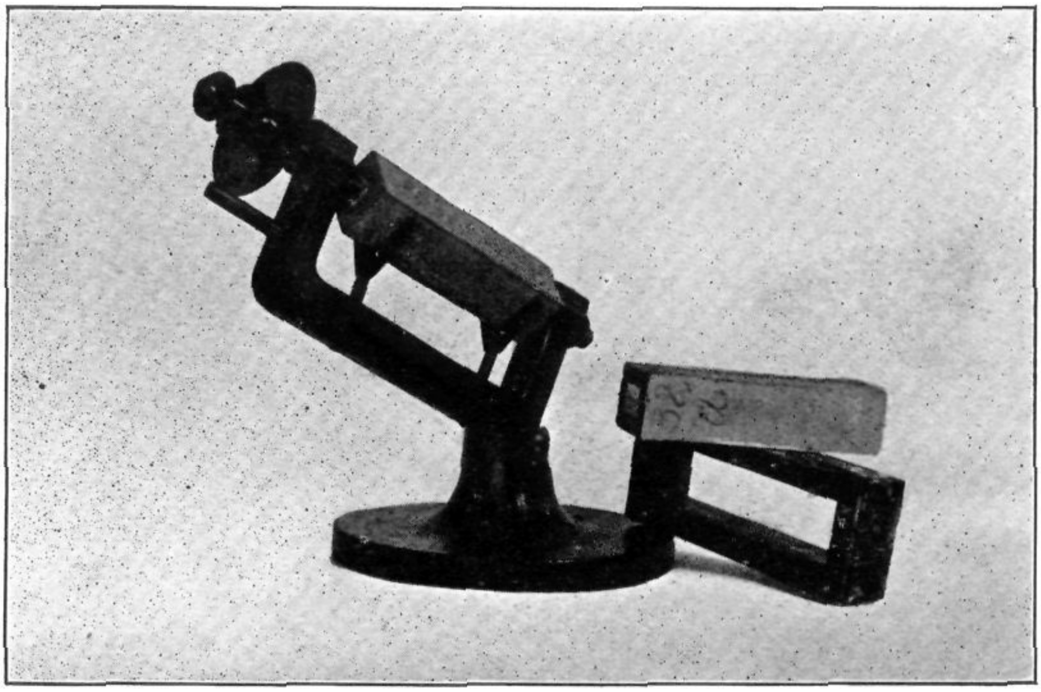
[1] This Journal, **24**, 248, 969; **25**, 1103; **26**, 1142.

angle of about 45°, so that the bar rests by its own weight, with the embedded glass plate against the lower contact piece of the micrometer. The forks compel the bar to always take the same position when being measured, provided the same surface and the same end are placed upward each time. This arrangement always insures the same point of contact for the two ends of the micrometer and eliminates any error due to inequalities in the embedded glass plates. The upper part of the micrometer consists of a screw advancing 1 mm. at each revolution provided with a graduated disc of 50 mm. diameter divided into one hundred parts, each division thus being large enough to enable thousandths to be estimated. The final pressure exerted on the bar is controlled by a friction head turning on the spindle of the micrometer screw.

The expansion bars are made in a split mould 25 mm. square and 102.5 mm. long. Before putting the cement into the mould, a small glass plate is fastened by fine copper wire firmly against each end of the mould so it shall be in the center of the end of the cement bar. These glass plates are cut from microscope slides and are about 12 mm. square. All four edges of each plate are ground to a bevel of about 45° and it is placed in the mould with the small surface against the metal. This insures the firm embedding of the glass in the cement. When these glass plates have been carefully cleaned and thus wired to the ends of the mould, the latter is filled with the cement to be tested in the same way as a briquette mould, special care being taken to insure thorough bedding of the glass plates. After striking off smooth, the mould is allowed to stand in moist air, and when firm enough the experiment number is scratched in. After twenty-four hours in moist air in the constant temperature room, the fine wires holding the glass plates are cut close to the bar, and the bar removed and measured. The brass mould was made 102.5 mm. long because the ordinary microscope slides from which the glass plates are cut average 1.25 mm. in thickness so that the length of the prism of cement on which the expansion is measured is 100 mm. This enables millimeters of expansion to be read directly as percentages.

In making measurements care should be taken that the glass plates are carefully cleaned. The bar is then to be placed gently in the supporting forks, right side up, and allowed to slide gently



against the lower contact piece. It is not to be pressed against it by any force except its own weight. It is easy to insure the same position of the bar in all measurements by seeing that the inscription is always up and in position to be read by the observer. When taking observations, the bar is to be pressed very lightly against the forks with one finger of the left hand while with the other hand the micrometer screw is gently turned until the contact point rests against the upper glass plate. In order to insure firm contact at both ends of the bar the fixed head of the micrometer screw is turned after contact with a pressure about equal to that exerted in winding an ordinary watch. The micrometer is then unscrewed about a half-turn until well clear of the bar and is then screwed down again *slowly*, this time by means of the milled friction head. When contact has again been made, the friction head is carefully turned approximately a revolution, so that the pressure on the expansion bar shall be that due to the friction of the movable head only. The reading of the micrometer is then taken, the head unscrewed until free, the bar loosened and the process repeated. Usually four or five such readings are made on each bar. The maximum variation in a series of five such observations will not exceed 0.003 mm. and is usually not over 0.002 mm. Different observers without more than a few minutes' initiatory practice will duplicate each other's readings within these same limits.

It is best to keep the bars, whether in water or air, together with the micrometer in a room of fairly constant temperature. The temperature coefficients of expansion of iron and cement are so close together that provided the bars and micrometer are at the same temperature, variations of a few degrees in the temperature of the room will not appreciably affect the measurements.

INFLUENCE OF FREE LIME.

Free lime has always been recognized as injurious in Portland cements, but it has been difficult to study its quantitative influence, because of the impossibility of determining by analysis how much of the lime in a clinker is free and how much is combined. It was decided to make a cement of otherwise normal composition which should contain a known amount of free lime. In order to provide a standard with which to compare such a cement, a normal mixture was prepared and burned as Expt. 77.

To a duplicate raw mixture was added calcite in grains coarse enough to remain as free lime in the cement (Expts. 78 and 81). These cements were made from L. W. marl and No. 5 clay whose composition has been given in Table I. The normal cement, 77, had the following percentage and molecular composition:

EXPERIMENT 77.

	Percentage.	Molecules.
SiO_2	24.52	100.
Al_2O_3	8.13	19.6
Fe_2O_3	2.79	4.3
CaO	61.66	270.7
MgO	2.89	17.7

This was burned in the rotary kiln at 1522°, which was as high a temperature as could be carried without causing the clinkers to stick together. The clinker was black, hard and brittle. A portion ground when fresh required 2.5 per cent. plaster of Paris to delay the initial set enough to work. With this amount, the initial set was ten minutes and final set twenty minutes. A pat twenty-four hours in air and twenty-four hours in boiling water remained perfect and hard. Bars 77 A and 77 B were made at that time. Another portion of clinker stored in the laboratory for forty days was ground with 1.5 per cent. plaster of Paris and took its initial set in three minutes and final in fifteen minutes. The pat test as before was perfect. The remainder of the cement with 1.5 per cent plaster of Paris was then stored, ground, an additional six months. Its initial set after that period was eight minutes and final two hours. Expansion bars 77 C and 77 D were made at that time. The further discussion of the behavior of this cement is found in connection with the following experiments. It only need be noted that, as was intended, it proved to be in every way a good cement.

The cements to show the influence of free lime (Expts. 78 and 81) were made from a raw mixture, a duplicate of Expt. 77, to which was added a weighed amount of pure calcite crushed and sized to pass a twelve-, but be retained on a twenty-mesh sieve. This relatively coarse calcite was mixed with the normal slurry which was moulded into cubes, dried and burned in the usual manner. It is fairly certain that such coarse calcite would remain almost wholly as free lime in the clinker. The mixture was burned at 1483°, a temperature a little below the average, but yielding a strong and apparently well-burned clinker. Assuming that all the lime from the crushed calcite remained in the free state, the clinker would contain 2.80 per cent. of free lime, and have the following percentage and molecular composition.

EXPERIMENTS 78 AND 81.

	Percentage.	Molecules.
SiO_2	23.83	100.
Al_2O_3	7.91	19.6
Fe_2O_3	2.72	4.3
Combined CaO	59.93	270.7
Free CaO	2.80	12.6
MgO	2.81	17.7

A portion of this clinker ground with 1.5 per cent. plaster of Paris required 23 per cent. of water for normal consistency and took its initial set in two hours and forty-five minutes. The final set was slow, but not exactly noted. A pat after twenty-four hours in air and twenty-four hours in boiling water was warped loose from the glass and very weak. Neat briquettes made at that time, kept in water and broken after seven days, twenty-eight days and six months showed, respectively, tensile strengths of 295, 630 and 862 pounds per square inch. Two expansion bars were made at this same time, 78 A to be kept in water and 78 B in air. The data of measurements are given in Tables II and IV at the close of the paper and the discussion is given below in connection with the following experiment. The other portion of clinker remaining unground was exposed outdoors in an open box during the month of June and after one month's exposure, was ground with 1.5 per cent. plaster of Paris as before. The cement then took 25 per cent. of water for normal consistency and gave an initial set of three minutes and a final set of five. After twenty-four hours in air and twenty-four hours in boiling water the pat was loose from the glass, slightly warped but very strong.

This cement then was manifestly unsound when fresh, as was to have been expected from the free lime, but behaved much better under the boiling test after the clinker had been stored exposed to the weather for one month. The unexpected fact shown is that this cement containing free lime was slow-setting when fresh, but after one month's storing became so quick-setting as to be useless. It is also to be noted that in spite of its free lime, the tensile tests up to six months were good.

It was deemed best to duplicate this experiment and Expt. 81 was accordingly made as an exact duplicate of Expt. 78, except that the temperature of burning was slightly higher, 1502° as compared with 1483° of the previous experiment. It being desired to determine the length of time required to completely hydrate free lime existing in clinker if the clinker was exposed freely to the weather, the main body of the clinker was thus exposed during the summer and samples were taken at the end of each month and tested for soundness by the boiling test. The data of the pat tests are on the next page.

This experiment confirms Expt. 78 in showing a relatively slow set on the fresh cement changing to an extremely quick set on exposure of the clinker to the weather for a few weeks. As would be expected, the presence of free lime caused nearly complete disintegration of the pat made from fresh cement. The progressive improvement in the behavior of the pats on boiling, rising to a perfect pat at the end of three months showed that by this time the free lime had probably become completely hydrated. The cement was still very quick-setting (see No. 4). On further exposure of the clinker to weather for a total of ten months, the pat still remained perfect but the cement with the same amount of gypsum added had become slow-setting, requiring nearly four hours for initial set (see No. 8). Storing the ground cement in the laboratory for the same period had a slight effect in the same direction (see No. 7). The conclusion is therefore reached that the bad effects of free lime may be eliminated by aging the clinker exposed to the weather, or the ground cement under cover. The cement may become very quick-setting during this process, but will probably get slower again, if sufficient time is allowed.

BENEFICIAL EFFECT OF AGING CEMENTS CONTAINING FREE LIME.

The beneficial effect of aging these cements has been in part brought out by the preceding study of the boiling tests, but it may be best studied quantitatively from the measurements of the expansion bars kept in water whose data are given in Table II, p. 1300, and discussed here, and from the measurements of bars kept in air which will be discussed under a separate heading further on in the paper.

The influence of free lime in cements used fresh and kept under water is best observed by comparing bar 78 A containing free

Treatment of cement.	Plaster of Paris added.	Water. Per cent.	Corresponding expansion bars.	Initial set.	Final set.	Result of pat test 24 hrs. in air and 24 hrs. in boiling water.
1. Fresh……………………………	1.5	23	Expt. 78, A and B.	45 min.(?)	1 hr.	Warped away from glass, badly cracked and easily rubbed to sand.
2. Clinker 1 mo. to weather……	1.5	23		Less than 15 min.		Warped loose from glass and checked.
3. Clinker 2 mos. to weather…..	1.5	24		Less than 4 min.		Loose from glass but very strong.
4. Clinker 3 mos. to weather …	1.5	24		Within 1 min.		
	2.0	24	Expt. 81, A and B.	?	?	Pat perfect.
5. Clinker 4 mos. to weather…..	2.0	23				Pat perfect.
6. Clinker 4 mos. to weather. Ground 4 weeks in lab.	2.0	23	Expt. 81, C and D.	5 min.	15 min.	Pat perfect.
7. Clinker 4 mos. to weather. Ground 6 mos. in lab.	2.0	23	Expt. 81, E and F.	7 min.	30 min.	Pat perfect.
8. Clinker 10 mos. to weather…	2.0	22	Expt. 81, G and H.	3 hrs. 45 min.	5 hrs. 30 min.	Pat perfect.

lime with the similar but normal 77 A. Bar 77 A, which has been immersed in water for five years, showed the gradual expansion usual with good cement and the slight drop in the curve at about six months which is also customary. The corresponding bar 78 A showed the effect of its free lime by an abnormal expansion during the first seven days. During this first week it expanded 0.220 per cent. which is more than the corresponding 77 A showed in five years. It continued to expand at a comparatively rapid but diminishing rate until after two months the rate of expansion had settled down to practically a normal rate, showing that the free lime had become completely hydrated by two months' immersion in water. The later history of the bar shows nothing abnormal, although its high expansion in its early history brings its total after five years to 0.451 per cent.

The effect of aging these cements before use is shown by bars 77 D and 81 B, C, E and G. Bar 77 D was made from the normal cement containing no free lime which had been ground with 1.5 per cent. plaster of Paris and then stored in the laboratory six months. The beneficial effect of aging even a normal cement is shown by its much greater constancy of volume as compared with the fresh cement. At the end of two months its expansion was only one-fifth as much as the fresh cement, and its last measurement showed a total expansion, after four years in water, of only 0.052 per cent. This cement also shows the customary slight contraction in volume after three months which in this case brings its volume slightly less than it was initially. This cement, 77, then, behaves throughout as a well-made cement should.

The similar cement, 78, containing 2.8 per cent. free lime showed abnormal expansion when worked up fresh. Expt. 81, which was a duplicate of 78, was purposely not worked up fresh, but was stored as clinker exposed to the weather for four months.

A portion of it was then ground with 2 per cent. plaster of Paris and an expansion bar was made (81 B) which placed in water showed no more expansion than a normal cement which had aged the same length of time. Another bar (81 G), made from a clinker exposed to the weather ten months, showed little difference in its behavior from a normal cement which had been aged. These bars with the corresponding pat tests indicate that the influence of free lime disappears completely if the clinker is stored open to the weather for four months prior to grinding, and that such cements will be more constant in volume than will most cements of proper composition but worked up fresh.

THE INFLUENCE OF FREE MAGNESIA ON PORTLAND CEMENT.

It was recognized over twenty years ago that magnesia might be a harmful constituent of cement. In 1888 the German Association of Portland Cement Manufacturers appointed a commission with R. Dyckerhoff as chairman to thoroughly investigate the question. This commission after a series of experiments lasting over five years reported in 1895[1] that they could not agree upon a unanimous report. Dyckerhoff maintained as the result of observations upon cements made by him that more than 4 per cent. of magnesia could not safely be allowed in Portland cement. The majority of the committee dissented from this opinion and cited instances of cements with much higher magnesia content which had stood severe tests and had been under observation for years enough to have developed any defects which might have been latent in them. They maintained that magnesia exerted no ill-effect provided the magnesia was calculated as replacing an equivalent amount of lime in the percentage formula

$$\frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} = 1.8\text{–}2.2.$$

The conclusions of the majority of the committee were apparently based not on cements which they had themselves manufactured, but on the analysis of commercial cements high in magnesia which had proved themselves safe.

Four years later other experiments were reported by Oskar von Blaese,[2] who manufactured cements containing varying percentages of magnesia. The raw materials were finely ground and burned in a fixed kiln, and the cements showed throughout a very great constancy of volume. The cements with higher percentages of magnesia showed abnormal expansion, but the conclusion of the author is that 5 per cent. of magnesia is entirely allowable in cements. Further evidence of the influence of magnesia was brought forward by Grauer,[3] who presented in 1902 results of five-year observations on the changes in volume of a number of cements containing magnesia up to 4 per cent. He found that

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[1] Thonindustrie Ztg. 19, 473.

[2] Ibid. 23, 214.

[3] Ibid. 26, II, 1031.

magnesia up to this amount exerted no marked harmful influence. Unfortunately, he made no experiments with cements containing over 4 per cent. magnesia.

It is curious that none of these investigators seem to have paid any attention to the possibility that the erratic behavior of magnesia was due to the form in which it existed in the cement. Free lime in cement has always been recognized as dangerous, but, when in proper combination with silica and alumina, it forms the principal constituent of cement. It seemed to us there was a possibility that magnesia, like lime, was harmful only in the free state, and that it might sometimes be in entirely harmless combination.

The first step in investigating this question was to determine whether magnesia could be made to combine with silica and alumina as lime does; in other words to make an all-magnesia cement. This successfully accomplished, the next step was to determine quantitatively the effect of magnesia existing undoubtedly in the free state. The problem then was to apply the knowledge thus gained to the solution of the difficult question of determining the equilibrium between free and combined lime, and free and combined magnesia. It is not claimed that anything more than a successful beginning has been made on this problem of equilibrium, but some light has been thrown upon it.

PREPARATION AND PROPERTIES OF AN "ALL-MAGNESIA" CEMENT.

Expt. 80 was made to determine whether magnesia could possibly completely take the place of lime and produce a hydraulic cement which did not show abnormal expansion. The raw materials used were No. 5 clay (for composition see Table I), and chemically pure hydrated magnesium carbonate containing 36 per cent. MgO. These were so proportioned as to give a clinker of the following percentage composition and molecular ratio. The cement necessarily shows a small amount of lime coming from the clay used.

EXPERIMENTS 80 AND 82.

	Percentage.	Molecules.
SiO_2	28.91	100.
Al_2O_3	9.79	20.0
Fe_2O_3	3.14	4.1
CaO	5.08	18.9
MgO	53.07	274.7
	99.99	

This was burned at 1496°. The clinker was apparently well burned, strong and of good appearance. It was ground with 1.5 per cent. of plaster of Paris. A pat required 21 percent. of water for normal consistency, took initial set in fifty-two minutes and final set in nine hours. After twenty-four hours in air and twenty-four hours in boiling water, the pat was perfect in appearance and firmly adherent to the glass, but if broken loose was weak as compared with good Portland cement and could be easily rubbed to sand between the fingers. Neat briquettes made from this cement and kept in water gave a tensile test of 27 pounds per square inch after seven days and 43 after twenty-eight days with a continuous gain to 162 pounds after two years. The difference shown by these tests between this cement and a regular Portland is one of degree only. A bar made from fresh cement and kept in water showed an expansion somewhat *less* than is normal for fresh Portland cement. The measurements extend for five years and are given in Table II.

A duplicate of this experiment was made as Expt. 82, the only difference being that the temperature of burning was somewhat higher—1538°. The clinker resembled that from the other experiment. A portion of the clinker was ground fresh with 1.5 per cent. plaster of Paris as in the previous experiment, required 23 per cent. of water instead of 21 for normal consistency, and set somewhat more rapidly, the initial set being twenty minutes and the final five hours. After subjecting to the boiling test the pat was perfect and stronger than in Expt. 80. After the clinker had lain in the laboratory for two weeks, another sample was ground and a pat was made. The initial set had become retarded in that time to one hour and thirty minutes and the final set to seven hours. After the remainder of the clinker had been stored in the laboratory four months, another sample was ground and an expansion bar made. This bar has been kept in water and under observation for four years, the full table of measurements being in Table II. The expansion at the end of four years is only 0.080 per cent., as compared with 0.100 per cent. on the duplicate experiment, 80, which was burned at a somewhat lower temperature and worked up fresh.

These experiments clearly show that it is possible to make a hydraulic cement whose molecular ratio $RO:RO_2+R_2O_3$ is practically that of many commercial Portland cements but in which the lime is almost entirely replaced by magnesia. This cement clinkers at a temperature about that for normal Portland and yields a cement which, except for its inferiority in ultimate strength, meets all the tests demanded of Portland. In fact five-year measurements in water show it to be superior to most cements in constancy of volume.

EFFECT OF ADDED FREE MAGNESIA AND COMBINED MAGNESIA.

The next step was to make a series of comparative tests to determine the effect of adding known amounts of free magnesia and combined magnesia to a finished cement. For this purpose fresh cement clinker was procured from one of our older Michigan mills. This clinker had been put through the ball mill so that most of it would pass a twenty-mesh sieve, but no gypsum had been added to it. It had the following composition:

EXPERIMENTS 83 AND 85.

	Percentage.	Molecules.
SiO_2	24.54	100.
Al_2O_3	6.80	16.4
Fe_2O_3	3.17	4.9
CaO	63.10	276.9
MgO	1.87	11.4

Portions of this crushed clinker were ground with the addition of 1.5 per cent. plaster of Paris, and varying proportions of free magnesium oxide and of crushed magnesian cement from Expt. 82 were added to it. The free magnesia was obtained by burning in the rotary cement kiln chemically pure magnesium carbonate at a temperature of not less than 1500°. The entire set of nine bars was worked up within two weeks. 83 A is cement ground without any addition save plaster of Paris. To B, C, D and E were added, besides, 1, 2, 3 and 4 per cent. respectively of hard-burned free magnesia while to F, G, H and I were added 2, 4, 6 and 8 per cent. of the magnesian cement, Expt. 82, approximately equivalent to 1, 2, 3 and 4 per cent. of combined magnesia. Tensile tests made on ten neat briquettes of each series extending over a period of three years did not indicate that the presence of free magnesia lowered the ultimate strength. Pat tests of the cements containing added magnesia after twenty-four hours in boiling water showed no signs of cracking or warping although occasionally and irrespective of the magnesia content, they were loose from the glass. The test of twenty-four hours in boiling water is therefore not to be relied on to indicate free magnesia even when present to the extent of 4 per cent.

The data of measurements in the nine bars of this series kept in water up to five years are given in Table III. Examination of the figures shows that the original cement (bar 83 A) showed, during the first three months, a relatively rapid expansion which seems to be characteristic of all fresh cements. During the next month it contracted slightly and slowly expanded again until at the end of a year it had reached the same volume as at three months. This drop in the expansion curve seems to be characteristic of all fresh cement and is probably associated with the usual decrease in ultimate strength of neat briquettes in a corresponding period. From one year to five years the expansion proceeded slowly but continuously. This bar, as well as the others described in this paper, will be kept under further observation.

Bars 83 F, G, H and I, containing 1 to 4 per cent. added *combined* magnesia, show the same general expansion as the original cement, but instead of causing a greater expansion this added combined magnesia has *diminished* the expansion slightly, probably because the added magnesian cement itself undergoes such slight changes in volume. After five years these four bars average 0.134 per cent. expansion while the original commercial cement showed 0.144 per cent.

Bars 83 B, C, D and E, on the other hand containing 1 to 4 per cent. of added *free* magnesia, show the same drop in the curve after three months that the others do, and up to this time there is nothing to indicate the presence of free magnesia. After one year, however, free magnesia to the extent of 2 per cent. or more begins to cause evident expansion, and its effect becomes progressively greater as time elapses, until at the end of five years we note that bar 83 E with 4 per cent. of free magnesia has expanded over 1 per cent. The bar at the end of this period is apparently strong and sound and will be observed further. Summarizing the results at the end of five years, we find the following percentages of expansion:

Original cement.............. 0.144

MgO added. Per cent.	A in free state. Per cent.	B combined. Per cent.
1	0.146	0.130
2	0.203	0.130
3	0.382	0.138
4	1.010	0.135

The above figures demonstrate conclusively that magnesia combined in the form of Expt. 82 does not cause expansion and show that the influence of free magnesia up to 1 per cent. is very slight. The dangers attending the presence of this constituent in larger amounts are forcibly shown by the above figures, but the insidious and slow development of the evil effects of free magnesia require further emphasis. Even cement 83 E with its 4 per cent. of free magnesia would have passed perfectly any standard physical tests, and yet after five years in cold water it has expanded over 1 per cent. and there is no indication that the end is reached. Indeed the expansion during the last year is nearly as much as the total of the preceding four years.

EFFECT OF AGING CEMENT CONTAINING FREE MAGNESIA.

After the bars for Expt. 83 were made, a certain amount of the ground mixtures was left. In order to confirm the results of Expt. 83 and also to observe the effect of aging the ground cement, a similar set of bars known as Expt. 85 was made from this surplus material. It was worked up after being kept in a basement cupboard for six months in bottles two-thirds of the time stoppered and the last two months with the stoppers removed. Bars 85 C and D form an addition to the series, being made from the crushed clinker stored a similar length of time in a cupboard but freely open to the air all the time. In all, nineteen bars were made in this series, ten being kept in water and nine in air. Four-year measurements of bars kept in water are given in Table III, while those stored in air are in Table IV.

A study of these figures on the bars of Expt. 85 in water shows that the first expansion, after seven days, averages less than two-thirds as much as in the cement not aged. The next point to be noted is that the contraction in volume observed in fresh cements after about three months is almost eliminated in this aged cement. The change in volume except for one or two slight exceptions is steadily an expansion, but after one year the measurements are still notably below the corresponding fresh cements. The last measurements are after four years with the following results as compared with the fresh cement at a corresponding period.

EXPERIMENTS 83 AND 85.

	Fresh cement. Per cent.	Aged cement. Per cent.
Original cement...........................	0.139	0.105
1 Per cent. free MgO added...........	0.144	0.150
2 " " " " "	0.190	0.165
3 " " " " "	0.253	0.240
4 " " " " "	0.562	0.615
1 " " combined MgO added...	0.129	0.115
2 " " " " " ...	0.124	0.107
3 " " " " " ...	0.130	0.099
4 " " " " " ...	0.130	0.084

The original cement aged six months after grinding and before using shows only 75 per cent. of the expansion of the cement worked up while fresh. The bars to which the magnesian cement was added show similar decreased expansion and the difference in favor of the aged cement is greatest in the cases of the bars with largest additions of the non-expansive magnesia cement. The bars with added free magnesia have, on the other hand, expanded practically as much as the fresh cement.

The net result of this experiment is to confirm the harmful and slowly appearing effect of free hard-burned magnesia in cement. Aging the cement before using retards the expansion for a year or two, but the relief is only temporary for after four years the expansion due to free magnesia is about as bad in the aged as in the fresh cement. The conclusion is therefore reached that aging will not prevent the evil effects due to free magnesia, although it may delay their appearance for a year. This is in contrast to the effect of aging cements containing free lime where the harmful effects of free lime may be completely removed by aging. The failure of the aging process to afford relief from magnesia is undoubtedly due to the extremely slow rate of hydration of this substance, which does not seem to hydrate in air at any measurable rate.

COARSENESS OF RAW MATERIALS AS A FACTOR CAUSING FREE LIME.

Under the heading "Influence of Free Lime," we have already discussed Expts. 78 and 81 to which such coarse particles of calcite were added that most of it was certain to remain as free lime in the finished cement. The effect of smaller differences in fineness, such as exist in marls from different sources, is shown by Expts. 74, 75 and 79. The L. W. marl used in Expt. 79 (and also in Expts. 77 and 78) was exceptionally uniform and almost impalpably finely precipitated calcium carbonate. The S. L. marl of Expt. 74 consisted largely of shells. It was ground to pass a 100-mesh sieve but the particles then were much coarser than those of L. W. marl. The M. and W. marl (Expt. 75) was intermediate between the two in fineness.

The effect of these differences in the physical properties of the marl is shown in Expts. 74, 75 and 79 where the three marls are combined with the same clay. Expts. 74 and 79 have nearly the same molecular formulas and are burned at practically identical temperatures. Yet 74 with coarser marl clearly shows free lime while 79 is sound. This is shown not only by the boiling tests but by the expansion bars. Bar 79 A from fresh cement showed after seven days in water an expansion of only 0.025 per cent. and cannot have contained a trace of free lime, while bar 74 A made from cement which had the advantage of being stored in the laboratory seven weeks after grinding and before being made up, showed after seven days in water an expansion of 0.190 per cent., nearly eight times as high as 79 A and only to be explained by the presence of free lime. Bar 74 D, made from the same cement stored as ground cement in the laboratory for seven and a half months, showed only normal expansion and confirmed the results previously observed in Expt. 81, that the effect of free lime completely disappears on sufficient aging.

Expt. 75 (medium grade marl) also shows considerable free lime, as is evidenced by the seven-day measurement on bar 75 A in water with its expansion of 0.200 per cent. The effect of aging in eliminating free lime is similarly shown in bar 75 D where the expansion on the seven-day measurement is reduced to 0.020 per cent. by storing the ground cement seven months.

The chemical compositions and molecular ratios of the cements 74, 75, 77 and 79 are given in the subjoined table.

	Percentage composition.				Molecular composition.			
	74.	75.	79.	77.	74.	75.	79.	77.
SiO_2	22.90	22.50	23.43	24.52	100.	100.	100.	100.
Al_2O_3	7.64	7.72	7.77	8.13	19.7	20.3	19.6	19.6
Fe_2O_3	2.81	2.70	2.67	2.79	4.6	4.5	4.3	4.3
CaO	59.59	62.99	58.92	61.66	280.2	301.5	270.7	270.7
MgO	7.05	4.06	7.21	2.89	46.7	26.9	46.0	17.7
CaO + MgO	......	......	......	......	326.9	328.4	316.7	288.4

It will be noted that the CaO molecular ratio increases in the order 79, 74, 75, but the difference between 79 and 74 is too small to account for the decided showing of free lime in 74 while it is absent from 79. The difference must be due to the coarser marl of 74. Neither should the free lime in 75 be ascribed to its somewhat higher lime ratio, for Expt. 105 from finely ground material reported in a previous paper gave a perfectly sound cement when burned at 1475° with higher RO ratio of 315.2 molecules of lime and 19.1 magnesia to 100 of silica. This same mixture, No. 105, before its very intimate grinding failed to give a sound cement even when burned at a temperature above 1600°. The details of this experiment showing influence of fineness of grinding on the clinkering process form the subject of a separate paper already published by one of us.[1]

These experiments emphasize the fact, which most mills now realize, that extremely fine grinding of raw materials is necessary to insure the production of cement which shall be sound, even when fresh.

FREE MAGNESIA CAUSED BY COARSENESS OF RAW MATERIALS.

There are five cements available for this discussion. The same lot of clay was used for all of them, but the basic constituents were from various sources, as stated below. The details regarding the manufacture of all of these cements have been given in the preceding portions of this paper. The data most important for this discussion are repeated here.

Expt. 80 and 82. "All-magnesia" cements. Very finely divided. Chemically pure magnesium carbonate used.

Expt. 77. Finely divided L. W. marl.

Expt. 79. Finely divided L. W. marl and finely divided magnesium carbonate.

Expt. 74. Coarser S. L. marl and finely divided magnesium carbonate.

Expt. 75. Moderately fine M. and W. marl.

Expt. No.	MgO. Per cent.	Molecules to 100 of SiO_2. MgO.	CaO.	CaO and MgO.	Temp. of burning.	Estimated free MgO. Per cent.
77…………	2.89	17.7	270.4	288.4	1522°	none
75…………	4.06	26.9	301.5	328.4	1482	2-3
74…………	7.05	46.7	280.2	326.9	1521	3+
79…………	7.21	46.0	270.7	316.7	1474	2-3
80…………	53.07	274.7	18.9	293.6	1496	none

Of these cements only the first in the table, Expt. 77, has a

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[1] This Journal, **25**, 1103.

low enough percentage of magnesia to pass the most rigid specifications. As has been shown already, the slight expansion of this cement when kept in water for five years assures us that it contains no measurable amount of free magnesia. The next cement in order (Expt. 75 with 4.06 per cent. MgO) has low enough magnesia to satisfy many of the specifications. It is, however, made from a coarser marl and is burned at a temperature which is not extraordinarily high, although it should have produced sound cement from an intimately ground raw mixture. The cement contains free lime, as previously noted. A portion of this cement was stored after grinding long enough to destroy the effect of free lime, and then worked up as bar 75 D, which was put in water and has now been under observation for four years. Its low initial expansion shows that the effect of the free lime has disappeared in the aging process, but its expansion at the end of four years reaches the figure of 0.177 per cent., far too high for a sound aged cement. It may fairly be compared with bar 77 D made from sound cement which had been aged about the same time, whose expansion in the same period was only 0.052 per cent., only one-third as much as the cement under consideration.

This tripled expansion of 75 D as compared with 77 D must, so far as we can see, be attributed to the presence of free magnesia. The amount of this free magnesia may be approximately estimated by comparing it with the measurements on Expt. 85 already reported, where varying amounts of free hard-burned magnesia were added to a sound cement which was then aged similarly to Expt. 75. By comparison with the bars of Expt. 85 we estimate that this cement, 75, contains between 2 and 3 per cent. of free magnesia. The reason for this free magnesia is probably to be sought in the relative coarseness of the raw material, which also prevented all the lime from combining. With finely ground raw materials, cement of this composition and burned at this temperature should show much better combination than this one does.

The third cement in the list, Expt. 74, with 7.05 per cent. magnesia, shows an expansion of the bar 74 D of similarly aged cement, amounting to 0.245 per cent. at the end of four years. In comparison again with bar 77 D the increase of 0.193 per cent. over 77 is attributable in the same way to free magnesia. Again estimating by comparison with Expt. 85, the amount of free magnesia required to give an expansion of 0.245 per cent., we arrive at the probable amount of free magnesia in this cement as a little over 3 per cent. This was burned at as high a temperature as is usual in practice but was made from shell marl as before noted and therefore contained both free lime and free magnesia.

Expt. 79 has very closely the same magnesia and lime ratios as 74 but was made from much more finely divided marl and was burned at a lower temperature. The amount of free magnesia indicated by the total expansion of 0.177 per cent. (bar 79 C) after four years as compared again with the 0.052 per cent. of bar 77 D indicates that the amount of free magnesia is the same as in Expt. 75, between 2 and 3 per cent. The burning temperature was about the same as 75 and the reason that the free magnesia is not higher is to be found in the finer subdivision of the raw material.

In view of the certain evidence of the presence of free magnesia in this cement, Expt. 79, special attention should be drawn to the fact that even the freshly burned cement stood perfectly the test of boiling a pat for twenty-four hours, and that neat briquettes showed a steady gain in strength from 575 pounds after twenty-eight days up to 911 pounds at the end of three years, with no apparent change at the end of the fourth year. This cement would then have passed all the physical tests required in the standard specifications adopted by the American Society for Testing Materials or the Board of Engineers of the United States Army. Yet it is now expanding at a rate which would arouse grave apprehensions had this cement four years ago been put into an important hydraulic undertaking in defiance of its high percentage of magnesia and relying solely on its good physical tests.

In conclusion and to show that much larger amounts of magnesia than those cited may be completely combined, reference may again be made to the all-magnesia cement, Expts. 80 and 82, which, made from finely ground materials and burned at a not unusually high temperature of 1496°, show not a sign of free magnesia.

EQUILIBRIUM BETWEEN FREE AND COMBINED LIME, AND FREE AND COMBINED MAGNESIA.

The lack of success experienced in making perfect cements with 4 and 7 per cent. magnesia was due in part to coarseness of the raw materials in Expts. 74 and 75. The only reproach that can be brought against Expt. 79 is that a higher burning temperature might have produced better results. Yet it was burned hot enough to produce good clinker and a perfectly sound cement judged by all usual standards. It seems comparatively easy to get magnesia into combination in the presence of a small amount of lime as shown in Expts. 80 and 82, but when, as is the case in Portland cements, the amount of lime is many times greater than the magnesia it is probable that the more reactive lime enters into combination before the inert magnesia and that to the magnesia falls the task of displacing the lime until equilibrium is reached. When equilibrium is reached, unless both the lime and magnesia are completely combined, there should be *both* free lime and free magnesia present. Expts. 74 and 75 both show this condition, but on account of the coarseness of the raw materials, it is not safe to assume that the free lime is due to the attainment of equilibrium.

The better case of Expt. 79. when the raw materials are finer, shows free magnesia but fails to show free lime. This may be due to lack of delicacy in the test, for we have no means of judging in advance what percentage of free lime would correspond to equilibrium for a given temperature and proportion of magnesia. It seems, however, plausible that the time of passage through the rotary kiln is too short to allow the attainment of equilibrium, and that part of the magnesia remains uncombined on account of its inertness. Cements burned in fixed kilns like those made in Germany by Dyckerhoff would have a better opportunity to attain equilibrium. Yet Dyckerhoff was not able, except in one instance, to obtain perfect cements with over 4 per cent. of magnesia. Von Blaese was able with a fixed kiln to obtain cements with higher percentages, which showed themselves quite constant in volume. It is to be noted, however, that the clay used by him was lean, containing less than 40 per cent. as much R_2O_3 as SiO_2. We believe that the relatively large amount of silica and the long duration of burning furnished the best conditions for bringing the magnesia into the combined state.

Our experiments differ in that they were made in a rotary kiln, and although we are not prepared to state that sound cements cannot be manufactured in a rotary kiln when the raw materials contain large amounts of magnesium carbonate, we feel safe in saying that if such cements can be manufactured, it will only be by paying the closest attention to the grinding of the raw materials and to the manner of burning, and that in the lack of a rapid test to determine the percentage of free magnesia it is far safer to stick to a 3 per cent. magnesia limit when the cement is to be used for important work under water.

The case of the influence of magnesia on cement seems to us to be parallel to the old discussion of the influence of phosphorus on steel. Many instances may be cited of steels high in phosphorus which have stood physical tests apparently satisfactorily. Yet engineers are unwilling to risk high phosphorus and are now insisting on a much lower percentage of that element in structural steel than was required a few years ago. It is now quite generally recognized among metallurgical chemists that the influence of an element such as phosphorus upon the properties of steel depends more upon the form in which that element exists than upon the total amount, and consequently if reliability is to be secured, the only safe course to follow is to require the objectionable element to be so low as to be harmless even if it exist in its most dangerous form.

The situation would be different provided the raw materials used contained magnesia already in combination with silica, as might be the case with some clays. An experiment has been made in this laboratory to determine how far lime would displace this harmless combined magnesia in burning a cement and throw the magnesia into the dangerous free form, but it has not been under observation years enough to enable us to give any judgment.

BEHAVIOR OF CEMENT BARS KEPT IN AIR.

In addition to the bars kept in water, duplicate bars of almost all these cements were kept on a shelf in a basement room of fairly constant temperature throughout the year, and measured regularly. The results of these measurements on bars left in air are given complete in Table IV and group the cements into two distinct classes, those that contain free lime, and those that do not contain free lime. The cements which do not contain free lime all contract in volume, and in a remarkably uniform manner, independent of composition. The smallest contraction noted at the end of four years is 0.300 per cent. and the highest 0.392 per cent. The larger figure is for a perfectly fresh cement (77 B) and the lower is for the same cement aged six months (77 C). In the same way Expt. 81 shows a contraction on the aged cement of 0.300 per cent. (81 F and H) while the fresh cement (81 A) has a contraction of 0.382 per cent. Free magnesia exerts no measurable influence, the bars of Expt. 85 with added free magnesia up to 4 per cent. being indistinguishable from one another.

Almost all these bars show a fairly regular diminution in volume with the exception of a break between the third and sixth month when there is a slight expansion followed nearly always by a decided contraction at the end of one year. This is probably related to the phenomenon previously alluded to in the review of the behavior of bars kept in water. The changes of volume in bars kept in air and water are in general the reverse of each other, and the simultaneous breaks in the curves are probably more than accidental coincidence but we are not prepared at present to offer an explanation of the underlying causes.

The cements containing free lime are exemplified in Expts. 74, 75 and 78. Bar 78 B, containing 2.75 per cent. free lime, is the only instance of a cement known to contain free lime which was worked up fresh. During the first seven days the contraction was practically normal, but expansion due to hydration of the lime commenced to be evident after that date and continued to increase at an accelerated rate until at the end of nine months the bar had expanded 1.17 per cent. and had cracked so badly that observations were discontinued. Of the other cements known to contain free lime, bar 75 B, aged thirty days ground, showed a contraction for fourteen days followed by an expansion, which at the end of five years amounts to 0.800 per cent. The same cement (bar 75 C) stored seven months showed a normal behavior throughout, contracting regularly up to 0.330 per cent. at the end of four years. Bar 74 B, in which the cement was aged seven weeks as ground cement, still showed the influence of some free lime, for although at the end of five years its volume is less than it was initially by 0.059 per cent., yet this contraction is less than it should be for cement containing no free lime. This same cement, bar 74 D, aged seven and one-half months after grinding, shows a contraction almost as large as a normal cement.

The effect of free lime on cement bars kept in air is to cause expansion, not, however, noticeable until after twenty-eight days. The hydration of the hard-burned lime in air is so slow that there may be continuous expansion up to five years or more. In case the amount of free lime is unusually high as in Expt. 78, the expansion may be great enough to cause disintegration. The normal behavior of cement bars is to contract in air and free magnesia exerts no measurable influence in this respect. Aging cement diminishes the contraction somewhat.

BEHAVIOR OF A CEMENT BAR ALTERNATELY IN WATER AND AIR.

It has been shown that cement bars stored in water normally expand and that bars stored in air contract. It is worth noting the effect of alternate exposure to air and water as bearing upon the behavior of cement sidewalks. A sample of clinker obtained from the same mill as Expts. 83 and 85 was stored in the laboratory for eight months and afterwards exposed to the weather for four months. The clinker was then ground with 1.5 per cent. plaster of Paris and the ground cement stored in the laboratory for five weeks. That this long aging had not caused any deterioration in the cement is shown by the fact that neat briquettes made at the time of the expansion bars gave a seven-day test of 420 pounds with increase of strength up to 737 pounds at the end of two years. From this cement two expansion bars were made and placed in water. 72 A kept in water showed very slight expansion as might have been expected from the long aging, the expansion at the end of four years being only 0.022 per cent.

Expansion bar 72 B was kept in water for four months and like 72 A remained almost constant in volume. It was taken out of the water and left in air for twenty-eight days when it contracted from —0.005 per cent. to —0.180 per cent. On being placed again in water, at the end of seven days it had expanded 0.150 to —0.030 per cent. and it remained practically constant for the next three weeks. It was again taken out of the water and placed in air and again contracted until at the end of twenty-eight days it had a contraction to 0.190 per cent., practically the volume which it had formerly assumed in air. It was now placed in boiling water for twenty-four hours and after cooling again showed an expansion to —0.030 per cent. as before after keeping in cold water.

This large alternate expansion and contraction as the result of alternate exposure to air and water gives some indications of the alternate strains to which cement walks are subject and may easily account for the appearance of hair cracks so common in such structures, especially where a mixture very rich in cement is used as the top coating.

SUMMARY.

Free lime in Portland cement will not only not be slaked during the mixing and setting of the cement but will not become completely hydrated even when the cement is immersed in water, until about fourteen days have elapsed. The result of this gradual slaking is to produce abnormal expansion of the cement. Any evil effects due to the presence of free lime in cements kept under water will be manifested within two months. In case free lime is present in cement used in structures above ground or where it is usually dry, the expansion due to hydration of the cement will be more gradual but several times greater in volume than when the material is under water. The expansion due to free lime slaking in the air may become so great after several months as to cause complete disintegration.

The deleterious effects of free lime may be completely removed by aging the ground cement or storing the clinker to weather until the pat will stand a perfect boiling test. Weathering the clinker for three months is usually sufficient. It is difficult to state the length of time necessary to properly age ground cement to eliminate free lime. It will not ordinarily be less than one month and may be much longer according to the conditions under which it is stored.

Cement which passes a perfect boiling test may safely be assumed to contain no free lime. The expansion of a bar of neat cement containing no free lime when kept in cold water for seven days is usually under 0.040 per cent., but occasionally may go as high as 0.060 per cent. A cement with 2.8 per cent. free lime showed an expansion of 0.220 per cent. in the same period.

The effect of magnesia like that of lime depends less upon its total amount than upon the form in which it exists. Combined magnesia like combined lime has no injurious effect in Portland cement. Magnesia combined with silica and alumina forms a hydraulic cement which is safe but as compared with Portland cement is too weak to be of any commercial value. Free magnesia has no appreciable affect in cement used above ground where it is continuously dry. If the cement is wet for a part or a whole of the time, the free magnesia will very slowly hydrate and cause expansion. Even where the cement is continuously immersed in water the expansion due to free magnesia is not appreciable until after two months and only becomes distinctly evident after a year. The hydration seems to be only well under headway at the end of the first year and expansion continues at an increasingly rapid rate for at least five years, and probably longer. Aging does not seem to diminish the deleterious effect of free magnesia in cement. This is to be expected, since the rate of hydration of hard-burned magnesia in air is almost imperceptibly slow.

The boiling test for twenty-four hours does not detect free magnesia as it does free lime. Cement containing as high as 4 per cent. of free magnesia has passed a perfect boiling test, yet the last measurement of this cement at the end of five years in cold water showed a total expansion of over 1 per cent., nearly half of which occurred during the fifth year after making.

This slow hydration of free magnesia with its accompanying expansion seems to be the probable cause of the expansion, frequently accompanied by more or less complete disintegration, so often noted in sidewalks, occurring several years after the walk has been laid.

One per cent. or less of free magnesia in cements kept under water causes little noticeable expansion even in neat cement; probably simply filling up the voids. Increased percentages of free magnesia cause cumulatively greater expansion until with 3 per cent. of *free* magnesia the expansion is too great to be at all safe.

In the manufacture of cement from raw materials containing magnesium carbonate, some portion of the magnesia will remain in the free state. This amount will increase with coarseness of raw materials, increasing percentage of lime and increasing percentage of magnesia. If the total magnesia does not exceed 3 per cent. it is not likely that well-made cement will carry enough of this magnesia in the free form to cause injurious expansion under any conditions of service. If the percentage of total magnesia rises above 3 per cent. there will be increasing probability of enough magnesia remaining in the free form to cause injurious expansion in large monolithic structures kept continuously or frequently wet. In structures where suitable provision can be made for expansion joints, a higher percentage of total magnesia is permissible than in monolithic structures. Magnesia should

TABLE II.—EXPANSION OF BARS OF NEAT CEMENT IN WATER.

All measurements represent percentage variation from original volume.

All measurements indicate expansion unless preceded by a — sign.

		Days.				Months.							Years.				
Expt.	No.	7.	14.	21.	28.	2.	3.	4.	6.	9.	12.	18.	2.	3.	4.	5.	Remarks.
74	A	0.190	0.226	0.240	0.240	0.290	0.310	0.330	0.350	0.363	0.370	0.423	0.447	0.499	0.550	0.582	Free CaO and free MgO.
	D	—0.005	+0.005	0.004	0.010	0.024	0.033	0.040	0.050	0.075	0.102	0.121	0.164	......	0.245	......	Aged. Free MgO.
75	A	0.200	0.240	0.265	0.270	0.305	0.315	0.330	0.350	0.355	0.355	0.383	0.390	0.407	0.370	0.432	Free CaO and free MgO.
	D	0.020	0.035	0.045	0.055	0.065	0.072	0.075	0.095	0.115	0.130	0.136	0.152	......	0.177	......	Aged. Free MgO.
77	A	0.038	0.055	0.060	0.070	0.098	0.112	0.120	0.135	0.132	0.130	0.163	0.158	0.170	0.180	0.190	Good cement used fresh.
	D	0.008	0.008	0.011	0.018	0.020	—0.005	—0.010	—0.005	+0.015	0.028	0.032	0.040	......	0.052	......	After aging.
78	A	0.220	0.260	0.280	0.295	0.340	0.355	0.363	0.385	0.390	0.390	0.414	0.412	0.421	0.441	0.451	Fresh. Free CaO.
79	A	0.025	0.045	0.050	0.070	......	0.110	0.168	0.150	0.151	0.160	0.204	0.218	0.250	0.330	0.310	7.2 % MgO. Fresh.
	C	0.005	0.015	0.015	0.010	0.020	0.025	0.030	0.035	0.076	0.089	0.104	0.127	0.145	0.177	......	7.2 “ “ Aged.
	E	—0.007	—0.001	—0.001	+0.003	......	0.032	0.036	0.052	......	0.095	0.117	0.140	0.180	......	......	7.2 “ “ “
80	A	0.022	0.030	0.040	0.040	0.040	0.040	0.040	0.050	0.032	0.032	0.057	0.062	0.082	0.100	0.102	All-magnesia. Fresh.
82	A	0.000	......	0.005	0.008	0.010	0.025	0.010	0.025	0.010	0.010	0.029	0.040	0.059	0.080	......	“ Aged.
81	B	0.030	0.030	0.025	0.026	0.030	0.035	......	0.045	0.063	0.077	0.082	0.090	0.099	0.105	......	Same as 78, but aged.
	C	0.005	0.010	0.010	0.010	0.013	0.005	0.005	0.025	0.044	0.049	0.051	0.059	0.071	0.070	......	“ “ 78, “ “
	E	0.000	0.000	0.000	0.010	0.020	0.035	0.035	0.043	0.048	0.050	0.068	0.062	0.081	0.092	......	“ “ 78, “ “
	G	0.020	0.025	0.038	0.038	0.053	0.065	0.073	0.081	0.086	0.089	0.103	0.101	0.115	0.121	......	“ “ 78, “ “

TABLE III.—EXPANSION OF BARS OF NEAT CEMENT IN WATER.

All measurements represent percentage variation from original volume.

All measurements indicate expansion unless preceded by — sign

		Days.				Months.							Years.				
Expt.	No.	7.	14.	21.	28.	2.	3.	4.	6.	9.	12.	18.	2.	3.	4.	5.	Remarks
83	A	0.030	0.038	0.045	0.055	0.080	0.100	0.080	0.090	0.090	0.100	0.112	0.116	0.132	0.139	0.144	Com. cement fresh.
	B	0.025	0.032	0.039	0.045	0.070	......	0.075	0.082	0.075	0.095	0.106	0.117	0.134	0.144	0.146	“ “ “ + 1% free MgO.
	C	0.020	0.030	0.040	0.050	0.073	0.094	0.075	0.096	0.078	0.113	0.133	0.150	0.170	0.190	0.203	“ “ “ + 2% “ “
	D	0.027	0.037	0.047	0.057	0.080	0.092	0.087	0.097	0.097	0.127	0.151	0.168	0.197	0.253	0.382	“ “ “ + 3% “ “
	E	0.030	0.040	0.052	0.065	0.090	0.110	0.104	0.120	0.120	0.158	0.172	0.223	0.290	0.562	1.010	“ “ “ + 4% “ “
	F	0.030	0.038	0.046	0.054	0.070	0.075	0.072	0.076	0.080	0.093	0.106	0.110	0.119	0.129	0.130	“ “ “ + 1% comb. MgO.
	G	0.026	0.032	0.040	0.049	0.070	0.089	0.080	0.080	0.070	0.088	0.101	0.107	0.119	0.124	0.130	“ “ “ + 2% “ “
	H	0.025	0.036	0.045	0.055	0.060	0.079	0.070	0.070	0.070	0.090	0.101	0.106	0.118	0.130	0.138	“ “ “ + 3% “ “
	I	0.021	0.030	0.040	0.048	0.060	0.072	0.070	0.070	0.070	0.096	0.104	0.110	0.120	0.130	0.135	“ “ “ + 4% “ “
85	A	0.020	0.030	0.040	0.040	0.040	0.050	0.050	0.070	0.088	0.085	0.089	0.094	0.108	0.110	......	Same cement aged.
	C	0.015	0.025	0.025	0.025	0.030	0.040	0.035	0.055	0.070	0.067	0.074	0.079	0.091	0.100	......	“ “ “
	E	0.020	0.035	0.040	0.040	0.045	0.045	0.055	0.078	0.098	0.098	0.106	0.122	0.127	0.150	......	“ “ “ + 1% free MgO.
	G	0.025	0.035	0.035	0.035	0.055	0.048	0.065	0.085	0 106	0.107	0.124	0.135	0.154	0.165	......	“ “ “ + 2% “ “
	I	0.010	0.030	0.035	0.040	0.035	0.055	0.060	0.085	0.110	0.115	0.136	0.154	0.185	0.240	......	“ “ “ + 3% “ “
	K	0.020	0.035	0.040	0.040	0.055	0.060	0.080	0.103	0.134	0.141	0.175	0.199	0.282	0.615	......	“ “ “ + 4% “ “
	M	0.020	0.025	0.030	0.030	0.043	0.045	0.060	0.070	0.084	0.082	0.093	0.096	0.109	0.115	......	“ “ “ + 1% comb. MgO.
	O	0.015	0.018	0.025	0.025	0.038	0.035	0.045	0.060	0.077	0.074	0.084	0.089	0.104	0.107	......	“ “ “ + 2% “ “
	Q	0.000	0.015	0.015	0.015	0.030	0.030	0.040	0.058	0.072	0.070	0.080	0.087	0.108	0.099	......	“ “ “ + 3% “ “
	S	0.002	0.002	0.002	0.003	0.005	0.012	0.022	0.032	0.054	0.052	0.062	0.069	0.081	0.084	......	“ “ “ + 4% “ “

TABLE IV.—CONTRACTION OF BARS OF NEAT CEMENT IN AIR.

All measurements represent percentage variation from original volume.

All measurements indicate contractions unless preceded by a + sign.

		Days.				Months.							Years.				
Expt.	No.	7.	14.	21.	28.	2.	3.	4.	6.	9.	12.	18.	2.	3.	4.	5.	Remarks.
74	B	0.129	0.137	0.138	0.139	0.107	0.081	0.060	0.046	0.010	0.110	0.048	0.089	0.077	0.032	0.059	Contains free lime.
	D	0.015	0.055	0.085	0.135	0.178	0.196	0.205	0.205	0.210	0.200	0.259	0.244	......	0.260	......	Aged till free lime removed.
75	B	0.115	0.120	0.118	0.110	0.050	0.000	+0.095	+0.155	+0.100	+0.090	+0.240	+0.209	+0.342	+0.739	+0.800	Contains free lime.
	C	0.040	0.075	0.110	0.165	0.230	0.250	0.290	0.290	0.285	0.265	0.328	0.308	......	0.330	......	Aged till free lime removed.
77	B	0.190	0.220	0.227	0.237	0.240	0.237	0.232	0.240	0.318	0.355	0.314	0.355	0.383	0.392	0.393	Good cement used fresh.
	C	0.025	0.072	0.108	0.139	0.195	0.222	0.260	0.250	0.255	0.247	0.302	0.282	......	0.300	......	After aging.
78	B	0.120	0.110	0.100	0.085	+0.080	+0.320	+0.775	+1.110	+1.170	Bar badly cracked.						Contains free lime.
79	D	0.078	0.115	0.160	0.208	0.260	0.270	0.310	0.300	0.295	0.292	0.367	0.353	0.380	0.388	......	7.2 % MgO. Aged.
81	A	0.090	0.120	0.195	0.230	0.275	0.295	......	0.335	0.315	0.306	0.365	0.355	0.380	0.382	......	Same as 78, but aged.
	D	0.085	0.170	0.180	0.250	0.225	0.285	0.295	0.285	0.285	0.303	0.353	0.354	0.365	0.375	......	" " 78, " "
	F	0.125	0.145	0.145	0.155	0.165	0.172	0.170	0.179	0.235	0.246	0.245	0.293	0.284	0.300	......	" " 78. " "
	H	0.155	0.180	0.165	0.167	0.170	0.180	0.170	0.176	0.225	0.247	0.242	0.292	0.292	0.300	......	" " 78. " "
85	D	0.107	0.165	0.180	0.210	0.260	0.260	0.270	0.265	0.265	0.316	0.335	0.366	0.378	0.385	......	Commercial. Aged.
	F	0.100	0.150	0.170	0.180	0.217	0.220	0.217	0.210	0.204	0.249	0.262	0.307	0.322	0.335	......	Com. Aged + 1 per cent. free MgO.
	H	0.135	0.185	0.195	0.205	0.235	0.255	0.240	0.240	0.225	0.273	0.286	0.324	0.337	0.355	......	Com. Aged + 2 per cent. free MgO.
	J	0.105	0.150	0.160	0.190	0.230	0.225	0.220	0.217	0.206	0.253	0.263	0.305	0.319	0.335	......	Com. Aged + 3 per cent. free MgO.
	L	0.110	0.170	0.170	0.200	0.240	0.240	0.240	0.235	0.229	0.274	0.290	0.325	0.346	0.360	......	Com. Aged + 4 per cent. free MgO.
	N	0.110	0.168	0.178	0.203	0.233	0.230	0.223	0.238	0.228	0.272	0.287	0.323	0.334	0.358	......	Com. Aged + 1 per cent. comb. MgO.
	P	0.110	0.160	0.175	0.195	0 230	0.220	0.230	0.235	0.225	0.272	0.290	0.325	0.339	0.355	......	Com. Aged + 2 per cent. comb. MgO.
	R	0.120	0.165	0.180	0.200	0.225	0.220	0.210	0.225	0.218	0.257	0.277	0.313	0.325	0.350	......	Com. Aged + 3 per cent. comb. MgO.
	T	0.110	0.160	0.180	0.190	0.210	0.200	0.200	0.220	0.217	0.264	0.278	0.313	0.311	0.330	......	Com. Aged + 4 per cent. comb. MgO.

not exceed 5 per cent. total when used even under these circumstances.

An increasingly large amount of cement is being used in the structure of buildings where it will never be exposed to the action of water. There is no ground for believing that magnesia even in the free form would cause trouble under such circumstances. Free lime, however, is more dangerous in these structures than where the concrete is to be kept damp, because the expanding lime increases its volume much more in air than in water. Concrete made from sound cement will normally contract in the air, and this contraction continues according to our measurements for at least five years and amounts with neat cement to about four-tenths per cent. Whether this contraction will be sufficient to seriously weaken structures such as floors deserves investigation.

Any cement worked up fresh will change its volume more than if properly aged. It will show a noticeable drop in the curve representing change of volume after about three months, a period which corresponds to that in which briquettes show a falling off in tensile strength. Cement should always be aged for work where constancy of volume is of the highest importance. The only disadvantage of aging lies in the tendency for a cement to become very quick-setting. If it is aged long enough, it reverts again to a slow-setting cement.

Leaving out of account free lime and magnesia the amount of expansion of a cement is apparently dependent upon the proportion and arrangement of the other constituents. The experiments here reported deal with cements with fairly low lime, and with alumina and oxide of iron also below rather than above the average. We have made cements richer in alumina and oxide of iron and also in lime, but observations have not as yet been carried out for a long enough period of years to warrant generalization. The data so far gathered confirm the general results given above but indicate that these cements higher in lime and alumina will be less constant in volume than those described here.

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