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THE APPLICATION OF THE FUNDAMENTAL KNOWLEDGE OF PORTLAND CEMENT TO ITS MANUFACTURE AND USE.*

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Too frequently the development of Portland cement is considered to have been solely a matter of plant routine. The fact that hydraulic limes, from which Portland cement was developed and which contained those constituents that it does, were first produced as a result of investigation is generally lost sight of. However the original producers of hydraulic cements brought forward their under-burned cement as a result of research, which showed them that lime must be burned with silicious or clayey material in order to give a true hydraulic cement.

The credit for the first original research belongs to Smeaton, who wished "to have a cement, the most perfect that was possible, to resist the extreme violence of the sea" in order to build the Eddystone Lighthouse about 1756. He therefore "resolved to take every opportunity in the evenings and intervals of my attendance on the work-yard, mould-room, etc., to go through a

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complete set of experiments on cement, so far as it concerned the subject I had in mind . . . . Having now found a species of materials, and a method of compounding them very competent to our purpose . . . . I was very desirous to get some light into some of the sensible qualities, that might probably occasion the difference, or at least become a mark of distinction. I therefore applied to my friend Mr. Cookworthy, whom I had found at all times ready to afford assistance . . . . He taught me how to analyze limestone." He then goes on to show how he made his analyses and found that "the most pure limestone was not the best for making mortar, especially for building in water . . . . even the Dorking lime, much esteemed for these uses at London, and in the country round about, is plainly nothing but a species of chalk, impregnated with clay, of which it makes one full seventeenth part of the original weight." We can add that in this country, the Portland cement industry had its inception in a region (the Lehigh Valley District) where limestone "impregnated with clay" occurs in great abundance.

The product made by Smeaton was not that now known as Portland cement, but what is known as hydraulic lime. Moreover the former name did not appear until about 1824, when Joseph Aspdin, a bricklayer of Leeds, took out a patent for making a cement from limestone and clay which was called Portland cement because of the resemblance of the set product to the stone quarried at Portland, England. Between this period and that of Smeaton, several cements had been produced, all as a result of investigation which showed the necessity of the presence of impurities in the limestone. The most notable of these investigators was L. J. Vicat, whose work entitles him to be "justly considered as the creator of the industry," according to such a recognized authority as Henry Le Chatelier.

However, none of these actually produced commercially what we now consider as Portland cement. The greater part of their product consisted of a soft burned material which corresponded to what we now know as Roman, Natural or Rosendale cement or hydraulic lime. If perchance some was "over-burned" so that a clinker was unintentionally produced, it was generally discarded and only the soft burned product went into use. The composition also had not developed into that used to-day, a much lower limed raw mixture being in use. Gradually the value of the hard

burned product was recognized, and with its recognition increased the desire to produce it, until about 1875 (in this country and possibly twenty years earlier abroad) we find Portland cement as we now have it—a commercial product.

From Smeaton to Vicat the investigative work was actively pursued in Sweden by Bergmann, in France by de Morveau and Collet-Descotels, and in Switzerland by Saussure. The first of the above proposed a theory which remained generally accepted until Vicat's work—a period of almost fifty years. This theory of Bergmann is of interest particularly as showing the methods employed in the research and to what erroneous conclusions they lead. Having found by chemical analysis alone, that certain hydraulic limes of Lena contained considerable amounts of manganese, he attributed the hydraulic properties of the material to this constituent. His illustrious reputation caused this theory to be generally accepted, and notwithstanding that de Morveau could find manganese in only one hydraulic lime of France, he refrained from contradicting Bergmann. Saussure in Switzerland found the same condition but again refrained from contradicting him, though he did maintain that clay could replace manganese, but would be inferior. The value of the chemical analyses so erroneously interpreted at that time remains to-day entirely too highly esteemed, and it is with difficulty that its proper place is recognized both in investigative and commercial usage at this late date.

Vicat's work stands out prominently in every respect. It was not undertaken to develop a product, as had been so much of the previous work, but was almost solely for the purpose of determining what a material was and what in the material caused it to react as it did with water. While he busied himself almost entirely with hydraulic limes, his method of working and reasoning was such as to cause it to be followed for years. His intense interest in these limes, especially when mixed with puzzolana, led him to materially underestimate the value of the Roman cements—the nearest approach to Portland cements at that time.

Following Vicat we have a number of investigations being carried on in France and Germany. The work in England was almost entirely dropped, but plant development rapidly pursued. Germany had taken up the investigation of hydraulic limes and Roman cements actively, the first investigator, John, being contemporaneous with Vicat. He was followed by Fuchs, Sefstroms,

Pettenkofer, Winkler, Feichtenger, Zulkowsky, Heldt, and Michaelis. Some of these produced in their studies Portland cement such as we have now, though the majority confined their attention to low burned products of either the high lime (hydraulic cement) or the low burned (Roman cement) type. One observation of Sefstroms is of particular interest. In his noting about 1827 the dusting of compositions corresponding to the formula 2CaO SiO_2 we have the first noting of what was but a few years ago shown by the American investigators of the Geophysical Laboratory to be the inversion of the beta form to the gamma form of this compound. In France the investigations of Vicat were continued by Berthier, Rivot, Fraemy, Landrein, and Merceron.¹

The advances either in Germany or France are not very striking when compared with that made by Vicat. Various formulæ were assigned to the different constituents, as a result of chemical analysis of either existing cements or of the set product, or of the products resulting from leaching the cements by either water or other solutions. The value of the constituents thought to be present, as hydraulic or cementing products, was hazarded as a result of these analyses, but there was a lack of general acceptance of these theories due to an appreciation of the lack of proper approach to the problem.

Le Chatelier by his work published in 1887 brought prominently into usage the microscope first used in cement investigation by Winkler. By using the microscope to examine the products produced by burning definite mixtures, by means of chemical analyses of these and of commercial products, he announced the composition of Portland cement to be a tricalcium silicate, tricalcium aluminate, "calcium ferrate" and "multiple silicates." These conclusions remained partly confirmed but never adequately disproven by such eminent foreign investigators as Michaelis, Oddo, Tornebohn, Rebuffet, Rohland, or our own Newberry and

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¹ It is not thought advisable in the space of a short paper to give the many references where the work of the above investigators can be found. These, together with a valuation of the work of each, may be found in the four following publications: "Experimental Researches on the Constituents of Hydraulic Mortars," Le Chatelier, translated by J. L. Mack, published by McGraw-Hill; "Cement," Betram Blount, published by Longmans-Green & Co., London; "Der Portland Zement," Schmidt, published by Konrad Wittwer, Stuttgart; "Die Chemie der hydraulischen Bindemittel," Kuhl and Knothe, published by S. Hirzel, Leipzig.

Richardson, until the eminent work of the investigators, especially Rankin, of the Geophysical Laboratory of the Carnegie Institution. It should be stated as a special credit to Le Chatelier, that while even the latter at first did not confirm the existence of the tricalcium silicate yet the final work of Rankin gave it the prominent place assigned to it by Le Chatelier. The very excellent work of Newberry must also be given a prominent place on account of the wide acceptance by the cement manufacturers of the ratio suggested by him as a means of controlling the composition.

The publications of the Geophysical Laboratory, in connection with their investigation of the system lime-silica-alumina, have given us a true insight into the constitution of Portland cement. Applying the phase rule by means of the best experimental methods of physical chemical attack, coupled with an extensive use of the petrographic microscope, they have shown that well-burned clinker contains tricalcium silicate, dicalcium silicate, tricalcium aluminate, and a certain amount of slag or glass high in oxide of iron.²

It is difficult to appreciate the enormous amount of experimental work done in this investigation, but some slight realization of it may be gained from the fact that "some 7000 heat treatments and subsequent optical examinations of the product" were made. The very stupendousness of the work precludes its duplication within any reasonable period, but at the same time the correctness of the conclusions has been checked many times in the course of work which included not only those compositions which are included in Portland cement but also all those of the entire ternary system. Here and abroad generally the results have been accepted as conclusive. In Germany the prejudice against accepting the existence of tricalcium silicate so strongly insisted upon by Le Chatelier, continues, and several poorly designed and poorly carried out investigations have been made to prove that this is a ternary compound containing a small amount of alumina.

In order to apply on a large scale certain of the generalizations made in some of the first papers of the Geophysical Laboratory the Bureau of Standards erected at its Pittsburgh branch an experimental cement plant during 1911. This was equipped with complete grinding apparatus and a 2' x 20' rotary natural gas kiln.

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² "Portland Cement," Rankin, JOURNAL OF THE FRANKLIN INSTITUTE, vol. 181, 747.

A series of burns was outlined in which a wide variation in the composition was maintained. After burning, a complete chemical and petrographic analysis was made. The clinker was then ground and from the resulting cement the different small physical test pieces were made, as well as concrete test pieces in the form of 6×12 cylinders, which were broken at various periods. Such an investigation would serve to show not only how the various constituents would affect the strength, but also how the strength would be affected by variations in the amount of the constituents. Another series on a smaller scale was carried out wherein pure alumina, silica and lime were used. These latter, on account of preventing contamination from kiln linings, were not made in the rotary kiln. Also in order to secure the silicates separately a higher temperature was desired than attainable in a rotary kiln. This series would serve to show the relative setting and hardening properties of constituents uninfluenced by the presence of a second or influenced by a definite amount of a second added by mechanical mixing after separate preparation.

These investigations, presented to the public partly in Bureau of Standards' Technologic Papers Nos. 43 and 78, have not only borne out the conclusions of the Geophysical Laboratory, but have applied them to elucidating the chemistry of hardening.

The much discussed tricalcium silicate was prepared containing little more than traces of alumina. It was found to have all the setting and hardening properties of ordinary Portland cement. The dicalcium silicate of the same degree of purity was found to harden so slowly that it had no commercial value. However, if allowed to remain in contact with water for a period of from two to three weeks it gradually hardened until at the end of three or four months it had as great a strength as the tricalcium silicate or Portland cement. The tricalcium aluminate when pure hydrated almost instantly with a marked evolution of heat and never secured a true set or hardening.

These conclusions naturally give rise to certain questions. If the tricalcium silicate has all the properties of Portland cement, why not manufacture it alone in the absence of the very slow setting dicalcium silicate or the non-hardening tricalcium aluminate? Has either the dicalcium silicate or tricalcium aluminate any essential functions either in the process of manufacture or usage? If the tricalcium aluminate alone reacts almost instantly with water

and does not set, how are these properties masked in the finished cement?

These questions require a study particularly of the work of the Geophysical Laboratory. The latter has shown that the tricalcium silicate starts to form from the oxides at 1400° C. through the intermediate formation of the dicalcium silicate. This combines at higher temperatures, or with a longer heating with more lime, to form the tricalcium silicate. This disintegrates at about 1920° to the dicalcium compound and free lime. But the most striking feature in regard to the tricalcium silicate is the fact that "it is found as a primary phase only within the ternary system." Hence the possibility of obtaining this pure at commercially obtainable temperatures in quantities at a cost to compete with the price of Portland cement is out of the question. The work of this Bureau does not show that such a pure product would have cementing qualities which would justify much greater cost than Portland cement. The possibility of using a cheaper material than alumina to form a ternary system is not likely, as by the use of clay, especially widely distributed and very cheap, two of the three oxides desired are readily obtained. The Bureau in its work used either the oxide of boron or chromium, neither of which is sufficiently cheap to compete with alumina. In this work not one but six successive burnings were required to produce the compound containing less than 2 per cent. of free lime. Why it would not be possible to produce it on a commercial scale under present methods is hence quite evident.

The dicalcium silicate forms much more readily than the tricalcium compound, especially in the presence of a third oxide, as alumina, and is not decomposable at its melting point. Mixtures of silica and lime such that this compound would form react rapidly and at commercially obtainable temperatures. The presence of alumina in small amounts decreases the temperature required to bring about the formation of the compound. This compound after a month or more of its slower hydration has a strength approximately equal to the higher lime compound, but its water of hydration is only about one-third the latter. It is the more stable product of the two silicates in respect to water and hence would be the more desirable to resist weathering so far as solubility is concerned, if it were not for the fact that after setting it has a very sandy structure and is not free of voids. It hence

contains cavities in which water may freeze or salts crystallize, and in this respect does not offer a good medium for weathering. The tricalcium aluminate by its rapid hydration assists in breaking up the granules of finely ground clinker and also in increasing to a slight degree the hydrating of the silicates. Any free lime existing in the clinker or that formed by the hydrating of the silicates, in the presence of gypsum added for regulating the set, very markedly reduced the reaction of the aluminate with water and actually gives this compound some cementing qualities. In the previous paragraph attention was called to the slow rate of hydration of the dicalcium silicate. The slow hydration noted and the open sandy appearance both require the presence of another material which will hydrate rapidly and to a denser mass. These two properties are furnished in a striking manner by the tricalcium silicate. It was found that mechanical mixtures of these two silicates in equal amounts produced a cement which had the desired density of Portland cement after hardening, and at late periods a very comparable strength. Later examinations of commercial clinker showed that in these mixtures the amount of high limed compound was low and that with mixtures of the correct proportion a product equal to Portland cement would doubtlessly have been obtained.

Before leaving the subject of pure compounds it would be desirable to call attention to certain of their properties which have been noted by different investigators, but in certain cases not fully explained. The presence of uncombined lime in these and in Portland cement has been a matter of much discussion. Thus, in the tricalcium silicate used in part of this investigation as much as 2 per cent. of free lime was noted, but the silicate was sound according to the usual test—because the test piece had attained a strength before test in excess of the disruptive force developed by the hydrating of the lime during the test. The dicalcium silicate hardens so slowly that it is likely that it would have to be aged a month before it would have sufficient strength to be sound in the presence of the same amount of lime. The dusting of dicalcium silicate and of low burned or too high silica Portland cement is a commonly noted phenomenon. This is due to the inversion of the beta to the gamma form of the dicalcium silicate with an increase in volume of about 10 per cent. Whether this inversion may be delayed to a late period, as for instance after the cement has gone

into a concrete, with consequent destruction of the concrete, has been discussed repeatedly. The Bureau has made a number of cements in which the clinker dusted slowly (it is surprising how much many clinkers will dust in the course of three or four years). But it has not been able to note any destruction of set cement in any form in specimens made of these cements. Disintegrated concretes made of commercial cements have been examined for the same purpose, and none of the gamma form noted. A number of investigators have questioned the possibility of hydration of the dicalcium compound. This has been due, however, to their not observing the phenomenon of its hydration over a sufficiently extended period. Test pieces made of it cannot be handled at the end of a week without breaking. At the end of a year they will have attained strength approximately equal to that of Portland cement, but will have acquired only about 5 per cent. water of hydration. Crystals of hydrated lime are plentiful in the specimens, showing the breaking up of the compound to a silicate of lower lime content. The tricalcium silicate will have acquired at the end of a year more than twice the water of hydration of the dicalcium compound. The former compound also gives off lime during its hydration. Many investigators have noted that the tricalcium aluminate sets and hardens. However this is another compound which decomposes at the melting point, giving off lime. If the two oxides, in the proportions to form $3\text{CaO Al}_2\text{O}_3$, are heated to the point of vitrification, $5\text{CaO } 3\text{Al}_2\text{O}_3$ and CaO result. The true tricalcium aluminate free of lime can be obtained only by heating the oxides for a long period at a temperature of about 100° below that required for vitrification (about 1450° , dissociates at 1535°). This mixture of $5\text{CaO } 3\text{Al}_2\text{O}_3$ and CaO sets and hardens rapidly and could be used as a very quick setting cement. It is this mixture which has been the subject of investigation, as it and not the true tricalcium compound has been obtained in by far the majority of cases. Chemical analyses will not determine whether the compound $3\text{CaO Al}_2\text{O}_3$ is formed. The microscope is essential to determine the free lime.

The work which the Bureau carried out in its rotary kiln has been of particular value in showing the amounts of the several constituents that may be obtained in general manufacturing practice, and how these affect the product as a cementing agent. In this work the composition of approximately 50 cements (each

made after burning a half ton of raw material) was varied so that the tricalcium silicate content ranged from a trace to approximately 51 per cent. The dicalcium silicate varied from 12 to 74 per cent., and the tricalcium aluminate from 14 to 33 per cent. These figures were obtained by petrographic examination of thin sections of clinker. The data have been studied in a great many ways—by the plotting of strength at various periods against the ratios suggested by Le Chatelier, Michaelis, Newberry and others, as obtained from the chemical analyses; by plotting the strength against the amount of the constituents as obtained by petrographic analyses, and by plotting the strength against molecular formula, calculated both

TABLE I.

Showing the effect of the di- and tricalcium silicates upon the strength, in pounds per sq. inch, at different ages, of cements in a 1:1.5:4.5 gravel concrete. Arranged in groups depending upon the $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio.

Average SiO_2 Al_2O_3	1.25	1.75	2.25	2.75	3.25	3.75	4.25	4.75
3 CaO SiO_2	36.3	22.0	30.2	26.1	16.2	31.4	21.1	7.6
3 CaO SiO_2 plus 2 CaO SiO_2	54.8	57.5	65.1	43.0	71.5	72.6	68.9	67.0
Strength at 4 weeks ..	1660	1205	1655	1315	960	1560	1560	570
Strength at 1.5 yrs. ..	2375	2265	2700	3110	2670	3215	3240	2705
Strength at 5 years ..	2650	3020	2960	3290	3170	3470	3610	3305

from the chemical and petrographic analyses. The majority of these show but little of interest, while others bring out striking facts. But the most striking feature of all is that composition or constitution are meaningless so far as predicting the quality of a cement unless the period of hardening is considered. This can be realized from what has been stated before in regard to the speed of hardening of the several compounds. Table I, presenting certain of the data, will show this fact, and at the same time illustrate one of the methods of presenting the data in such a tabular form as will show a comparison of one of the common ratios with changes in constitution and with strengths produced in concrete at certain ages.

The data in Table I have been arranged by placing each of about 50 cements, all made at the Bureau, in one of several

groups depending upon whether the silica-alumina ratio lay between 1.00 and 1.50; 1.50 and 2.00; 2.00 and 2.50, etc. In the table the first group above is given in the second column under the ratio 1.25, the second under the ratio 1.75, etc. These ratios were obtained from the analyses of the clinker by reducing these by calculation to the 5 compounds—silica, alumina, iron oxide, lime and magnesia as equaling 100 per cent. The amounts of the two silicates were obtained from petrographic analyses of thin sections of the same clinker. In the table the amount of either constituent is the average of all the cements in the group. The strength was the average of the 6 x 12 concrete cylinders for all the cements in the group.

The difficulty of deriving any conclusions from such a tabula-

$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$	CaO equivalent to $2.5\text{SiO}_2 + 1.6\text{Al}_2\text{O}_3$	CaO by analysis	3CaOSiO_2	2CaOSiO_2	Strength of 1:1.5:4.5 concrete tested at		
						4 weeks	1.5 yr.	5 yrs.
2.29	2.17	65.8	64.1	61.8	16.8	2380	3845	4510
2.71	2.26	64.9	65.1	51.5	18.0	2480	4260	4750
3.35	2.33	65.0	65.9	49.8	22.0	2700	4530	5150
1.67	2.16	64.5	64.5	29.5	25.0	1925	3130	4180

tion is immediately apparent, but the reason for the difficulty is not so evident. It is, however, due to the fact that in any group we have the tricalcium silicate ranging from a very small amount to a very large one—as for instance in the group with a ratio of 3.25 it ranges from a trace to 49.8 per cent. In other words a ratio depending upon the composition may classify as similar, cements which differ widely in their constitution. The same applies to all other ratios that have been proposed, whether they are based upon either a percentage or a molecular basis. This is further illustrated in the following tabulation of data secured from the examination of but four cements and the concrete made from them.

It is clearly evident from the above that the silica-aluminum ratio in these four cases again fails as a criterion of the value of a cement; that the lime-silica plus alumina ratio as well as the Newberry formula, shown at the top of the third column, does not predict the amounts of the constituents although for late periods

it is a fair index of the strength. The failure of the lime-silica plus alumina ratio can be readily appreciated from the wide variation in the relative amounts of silica or alumina that is possible and yet have their sum constant. The use of molecular quantities instead of percentages does not materially affect the significance of this ratio derived from several cements, although it does change the numerical value.

The Newberry formula, on account of its very wide application in plant control, was studied more closely by grouping 23 cements which did not deviate too much from normal commercial composition into three groups. In the first group the average lime content, as found by analysis, was in excess of that calculated by the Newberry formula; in the second it had approximately

CaO equivalent to $2.5\text{SiO}_2 + 1.6\text{Al}_2\text{O}_3$	CaO by analysis	$3\text{CaO} \cdot \text{SiO}_2$			$2\text{CaO} \cdot \text{SiO}_2$	Strength of 1:1.5:4.5 concrete tested at		
		Average	Maximum	Minimum		4 weeks	1.5 yr.	5 yrs.
59.8	65.6	40.8	43.1	37.2	14.3	1865	2565	3000
65.3	64.9	38.9	51.8	23.4	26.1	2030	3435	3735
70.8	62.6	25.5	44.7	14.3	38.3	1400	2775	3210

the same value, and in the third the lime content was considerably below that derived from the formula. The above tabulation shows the results of this grouping, together with the average strength of the cements in the group and data concerning the constituents.

Again the formula apparently is of no service in predicting the constitution, but the failure is due either to differences in degree of burning or in composition. Thus the compositions of the cements showing maximum and minimum tricalcium silicate in the second group are very similar, but the one with minimum tricalcium silicate was decidedly underburned and unsound—although it had a strength of 3765 pounds per square inch in the concrete at the end of five years. In the third group the cement with the minimum tricalcium silicate was one with a high alumina content and low lime and silica, whereas the one with the maximum content was a low alumina but high lime and silica content. However, an analysis of the data from all the cements shows that this formula

is the superior of any of the ratios ever suggested. But even it cannot be used to make deductions as to the quality of a cement from the results of chemical analyses, particularly on account of the latter not showing the degree of burning.

How the petrographic analyses will predict the cementing qualities can be inferred from the above tables and discussions. It can also be grasped by a study of Figs. 1 and 2. In preparing these, the clinker has been considered as being composed of but three

FIG. 1.

constituents—the dicalcium and tricalcium silicates and the “flux.” These, as determined by the petrographic microscope, embrace all the constituents and hence equal 100 per cent. In the “flux” is embraced the tricalcium aluminate, the possible “ferrites” and the “glass” more or less colored by the iron oxide. By simply dividing in each analysis the percentage of each constituent by the per cent. of tricalcium silicate, we obtain a formula for each cement of the type—

In all cases the first constituent being unity we may plot the location of the other two on ordinary rectangular coordinate paper.

These locations can then be indicated by such marks as will indicate as to which of several groups it belongs in so far as its strength at any age is concerned. This procedure has been followed in preparing Figs. 1 and 2.

From these it will be noted, as previously stated, that the effect of the tricalcium silicate at the four-week period is very marked in producing high early strengths. This is shown by the fact that those cements low in dicalcium silicate and "flux" fall in the

FIG. 2.

lower left hand corner of the figure, while the locations of the others are stretched out across to the upper right hand corner. The location of each cement is indicated by one of three marks depending upon the strength of the cement as indicated by the concrete specimens. In the case of the four-week specimens, the marks indicate strengths ranging from 345 pounds per square inch to 2700 pounds, while at five years the strengths range from 2110 pounds to 5150 pounds. As at the former period the maximum value is about six times the minimum, while at the latter period the maximum is but two and a half times the minimum, the effect of the dicalcium silicate in conferring strength with age is readily seen.

These figures also present the opportunity of deriving a formula for cement of best general strength qualities. They show that when the dicalcium silicate exceeds 1.5 molecular ratios the strength at four weeks will be low, though for best results this should not exceed 1.0; but if late strengths are considered then it may reach 2.0 and be of good quality. The flux should not exceed 1.0 in any case. Hence the formula would appear for early strength as

If the flux were pure tricalcium aluminate this formula would reduce to a percentage composition of 66.9 per cent. lime, 18 per cent. silica, and 15.1 per cent. alumina. Such a composition, however, would not be obtained from averaging the chemical analyses of the cements in question, neither would it represent the composition of commercial cements. Hence we have rather strong evidence that the "flux" contains silica as well as all the alumina and approximately all of the iron oxide. It indicates quite clearly, however, that the two silicates are likely present in equal molecular ratios. A mixture of the two silicates only in this ratio would give 30 per cent. silica and 70 per cent. lime. Hence the percentage of silica by 2.33 equals the percentage of lime, which is rather a close approximation to Newberry's ratio of 2.5. It is, however, very interesting to note that a purely scientific investigation, carried out entirely from the viewpoint of constitution, should confirm commercial Portland cement manufacturing practices in the use of present compositions.

It is evident that so far as early strength is concerned a cement of relatively high tricalcium silicate content is desired (see Figs. 3 and 4). Such a cement not only gives high early strengths but does not apparently lose strength with age. (It can be readily noted, however, that it does not have a high rate of strength increase with age.) Therefore the possibility of producing cements with a high content of this constituent is very attractive. The use of other fluxing or catalyzing agents than alumina have been suggested. The iron oxide occurring as an impurity in the clay and magnesia as an impurity in the limestone act in this capacity, but cannot be used to a greater extent than that now done commercially without adversely affecting the required properties. The former, in excess, gives a slow setting product and the latter in

FIG. 3.

Upper.—Photomicrograph of a section of clinker of normal composition, nicols of microscope crossed. Note the large, poorly defined grains and lack of crystalline structure; contrast with lower photomicrograph of a section of clinker of approximately 17 per cent. silica, and 11 per cent. alumina content, and note large crystals of tricalcium silicate. Such a cement is not quick setting and deports itself in the kiln as one of normal composition. Magnification in both cases—135 diameters.

addition to slow hardening gives difficulties in manufacture through the formation of excessively large clinker which reduces kiln output.³ The Bureau in its experimental plant made a series of burnings using calcium fluoride to replace some of the limestone and another in which boracic acid was used. The results were disappointing, as in both cases a slow setting and hardening product was obtained, although the lime content exclusive of magnesia was carried close to 70 per cent. However, under these conditions the cements were sound, although the test pieces had to be aged 48 hours before testing, as at earlier periods final set had not been acquired.

High tricalcium silicate can also be obtained by increasing the lime content and reducing the silica. This demands a higher temperature for burning, which in turn increases the cost of production if present procedure is followed. The possibility of an entire change of production procedure is attractive and of interest. It is well known that burning at a lower temperature for a longer period will produce the same result as burning at a high temperature for a shorter period. Hence the suggestion of trying kilns of the tunnel type instead of the rotary type. For use in such a kiln the raw material after grinding would be briquetted, placed upon cars and passed through the tunnel, a certain section of which would be heated to the desired temperature. The heated products of combustion could be directed to a waste heat boiler or to pre-heating the briquettes entering the kiln. This type of kiln, so far as fuel conservation is concerned is the most economical now in use and that it could be used to reach a temperature as high as that required for burning cement is evidenced by its usage for burning fire brick. Modern machine methods for making, molding and handling brick would reduce the apparent cost of this part of the procedure to a minimum. The economy of such a kiln is further realized by the fact that practically the entire section of the kiln is filled with the charge, while in the rotary kiln only a very small section is in use at any time.

Another suggested method is that of the use of admixed fuel in the raw material in the form of coke breeze, anthracite culm,

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³ *Technologic Paper No. 102 of the Bureau of Standards*, "The Properties of Portland Cements Having a High Magnesia Content," gives the results of a study of the effect of magnesia in cements conducted along the lines of the investigations under discussion.

FIG. 4.

Upper.—A photomicrograph of a section of clinker of normal composition, nicols crossed, magnification 90 diameters. Lower.—Of a section of high alumina cement, magnification 40 diameters. See remarks under Fig. 3.

etc. Some preliminary work at the Bureau indicates that the combustion of the fuel in such close contact with the raw material as is brought about by this procedure materially reduces the temperature and fuel required. Further confirmatory work on a large scale is contemplated and partly under way.

The oft repeated suggestion of fusing the clinker in something like a blast furnace will not be quieted until it has been actually shown to be a success or failure. This like the previous suggestion when carried out in a modified blast furnace carries with it the use of a solid fuel in contact with the raw material. Recently considerable attention has been directed to "fused cement" being produced in an electrical furnace in France. This is not, however, Portland cement (which latter must be considered silicates of high lime content with the tricalcium aluminate as a minor constituent), but is one or both of the highly aluminous lime aluminates ($\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$), with a low limed silicate or silico-aluminate of lime as the minor constituent. This class has been under investigation for a number of years by the Bureau, whose recent publication, Technologic Paper No. 197, gives the results. They are indeed wonderful cements, but do not require fusing for manufacturing, but on the other hand require a source of cheap alumina, which is not available in this country. Fused Portland cements of usual composition do not appear very desirable or necessary. They would require excessive cost in burning and subsequent grinding. Also it is a matter of daily practice to secure cements free of uncombined lime in the ordinary clinkering process. Harder burning, even to the point of fusion, cannot secure more or even a different combination of the compounds, unless the lime content were increased beyond that usually used. In such a case a higher temperature would be required to complete the reaction between the dicalcium silicate and the lime, the temperature needed depending entirely upon the amount of lime present in excess of that now commercially used. On the other hand it should be borne in mind that at 1900° the tricalcium silicate decomposes into the dicalcium and free lime. At that temperature the decomposition is complete, but starts considerably lower. Hence in a fused clinker of the usual composition, rapidly cooled, free lime would be present.

At the present time there is but one standard for Portland cement, no matter into what use it ultimately goes. Is this good

practice? The answer must be in the affirmative if considered from the viewpoint of our present knowledge of cement testing. The practical cement user, however, has answered the question negatively in many cases—when he uses one or more brands in preference to others for certain classes of work or at certain periods of the year. In this connection may be cited the belief that certain brands always produce a non-dusting floor, while other brands produce a dusting floor. In all cases the various brands invariably meet the requirements of the standard. The requirements of the latter do not bring out the differences which usage has found to exist. Hence for certain uses special tests will have to be devised which will determine the desirability of any brand over another for any particular case. The question arises as to what is a particular case. Should cements for massive construction be different from those for road construction, or for interior pavement or for seawater or alkali work, or for reinforced concrete? The former does not of necessity demand high tensile or compressive strength like the latter, while for the pavement strength is of relatively minor importance when compared with non-dusting. For seawater or alkali resisting work the physical properties are relatively of minor importance when compared with the need of resistance to chemical action.

High compressive strength can be secured by a high tricalcium silicate content, a silica content of about 20 per cent., a usual alumina content and hard burning of such a raw mixture ground more finely than is usual. Such a cement, however, is brittle and of low tensile strength after an early age, hence it is not desirable for road work. It commends itself for floors but requires special skill in handling or it will dust continuously. Material changes in our present tests would have to be made to show the value of any marked changes in methods or procedure of manufacture. Earlier strength tests than seven days would be required; both a tensile and compressive test would have to be considered and a test to determine the coefficient of expansion with age. If by change in composition it can be shown that a cement more resistive to salt action can be secured it may be necessary to incorporate further chemical determinations in our specifications. The possibility of determining the quality of the cement in a concrete at a late age by an accelerated test, in other words determining its cementing qualities when it has largely hydrated, is worthy of much research.

Hence aging at higher temperatures in an atmosphere of water vapor should be a subject of much further and more logical work than heretofore.

This is truly the "Cement Age," but the development of the cement is in its infancy notwithstanding that in this country, where it has secured its widest and most daring application, it is hardly more than fifty years old. But the industry while growing old has developed too broadly physically and too narrowly mentally. After the first few years of a well-balanced development the environments furnished such strenuous physical exercise in developing a market against foreign competition and keeping up with the market once developed, that a magnificent physique was developed but mentally equipped only to keep this physique of production in condition. Recently, however, cost problems and service questions (in particular) have forced the industry to consider its mental shortcomings, and it is now engaged in overcoming these by such thought of technical matters along various lines as serve to demonstrate that it will be able to discuss and settle them in due course along well-developed scientific lines.

The Application of Anode Rays to the Investigation of Isotopes. G. P. THOMSON. (*Phil. Mag.*, November, 1921.)—The author of this paper is the son of Sir J. J. Thomson. Among British physicists there is at least one other of the second generation, Lord Rayleigh. In this connection the names Bernouilli and Berthelot will suggest themselves to the reader. Perhaps there is no better illustration of the transmission of scientific ability from father to son than in the case of R. Kohlrausch whose two sons, W. and F. Kohlrausch, both won distinction and two of whose granddaughters were wedded to men of scientific attainments, W. Hallwachs in Leipzig and Professor Day in Washington.

There are four ways of getting positively charged metallic atoms in the search for isotopes by electromagnetic analysis:

1. By sending an electric discharge through a volatile compound of the metal. Aston used this method with nickel carbonyl, but it is limited in application.

2. Dempster's method of volatilizing a metal, not yet fully described.

3. Positive particles emitted by salts heated for the purpose. A very low pressure in the gas is required.

4. Anode rays given off by an anode under bombardment by gaseous ions. In this method a moderately high pressure is used.

The last method was employed in the present research. The