Frontispiece. .....showing apparatus used

THE HYDROLYTIC EFFECT OF ALCOHOL-WATER MIXTURES ON PORTLAND CEMENT

by

C. C. QUENELLE

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"From the days of antiquity to the present time man has utilized cementitious materials in the construction of dwelling places, dams, roadways, bridges, et cetera. The natives of the Southwest still use the primitive material, "adobe" clay. As the necessity for stronger and more weather-resistant materials developed, other substances were found or produced. Limestone was burned by the ancients, and mixed with sand, and sometimes a volcanic scoria "puzzolana" to produce a cement which has served in the construction of great architectural masterpieces. The utilization of argillaceous limestone and the application of higher temperatures have led to the development of the much stronger product which is now known as portland cement."[1]

The name Portland Cement was given in 1824, by an Englishman named Joseph Aspdin[2] by virtue of the close resemblance of his product to a natural building rock occurring near the town of Portland in England. To Aspdin is commonly given credit for the invention of Portland Cement because it was he who first obtained a patent on it. But like many so called discoveries, portland cement was not discovered suddenly, or by one man. The evolution of this cement had been a

gradual process, and many chemists and engineers had contributed information which led inevitably to the final production of this new cement.

The constitution of portland cement and the properties of its constitutients and the reactions they undergo hawe remained somewhat of a scientific mystery even to the present day. Much study has been given to this subject, some of the ablest students of their day giving their lives to the pursuit of this problem.

In 1756 John Smeaton[1], an English engineer, made the most important discovery that limestones which contain a considerable proportion of clay are distinctly superior to purer limestones for the making of hydraulic cements. In 1780, Higgins[3] observed that when limestone or chalk is suddenly heated to the highest degree, it vitrifies in the parts which touch the fire vessels or furnace or fuel, and the whole of it becomes incapable of slaking freely or acting like lime. Limestone is more apt to vitrefy in such circumstances as it contains more gypseons or argillaceous particles, and oyster shells or cockle shells vitrify more easily than do limestone or chalk.

The earlier engineers did not seem to be much concerned as to the process by which a hydraulic cement was formed. They were mostly interested in the materials and the technique of manufacture and not so greatly interested in the

underlying causes of why certain combinations of materials and technique produced specific results. John Grant[4] stated in 1865 that the manufacture of portland cement is not one of complex character although it requires the exercise of extreme care in the admixture of its two simple and well known ingredients, clay and chalk.

It naturally follows then that the theories of the earlier engineers and chemists on the constitution of portland cement were those of speculation and not of intelligently directed experimentation. In general, these theories were of three types: (1) That clinker consists of a mixture of anhydrons lime and silica which combine when brought in contact with water; (2) That some of the lime and silica are caused to combine by the burning process forming a mono- or possibly a di-calcium silicate, and leaving an excess of free lime, and (3) That clinker consists of hydraulic calcium aluminate, silicates, and free lime, which combine during the hardening process.[1]

After this earlier period, the investigation of portland cement took on a more scientific atmosphere. Henry Le Chatelier[5] was among the first and the ablest of these investigators. Although handicapped by very limited means for measurements of precision, he succeeded in discovering and postulating many points which today are acknowledged to be

facts.

Without giving the details of Le Chatelier's work, we can, by showing the results of his investigations, show the object of our own.

In his earlier papers, Le Chatelier held that the ortho-silicate, 2 CaO.SiO_2 was the chief, if not the only hydraulic constituent of portland cement. Other compounds he held to be present were 3 CaO. Al_2O_3 occassionally with lime; 3 CaO. 2(Fe,Al)$_2$ O_3, a deep brown-colored alumina-ferrite of lime; and certain very small crystals, probably magnesium compounds. He later reported, however, the disilicate to be essentially non-hydraulic. Le Chatelier later believed in the existence of a tribasic silicate, 3 CaO. SiO_2 in cement clinker. He claims to have prepared this compound by decomposing the chlorsilicate with water vapor at a temperature above 450° C. He wrote the reaction as follows: 2 Ca O. SiO_2 . $CaCl_2$ plus H_2O = 3 CaO. SiO_2 plus 2 HCl. The reaction was incomplete, however, but the product seems to have possessed properties of setting and hardening similar to those of portland cement. He found it to show no signs of swelling or cracking, which he regards as a certain indication of the presence of free lime. Le Chatelier summarized his work as follows," the absence of free lime in portland cements of good quality is

very certain; the existence of the aluminate is only probable."

In his work on the calcination or burning process, Le Chatelier found that with a large excess of lime, the final products will be quicklime, tricalcium silicate, and tricalcium aluminate. By diminishing the quantity of lime, we would have these two salts and no quicklime. This makes the determination of the amount of lime to be used, a very important factor in the manufacture of cement.

Wilhelm Michaelis[6] was another investigator who did some very important work on portland cement. He believed the MgO and Fe_2O_3 to be combined in the ratio 2 MgO or 2 CaO to 1 Fe_2O_3. The tricalcium ferrite did not exist, he believed, and any excess CaO went into solution and caused unsoundness.

Zulkowski[1] believed cement clinker to be a mixture of free CaO and a double silicate of lime and alumina of the formula: $4\ CaO.\ Al_2O_3.\ 2\ SiO_2$. The method used by Zulkowski for determining the free CaO consisted in treatment of the cement with a dilute solution of hydrochloric acid. This method is open to the objection that with dilute acids, more or less hydrolysis of calcium silicates and aluminates takes place with the liberation of free lime.

Meyer[1] conducted a brilliant study as a result of which he concurred with Le Chatelier in the essential points on the constitution. In 1901, he wrote: "In fact we

have no evidence to prove the existence of free lime in anhydrous cement. On the contrary, we may conclude by microscopic examination, or by observing the effect of the addition of a small quantity of strongly calcined lime, or by noting the effect when such lime is present due to underburning, that it is certainly impossible that free lime may be present in a Portland Cement of good quality."

Another thing which makes the determination of free lime in Portland Cement a very important factor in its manufacture is the development of proportioning formulas.

Le Chatelier was among the first to propose definite formulas for proportioning the raw mixture in terms of the principle oxides, CaO, MgO, SiO_2, Al_2O_3, and Fe_2O_3. On the basis of his previous investigations on constitution, it seemed altogether justifiable to Le Chatelier that the composition of clinker should be rigorously defined by two limits for lime. The clinker should not, he argued, contain any free lime, as this produces unsoundness in the product. That is, the molecular ratio $\frac{CaO}{SiO_2}$ must not be greater than 3, since the tricalcium silicate is the most basic of the silicates in cement. On the other hand, the presence of too great an amount of the dicalcium silicate, $2CaO.SiO_2$, seemed undesirable to Le Chatelier[5], since he believed that he had found this compound to disintegrate spontane-

ously (dust) and to be nonhydraulic. When an excess of lime is present, he believed the compounds formed to be 3 CaO.SiO_2 and 3 CaO. Al_2O_3. Thus the upper limit for CaO in which the assumption is made that MgO may replace CaO, is expressed by:

$$\frac{CaO \text{ plus } MgO}{SiO_2 \text{ plus } Al_2O_3} \quad \text{not greater than 3.}$$

S. B. and W. B. Newberry[7] also did some work which proved that an excess of lime tended to cause unsoundness in portland cement. After doing experiments with mixtures containing various ratios of CaO and SiO_2 and CaO and Al_2O_3, they proposed the formula $x(3CaO.\ SiO_2)$ plus $y\ (2\ CaO.\ Al_2O_3)$ in which x and y vary in accordance with the relative amounts of SiO_2 and Al_2O_3 present. On preparing synthetic cements in accordance with the above formula, in contradistinction to that of Le Chatelier[5], $x(3\ CaO.\ SiO_2)$ plus $y\ (3\ CaO.\ Al_2O_3)$, they found their own to apply, while, by the latter, the excess of CaO required to combine with the Al_2O_3 as 3 CaO. Al_2O_3 over that required to combine as 2 CaO. Al_2O_3 was found to remain in the free state so far as could be inferred from their tests. The product was unsound in all cases, and increasingly so as the Al_2O_3, and consequently the excess CaO, was increased.

Jean Hendrickx[1], a Frenchman, has done a great deal of work on portland cement. The essential thing to him

is not the manner of combination, but the ratio in which the silica, and lime must be proportioned. Hendrickx believes the major problem of the cement chemist becomes that of causing the first limit for lime to coincide with the second.

The whole problem then, is to develop a satisfactory and expedient method for the determination of free lime. As stated before, the method used by Zulkowski[1] consisted in treatment of the cement with a dilute solution of hydrochloric acid. The objections to this method have already been given. Harts[1] method consisted of extraction of the free lime with a 10% alcoholic solution of iodine. Wormser[1] and Spanjer[1] reported large amounts of free lime obtained first in alcoholic solution of aluminum chloride and, later, by a method using solid aluminum chloride and ammonium oxalate. Rebuffat extracted CaO with sugar solutions. Many methods employing aqueous solutions have been used repeatedly in spite of admonitions by Michaelis that such reagents could not give exact results, and the report of Rohland that quantitative proof of the existence or non-existence of free CaO or $Ca(OH_2)$ could not be obtained by purely chemical means.

No wholly satisfactory method for determining free lime in portland cement has been found. However, there appears to be no reason for Rohland's report and, while there is some foundation for Michaelis' theory as to acqueous solu-

tions, the results of the investigation recorded herein, prove that, to a certain extent, he was incorrect.

There is only one method known to us that gives entirely dependable results. This is the method of Lurch and Bogue which is as follows: Weigh accurately about one gram of freshly and finely ground cement into a 250 c.c. Erlenmeyer flask. Add 25 to 30 c.c. absolute alcohol, 5 to 6 c. c. glycerol and about 10 drops of phenolphthalein. Heat to boiling and titrate while hot with standard Ammonium Acetate in alcoholic solution until the pink color disappears. Boil again for a minute and, if the pink color reappears, run in more Ammonium Acetate and again boil, continuing the process of alternately boiling and titrating until the pink color fails to reappear after boiling for about three minutes.

The main objections to this method are the time and care required. The smaples must be watched and agitated constantly to prevent loss by "bumping". The time required to complete the titration of a sample of cement may vary from a few minutes to more than an hour depending on the fineness of grinding, the vitreous nature of the cement, and the quantity of free lime present, but with any appreciable amount present, the time required is likely to be more than an hour.

Water is objectionable, of course, as the solvent for lime in portland cement owing to its hydrolytic action

upon calcium aluminates and silicates which results in the liberation of free lime. The extent of this, however, could hardly be tremendous in view of the fact that in accepted methods of analysis in the past it has been the solvent. Its use is desirable from the standpoint of convenience and economy, and its solvent action upon lime. It seemed desirable to determine whether the hydrolytic action of water on cement might not be reduced to a negligibly small effect by the addition of alcohol, without at the same time, reducing its solvent action for lime too greatly. Due to the fact that CaO is more soluble in water than glycerol, we believed that an acqueous solution would be preferable to the Lurch and Bogue solvent. We also believed the CaO could be extracted from the cement and, in this way, eliminate the constant attention required by the method of Lurch and Bogue. Due to its low volatility, glycerol could not be used with alcohol in an extractor.

We first prepared nine mixtures of alcohol and water ranging for 10 percent to 90 percent. We used Wiley extractors in this work. Nine of these were placed in a row as shown in the frontispiece, and a different strength solution placed in each of them. The extractors operate in this manner: The sample is placed in the crucible which has a perforated bottom, heat is applied to the bottom of the tube,

the solution volatilizes and is condensed and drops from the point of the condenser down on the sample. Since our sample was powdered, some sort of a mat was required for the bottom of the crucible. We, at first, used a filter paper cut to fit, but later found a thin asbestos mat to be more satisfactory.

We then weighed samples from a standard cement and "run" them in the extractors for approximately eight hours.

We then titrated the solutions, using phenolphthalein in alcoholic solution as indicator, against an aqueous solution of HCl whose CaO value was 0.002405 grams per c. c.

Our results were as follows:

Sample No. I.

Solution 10% C_2H_5OH - 90% H_2O by weight

Weight of sample = 4.0028 grams

titer = 1.5 c. c.

Percent CaO = 0.0896

Sample No. II.

Solution 20% C_2H_5OH - 80% H_2O

Weight of sample = 3.6815 grams

titer = 0.6 c. c.

Percent CaO = 0.0365

Sample No. III.

Solution 30% C_2H_5 OH - 70% H_2O

Weight of sample = 5.2581 grams

titer = 0.35 c. c.

Percent CaO = 0.0160

Sample No. IV.

Solution 40% C_2H_5 OH = 60% H_2 O

Weight of sample = 4.2899 grams

titer = 0.35 c. c.

Percent CaO = 0.0196

Sample No. V.

Solution 50% C_2H_5 OH - 50% H_2O

Weight of sample = 4.4452 grams

No color

Sample No. VI.

Solution 60% C_2H_5 OH - 40% H_2O

Weight of sample = 3.9983 grams

No color

Sample No. VII.

Solution 70% C_2H_5 OH - 30% H_2O

Weight of sample = 3.5835 grams

No color

Sample No. VIII.

Solution 80% C_2H_5 OH - 20% H_2O

Weight of sample = 4.6454

No color

Sample No. IX.

Solution 90% C_2H_5OH - 10% H_2O

Weight of sample = 4.3008

No color

The results of this "run" left us with the choice of two conclusions. Either the 10 percent solution was extracting the free lime and the extraction power of the other solutions varying inversely as their alcohol content and losing their power totally at the 50 percent strength or else, the sample contained no free lime and the results were

due to hydrolysis which stopped with the 50 percent solution.

In our next series of samples, we used only the 10 and 50 percent solutions. Our results, after four hours, were as follows:

SAMPLE NO. I.

Solution 10% C_2H_5OH - 90% H_2O

Weight of sample = 1.1665 grams

titer = 0.2 c. c.

Percent CaO = 0.0412

Sample No. II.

Solution 10% C_2H_5OH - 90% H_2O

Weight of sample = 1.5542 grams

titer - .2 c. c.

Percent CaO = 0.0309

Sample No. III.

Solution 10% C_2H_5OH - 90% H_2O

Weight of sample = 1.1112 grams

titer = 0.175 c. c.

Percent CaO = 0.0378

Sample No. IV.

Solution 50% C_2H_5 OH - 50% H_2O

Weight of sample = 0.8970 grams

No color

Sample No. V.

Solution 50% C_2H_5 OH - 50% H_2O

Weight of sample = 1.1471

titer = .025 c. c.

Percent CaO = 0.0052

Sample No. VI.

Solution 50% C_2H_5 OH - 50% H_2O

Weight of sample = 1.2651 grams

No color

We were still getting results from our 10 percent solution but none from the 50 percent. We later discovered this to be due to a lack of water in the condensate

from the 50 percent solution on account of a lack of boiling.

Our next operation was to run a sample of the cement by the method of Lurch and Bogue to determine what percent, if any, of CaO was present. To our encouragement, We found no trace of free lime in the sample after 15 minutes of boiling with the alcohol-glycerol mixture.

It was now a question entirely of hydrolysis and the problem was to find at what point the hydrolysis stopped. In our next series of samples, we ran one with pure water. The result of this was astounding, the results from the pure water and the 10 percent alcohol differing by more than 19 percent. After running this series 5 hours, we arrived at the following results:

Sample No. I.

Solution - distilled water

Weight of sample = .8007 grams

titer = 6.5 c. c.

Percent CaO = 1.952

Sample No. II.

Solution 10% C_2H_5OH - 90% H_2O

Weight of sample = 1.0843 grams

titer = 0.4 c. c.

Percent CaO = 0.0886

Sample No. III.

Solution 20% C_2H_5 OH - 80% H_2O

Weight of sample = 1.1544 grams

titer = 0.15 c. c.

Percent CaO = 0.0312

Sample No. IV.

Solution 30% C_2H_5 OH - 70% H_2O

Weight of sample = .8201 grams

titer = .05 c. c.

Percent CaO = 0.0146

Sample No. V.

Solution 40% C_2H_5 OH - 60% H_2O

Weight of sample = .7965 grams

titer = .05 c. c.

Percent CaO = 0.0150

Sample No. VI.

Solution 50% C_2H_5 OH - 50% H_2O

Weight of sample = .9855 grams

titer = 0.05 c. c.

Percent CaO = 0.0122

Sample No. VII.

Solution 60% C_2H_5 OH - 40% H_2O

Weight of sample = 0.8666 grams

titer = .025 c. c.

Percent CaO = 0.00698

Sample No. VIII.

Solution 70% C_2H_5 OH - 30% H_2O

Weight of sample = 1.0132 grams

titer = .015 c. c.

Percent CaO = 0.0036

Sample No. IX.

Solution 80% C_2H_5 OH - 20%

Weight of sample = 0.8948 grams

No color

In this last series of samples, we used a smaller amount of solution and, with the aid of boiling beads, secured more vigorous boiling than in the previous cases. We attribute the lack of hydrolysis by the stronger solutions in the previous cases to a lack of water in the condensate. In this last series, the solutions boiled continuously.

We can now be certain that with a solution containing 80 percent alcohol and 20% water, there is no hydrolysis of the calcium aluminates and silicates in portland cement.

Our next problem was to determine whether or not the 80 percent alcohol contained enough water to dissolve the CaO in the cement.

We prepared a sample by mixing some pure CaO with the sample of cement we were using and ran samples from

it in the extractors. Both the 80 and 90 percent solutions showed color upon the addition of phenolphthalein but the results did not check. There are several good reasons for this. First, it was impossible to secure a uniform sample even with the most careful mixing, and, secondly, with the type of extractor used in this work, it was impossible to treat the sample uniformly since only the part laying directly under the point of the condenser was exposed to the drops. Another disadvantage of this extractor is that it was originally devised to be used with no mat in the bottom of the crucible but, since our sample was powdered, it was necessary to use a mat. This prevented the condensate from running through as rapidly as it was condensed and the crucible soon filled.

We believe we have disproved the theory that solutions used in the determination of free lime in portland cement must be entirely anhydrons. We also believe that if a suitable extractor can be designed to treat the sample uniformly, the cement chemist can start his samples going with an 80 percent solution of alcohol and then go about his other work without giving his entire attention to the determination of free lime. This would be a great saving of time and would

also give the chemist the exact percent of free lime which is not obtained by the present day physical methods.

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CHEMICAL LABORATORY

1929 DATE

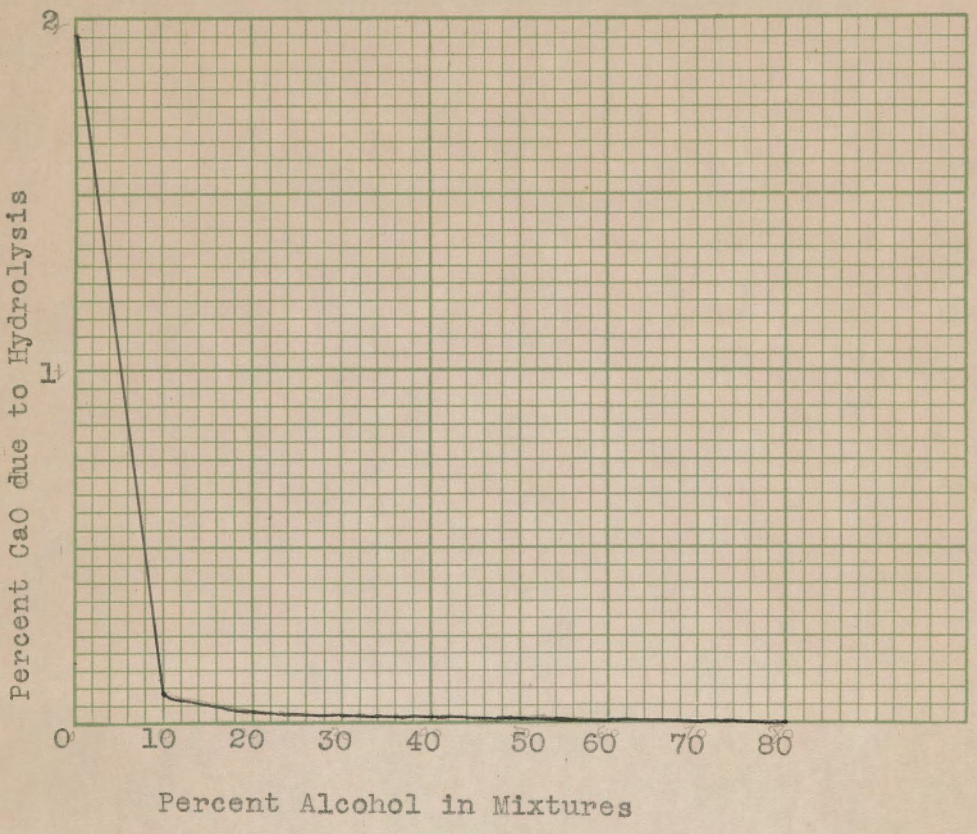

FIG. NO. 1

TITLE:- The Hydrolytic Effect of Alcohol-Water Mixtures on Portland Cement

INTERPRETATION OF CURVES

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APPROVAL

The foregoing thesis is hereby approved as a creditable study on an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it is submitted.

It is to be understood that by the approval of the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

Name Judson A. Robertson

Title Professor of Chemistry