

A STUDY OF THE RATE OF FORTIFICATION
OF FREE LIME IN CONCRETE SUBJECTED TO
ALTERNATE HEATING AND COOLING IN A WATER BATH
AND ITS EFFECT ON THE DISINTEGRATION
OF THE CONCRETE

by

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INTRODUCTION

This research was carried out in an attempt to determine the effect of Free Lime on the disintegration of concrete subjected to alternate heating and cooling in a water bath containing water relatively high in bicarbonates.

D. C. Taylor (*) of the Department of Applied Mechanics of Kansas State College, in his research on the volume change of concrete subjected to the above mentioned heating and cooling test, has observed that concrete cylinders placed in the bath begin to disintegrate after a certain number of cycles depending upon the cement from which the concrete was made. The method of disintegration was peculiarly similar to that observed in concrete pavements and structures which are exposed to surface water. Checks first appeared, and these gradually developed into cracks. Continued treatment eventually reduced the strength of the specimens to only a fraction of its original value.

It was noticed that when the cracks began to form, a ridge of white, insoluble material appeared on them which suggested the possibility that it might have been squeezed

(*) Unpublished data in the files of the Department of Applied Mechanics, Kansas State College.

from the interior by some internal pressure. Chemical analysis showed the white, insoluble material to be CaCO_3 , and a calculation of the change in volume of Ca(OH)_2 going to CaCO_3 shows that there is an increase of sixteen and eight-tenths per cent, so that it would not be at all impossible for the pressure exerted by the forming of the carbonate from the Ca(OH)_2 of the concrete to cause the specimen to crack.

The bicarbonate content of the water used in the bath is approximately 350 parts per million. This varies from day to day, but it is relatively high at all times and provides an excellent opportunity for the formation of CaCO_3 in the specimens.

HISTORICAL AND THEORETICAL

Composition of Portland Cement

Portland cement is composed of the following constituents: Al_2O_3 , CaO , SiO_2 , Fe_2O_3 , MgO , and SO_3 , together with a small amount of such impurities as K_2O , Na_2O , MnO_2 , etc. These impurities rarely exceed two per cent and are generally believed to have no effect upon the properties of the cement.

The manner in which the above constituents combine to

form compounds has been studied by several investigators. Bogue (1) has perhaps done the finest work in this field. He has found that the main compounds of Portland cement are: $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$, $3\text{CaO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, MgO , CaSO_4 , and a small amount of uncombined CaO . There are also known to be small amounts of several other "freak" compounds which apparently occur only when the conditions are just right.

The Origination of the Free Lime

With the compounds of Portland cement definitely known, investigations have turned toward the reactions which occur when Portland cement is mixed with water. Those who have worked on this phase are in agreement that when the compounds of Portland cement are mixed with water they hydrolyze, going to less basic compounds, and at the same time liberating $\text{Ca}(\text{OH})_2$. There is considerable controversy, however, over the extent to which this hydrolysis goes. Tippmann (2), who represents one extreme, believes that the hydrolysis of the calcium silicates is complete, and that the hardening of Portland cement is due to the crystallization of the liberated $\text{Ca}(\text{OH})_2$ and the simultaneous dehydration of the silica gel. He has found that $\text{Ca}(\text{OH})_2$ does not form crystals in the absence of CaSO_4 , and he believes that

sugar prevents the hardening of Portland cement mortar by preventing the formation of crystalline Ca(OH)_2 .

Dorsch (3) has been unable to duplicate the results of Tippmann, and most of the latter's statements are refuted.

Hoyanagi (4) studied the hydration of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ by a photographic method. He finds that in addition to crystals of Ca(OH)_2 there appear crystals whose composition approaches $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10.5\text{H}_2\text{O}$.

Colony and Snader (5) report that, when $2\text{CaO}\cdot\text{SiO}_2$ is gaged with water and made into test pieces, Ca(OH)_2 is liberated, the other product being amorphous hydrated calcium silicate whose composition approaches $\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$. The amount of crystalline Ca(OH)_2 which is formed is dependent upon the amount of water used in making the test pieces. For $3\text{CaO}\cdot\text{SiO}_2$ they find that the hydrolysis takes place much more rapidly and yields more Ca(OH)_2 than $2\text{CaO}\cdot\text{SiO}_2$. In the end the silicate approaches the same composition as the product obtained by the hydrolysis of $2\text{CaO}\cdot\text{SiO}_2$. As to strength the $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ was the better at the end of six months. The $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ also hydrolyzed, giving Ca(OH)_2 and a less basic aluminate. It liberates a large amount of heat during the process and exhibits what is called a flash set. At the end of six months it had a strength equal to eighty-two per cent of tri-calcium silicate.

In a somewhat similar study, Lerch and Bogue (6) prepared a number of the compounds which normally occur in Portland cement. The hydration and hydrolysis of these compounds were studied individually. The results for $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{SiO}_2$ are given in Table 1, and are based upon the reactions

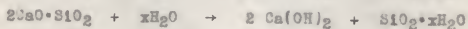
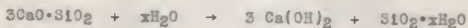


Table 1. Per Cent Hydrolysis of Calcium Silicates, and Their Compressive Strengths at Various Ages.

PER CENT HYDROLYSIS AT VARIOUS AGES								
	1 da.	3 da.	7 da.	28 da.	3 mo.	6 mo.	1 yr.	2 yr.
C_3S	15.5	20.8	23.5	24.7	24.8	26.4	26.2	26.3
C_2S_β	.1	.1	.3	.8	.8	.5	.9	.9
$\text{C}_2\text{S}_\gamma$.1	.1	.1	.1	.1	.5	.5	.5
COMPRESSIVE STRENGTHS AT VARIOUS AGES IN POUNDS PER SQUARE INCH								
	1 da.	3 da.	7 da.	28 da.	3 mo.	6 mo.	1 yr.	2 yr.
C_3S	1450	2800	5960	7100	7100	9690	10300	11300
$\text{C}_3\text{S} + 5\%$ CaSO_4	1770	2780	5830	6760	6330	8700	9800	11300
C_2S_β	0	60	140	910	5160	7560	10250	14350
$\text{C}_2\text{S}_\beta + 5\%$ CaSO_4	0	90	220	1200	3900	7700	9800	12600
$\text{C}_2\text{S}_\gamma$	0	15	15	40	70	100	130	330
$\text{C}_2\text{S}_\gamma + 5\%$ CaSO_4	0	15	15	40	60	140	190	480

Boyanaqi (7) concludes from his results that when Portland cement is treated with water the $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ first becomes hydrated to $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10.5\text{H}_2\text{O}$ and that this reaction is the chief cause of setting. If CaSO_4 is present, crystals of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 36.6\text{H}_2\text{O}$ are formed. $3\text{CaO}\cdot\text{SiO}_2$ and $2\text{CaO}\cdot\text{SiO}_2$ hydrolyze, giving a large amount of free $\text{Ca}(\text{OH})_2$ and amorphous colloidal $\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$. The hardening of the cement is due to the inclusion of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10.5\text{H}_2\text{O}$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 36.6\text{H}_2\text{O}$, and $\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$ gel in the voids between the $\text{Ca}(\text{OH})_2$ crystals.

As was stated before, investigators are agreed that Free Lime is liberated in all cases. Just how much is liberated by each constituent compound and what part the liberated lime plays in the setting and hardening process are still not very well understood.

Effect of the Free Lime on the Disintegration of Concrete

$\text{Ca}(\text{OH})_2$ being a fairly active ingredient of hydrated cement, it seems probable that it is an important factor affecting the durability.

Burke (8) believes, as a result of numerous experiments, that the disintegration of concrete test pieces by the action of sulfate waters is due to the formation of $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ from

$\text{Ca}(\text{OH})_2$, and the accompanying volume change. His calculations show that there is no volume change in the $\text{Ca}(\text{OH})_2$ going to CaCO_3 and therefore there could be no deterrent effect charged to carbonate waters.

Thorvaldson (11), in a study of the action of sulfates on Portland cements by volume stability measurements, concludes that all cements high in lime and containing normal amounts of Al_2O_3 have low resistance to the action of sulfate water. Increasing the amount of Fe_2O_3 and decreasing the Al_2O_3 make the cement more resistant.

Probst and Dorsch (12) find that, of specimens immersed in solutions of CaSO_4 , Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, MgCl_2 , and sugar, the high early strength (high lime) cements were the least resistant, and the aluminous cements were the most.

Paul (13) believes that the lack of durability of concrete pavements has become more pronounced in recent years with the use of high lime cements. He presents evidence to show that durability is inversely proportional to the $3\text{CaO}\cdot\text{SiO}_2$ content of the cement used. He believes that the problem of increasing the life of concrete roads can be solved by the production of low lime cements in which the $3\text{CaO}\cdot\text{SiO}_2$ content is less than forty per cent.

Brady (9) reports that the storage of cement mortars in CO_2 results in a much greater shrinkage than in air. It

appears that CO_2 reacts not only with the $\text{Ca}(\text{OH})_2$ present, but also with the $\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$ gel.

Westerberg (10) believes that the disintegration produced by water percolating through concrete is dependent not only on the chemical composition of the water, but also on the rate of flow. Water high in H_2CO_3 has a very destructive action; whereas a neutral water, especially one with a high lime content, may actually improve the watertightness of the concrete.

Roscher-Land (14) gives the absorption of CO_2 and the formation of calcite as the cause of crumbling or sanding of aluminous cements.

Methods of Determining Free Lime

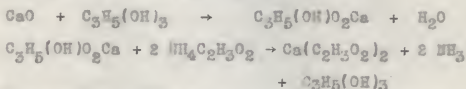
Numerous methods have been advanced for determining free CaO in cements, but of them only about three or four have proven very satisfactory.

It is quite generally conceded that, due to the relative ease with which the compounds of Portland cement hydrolyse, any process for the extraction of the lime by the use of aqueous solutions will give erroneous results. Therefore, all such methods will be eliminated from this discussion.

The glycerol method of Ealey (15) was first used for the determination of free CaO in sand lime bricks and like

materials. Lerch and Bogue (16) later found that the method could be satisfactorily employed for the determination of free CaO in the presence of calcium silicates and aluminates.

The method depends upon the reactions:



The calcium glycerate solution is basic enough to turn phenolphthalein, and when $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ is added, NH_3 is liberated equivalent to the amount of CaO in the sample, and the solution turns colorless.

The lime is dissolved by a solution of glycerol in absolute alcohol in the ratio of one part of glycerol to five of alcohol, and is then titrated by a standard solution of ammonium acetate in absolute alcohol.

CaO is quite insoluble in the cold solution of alcohol-glycerol, but becomes fairly soluble in a hot solution, necessitating the use of some means of heating the solutions. Even with heating, the solution of the lime by the glycerol is quite slow, and the determination requires from six to eight hours to complete.

Lerch and Bogue (17) in a later paper recommend several minor changes in the procedure for the determination of uncombined lime in Portland cement, the principal one being

a change in the concentration of the phenolphthalein solution used in the titration. A change was also made in the amount of alcohol-glycerol to be used per determination.

Rodt (18) has investigated the glycerol-ammonium acetate method for the determination of Free Lime in hydrated cement, and has found that it can be used satisfactorily provided the concentration of the phenolphthalein solution is increased as Lerch and Bogue (17) had already recommended. He also found that as much as one cubic centimeter of water in the alcohol-glycerol solution did not noticeably affect the titration in any case, and that as high as five cubic centimeters in thirty of alcohol-glycerol did not affect the titration on some cements.

Brandenburg (19) has found that the addition of one gram of anhydrous BaCl_2 to the sample of cement after the alcohol-glycerol has been added greatly expedites the liberation of the lime. The addition of BaCl_2 was found to be negative toward CaCO_3 , MgO , CaSO_4 , and other compounds which might be present in cement. He reports that the time between titrations may be greatly shortened and that the end point is much more easily read.

Brandenburg has found that results obtained with the aid of BaCl_2 are a trifle higher than those obtained without, but that the results are consistently high; and he believes

that the true CaO content is more nearly approached when BaCl_2 is used than by the standard method.

Another method recommended for the estimation of Free Lime in concrete depends upon the determination of the heat of hydration of the Free Lime in a calorimeter.

Bessey (20) gives the following procedure: Heat ten grams of pulverized concrete at 350°C . for one-half hour, cool, and then determine the heat of hydration in a calorimeter.

Heat another ten grams of the same concrete at 550°C . for one-half hour. This decomposes Ca(OH)_2 . Determine the heat of hydration of this sample. From the difference of the two heats of hydration the Free Lime content can be calculated. A correction factor must be applied to the results, but it is constant for the apparatus, and very good results are reported to be obtained.

A method of determining Free Lime based on the extraction of the lime with a phenol-alcohol solution is described by Konarszewski and Lukaszewig (21). They recommend the following procedure: Boil a one gram sample of cement with 25 cc. of a mixture 1:1 phenol and absolute alcohol under a reflux for several hours. Filter off the undissolved cement with a glass filter, and wash the residue with absolute alcohol. Remove the alcohol by distillation, and then add

100 cc. of distilled water to the residue of the distillation. This liberates the lime, and it can then be titrated with standard HCl, using methyl orange for an indicator.

EXPERIMENTAL

Apparatus

The Heating and Cooling Apparatus. The water bath used for heating and cooling the specimens consists of a copper tank 48 in. by 39 in. and 10 in. deep. The tank is equipped with a solenoid valve and a time clock which alternately admits cold water and steam directly into the water of the bath. Appropriate baffles are provided to insure proper circulation.

The temperature of the bath varies over the range of 20° to 80° C., and the rate of flow of steam and water is so adjusted that it takes approximately thirty minutes for the temperature of the water to go from one extreme to the other. Thus one cycle is completed every hour.

In order to obtain a better idea of the effect of the water in the bath on the specimens, it was thought advisable to subject part of the specimens to the same bath with the exception that distilled water be substituted for the tap water. This was accomplished by building copper tubes which could be placed directly into the bath. The tubes were made

2½ in. in diameter and 26 in. long, and were closed at one end only. Each tube was equipped with two small hose connections placed 1 in. from each end. Three tubes were made, each being large enough to hold six 2 by 4 in. cylinders.

The specimens were placed in the tubes and rubber stoppers inserted in the open ends. The tubes were then connected in parallel to a large bottle of distilled water, and placed in the water bath. The distilled water was allowed to flow through the tubes at the rate of about 1½ gal. per tube every day.

The possibility that part of the lime might be leached out of the specimens by the above treatment was suggested, and in order to determine whether this were true or not three more copper tubes were built of the same dimensions as those above but without the hose connections. Cylinders were merely placed in these tubes and the remainder of the space filled with water; then a No. 12 rubber stopper was inserted. In order to allow for the expansion of the water in the tube while being heated, it was necessary to make a small hole in the stopper and connect this with a small reservoir by means of a rubber tube. The water on these specimens remained unchanged throughout the test.

Apparatus for the Determination of the Free Lime. The alcohol-glycerol method for the determination of the lime was chosen, and the procedure as outlined by Lerch and Bogue (17) was followed with a few minor changes.

The apparatus used for this determination consisted of a steam bath with spaces for four flasks. The reflux condenser used for the extraction was a 45 cm. length of 6 mm. glass tubing. Cork stoppers were used to connect the flask to the condenser.

In order to do away with the necessity of removing the condenser from the flask every time a titration was to be made as was outlined by the standard method, a burette was attached to each individual flask. A 5 cm. length of capillary tubing served as a tip for the burette and at the same time prevented an undue amount of the titrating solution's being washed out of the tip by the refluxing liquid during the extraction period.

In order to protect burettes and solution in them from the heat of the steam bath, several layers of heavy cardboard were placed over the top of the bath. Holes were cut in the cardboard just large enough for a 250 ml. erlenmeyer flask.

In spite of the precautions some heating of the burettes and solutions occurred, but as exactly the same conditions prevailed during the standardization as during actual deter-

minations any error which might have occurred due to volume change should have been compensated for.

A clean white towel was placed entirely over the top of the steam bath to provide a white background against which to make the titrations. An electric light was placed squarely over the center of the steam bath which greatly facilitated the detection of the end point.

Crushing and Grinding Equipment. Grinding equipment consisted of a small jaw crusher, a Braun pulverizer, and a one-quart porcelain pebble mill. Steel balls were used in the mill in place of the usual porcelain ones.

Choosing the Cements

Ten commercial cements were available whose chemical analysis and compound composition pretty well cover the range for Portland cements. Out of these ten cements three were chosen whose chemical analysis and compound composition as determined by the Ash Grove Cement Company of Chanute, Kansas, are given in Table 2. These three were chosen because they represent high, low, and intermediate lime cements, and also because there was such a wide variation in the $3\text{CaO}\cdot\text{SiO}_2$ and $2\text{CaO}\cdot\text{SiO}_2$ content.

Table 2. Chemical Analysis and Compound Composition of Cements Investigated.

	No. 6	No. 9	No. 10
SiO ₂	21.36%	22.10%	19.68%
Al ₂ O ₃	5.33	5.42	5.90
Fe ₂ O ₃	4.51	5.22	2.26
CaO	61.35	58.45	67.15
MgO	3.99	2.80	1.03
SO ₃	1.72	1.96	2.04
Loss	1.13	3.66	2.52
Total	99.39%	99.61%	100.58%
Insoluble residue	.07%	.23%	.08%
Free CaO	.15	.42	2.01
CaSO ₄	2.90	3.30	3.50
4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	13.70	15.80	6.80
3CaO·Al ₂ O ₃	5.15	5.05	11.70
2CaO·SiO ₂	31.50	48.50	5.50
3CaO·SiO ₂	39.50	19.00	67.50

Preparation of Specimens

Preliminary test pieces were made of the high lime (No. 10) and the low lime (No. 9) cements in the form of 2 by 4 in. cylinders. These cylinders were made of cement, Kaw River sand, and $\frac{1}{2}$ in. limestone aggregate in the ratio 1:2.35:2.95 by weight. A water/cement ratio of 6.75 gallons per sack of cement was used. The cylinders were removed from the molds at the age of one day and placed in the moist closet, which is maintained at 70° F. At the age of 28 days

part of them were placed in the open water bath, where they were subjected to heating and cooling.

These cylinders were tested for Free Lime at several ages, and compared with the specimens which had not been placed in the bath. The results of these tests indicated that the lime was increasing in amount rapidly enough that the change could be detected over a period of several weeks.

After the results of the Free Lime determinations on the first set of specimens were obtained, another set, consisting of twenty-four specimens of each of the three chosen cements, was made. The same sand and aggregate were used, but the mix and water/cement ratio were changed. The new mix was 1:2.34:1.96 and the w/c ratio was 5 U. S. gallons per sack.

The cylinders were made twelve at a time. They were removed from the molds and placed in the moist room at the age of one day.

At the age of fourteen days all but six cylinders of each cement were removed from the moist room. Those removed were disposed of as follows: six of each cement were placed in the open water bath; six of each cement were placed in the sealed tubes with no provisions for changing the water on them; six of each cement were placed in the water change tubes described previously.

At a later date the third set of specimens was made, for

the purpose of determining the rate of formation of the lime and the rate of combination of the cement with water at early ages.

Twenty-four individual specimens were made, eight of each cement, using the identical mix and w/c ratio used in the previous set of specimens. The cement, sand, and aggregate for each specimen were weighed separately and placed in a six-ounce, friction top, tin ointment box. The constituents were then thoroughly mixed with water which was added from a burette. The lids were placed on the cans, and they were set aside until the time of testing. One hundred grams of material was used for each specimen. These specimens were not subjected to the heating and cooling test.

Procedure and Results

When a specimen had reached the age at which it was to be tested, it was placed in the air oven maintained at 120 to 130° C. and dried for a period of not less than twenty-four hours. It was then put through the jaw crusher, and broken into about one-fourth inch pieces. These were next run through a small Braun pulverizer, which reduced the size of the pieces to passing a No. 28 mesh sieve.

The sample, which weighed approximately 450 grams, was then quartered, and one-fourth of it was placed in the pebble

mill and ground until it would 100% pass a No. 125 mesh screen. The sample was again dried for a period of an hour or more, and placed in a properly labeled bottle. For the Free Lime determination, 2 grams of this sample was weighed and transferred to a 250 ml. erlenmeyer flask. Sixty cc. of the alcohol-glycerol solution were added, and if anhydrous BaCl_2 was used, approximately 1 gram was added. The condenser and burette were attached to the flask, which was then placed on the steam bath. As soon as an appreciable pink color developed it was discharged with the standard ammonium acetate solution from the burette. When the pink color failed to return, the burette was read, and the lime value calculated from the titration.

The ammonium acetate solution was standardized with pure lime, prepared by heating .2 gm. of C.P. CaCO_3 at $900-1000^\circ\text{C}$. to constant weight in a platinum crucible. The crucible was cooled and quickly weighed with the cover on. The lime was then transferred to an erlenmeyer flask and treated exactly in the manner described above.

Solutions for the Free Lime determination were prepared from absolute alcohol made by refluxing 95% ethyl alcohol with quick lime in the ratio of 300 grams of lime to each liter of alcohol. After the refluxing period, the alcohol was distilled off, and was again treated with lime and re-

fluxed for some time. The alcohol was again distilled off, and was protected from moist air by tubes of CaCl_2 .

Later a commercial grade of absolute ethyl alcohol was used. This alcohol tested 99.87% water free. No difference in results could be detected between the two sets of solutions.

The alcohol-glycerol solution was prepared by mixing absolute alcohol and C.P. glycerol in the ratio of five to one. To this solution 2 ml. of a phenolphthalein solution prepared by dissolving 1 gram of phenolphthalein in 100 cc. of absolute alcohol were added for every liter of solution.

The ammonium acetate was prepared by dissolving 16 grams of C.P. ammonium acetate in 1 liter of absolute alcohol. This gives a solution of which 1 cc. is approximately equal to .006 grams of CaO .

The first group of specimens was used for the main part to determine whether the tentative modification to the Free Lime method as suggested by Brandenburg (19) could be successfully used.

The cement samples were analyzed for Free Lime both with and without the addition of BaCl_2 . Different lime values are shown for the cements because they were stored under different conditions. Part of the cement was in air tight cans, while the remainder was stored away in a dry place, but unprotected

from the air. The cements which were used in making the specimens were taken from large cans with loosely fitting covers which did not provide protection of the cement from the air.

In all cases where $BaCl_2$ was added, the amount was approximately one gram. Apparently some carbonation had taken place in those cements which were not protected from the air, as shown by the lower results.

Table 3. A Comparative Analysis of Cements Nos. 6, 9, and 10, Showing the Effect of the Conditions of Storage and the Use of $BaCl_2$.

CEMENT NUMBER	CONDITION OF STORAGE	$BaCl_2$	FREE LIME PER CENT
10	Unprotected from air	No	1.85
10	" " " "	Yes	2.25
10	Sealed can	No	2.08
10	Sealed can	Cement Co.'s analysis	2.01
10	" "	Yes	2.41
6	Unprotected from air	Yes	0.33
9	Unprotected from air	Yes	0.60

Table 4 gives the results obtained on the first set of concretes, which were made from cements No. 9 and No. 10 with a mix of 1:2.35:2.95 by weight. The w/c ratio was 6.75 U. S. gallons per sack. This group of specimens was placed into the open water bath, and was not protected from the water in any way.

Table 4. Comparative Analyses of Concretes Made from Cements Nos. 9 and 10 for Net Free Lime, Showing the Effect of the Condition of Treatment Prior to Test and the Use of $BaCl_2$.

NUMBER OF CEMENT FROM WHICH MADE	CONDITIONS OF TREATMENT PRIOR TO TEST	$BaCl_2$	TOTAL FREE CaO	NET FREE CaO
10	28 da. in moist room	No	2.38	2.02
10	"	Yes	2.69	2.33
10	28 da. moist, 7 in bath	No	2.67	2.31
10	"	Yes	2.76	2.40
10	28 da. moist, 21 in bath	Yes	3.14	2.78
9	28 da. moist	No	0.70	0.60
9	"	Yes	1.05	0.95
9	28 da. moist, 7 in bath	No	0.85	0.75
9	"	Yes	1.08	0.98
9	28 da. moist, 21 in bath	Yes	1.17	1.07

The net Free Lime, produced by reaction with H_2O , was calculated by subtracting the per cent of lime which, according to previous calculations, was in the specimens before the water was added. This introduces a small error because the value for original lime is based on the dry weight of the ingredients, whereas to be correct it should be based on the weight of the dry ingredients plus the weight of water held in combination at the time of the test. However, no adequate provision was made for the determination of the combined water in this or the next group of specimens.

The results show that in every case where $BaCl_2$ was added the CaO content was somewhat higher than that obtained by the standard method. However, in the cases where $BaCl_2$

was added the end point was reached in approximately one-half the time required for the standard method. The BaCl_2 addition determinations also had the advantage that after the end point was once reached continued boiling for several hours failed to produce any return of the pink color.

Further tests of the BaCl_2 method included adding a weighed amount of lime to several of the samples and then determining the total lime from the titration. The lime added was determined from the titration in each case by subtracting the amount of lime which was originally in the sample of concrete. Results of these determinations are given in Table 5.

Table 5. The Analyses of Concretes to which a Known Amount of Lime Was Added as a Check on the Use of BaCl_2 .

LIME ADDED BY WEIGHT	LIME ADDED AS CALCULATED FROM THE TITRATION
.1110 grams	.1106 grams
.1154 "	.1160 "
.0530 "	.0751 "
.0626 "	.0630 "

It was found that the titration depended somewhat on the amount of BaCl_2 added, but the variation was not sufficient to require the accurate weighing of the BaCl_2 each time.

After a study of the above data it was believed that the modification for the Free Lime method (19) could be used

to advantage in the determinations. The time factor being an important one, an opportunity to run a determination in four hours which ordinarily required eight hours could not be easily overlooked. Even though the results are a trifle higher than those obtained by the standard method, it was believed, as Brandenburg (19) suggests, that due to the increased sharpness of the end point the BaCl_2 addition probably gives results nearer to the true values than the standard method.

A comparison of the lime content of the specimens at the several ages as shown in Table 2 would clearly indicate that the lime was increasing rapidly enough to be detected by the glycerol method over the test period.

The second set of cylinders, which were made using a mix of 1:2.34:1.96 by weight, and w/c equal to 5 U. S. gals. per sack, were subjected to the several different methods of treatment in the water bath. All specimens were moist cured for fourteen days, and the ages given in tables refer to the age of the specimen in weeks after the test was begun in the bath. The true age would be the age given plus two.

The results of the Total Free Lime determinations are given in Table 6. BaCl_2 was used in making the Free Lime determinations.

Table 6. The Analyses for Total Free Lime of Concretes Made from Cements Nos. 6, 9, and 10, Showing the Effect of Ageing and Different Treatments in the Water Bath.

AGE IN WEEKS	SPECIMENS IN OPEN WATER BATH	SPECIMENS IN SEALED TUBES	SPECIMENS IN WATER-CHARGE TUBES	SPECIMENS IN MOIST ROOM
<u>Free CaO in Concrete Made from Cement No. 6</u>				
1	2.06%	1.81%	2.02%	1.98%
2	1.97	1.91	2.03	1.94
3	1.90	1.88	2.04	2.06
7	1.96	1.79	1.95	2.06
<u>Free CaO in Concrete Made from Cement No. 9</u>				
1	1.34%	1.39%	1.16%	1.29%
2	1.29	1.44	1.50	1.30
3	1.46	1.46	1.48	1.26
7	1.25	1.20	1.23	1.43
<u>Free CaO in Concrete Made from Cement No. 10</u>				
1	3.26%	3.23%	3.64%	3.10%
2	3.43	3.43	3.52	3.57
3	3.46	3.74	3.35	3.36
7	3.14	3.48	3.31	3.48

The results obtained from this set of specimens were disappointing. They did not seem to bear out those obtained from the preliminary set at all. No trends could be observed whatever at the end of seven weeks in the bath. Possibly this was due to the manner in which the specimens were made. Undoubtedly there was some error introduced in this manner because with a mixture as non-homogeneous as the one used it

would be practically impossible to get the same amount of each ingredient into each cylinder unless they were made individually.

The specimens in the third group, which were made individually and sealed in cans immediately after they had been mixed, were tested for lime over a period of one week only. When the age for the test came due, the concrete was either dug out of the can with a spatula, or, if it was too hard for this, was cracked up by striking the bottom of the can with a hammer. The can and specimen were placed in the oven and dried for 24 hours at 120 to 130° C. The sample was then weighed and afterward was ground to passing a No. 125 mesh sieve, just as previous specimens had been.

The results of the Free Lime determinations on this group of specimens are given in Table 7.

Table 7. Comparative Data on the Free Lime in Concretes Made Individually and Sealed Immediately in Cans, Showing the Effect of Ageing.

AGE IN HOURS	SPECIMEN No. 6		SPECIMEN No. 9		SPECIMEN No. 10	
	TOTAL FREE CaO	NET FREE CaO	TOTAL FREE CaO	NET FREE CaO	TOTAL FREE CaO	NET FREE CaO
1/2	0	0	.02	0	.36	0
1	0	0	.02	0	.32	0
3	.06	0	.15	.04	.49	.07
6	.12	.06	.20	.09	.73	.31
12	.21	.15	.19	.08	1.06	.64
24	.87	.81	.67	.56	1.80	1.38
72	1.67	1.61	1.30	1.09	2.98	2.56
168	1.92	1.86	1.44	1.33	3.15	2.73

Table 7 (cont.)

AGE IN HOURS	SPECIMEN No. 6		SPECIMEN No. 9		SPECIMEN No. 10	
	TOTAL FREE CaO	NET FREE CaO	TOTAL FREE CaO	NET FREE CaO	TOTAL FREE CaO	NET FREE CaO
3 wks.*	1.93	1.87	1.29	1.18	3.10	2.68
4 wks.*	1.94	1.88	1.30	1.19	3.57	3.15
5 wks.*	2.06	2.00	1.26	1.15	3.36	2.94
9 wks.*	2.06	2.00	1.43	1.32	3.48	3.06

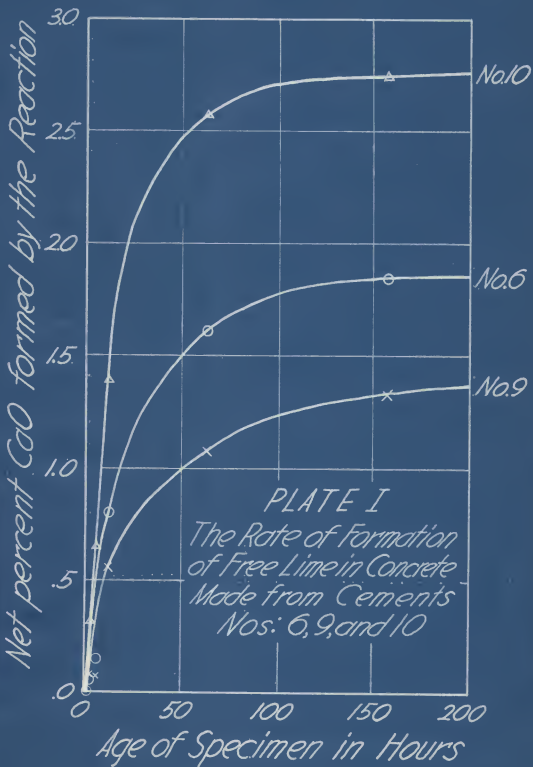
*These results were taken from the previous set of specimens, using the data obtained from those cylinders which were stored in the moist closet.

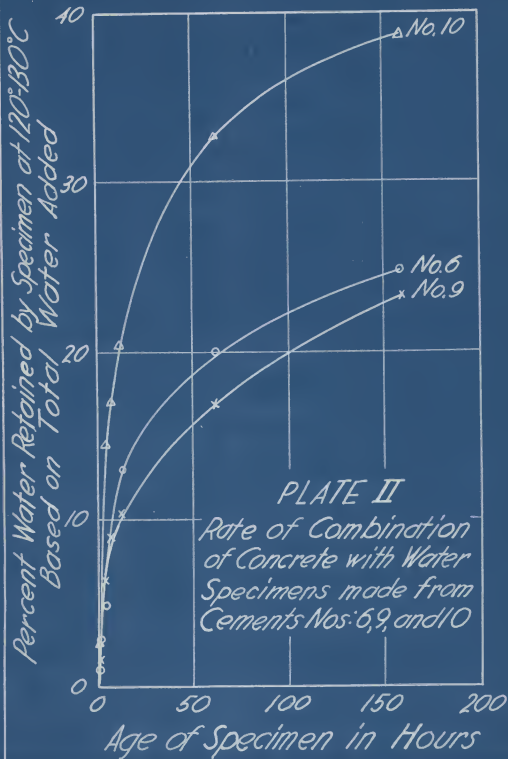
The net Free CaO was obtained by subtracting the Free CaO which was in the dry ingredients before the addition of the water. This was calculated for the three cements to be: No. 6, 0.06%; No. 9, 0.11%; No. 10, 0.42%.

Data showing the amount of water which was retained by the same specimens when they were heated at 120-130° C. in an air oven are given in Table 8.

Table 8. The Amount of Mixing Water Retained at 120-130° C. by Concrete Made from Cements Nos. 6, 9, and 10, at Different Ages.

AGE IN HOURS	NUMBER 6		NUMBER 9		NUMBER 10	
	GRAMS OF WATER RETAINED	PER CENT OF TOTAL WATER	GRAMS OF WATER RETAINED	PER CENT OF TOTAL WATER	GRAMS OF WATER RETAINED	PER CENT OF TOTAL WATER
1/2	.10	1.30	.13	1.69	.17	2.21
1	.08	1.04	.08	1.04	.20	2.60
3	.22	2.86	.13	1.69	.43	5.60
6	.38	4.95	.50	6.50	.94	12.22
12	---	---	.70	9.10	1.33	17.30
24	.99	12.9	.88	10.14	1.56	20.30
72	1.54	20.0	1.29	16.78	2.52	32.8
168	1.86	24.45	1.33	23.80	2.98	38.8





The per cent of total water, as shown in Table 8, was calculated by dividing the grams of water retained by the total weight (7.7 grams) of mixing water used for each specimen.

The above data are shown on Plates I and II.

Plate I and the accompanying data show that the high lime cements undoubtedly liberate more Free Lime when they are mixed with water.

It was noted that the Free Lime curves had become almost horizontal at the early age of one week, but the curves showing the rate of combination with water were still rising fairly rapidly at this time. The water which was being taken on after the period of one week must be due to hydration reactions rather than hydrolysis.

The data indicate that in none of the specimens was lime liberated before a time of about three hours had elapsed. Whether this has any bearing on the time of setting is not known.

The setting time of the three cements is given in Table 9.

Table 9. Time of Setting of Cements Nos. 6, 9, and 10.

CEMENT NUMBER	SETTING TIME IN HOURS	
	INITIAL	FINAL
6	4:00	5:15
9	2:25	5:00
10	1:45	3:30

An interesting observation arose from the calculation of the amount of lime left in combination in the cements after a period of one week. This calculation was made by first subtracting the original Free Lime and the lime held in combination as CaSO_4 from the total lime in the cements. This was done because it is definitely known that these compounds do not liberate lime when they are wetted. Then the Free CaO produced by the reaction was calculated over to the per cent Free CaO in terms of the cement and subtracted from the total CaO in the cement as determined by the chemical analysis. This gives the amount of CaO remaining chemically combined, as shown in the following equations:

No.	Total CaO	- (CaO in CaSO_4)	+	Free CaO	+ Net Free CaO	=	% combined CaO
6	61.35	- (1.20	+	.15	+ 10.05) =	49.95%
9	58.45	- (1.37	+	.42	+ 7.20) =	49.46%
10	67.15	- (1.43	+	2.01	+ 14.91) =	48.80%

Whether or not this was merely a coincidence is not known, but if further experiments should bear out what the results above indicate it would be a simple matter to calculate the per cent of hydrolysis of each of the compounds in the cement. It remains a striking fact that three cements varying as widely as the three studied do in both chemical analysis and compound composition should, at the end of one week after being mixed with water, approach a state in which

the same amount of lime was held chemically combined in all three.

It had been hoped that the length of the test would be sufficient that the specimens placed in the open water bath would show evidence of cracking, and that some thin sections could be made. However, at the date of writing, none of the specimens shows any evidence of cracks. The specimens all show some carbonation on the surface, with No. 10 showing this the most as would be expected, and No. 9 the least.

It was interesting to note that the Free Lime determinations at the early ages on the last group of specimens showed no lime even when $BaCl_2$ was added. Theoretically, there was sufficient lime present for a very small (.1 to .2 cc.) titration in several cases, but with the indicator used, so small a titration would not be sufficient to show any change. This would indicate that the $BaCl_2$ was not causing some lime to be liberated from the cement compounds which would account for the high results given by this method.

When $BaCl_2$ was used no difficulty whatever was encountered in obtaining checks on duplicate determinations. Rarely did duplicates fail to check within .2 cc., and in many cases checks were obtained with no more than .05 cc. difference between two determinations.

SUMMARY

Concrete specimens were made of three cements varying widely both in chemical analysis and compound composition. These specimens were analyzed for Free Lime by the alcohol-glycerol ammonium acetate method at several ages and under different conditions of treatment prior to the free CaO determinations.

Data and results are given which show that after a period of one week nearly all the "Free" lime has been liberated, but that the specimens are still combining with water fairly rapidly.

Specimens which were subjected to alternate heating and cooling in a water bath showed no more lime at the end of seven weeks than did those specimens which were in the moist room.

Calculation shows that concrete specimens, made exactly alike in everything but the cement, at the age of one week all contain nearly the same amount of lime in chemical combination. Whether any significance can be attached to this fact has not yet been determined.

Results are given which indicate that the use of $BaCl_2$ (anhydrous) to expedite the Free Lime determinations does not liberate lime which would otherwise remain in combination.

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*Original not seen.

