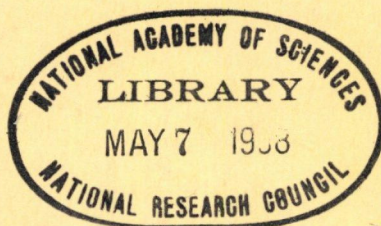


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" Bulletin 171

*Alkali-Aggregate  
Reaction*



**National Academy of Sciences—**

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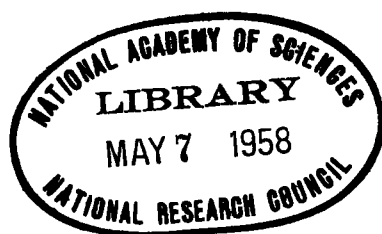
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# Evaluation of the Quick Chemical Test For Alkali Reactivity of Concrete Aggregate

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Division of Engineering Laboratories, Denver, Colorado

Since its publication in 1947, the quick chemical test for alkali reactivity of concrete aggregate has been used by many laboratories, and the procedure was accepted as a tentative standard by the American Society for Testing Materials in 1952 (Method C 289). The significance and reliability of the test are evaluated in the light of our experience and that of others.

As was indicated in the original publication of the method, anomalous results can be obtained if certain rocks or minerals are present. Moreover, reproducibility of results commonly is not satisfactory, primarily because chemical equilibrium is not established between the sample and the solution. Hence, the concentration of silica in solution and the reduction effected in the alkalinity of the solution are influenced by all aspects of the procedure, both during and following the reaction period.

In order to elucidate these matters, the following factors were investigated: (1) presence in the aggregate of minerals effecting extraneous reduction of alkalinity, including dolomite, antigorite, and calcite; (2) effect of agitation during the reaction period; (3) preliminary acid treatment of samples to remove carbonates; (4) measurement of pH during titration to determine the reduction of alkalinity; (5) modification of filtering procedures; and (6) variation in volume and concentration of the NaOH solution.

The results are summarized and discussed. The findings do not justify modification of the test procedure at this time. However, it is recommended that a petrographic examination of the aggregate be performed as a guide to evaluation of the results of the chemical test.

● THIS REPORT covers experience with the procedure developed in 1945-47 by the Engineering Laboratories of the Bureau of Reclamation, United States Department of the Interior, to determine quickly the potential reactivity of an aggregate with alkalis released during the hydration of portland cement (1). The procedure later was modified in certain respects and adopted by the Corps of Engineers, United States Army (Method CRD-C 128-48, 49, 50, and 52) (2), and as a tentative method of test by the American Society for Testing Materials (Method C 289-52T and 54T) (3). The method is commonly called the "quick chemical test." It has been widely applied in the testing of aggregates in this country (4, 5, 6, 7, 8).

Experience has indicated problems with reproducibility of the method and, in some instances, with reliability of the results. These justify review of the test procedure, the significance of the data obtained by the test, and investigations by ourselves and others to improve its reproducibility and reliability.

## DEVELOPMENT OF THE METHOD

The original procedure of the chemical test was published in 1947 (1). Conclusions on the validity of the method were based upon application of the test to approximately 70 sands, gravels, rocks, and minerals whose deleterious or innocuous character has been established by mortar test; 22 of the materials were known from service records to be deleteriously alkali-reactive. It was shown that the results of the method could be used to subdivide the tested materials correctly into those which are deleteriously alkali-reactive and those which are not according to a mortar bar test similar to ASTM Method C 227 (3) and available service records. Additional data on results of the tests

were published subsequently, at which time the criteria indicating deleterious degrees of alkali reactivity were modified slightly (4).

The test involves crushing and washing of the sample of the aggregate so as to obtain a specimen in the No. 50-100 size range; 25 grams of the prepared aggregate are placed in a specially designed reaction vessel with 25 milliliters of 1-N NaOH solution. The vessel is sealed and stored at 80 deg + 1 deg for 24 hours, whereupon the residual liquid is filtered off with minimal agitation of the solids. The filtrate is analyzed for dissolved silica, and the reduction effected in the alkalinity (basicity) of the solution is determined by titration. The potentially deleterious or innocuous character of the aggregate is established by plotting the determined values of silica concentration ( $S_C$ ) in millimoles per liter as the abscissa against the reduction of alkalinity ( $R_C$ ) and noting whether the point so located lies to the left or the right of a line found empirically to separate equivalent data points representing aggregates whose degree of reactivity was established in the original work.

Review of the data indicated that not only was the potentially deleterious or innocuous character of the aggregate established, but also that correlations could be established between the chemical quantities determined and the rate and magnitude of the expansion of the mortar bars. Thus, it was found that the proportion of the deleteriously reactive type giving the maximum mortar expansion (the so-called "pessimism" proportion) and the rate of mortar expansion correlated inversely with the reduction in alkalinity established in the chemical test. Other important relationships were established also.

On the other hand, the original investigation demonstrated that certain rocks and minerals could effect an extraneous reduction in alkalinity, with resulting spurious increase in  $R_C$ . Carbonates of magnesium or ferrous iron cause difficulty in this way. It was shown that the tests indicated the deleterious degree of alkali reactivity when a quartz aggregate contained as little as 1 percent of opal, whereas a similar combination of dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) was indicated to be innocuous. This effect results from precipitation of hydroxide as a hydroxide of magnesium or ferrous iron, and a consequent increase in  $R_C$  above the value produced as a result of alkali-silica reaction. The data point representing the aggregate thus is shifted upwardly and possibly across the boundary between innocuous and deleterious materials.

However, the data demonstrated that the valid and definite indication of deleteriousness would be obtained if the aggregate contained 2.5 percent of opal. Apparently the extraneous precipitation of hydroxide is halted or prevented in the presence of moderate or high proportions of silica in solution. If an aggregate contains 5 percent or more of opal, the values of  $S_C$  and  $R_C$  are similar whether the bulk of the aggregate is dolomite, quartz, or other minerals.

The published account of the test and its application created widespread interest throughout the country and it was introduced into testing procedures by numerous laboratories. In 1949, the Corps of Engineers included the procedure into their "Handbook for Concrete and Cement" as Method CRD-C 128 (2).

Available data and experience with the method were reviewed by Subcommittee II-b on Chemical Reactions of Aggregates in Concrete, ASTM Committee C-9 on Concrete and Concrete Aggregates, and in 1952 a tentative method of test covering the procedure was issued (ASTM Designation: C 289-52T, Tentative Method of Test for Potential Reactivity of Aggregates (Chemical Method) (3)). Many of the details of the tentative method were based upon work of the Corps of Engineers, United States Army (8). The tentative method included specific instructions and fixed several details of procedure not defined adequately in the original publication, but departed substantially from the original procedure only in the titration and calculation to determine the reduction of alkalinity ( $R_C$ ). As a result of extensive study and discussion, this change was rescinded in 1954 so that ASTM Method C 298-54T conforms closely with the original procedure.

#### STUDIES BY THE CORPS OF ENGINEERS

In May 1949, the Waterways Experiment Station, Corps of Engineers, United States Army developed an extensive program to investigate the quick chemical test (their Method CRD-C 128-49) (2) and the mortar bar test (their Method CRD-C 123) (2), particular-

ly to establish causes and means to control unsatisfactory reproducibility (8). The program concerning the chemical test comprised all of the Corps of Engineers Division Concrete Laboratories, seven in number, and the Petrographic Laboratory, Division of Engineering Laboratories, Bureau of Reclamation, Denver, Colorado. Portions of six aggregates were distributed to the participating laboratories both in original condition and after preparation of the material for test by the Waterways Experiment Station. Each was tested three times in triplicate in accordance with Method CRD-C 128-49.

Statistical analysis of the resulting data indicated that inadequate reproducibility was due to lack of proper detail in the specification of the procedure. Accordingly, the description of the method was modified extensively so as to specify more rigorously the equipment; techniques; and procedures; the statement of tolerances, such as in preparation of reagents; analytical procedures; preparation of the aggregate for testing; and filtration following the reaction period. The modified procedure was designated Method CRD-128-50.

Tests were repeated, employing only one aggregate (a chert gravel from Arkansas). In Phase I of this portion of the program, the aggregate was processed at the Waterways Experiment Station and distributed to the cooperating laboratories for testing. In Phase II, the natural gravel was submitted to each cooperating laboratory for processing. The finished sample for testing was then returned to the Waterways Experiment Station for performance of the chemical test. Results are summarized in Table 1.

Agreement among the laboratories is adequate, although three results in Phase I differ markedly from the others. Agreement among the laboratories was better in this series, involving only one aggregate, than in the previous series, involving six aggregates. The improvement observed is the result of the increased reproducibility of  $S_c$ . Reproducibility of  $R_c$  remained about the same for most of the laboratories.

TABLE 1

RESULTS OF A COOPERATIVE TEST ON ASTM METHOD C 289 SPONSORED BY THE CORPS OF ENGINEERS, UNITED STATES ARMY<sup>1</sup>

Laboratory	Data on $S_c$						Data on $R_c$					
	Phase I			Phase II			Phase I			Phase II		
	$S_c$	$SD^2$	$CV^3$	$S_c$	$SD^2$	$CV^3$	$R_c$	$SD^2$	$CV^3$	$R_c$	$SD^2$	$CV^3$
WES	163.6	2.6	1.6	163.6	2.6	1.6	75.5	3.0	4.0	75.5	3.0	4.0
BR	166.2	3.8	2.3	174.4	5.8	3.3	70.6	3.9	5.5	76.2	3.4	4.5
ORD	155.4	13.7	8.8	178.8	3.8	2.1	96.0	5.9	6.1	78.4	2.8	3.6
MRD	174.2	4.0	2.3	164.3	6.4	3.9	72.7	2.1	2.9	79.4	3.7	4.7
SWD	176.9	5.6	3.2	187.0	2.4	1.3	131.7	15.0	11.4	76.3	3.2	4.2
SPD	190.7	3.5	1.8	180.9	2.7	1.5	68.3	6.5	9.5	77.4	2.4	3.1
SAD	133.8	4.2	3.1	162.8	2.6	1.6	85.6	3.0	3.5	73.9	3.3	4.5
NPD	202.4	0.9	5.4	168.9	4.1	2.4	82.6	4.4	5.3	69.1	5.5	8.0
Grand avg	170.4	6.0	3.5	172.7	3.8	2.2	85.4	5.5	6.4	75.7	3.4	4.5
Over-all	---	7.1	4.2	---	4.1	2.4	---	6.7	7.8	---	3.5	4.6

<sup>1</sup> Test conducted in accordance with ASTM Method C 289-52T on one sample of chert gravel, Murfreesboro, Arkansas ( $\frac{3}{4}$ - to  $\frac{3}{8}$ -inch fraction). In Phase I material processed at Laboratory WES was tested by the indicated laboratories. In Phase II material processed at the indicated laboratory and tested at Laboratory WES. The table is taken from Table 40 of Reference 8.

<sup>2</sup> Standard deviation.

<sup>3</sup> Coefficient of variation.



TABLE 2

AGGREGATE MATERIALS USED IN INVESTIGATION OF THE QUICK CHEMICAL  
TEST FOR ALKALI REACTIVITY (ASTM METHOD C 289-54T)

Aggregate No.	Identification and Source	Maximum Expansion of Mortar at 1 Year Percent <sup>1</sup>
1	Arkose, Byllesby Dam, Virginia	<sup>2</sup> 0.147
2	Novaculite, Hot Springs, Arkansas	0.561
3	Sand, Sargent, Nebraska (Lab. No. M-915)	0.114
4	Sand, Scottsbluff, Nebraska (Lab. No. M-436)	0.088
5	Gravel, Phoenix, Arizona (Lab. No. M-659)	0.107
6	Gravel, Mullen Dam site, Nebraska (Lab. No. M-226-B)	0.096
7	Gravel, Scottsbluff, Nebraska (Lab. No. M-436)	---
8	Phyllite, Buck Dam, Virginia	<sup>2</sup> 0.310
9	Sand, Eklutna Dam site, Alaska (Lab. No. M-1060)	0.098
10	Gravel, Eklutna Dam site, Alaska (Lab. No. M-1060)	0.061
11	Sand, near Saco, Montana (Lab. No. M-365 to M-371)	---
12	Sand, Carryhurst, Utah (Lab. No. M-672)	0.090
13	Sand, Canyon Ferry Dam, Montana (Lab. No. M-310)	0.117
14	Sand, Canyon Ferry Dam, Montana (Lab. No. M-290)	0.089
15	Sand, Black Canyon Dam, Idaho	0.056
16	Sand, near Grand Coulee Dam, Washington (Lab. No. M-675)	<sup>3</sup> 0.075
17	Felsitic rhyolite, Mojave, California	0.045
18	Gravel, near Marsh, Montana (Lab. No. M-425)	0.093
19	Gravel, near Marsh, Montana (Lab. No. M-424)	0.126
20	Chalcedony, Serro do Mar, Brazil	0.264
21	Chalcedony, Lead Pipe Springs, California	0.940
22	Gravel, Hoover Dam, Arizona (Lab. No. M-610A)	0.159
23	Sand, White Narrows Dam site, Nevada (Lab. No. M-509)	0.122
24	Sand, Willow Creek, Colorado, (Lab. No. M-626)	0.095
25	Gravel, Putah Creek, Yolo County, California (Lab. No. M-1539)	0.049
26	Sand, near Marsh, Montana (Lab. No. M-425)	0.063
27	Basalt from Aggregate No. 16, above	0.028
28	Sand, Putah Creek, Yolo County, California (Lab. No. M-1540)	0.090
29	Sand, Platoro Dam site, San Luis Valley, Colorado (Lab. No. M-421)	0.119
30	Sand, Platoro Dam site, San Luis Valley, Colorado (Lab. No. M-422)	0.119
31	Sand, Putah Creek, Yolo County, California (Lab. No. M-1539)	0.108

TABLE 2 (Continued)

32	Sand, near Merrill, Oregon (Lab. No. M-440)	0.154
33	Rhyolite tuff, Castle Rock, Colorado	0.400
34	Andesites and rhyolites, Bill Williams Ranch, Arizona	0.723
35	Siliceous, magnesian limestone, Paso Robles, California	<sup>2</sup> 0.361
36	Dolomite, Tuckahoe, New York	0.026
37	Graywacke, near Monticello Dam, California	0.035
38	Serpentine, Warren County, New York	0.030
39	Quartzite, Sioux Quartzite, Jasper Stone Company, South Dakota	---
40	Rhyolite porphyry, Deadwood, South Dakota	0.041
41	Sand, near Marsh, Montana (Lab. No. M-424)	0.074
42	Sand, Blue River, Kansas	0.064
43	Sand, Republican River, Kansas	<sup>2</sup> 0.167
44	Sand, Friant Dam, California	0.072
45	Slate, source unknown	0.192
46	Opal, Quincy, Washington	1.610
47	Quartz, Buffalo Park, Colorado	0.033
48	Marble, near Marble, Colorado	0.022
49	Prochlorite, Chester, Vermont	<sup>3</sup> 0.042
50	Scolecite, Challis, Idaho	---
51	Pectolite, Patterson, New Jersey	---
52	Prehnite, West Patterson, New Jersey	---

<sup>1</sup> Except as otherwise indicated bars are 1 by 1 by 10 inches in size; mix parts 1:2; water-cement ratio = 0.40 by weight; aggregate graded 20 percent by weight each No. 4-8, 8-16, 16-30, 30-50, and 50-100; cured 24 hours or 7 days in fog room at 70° - 73.4° F; then stored at 100° F in sealed cans in the presence of moisture; alkali content of the cement: Na<sub>2</sub>O = 1.16-1.30 percent; K<sub>2</sub>O = 0.04-0.12 percent.

<sup>2</sup> Bars are 2 by 2 by 10 inches in size; mix parts 1:2; water-cement ratio = 0.40 by weight; aggregate graded 19 percent by weight each No. 4-8, 8-16, 16-30, 30-50, 50-100 and 5 percent passing No. 100; cured 7 days in fog room at 70° F, then stored in sealed cans in the presence of moisture; alkali content of cement: Na<sub>2</sub>O = 1.30 percent, K<sub>2</sub>O = 0.12 percent.

<sup>3</sup> Test performed on previous sample from same source.

## CHANGE OF PROCEDURE TO IMPROVE REPRODUCIBILITY AND RELIABILITY OF THE METHOD

### Continuous Titration

One cause of variation in the value of R<sub>C</sub> is observation of the colorimetric end point during titration. Also, it is possible that titration to pH values other than that of the phenol-phthalein end point or even the trajectory of the pH with titration might yield more significant and reproducible data.

The chemical test was performed on eight aggregates (Nos. 21, 27, 34-39, Table 2) of various lithologic types in accordance with the stipulated procedure, except that S<sub>C</sub> was not determined, and the titration was followed continuously by means of a pH meter. Distinctly different curves are obtained for the materials, the potentially deleterious materials producing filtrates of lower pH than are produced by innocuous siliceous aggregates (Figure 1). Dolomite also reduces the pH of the filtrate, but the shoulder at pH 9 to 8.5 resulting from titration of the carbonate in solution is characteristic and permits separation of this curve from those produced by potentially deleteriously reactive aggregates. Nevertheless, it is apparent that difficulties would be encountered if a potentially deleteriously reactive siliceous dolomite were tested.

## Rotation of Reaction Vessels; Determination of Change of Alkali Concentration

Probably the most fundamental cause for difficulty in obtaining satisfactory reproducibility in the test is the lack of attainment of equilibrium in the reaction vessels. This condition is unavoidable in any chemical procedure to evaluate alkali reactivity of aggregate, inasmuch as attainment of equilibrium manifestly would mask the inherent differences in rate and magnitude of reaction to which differing rocks and minerals are susceptible. Nonetheless, if the contents of the reaction vessel were maintained in a quasi-homogeneous condition, the reactions could proceed farther and approach more closely a condition of equilibrium. This can be accomplished by appropriate continuous agitation during the reaction period.

A mechanism designed for use in a previously developed chemical test for alkali reactivity of pozzolans (9) was used to cause continuous end-over-end rotation of the reaction period. The chemical test was performed as stipulated on 14 aggregates of various lithologic types, except that continuous agitation was supplied.  $S_C$  was determined, and the concentration of sodium and potassium in the filtrate was measured by flame photometry.

Agreement between duplicate determinations was remarkably good (Table 3). The titration curve shows features similar to those observed previously (Figure 2). However, three potentially deleterious aggregates (Nos. 2, 31, and 43) produced curves lying within the zone occupied by curves representing innocuous aggregates. Aggregates No. 42 and 43 produced almost identical curves, even though Aggregate No. 42 is innocuous and Aggregate No. 43 is potentially deleterious.

The reduction in alkali concentration is calculated as the difference between the sodium concentration of the original NaOH solution and the sum of the sodium and potassium in the filtrate. The potassium concentration usually is negligible, but several aggregates released substantial amounts of potassium into solution. The results of the test are plotted in Figure 3, indicating the reduction in alkalinity alternately as  $R_C$  and the equivalent reduction in alkali concentration. Results of the standard test on these aggregates are shown also. Introduction of agitation produces substantial shifts in the position of the data points.  $S_C$ , determined after agitation, is equal to or greater than

$S_C$  determined in the standard test.  $R_C$  usually is reduced by introduction of agitation, although for two aggregates, the reverse is true. The reduction of alkali concentration usually is close to  $R_C$ . This procedure justifies further investigation. Its adoption would require shifting of the boundary line considerably to the right.

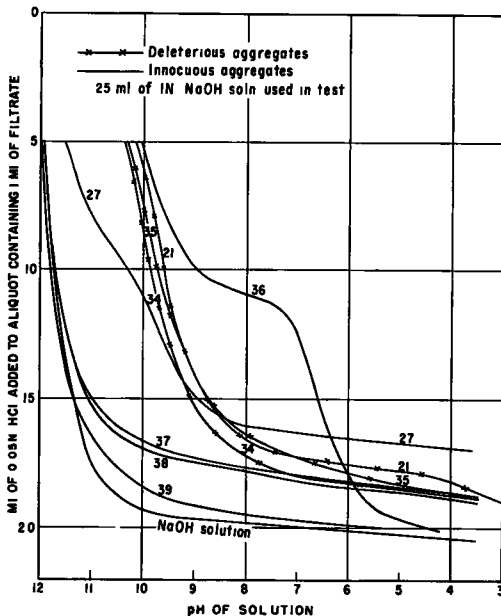


Figure 1. Titration curves obtained on the filtrate from the quick chemical test (ASIM Method C 289-54T).

## Modification of the Reaction Vessel; Reduction in Amount of NaOH Solution

One of the important reasons for the variation observed in duplicate or triplicate determinations in the current procedure of the chemical test is the existence during the reaction period of a large amount of solution above the solids. In the presence of reactive materials, this portion of the solution differs in composition from the solution in the interstices of the sample because diffusion does not keep pace with the chemical reaction. In the interstitial solution, the concentration of alkalis becomes low and the concentration of silica becomes high with respect to the supernatant solution, the degree of variation

**TABLE 3**  
**DUPLICATE VALUES OF  $S_C$  AND  $R_C$  IN TEST INCLUDING CONTINUOUS**  
**AGITATION OF REACTION VESSELS<sup>1</sup>**

Aggregate No. <sup>2</sup>	$S_C$ , mM/1		$R_C$ , <sup>3</sup> mM/1	
	1	2	1	2
2	336	338	20	25
15	76	77	85	90
16	229	227	117	122
17	67	66	72	72
20	864	868	102	82
21	1,032	1,036	72	82
25	199	197	144	146
27	397	399	202	192
31	228	222	205	207
33	956	936	302	292
40	58	60	82	72
42	60	62	35	38
43	76	77	28	30
44	65	63	60	62

<sup>1</sup> ASTM Method C 289-54T except for continuous end-over-end rotation of reaction vessels at about 30 rpm during the reaction period.  $R_C$  was determined by analysis for alkalis, rather than by titration (see footnote 2 below).

<sup>2</sup> See Table 2 for identification of the aggregates.

<sup>3</sup> Reduction in alkalis (Na+ and K+); NA + and K+ determined by flame photometry at conclusion of test; reduction calculated by subtracting the sum of the concentrations of Na+ and K+ from the original concentration of Na+.

depending upon the kind and degree of reaction taking place. The concentration of alkalis and silica in the filtrate depends upon details of the techniques used during filtration, especially the degree of agitation used before drainage of the solution and the completeness with which the solution is extracted from the solids. Particularly for highly reactive aggregate, the composition of the filtrate depends largely on the magnitude of the vacuum attained, the time allowed for filtering, and whether the supernatant liquid is decanted through the filter first or stirred with the aggregate.

In order to reduce these variables, a number of the reaction vessels were modified to include a bottom drain (Figure 4). A series of tests was carried out with 25 grams of sample prepared as stipulated in the procedure, but only 10 milliliters of 1-N NaOH solution were added. The aggregates were selected so as to study more closely those producing mortar expansion in the range 0.040 to 0.160 percent at 1 year. Ten milliliters of solution is sufficient to saturate the sample, but very little excess supernatant liquid is present. After the specified reaction period, the cover to each vessel was loosened to vent air, the cap was removed from the drain, and vacuum was applied to the bottom. The filtrate recovered usually exceeded 6 milliliters. The analytical procedure was carried out as stipulated, except that 5 milliliters of the filtrate were diluted to 100 milliliters rather than 10 milliliters to 200 milliliters.

An attempt was made to classify the resulting data points into three groups on the basis of mortar bar expansion; namely: (1) innocuous (less than 0.080 percent expansion in 1 year); (2) marginal activity (0.080 to 0.150 percent expansion in 1 year); and (3) deleteriously reactive (more than 0.150 percent expansion in 1 year (Figure 5). In the figure, a line has been drawn between the area occupied by the innocuous aggregates and the others. Data points representing two of the aggregates (Nos. 10 and 24) lie on the wrong side of the line. Nevertheless, the relationships are sufficiently good to de-

<sup>1</sup> See footnotes 1 and 2 to Table 2.

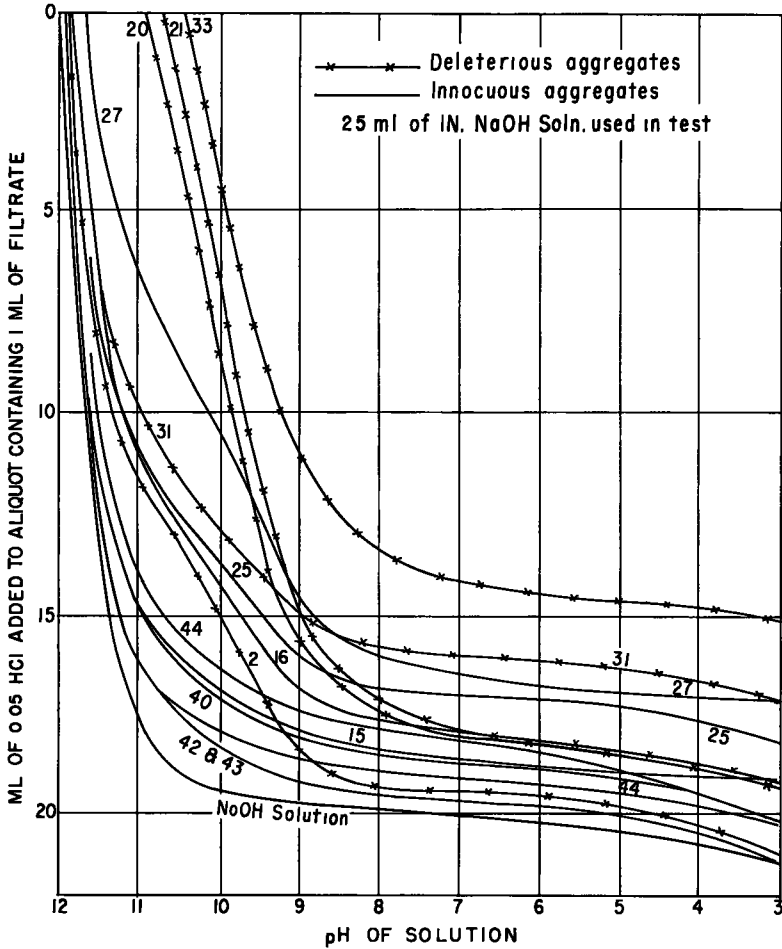


Figure 2. Titration curves obtained on the filtrate from the quick chemical test after continuous agitation during the reaction period.

monstrate conclusively that the factors determined by this modification of the chemical test relate rather closely to the processes resulting in expansion of mortar bars containing alkali-reactive aggregate and high-alkali cement.

An attempt to divide the aggregates on the basis of an expansion of 0.100 percent at 1 year likewise leaves anomalies. Points 9, 10, 18, and 28 would fall to the left of such a boundary, and the boundary must lie to the left of Points 29 and 8. In this situation, Points 3, 4, 12, and 14 are located erroneously to the right of the boundary.

Note that this is a severe test of the criteria to be applied to the results of the test. Of the 34 aggregates included in this phase of the program, 25 produced mortar expansion in the range 0.040 to 0.160 percent at 1 year. Some of these aggregates may be potentially more deleterious than indicated because the optimum ratio of alkalis to reactive siliceous material may not have been achieved in the mortar bars.

In any event, this procedure was not followed further because of these anomalous or erroneous indications.

It is appropriate here to comment briefly upon a moist-stored mortar test, such as ASTM Method C 227, as a basis for evaluating other tests designed to determine the potential alkali reactivity of concrete aggregate. In our opinion, moist-stored mortar tests, such as ASTM Method C 227 and the analogous procedure used by the Bureau of Reclamation, are the most widely available and generally applicable techniques by which deleterious alkali reactivity of aggregates or cement-aggregate combinations can be re-

cognized. Nevertheless, these tests are not completely dependable either for predicting reactivity of particular cement-aggregate combinations or for determining the deleterious degree of reactivity to be expected in use of a given aggregate with high-alkali cements in general. For example, a certain aggregate known to produce a deleterious degree of alkali-aggregate reaction in structures fails to produce significant expansion in moist-stored, high-alkali mortars in the laboratory (10). Reproducibility of the mortar test is usually not satisfactory either within the laboratory or from laboratory to laboratory, not only because of lack of uniform procedures but also because the inherent reactivity of given cements varies with storage in the laboratory and from shipment to shipment from the mill. Hence, in evaluating an alternative procedure, such as ASTM Method C 289-54T, we should not assume that there are available other methods which are free from significant difficulties.

#### Variation of Concentration of the NaOH Solution

Two groups of tests were designed to investigate the significance of the concentration of NaOH solution, using a procedure identical with that described in the previous section, except that concentrations of 0.5 N and 1.5 N were used.

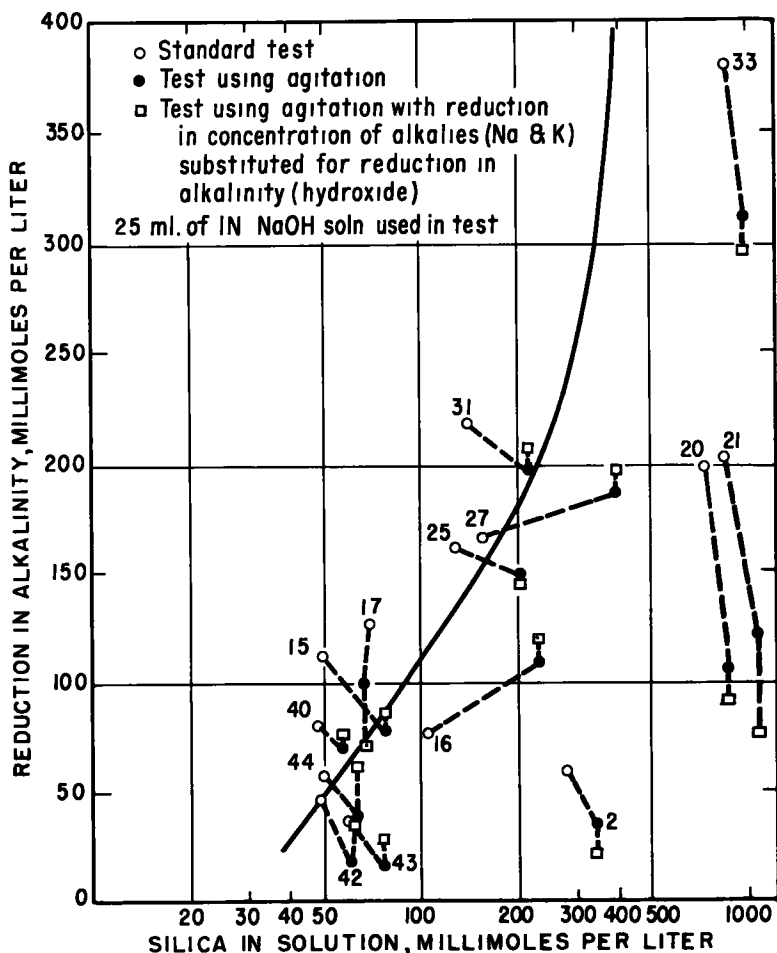


Figure 3. Correlation of results of the quick chemical test (ASTM Method C 289) with results obtained after continuous agitation during the reaction period. Reduction in alkalinity ( $R_c$ ) is compared with the reduction in concentration of alkalis.

The results are shown in Table 4. No improvement in reliability of the method is indicated.

### EXTRANEOUS EFFECT OF CERTAIN MINERALS

#### Effect of Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) and Antigorite ( $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ )

As was indicated in the original work on the chemical test, dolomite and probably magnesium and ferrous carbonates produce a reduction in alkalinity unrelated to alkali-silica reaction. This reduction is caused by precipitation of hydroxyl as hydroxides of magnesium or ferrous iron. Similarly, it was suspected that certain magnesium silicates might also produce spurious changes in  $R_c$ .

In order to investigate these effects more completely, the chemical test was applied to a series of mixtures of opal (Aggregate No. 46) with dolomite (Aggregate No. 36), serpentine (Aggregate No. 38), and quartz (Aggregate No. 47, respectively, the opal content of the mixtures ranging from 0.1 to 2.5 percent, by weight of the test sample. The opal was added in the form of granular material in the No. 50-100 size range.

Because some investigators had suggested informally that the activity of the dolomite and other minerals might indeed play a role in alkali-aggregate reactions, a series of mortar bars was prepared and tested in accordance with the procedure similar to ASTM Method C 227 (3). The aggregates were mixtures of the same constituents in the same proportions employed in the sample for the chemical test.

The results of the chemical test indicate that all of the mixtures of serpentine employed (including up to 2.5 percent of opal) and the dolomite-opal mixtures containing up to 1.50 percent of opal are innocuous (Figure 6). The data point representing the serpentine-opal mixture containing 2.5 percent of opal is close to the boundary separating innocuous from deleterious aggregates. On the other hand, all of the quartz-opal mixtures are indicated to be potentially deleteriously alkali reactive.

In the mortar bars, all of the aggregates containing more than 0.25 percent of opal produced expansion greater than 0.1 percent in 1 year, regardless of the composition of the remainder of the mixture. Hence, the result of the chemical test is in error for the serpentine-opal mixtures containing 0.25 to 2.5 percent of opal and for the dolomite-opal mixtures containing 0.25 to 1.50 percent of opal. The result of the quartz-opal mixture containing 0.10 percent of opal is in error also since a deleterious indication is obtained in spite of the lack of significant expansion in the mortar bar test.

Difficulty of this type might be avoided by analysis for sodium and potassium rather than by determination of reduction of alkalinity as a function of the reduction of titratable hydroxyl ion. Sodium is not removed from solution by the precipitation of the secondary hydroxides, whereas the reduction in alkalinity effected by the alkali-silica reaction does correlate with a reduction in the concentration of total of sodium and potassium in solution. The close relationship of reduction of titratable hydroxyl ion to reduction of total sodium and potassium has been demonstrated in extensive tests of pozzolans by somewhat similar procedures (9). This point is discussed further below.

#### Effect of Calcite ( $\text{CaCO}_3$ )

The possible effect of calcite on results of the chemical test originally was ignored because tests applied to marble or limestones containing minimal proportions of silica or silicate minerals produced virtually no re-

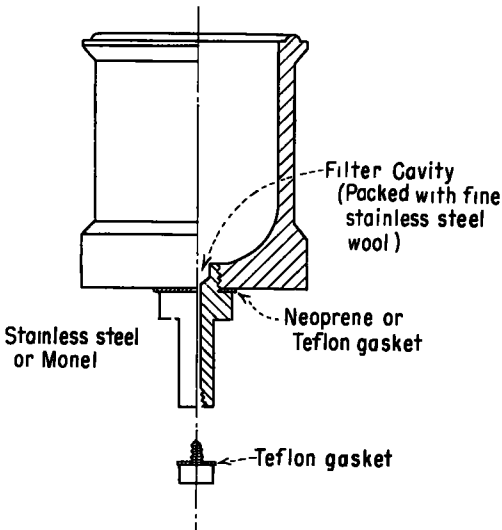


Figure 4. Modified reaction vessel used in filtration by drainage at the bottom.

duction in alkalinity or release of silica into solution. Conversely, several opaline or chalcedonic limestones known to be deleteriously alkali reactive were indicated as being deleterious by the chemical test. Nevertheless, calcium carbonate is slightly soluble in alkaline solutions, and the thought finally arose that calcium released into solution by calcium carbonate might cause spurious reductions of  $S_c$  by the precipitation of one or more calcium silicates.

Two series of mixtures of opal (No. 46), calcite (No. 48), and quartz (No. 47) were prepared and subjected to the test in order to study possible effects of this type. The test was conducted in accordance with standard procedure, except that only 10 milliliters of sodium hydroxide was added to each container, and the bottom-drain procedure was employed. All of the mixtures in both series included 2 percent by weight of opal in the No. 50-100 size range. Calcite constituted 4, 16, 40, and 98 percent of the mixture, the residual being quartz in the No. 50-100 size range. In one series, the calcite was introduced as granular material in the No. 50-100 size range, whereas in the other the calcite was introduced in the No. 100-200 size range. (The mixture con-

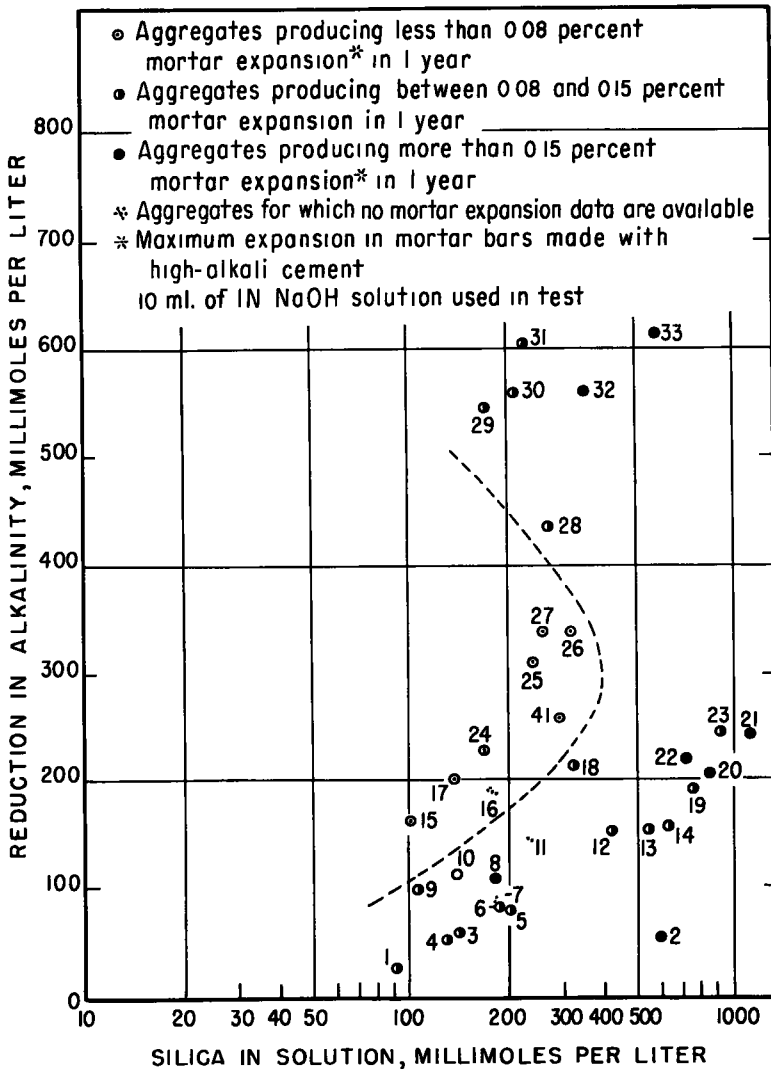


Figure 5. Results of the quick chemical test including bottom-drain reaction vessels and use of only 10 ml 1 N Na OH solution.



**TABLE 4**  
**EFFECT OF CONCENTRATION OF NaOH SOLUTION ON RESULTS OF THE QUICK CHEMICAL TEST<sup>1</sup>**

Aggregate No. <sup>2</sup>	Concentration of NaOH SOLN Used--Determined Values for R <sub>C</sub> and S <sub>C</sub>					
	0.5 N NaOH		1.0 N NaOH		1.5 N NaOH	
	S <sub>C</sub> , mM/1	R <sub>C</sub> , mM/1	S <sub>C</sub> , mM/1	R <sub>C</sub> , mM/1	S <sub>C</sub> , mM/1	R <sub>C</sub> , mM/1
1	56	42	92	26	123	45
5	78	58	203	79	306	91
6	106	70	190	84	264	103
8	60	71	184	108	328	155
12	167	120	420	152	712	203
18	78	159	316	212	508	275
22	228	141	726	220	1,816	321
26	76	252	316	337	748	432
28	84	340	269	434	440	493
29	—	—	172	547	1,104	655

<sup>1</sup> ASTM Method C 289-54T except as follows: (1) 10 ml NaOH solution in indicated concentration; (2) solution extracted at conclusion of reaction period by bottom drain; (3) R<sub>C</sub> not corrected by use of a blank.

<sup>2</sup> See Table 2 for identification of the aggregates.

taining 98 percent of calcite was not included in the latter series.)

The results demonstrate that calcium carbonate causes a change in the values of S<sub>C</sub> and R<sub>C</sub>. R<sub>C</sub> is increased progressively with addition of calcium carbonate, the reduction being greater with addition of the finer calcite (Figure 7). S<sub>C</sub> is decreased in the tests of this series as the proportion of calcium carbonate is increased.

In another determination following the same test procedure, mixtures of a deleteriously reactive slate (No. 45) and quartz (No. 47), or calcite (No. 48) were tested to determine the effect of the calcite on the values of R<sub>C</sub> and S<sub>C</sub>. All constituents of the mixture were prepared as stipulated in the procedure to the No. 50-100 size range. The quartz and calcite constituted 20 percent by weight of the respective mixtures.

As was found with the quartz-opal-calcite mixture, the value of R<sub>C</sub> is higher for the slate-calcite mixture than for the slate-quartz mixture. Surprisingly, the value of S<sub>C</sub> is higher also.

Apparently, calcium released by calcite (calcium carbonate) into an alkaline solution containing dissolved silica causes precipitation of calcium silicate carrying adsorbed or combined alkalis, in this instance primarily sodium. This action reduces the concentration of alkalis in solution, with consequent reduction of titratable hydroxyl ion. If sufficient silica is precipitated, S<sub>C</sub> may decrease because of depletion of soluble silica. Also, if the alkalinity of the solution is decreased sufficiently, the concentration of silica at saturation may be reduced. At intermediate or low values of S<sub>C</sub>, the data indicate that the concentration of silica may increase as a result of reaction of calcium released from calcium carbonate.

In none of these determinations did the added calcite cause a data point to shift across the boundary separating innocuous and deleterious aggregates. It is probable that aggregates otherwise falling close to but to the right of the boundary will be shifted across it as a result of such action. However, the shift to the right (higher S<sub>C</sub>) evident for Aggregate No. 45 produces a trajectory tending to parallel the boundary and so reduces this possibility.

#### EFFECT OF PRELIMINARY ACID TREATMENT OF THE SAMPLES

As a means to eliminate the extraneous effect of carbonates on the results of the chemical test, preliminary acid treatment of the prepared samples was investigated.

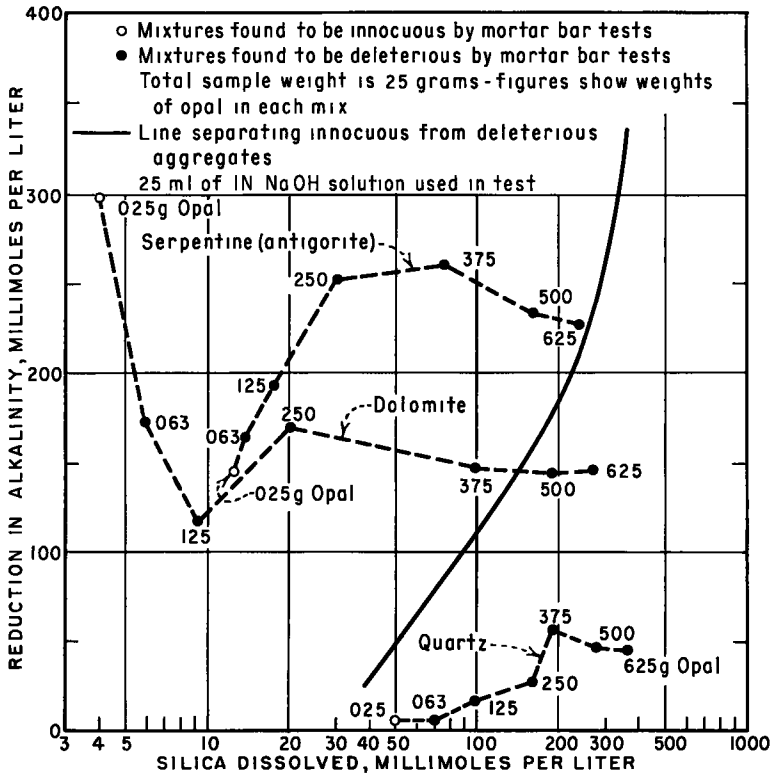


Figure 6. Results of the quick chemical test (ASTM Method C 289-54T) on mixtures of dolomite, serpentine, and quartz with opal.

Because certain silicate minerals decompose in hydrochloric acid and might therefore cause erroneous results, several zeolites and prochlorite were included also in the series of tests.

Twenty-five grams of the No. 50-100 size prepared material were treated in beakers with 500 milliliters of 1:10 HCl and heated to near-boiling. After 1 hour of heating, the supernatant liquid was decanted and another 500 milliliters of the acid added and the heating repeated. After decantation of the acid solution, the residuum was washed five times with 500 milliliters of distilled water and then dried in an oven at 105° C. Each residue was then subjected to a stipulated procedure.

The results demonstrate that the zeolites tested; namely, scolecite, pectolite, and prehnite (Nos. 50, 51, and 52, respectively), were partially or completely decomposed by the acid treatment, and high values of  $S_C$  are obtained (Table 5).  $R_C$  is high for the scolecite and pectolite. The prochlorite apparently is not decomposed by the acid treatment.

Surprising relationships are developed in the tests of the aggregate materials. These are largely inexplicable at this time. However, the results indicate clearly that such a procedure cannot be applied routinely as a part of this test.

### CONCLUSIONS

1. ASTM Method C 289-54T is a useful means to evaluate potential deleterious reactivity of aggregates with cement alkalis. It is especially valuable because it yields results within 2 work days.

2. Reproducibility of the method is acceptable in view of the difficulties inherent in evaluating the alkali-aggregate reaction and the limited reproducibility of alternative procedures, provided the stipulated procedures are followed in all details and the specified equipment and apparatus are used.

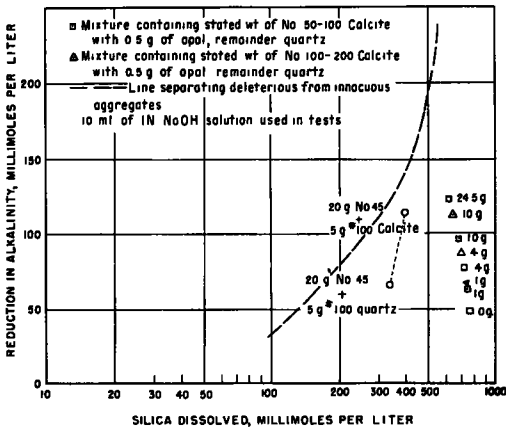


Figure 7. Results of the quick chemical test (ASTM Method C 289) on mixtures containing calcite (calcium carbonate).

of the several minerals, it is recommended that petrographic examination be applied in conjunction with performance and interpretation of the chemical tests.

5. No changes are recommended in the procedure (ASTM Method C 289-54T) at this time. Additional work on the procedure is justified, especially in use of agitation of the vessels during the reaction period, reduction of the volume of NaOH solution used, use of a bottom drain on the vessels, and evaluation of reduction of alkalinity by determination of the change of concentration of sodium and potassium rather than of reduction of the titratable hydroxyl ion. Determination of  $R_C$  by analysis for sodium and potassium probably will remove a large part of the spurious effects induced by magnesium, ferrous carbonates, and hydrous silicates.

3. Reliable results are not obtained with the method if certain minerals or rocks are present. Magnesium and ferrous carbonates (dolomite, magnesite, and siderite) and the hydrous magnesium silicate antigorite (serpentine) have been identified as minerals producing spurious increase in the reduction of alkalinity and concentration of silica. Calcite (calcium carbonate, the essential constituent of limestone and marble) causes an increase in the reduction of alkalinity and changes of the silica concentration if alkali-reactive siliceous phases are present in the aggregate. The effects of calcite are not expected to produce an erroneous indication of potential alkali reactivity of an aggregate unless the potential reactivity is marginal.

4. Because of the extraneous influence

TABLE 5

EFFECT OF PRELIMINARY ACID TREATMENT OF AGGREGATE ON RESULTS OF THE QUICK CHEMICAL TEST<sup>1</sup>

Aggregate No. <sup>2</sup>	With Prior Acid Treatment		Standard Procedure	
	$S_C$ , mM/1	$R_C$ , mM/1	$S_C$ , mM/1	$R_C$ , mM/1
8	184	82	91	76
16	152	77	104	77
28	656	139	149	214
31	544	202	142	218
34	360	171	720	184
35	352	65	650	240
38	340	531	7.5	236
49	32	2		
50	188	311		
51	552	109		
52	172	45		

<sup>1</sup> See accompanying text for the procedure used in the acid treatment.

<sup>2</sup> See Table 2 for identification of the aggregates.

REFERENCES

1. Mielenz, R. C., Greene, K. T., "Chemical Test for the Reactivity of Aggregates with Cement Alkalies; Chemical Processes in Cement Aggregate Reaction," Proceedings, American Concrete Institute, 44, 193(1947).

2. Corps of Engineers, United States Army, "Handbook for Concrete and Cement," Waterways Experiment Station, Vicksburg, Mississippi (August 1949) with supplements.
3. American Society for Testing Materials, "ASTM Book of Standards," Part 3 (1955).
4. Mielenz, R. C. , and Witte, L. P. , "Tests Used by the Bureau of Reclamation for Identifying Reactive Concrete Aggregates," Proceedings, American Society for Testing Materials, 48, 1071 (1948) and discussion.
5. Slate, F. O. , "Chemical Reactions of Indiana Aggregates in Disintegration of Concrete," American Society for Testing Materials, 49, 954 (1949).
6. Lerch, W. , "Studies of Some Methods of Avoiding Expansion and Pattern Cracking Associated with the Alkali-Aggregate Reaction," American Society for Testing Materials, Special Technical Publication No. 99, 153 (1950).
7. Lerch, W. "Chemical Reactions of Concrete Aggregates," American Society for Testing Materials, Special Technical Publication No. 169, p 334 (1955).
8. Corps of Engineers, United States Army, "Tests for Chemical Reactivity between Alkalies and Aggregate, Report No. 1, Quick Chemical Test," Technical Memorandum No. 6-368, Waterways Experiment Station, Vicksburg, Mississippi, 39 p (1953).
9. Mielenz, R. C. , Greene, K. T. , Benton, E. J. , and Geier, F. H. , "Chemical Test for Alkali Reactivity of Pozzolan," Proceedings, American Society for Testing Materials, 52, 1128 (1952).
10. Hester, J. A. , and Smith, O. F. , "The Alkali-Aggregate Phase of Chemical Reactivity in Concrete, Part II, Deleterious Reactions Observed in Field Concrete Structures," American Society for Testing Materials, in press.

# Miscellaneous Observations on the Alkali-Aggregate Reaction and the Ionic Charge on Hydrated Cement

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It has been demonstrated by an interferometric technique that calcium hydroxide has an inhibiting effect on the alkali aggregate reaction, and it has also been demonstrated that opal may be caused to swell in the absence of any cement membrane. The fact that aggregates are attacked more rapidly in a settling cement sludge than in the supernatant liquid has been explained by the higher pH values in the sludge. The magnitude and polarity of the excess ionic charge on various portland cements has been determined by a procedure which used the silver-ammonia-bromide complex as the indicator ion, and it appears that this ionic charge may be a contributing factor in the swelling and shrinking of hydrated cement.

● STANTON demonstrated in 1940 (1) that reaction between high-alkali cement and certain aggregates could cause disintegration of concrete. Since that time much work has been done to better understand the reactions involved (2, 3, 4). In the present work, several methods of study have been used which confirm to a great extent the work of earlier investigators. The interferometric technique was used to determine the volume changes of opal, various glasses and neat portland cement paste in buffer solutions at various hydrogen ion concentrations. Further information on the reasons for the volume changes which occur in the alkali-aggregate reaction is furnished by the nature of the ionic charge on aggregates and cement. Measurements were also made of the pH of the cement sludge and the supernatant liquid in order to give further information on the cause for the greater reaction exhibited in the sludge than in the liquid.

## EXPERIMENTAL PROCEDURES

The chemical durability of opal, hydrated cement and certain glasses as indicated by their surface alteration was determined by an interferometric procedure (5). In this method, one surface of the specimen is polished sufficiently flat to give interference bands when placed under an optical flat. The sample is then immersed one-half its depth in a test solution and the surface of the solution covered with an oil layer to prevent evaporation. The system is maintained at 80 deg C for a definite period, usually 6 hours, and the sample is then removed, washed, and dried. Using the unexposed portion of the sample as a reference plane, the chemical attack on the exposed surface is measured by determining the displacement of the interference fringes by means of the conventional Pulfrich interferometer equipped with an unfiltered helium lamp for illumination. This chemical attack or surface alteration of the specimen may be a corrosion of the surface exposed to the solution; or the attack may be made evident by a swelling or increase in thickness of the specimen. In this paper, any solution or corrosion of the surface made evident by decrease in thickness of the specimen is designated as attack, and any increase in thickness of the specimen caused by the chemical reaction is designated as swelling. To conform to previous publications, (5, 6) swelling of the specimen is plotted in each case as a negative attack. Should the reaction be too rapid or severe, shorter exposures or lower temperatures must be used and the result estimated for 6 hours and 80 deg C to put all data on a comparable basis.<sup>1</sup>

For the determination of the magnitude and the polarity of the uneven distribution of migratable ions (6) between the outer solution and the solid phase, samples of approximately 10 g were prepared by being crushed and passed through a No. 50 and retained

<sup>1</sup> This estimation was based on the formula shown in "Studies of the Chemical Durability of Glass by an Interferometer Method," Donald Hubbard and Edgar H. Hamilton, Jour. Res. NBS 27, 143-157, Aug. 1941, RP1409.

TABLE 1  
CHEMICAL COMPOSITIONS

	Corning 015 <sup>a</sup>	BaC 572 <sup>b</sup>	BSC 517 <sup>b</sup>	F 620 <sup>b</sup>	Soda-Flint <sup>b</sup>	Pyrex <sup>c</sup>	Fiber-Glass <sup>d</sup> Type E	Li <sub>2</sub> O-SiO <sub>2</sub> <sup>b</sup> Glass	F-40 <sup>b</sup>	Opal <sup>e</sup>	Opal <sup>f</sup>
Na <sub>2</sub> O	22	0.4	8.4	3.6	20	3.8					
K <sub>2</sub> O		7.7	11.8	5.2		0.4					
Li <sub>2</sub> O								23.9			
CaO	6						16.0				
BaO		30.8							30		
PbO				45.1	20						
ZnO		7.2	0.5								
B <sub>2</sub> O <sub>3</sub>		3.6	12.4			12.9	9.5				
As <sub>2</sub> O <sub>3</sub>		0.2	0.5	0.5							
Sb <sub>2</sub> O <sub>3</sub>		0.4									
SiO <sub>2</sub>	72	49.7	66.4	45.6	60	80.5	55.0	76.1	50	93.09	90.38
Al <sub>2</sub> O <sub>3</sub>						2.2	14.5			0.87	2.72
Fe <sub>2</sub> O <sub>3</sub>										0.11	0.54
MgO							5.0				
Ign. Loss										5.40	5.32
HF Res. <sup>g</sup>										1.51	4.30
TiO <sub>2</sub>									20		

<sup>a</sup>MacInnes, D. A. and Dole, M., "The Behavior of Glass Electrodes of Different Compositions" Jour. Am. Chem. Soc., Vol. 52, p. 29, (1930).

<sup>b</sup>Compositions of batch material.

<sup>c</sup>Phillips, C. J., "Glass, the Miracle Maker," p. 47, Pitman Pub. Corp., New York.

<sup>d</sup>O'Leary, M. J. and Hubbard, D., "Some Properties of a Glass Used in Paper Manufacture" Jour. Research NBS, Vol. 55, (1955) RP 2599.

<sup>e</sup>Selected clear pieces, used in interferometer flats.

<sup>f</sup>Run-of-mine grade, used in expansion bars.

<sup>g</sup>The HF residue was fused and dissolved, and "R<sub>2</sub>O<sub>3</sub>" precipitated with NH<sub>4</sub>OH and ignited. The Fe<sub>2</sub>O<sub>3</sub> was determined in the ignited precipitate and the remainder of the R<sub>2</sub>O<sub>3</sub> assumed to be Al<sub>2</sub>O<sub>3</sub>.

on a No. 140 U. S. Standard Sieve. The samples were then leached for various periods of time in distilled water at 80 deg C. with occasional agitation. The liquid and solid phases were separated by decantation, then the solid phase was treated for 5 minutes in 50 ml of saturated Ag(NH<sub>3</sub>)<sub>2</sub>Br solution in full strength aqueous ammonia. The samples were again separated from the liquid phase by decantation and after adding water the samples were acidified with concentrated H<sub>2</sub>SO<sub>4</sub> in order to precipitate and eliminate any adsorbed AgBr. The excess Ag<sup>+</sup> or Br<sup>-</sup> ions remaining in the solid phase were then titrated potentiometrically, using the Ag, AgBr electrode and the glass half-cell as the indicator and reference electrode, respectively. All potentiometric measurements were made at room temperature, using a Beckman model G pH meter.

## RESULTS AND DISCUSSION

### Inhibiting Effect of Calcium Hydroxide on the Alkali-Aggregate Reaction

There appears to be a considerable difference of opinion as to the role of calcium hydroxide in the alkali-aggregate reaction. Hester and Smith (7) believe that calcium hydroxide is necessary for the progressive effect of the expansive alkali-aggregate reaction. On the other hand, Powers and Steinour (8) believe that under certain conditions calcium hydroxide inhibits this reaction. Osmotic flow rates of alkaline solutions, determined by Verbeck and Gramlich (9), in the presence and absence of calcium hydroxide appear to confirm the latter hypotheses. Observations of other workers place the role of calcium hydroxide somewhere between these more or less extreme views. For example: Kalousek (10) and Parsons and Insley (11) suggest the possibility of calcium hydroxide reacting to form a semipermeable membrane across which expansive pressures can be developed, and Vivian states (2, Bull. 256 p. 78) that "Calcium hydroxide is not required for the production of gel or sol. . . . ."

In order to further test the effect of calcium hydroxide in sodium hydroxide solutions,

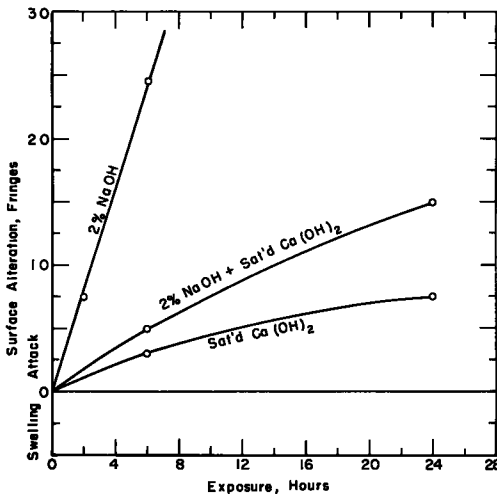


Figure 1. Chemical durability (surface alteration) of barium crown glass 572 illustrating the inhibiting effect of saturated calcium hydroxide solution when added to a 2 percent solution of sodium hydroxide. Exposure at 80 deg C.

the NaOH solution is only about  $\frac{1}{5}$  that of the untreated specimen; that is, both for the glass above and for this opal the effect of the calcium hydroxide is to decrease the rate of attack about 5 fold.

The effect of this inhibiting action is perhaps also made evident in a photograph of grains of opal in a mortar bar where the outside of the aggregate grain remains hard and glassy while the inside has reacted and is very soft (see Fig. 3).

### Swelling of Opal

Many investigators who have worked on the alkali-aggregate problem have tried to demonstrate the swelling of opal in alkaline solutions in the absence of any cement paste or other osmotic membrane (9, p. 17). The swelling of opal has been demonstrated by an interferometric method in acid solutions (5); however, in alkaline solutions, such as are present in cement pastes, there is a simultaneous effect of swelling and attack such that any swelled material on the polished specimen will quickly slough off or dissolve in the excess solution.

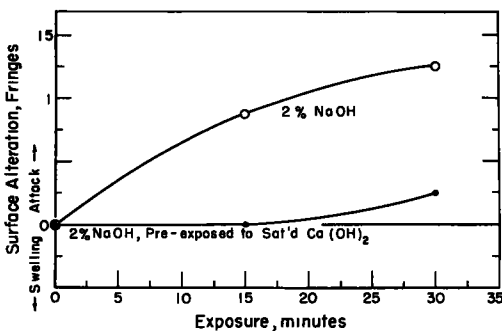


Figure 2. Chemical durability (surface alteration) of opal in 2 percent sodium hydroxide at 80 deg C. One sample untreated and one pre-exposed to saturated calcium hydroxide solution for 6 hours at room temperature.

opal and a synthetic glass aggregate were tested for chemical durability or surface alteration by an interferometric procedure.

The chemical durability of a barium crown glass (BaC 572), (see Table 1), exposed over a period of 24 hours in various solutions is illustrated in Figure 1. It can be seen that the attack on the glass in 6 hours in saturated calcium hydroxide is about  $\frac{1}{4}$  fringe, and in 2 percent sodium hydroxide 10 times this amount, or about  $2\frac{1}{2}$  fringes. The inhibiting effect of calcium hydroxide can be seen when 2 percent sodium hydroxide is added to saturated calcium hydroxide solution. The attack (instead of being additive) is decreased from  $2\frac{1}{2}$  fringes to  $\frac{1}{2}$  fringe, or about 5 fold.

The same effect is illustrated in a slightly different way for a natural aggregate in Figure 2 where the surface alteration of opal (see Table 1, Opal<sup>e</sup>) in 2 percent sodium hydroxide is seen to be about  $1\frac{1}{4}$  fringes for the 30 minute exposure. But when the opal specimen is first exposed to saturated calcium hydroxide solution for 6 hours at room temperature the attack in

6 hours at room temperature the attack in

In order to eliminate this loss of reacted material, a method of testing aggregate samples by the interferometric procedure without a large excess of solution was devised. Instead of suspending the test piece in the solution, the sample was laid flat and a drop of solution was placed on the surface. As the drops evaporated, distilled water was added to bring them as near as possible to the original size and

concentration. After various periods of exposure the sample was carefully washed and dried as usual, and then viewed under the interferometer.

Figure 4 (A, B, and C) shows the swelling effects of different solutions on a sample of lithia-silica glass. Figure 4A illustrates the swelling caused by a drop of acid buffer<sup>2</sup> at a pH of 2.0. Swelling caused by a drop of saturated calcium hydroxide solution is shown in Figure 4B, and by a drop of 2 percent sodium hydroxide solution in Figure 4C. The ragged effect shown in 4C is caused by the fact that the solution tends to spread over the surface of the sample rather than maintain itself in the form of a drop with definite edges. The difficulties encountered with the lithia-silica glass and sodium hydroxide are increased when natural opal is used because the drop evaporates at elevated temperatures, and at room temperature the reaction is too slow to give entirely satisfactory results for photographic reproduction. However, Figure 4D does show a slight swelling of the opal surface when treated with a drop of 2 percent NaOH solution.

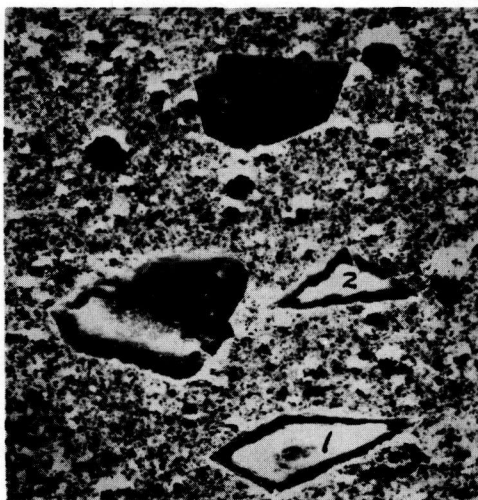


Figure 3. Polished section of opal in high-alkali cement. Note particularly the angular grains (No. 1 and 2) showing reaction in the center portion (soft and white) and the dark (apparently unreacted) outer edge about 50 microns in thickness (Reproduced from Ref. 5).

#### Reaction in Cement Sludge

In a previous investigation of chemical durability by the interferometric procedure, it was observed that the reactive aggregate was always more vigorously attacked in the settling cement sludge than in the supernatant aqueous extract both in the high and low alkali cements (5, Figs. 7, 8, and 9). Although the observation was noted, no reason for this increased attack was available at that time.

At the higher pH values in Figure 5, it can be seen that a small increase in pH causes a large increase in the attack on the standard reactive aggregate (Pyrex Brand Glass 7740). Because of this fact and because the Pyrex is attacked more rapidly in the settling cement sludge than in the supernatant liquid (Fig. 6A and B) it would appear that the pH of the sludge must be higher than the pH of the supernatant liquid.

In order to verify this experimentally, pH determinations were made in both areas by means of the glass electrode. In order to eliminate the "suspension effect" (13, 14) the measurements were made with the reference electrode in the supernatant liquid and with the glass electrode in the phase being tested. The pH was always found to be higher in the settling cement than in the clear solution.

A comparison of the difference in pH between the sludge and liquid, with the durability curve in the alkaline range in Figure 5, indicates that the difference of about 0.1 pH as shown in Table 2 could readily account for the observed difference in durability between the aqueous extract and the settling cement sludge illustrated in Figures 6A and 6B).

This observed difference in pH between the two areas of the solution then raises the question as to how the higher alkalinity in the settling cement sludge is brought about.

In the section immediately following it is shown that the non-migratable ions associated with the hydrated portland cement grains are positively charged. These non-migratable positive charges will attract into the sludge phase any negative migratable ions (namely hydroxyl ions) thus causing a greater concentration of  $\text{OH}^-$  ions in the sludge

<sup>2</sup> Britton-Robinson Universal Buffers (12).



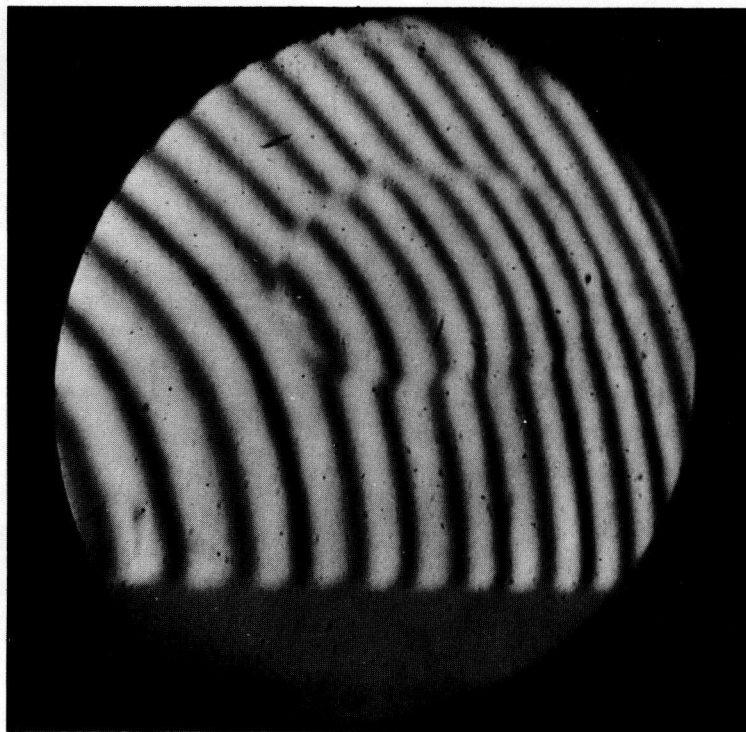


Figure 4A. Interferometric pattern showing swelling on a  $\text{Li}_2\text{O-SiO}_2$  glass caused by a drop of buffer at pH 2 in 24 hours.

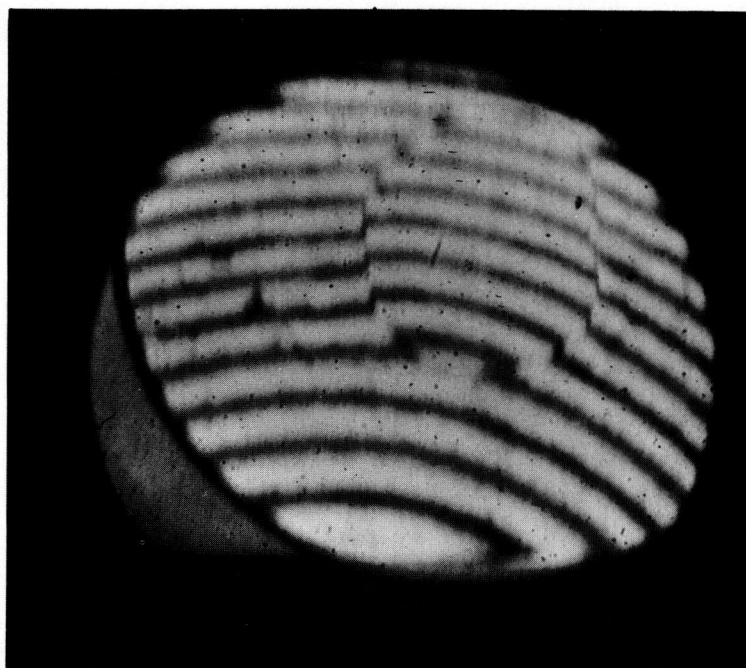


Figure 4B. Interferometric pattern showing swelling on a  $\text{Li}_2\text{O-SiO}_2$  glass caused by a drop of saturated calcium hydroxide solution in 48 hours.

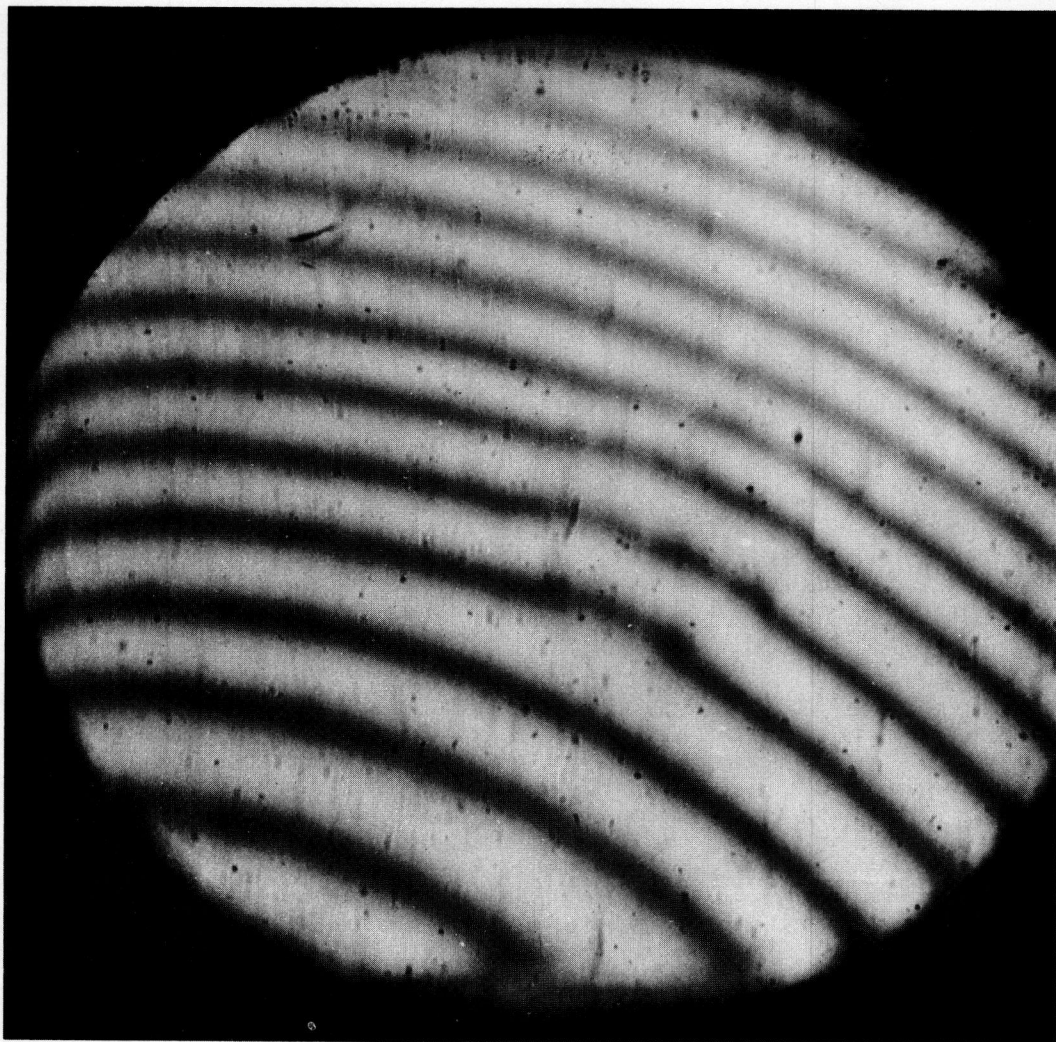


Figure 4C. Interferometric pattern showing swelling on a  $\text{Li}_2\text{O-SiO}_2$  glass caused by a drop of a 2 percent solution of sodium hydroxide in 48 hours.

phase than in the supernatant liquid. This increased concentration of  $\text{OH}^-$  is directly responsible for the higher pH values shown in Table 2.

#### Ionic Charge on Hydrated Cements

The subject of the possible ionic charge on hydrated cement has been reviewed by Pontoppidan<sup>3</sup> and it appears that there is as much evidence for a positive as for a negative charge on hydrated portland cement.<sup>4</sup>

The excess ionic charge on hydrated portland and high alumina cement is given in

<sup>3</sup> Pontoppidan, C., Discussion, "The Chemistry of Retarders and Accelerators." International Symposium on Chemistry of Cements, Stockholm 1938. Ingeniorsvetenskapsakademien, Stockholm, pp 364-69.

<sup>4</sup> More recent work also gives inconclusive evidence as to the ionic charge during early stages of hydration. (Ernsberger, Fred M. and Wesley G. France, "Portland Cement Dispersion by Adsorption of Calcium Lignosulfonate" Industrial and Engineering Chem., Vol. 37, pp 598-600 (1945)).

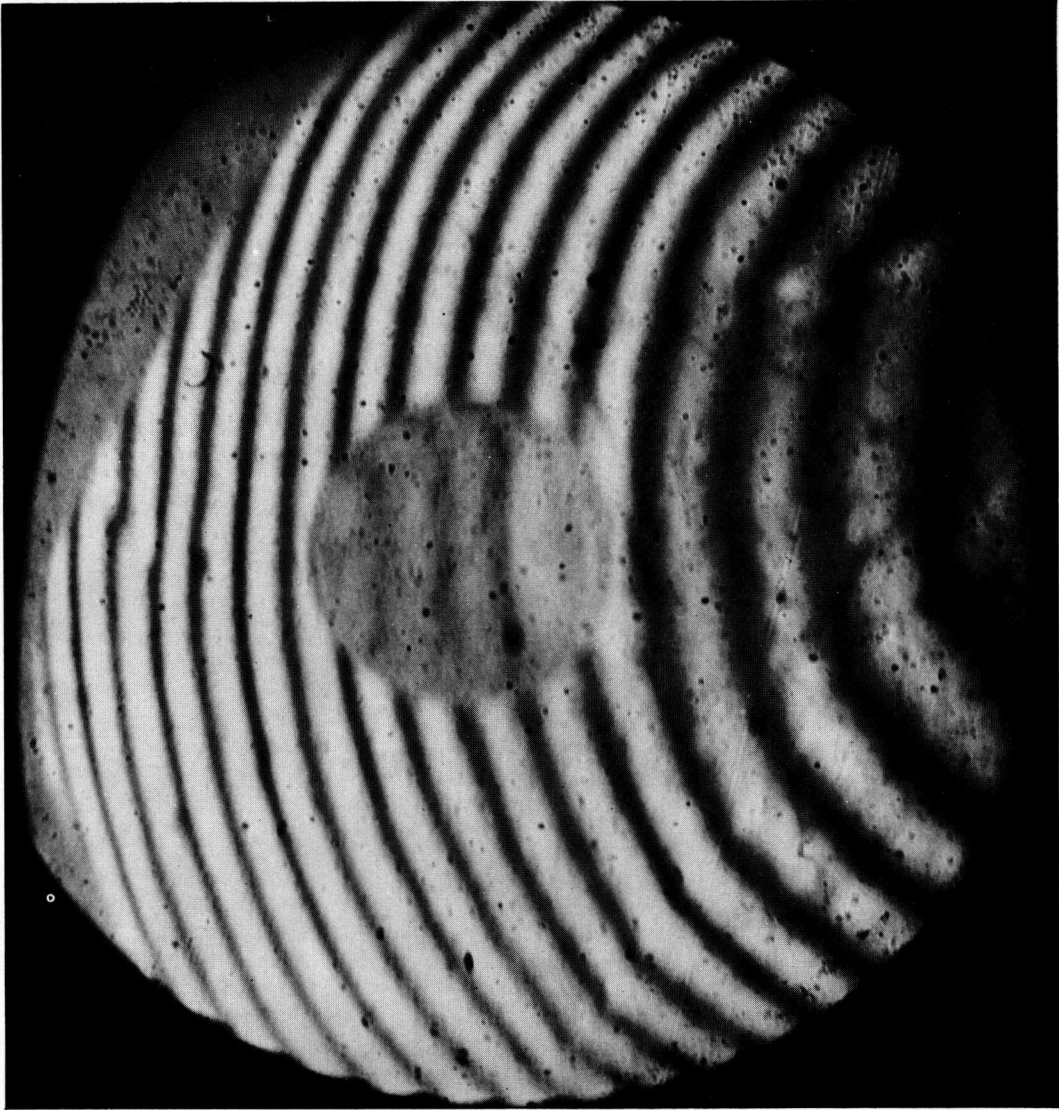


Figure 4D. Interferometric pattern on opal showing swelling caused by a drop of a 2 percent solution of sodium hydroxide in 6 hours.

Figure 7 as a function of leaching time.<sup>5</sup> In order to determine at what point during hydration the cement acquires this charge, additional determinations of the uneven distribution of migratable ions were made starting with the unhydrated cement and using a modification of the regular procedure. A mixture of 10 grams of cement and 50 cc of distilled water was made and then stirred periodically to prevent solidification of the cement. The liquid was separated from the solid phase by filtration rather than by decantation and a correction was made for the negative ionic charge of the filter paper of about  $13 \times 10^{-4}$  m-eq/gram (milli-equivalents per gram of sample). Also because of the difficulty of acidifying the solid phase the supernatant liquid was tested rather than the cement grains themselves and the equal but opposite results were reported, as the excess ionic charge on the cement.

<sup>5</sup> The neat cement was mixed as for regular autoclave bars (15), then stored one day in the moist cabinet and seven days in water before test.

TABLE 2

OBSERVED DIFFERENCES IN pH BETWEEN THE AQUEOUS EXTRACT AND THE SETTING SLUDGE FOR A LOW- AND A HIGH-ALKALI CEMENT<sup>a</sup>

Cement Type	Alkalinity		Difference pH
	Extract pH	Sludge pH	
Low alkali	12.52	12.66	0.14
High alkali	12.60	12.70	0.10

<sup>a</sup>Analysis of cements in Table 3.

The results for the portland cement at five different temperatures are plotted in Figure 8. Although the general shapes of the curves are surprisingly similar there are also significant differences. An apparent equilibrium is reached at successively greater values at 80, 60 and 40 deg C respectively. And, although this apparent equilibrium at 20 deg and 10 deg is not reached even after 8 days it appears that the final values at these temperatures will also be successively greater. This same effect may be seen in the family of curves in Figure 9 where the uneven distribution of migratable ions is plotted as a function of temperature.

These positive ionic charges are quite characteristic of various portland cements as shown in Figure 10 where the uneven distribution of migratable ions is plotted for samples of type I, II, III, IV and type V cements (16). These samples were chosen from 203 cements used in a series of long time tests (17). The chemical analysis of these cements is given in Table 3 where the number of the sample corresponds to the number in this original report, and the cements chosen were those having a fineness as near as possible to that of the type II cement.

In Figures 11 and 12 the ionic charge on a high alumina cement is plotted as a function of time and temperature respectively. In Figure 11, note that as with the portland cements the initial charge is almost zero, but there is a rapid reversal of charge from positive to negative at about 6 hours on the 30 deg and 40 deg C curves. And also, in contrast to the curves for the portland cements, the shapes of the curves for the high alumina cement show a marked difference at the various temperatures. It has been amply demonstrated that supersaturation and precipitation occurs during the hydration of cements (18, and 19). A comparison of the curves in Figures 11 and 12 with those of Wells (18, Fig. 8) and Assarson (19, Fig. 1) shows a characteristic reversal of properties in the early stages of hydration. Also, the effects illustrated in Figure 11 are compatible with phase changes as shown by X-ray studies on a cement of the same type over a similar temperature range (20). In these X-ray studies monocalcium aluminate hydrate appears to be the major phase at 24 deg C, diacalcium aluminate hydrate the major phase at 35 deg C and tricalcium aluminate hydrate the major phase at 50 deg C and 80 deg C, with smaller amounts of unidentified phases occurring at each temperature. However, before any attempt at correlation is made be-

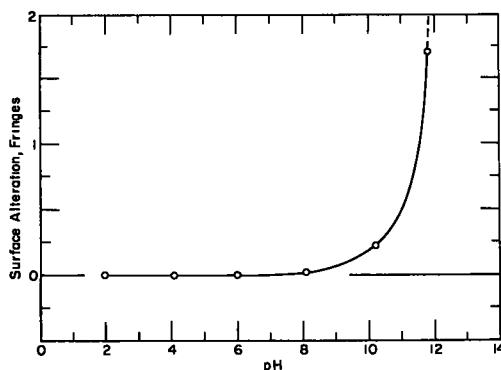


Figure 5. Chemical durability (surface alteration) of Pyrex over pH range from 2 to 11.8. Exposure 6 hours at 80 deg C.

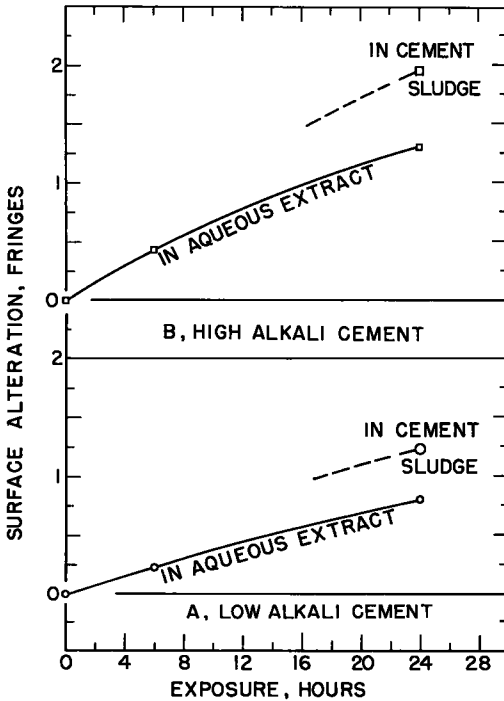


Figure 6. A. Chemical durability (surface alteration) of Pyrex in aqueous extracts from a high alkali cement compared with durability in the settling cement sludge. Exposure at 80 deg C. B. Chemical durability (surface alteration) of Pyrex in aqueous extracts from a low alkali cement compared with durability in the settling cement sludge. Exposure at 80 deg C.

could have a greater effect on the ionic charge than would the major phases identified in the hydrated cement.

Figure 12 shows much the same effect as Figure 11 in a different manner, with the uneven distribution of migratable ions plotted as a function of temperature for various hydration periods. Note that there is an inflection point in all the curves (except that for the 6 hour leach) between 20 deg C and 30 deg C, and a maximum ionic charge for all periods of exposure at some temperature above 40 deg C.

A study of Figures 8 and 11 shows that portland cement reaches its greatest positive charge, and alumina cement its greatest negative charge only after several hours of hydration, even at the higher temperatures tested.

### Expansion of Cement

The expansion and contraction shown by aggregates is also exhibited by neat cement pastes. The mechanism and cause of the swelling and shrinking of hydrated cement pastes have been the subject of much study. One of the most often referred to, and perhaps the first reference to the importance of shrinkage in the hardening of cements, is that of Michaelis (21, 22). Numerous investigators have since studied the swelling and shrinking of cement pastes, mortars and concretes (23), and a theory of swelling and shrinking of neat cement during hydration has also been given in a comprehensive discussion by Powers and Brownyard (24). Eitel (22, p. 1219) states that "It is possi-

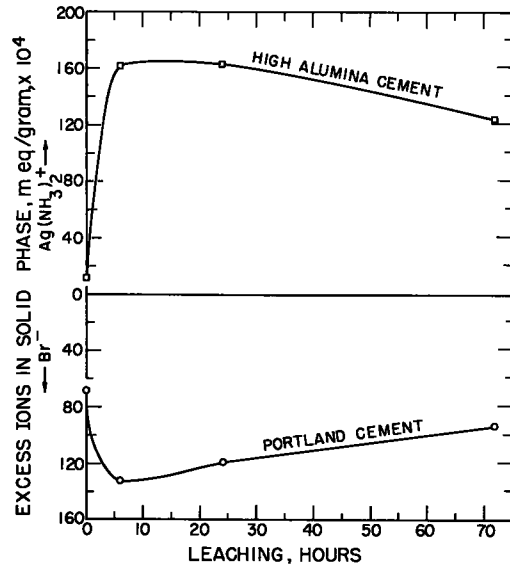


Figure 7. Ionic charge (or the uneven distribution of migratable ions [ $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{Br}^-$ ] between the solid and liquid phases) on portland and alumina cements after leaching in distilled water. Cement samples hydrated 7 days at 25 deg C. before leaching.

tween the charges illustrated and these different phases, extensive work should be done on pure components, both on the determination of phases and on the determination of ionic charges. As a matter of fact, it is possible that the unidentified phases (or even aluminum hydroxide gel which would not show up in X-ray studies)

TABLE 3  
CHEMICAL ANALYSIS AND FINENESS OF CEMENTS

Cement	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	SO <sub>3</sub>	MgO	Loss	Insol.	Na <sub>2</sub> O	K <sub>2</sub> O	CaSO <sub>4</sub>	Li <sub>2</sub> O	SrO	Fineness Air Permeability	
														am <sup>2</sup> /g	am <sup>2</sup> /g
Type I #9	20.2	7.0	2.6	62.7	2.1	3.0	1.1	0.4	0.38	0.88	0.02	0.38	0.38	3410	3410
Type II Low Alk.	22.6	4.5	3.2	65.1	1.7	1.2	1.5	0.2	0.00	0.29	0.01	0.15	0.10	3410	3410
Type III #103	23.5	3.3	2.9	65.5	2.2	0.8	1.4	0.0	0.00	0.39	0.01	0.10	0.10	3960	3960
Type IV #107	23.2	5.2	4.1	63.2	1.8	1.0	0.9	0.0	0.15	0.30	0.01	0.14	0.07	3430	3430
Type V #116	24.6	3.6	2.5	65.0	1.4	1.8	0.8	0.1	0.12	0.30	0.01	0.07	0.07	3380	3380
High Alkali	21.6	6.0	2.5	63.3	2.3	1.9	1.1	0.2	1.10	0.09					

TABLE 4

EXCESS IONIC CHARGE RETAINED BY PORTLAND CEMENT UPON HYDRATION AT VARIOUS TEMPERATURES USING Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> AND Br<sup>-</sup> AS THE INDICATOR IONS

Hydra- tion Time	Excess ions retained within the solid phase after hydration at the following temperatures													
	10 deg C.		20 deg C.		40 deg C.		60 deg C.		80 deg C.					
Days	m. eq/g	Br-	m. eq/g	Ag+	Br-	m. eq/g	Ag+	Br-	m. eq/g	Ag+	Br-	m. eq/g	Ag+	Br-
0	<1.2x10 <sup>-4</sup>	-	<1.2x10 <sup>-4</sup>	-	<1.2x10 <sup>-4</sup>	-	<1.2x10 <sup>-4</sup>	-	<1.2x10 <sup>-4</sup>	-	<1.2x10 <sup>-4</sup>	-	<1.2x10 <sup>-4</sup>	-
1/4	-	2x10 <sup>-4</sup>	-	7x10 <sup>-4</sup>	-	32x10 <sup>-4</sup>	-	85x10 <sup>-4</sup>	-	103x10 <sup>-4</sup>	-	137x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>
1	-	42x10 <sup>-4</sup>	-	102x10 <sup>-4</sup>	-	155x10 <sup>-4</sup>	-	162x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>
2	-	112x10 <sup>-4</sup>	-	160x10 <sup>-4</sup>	-	182x10 <sup>-4</sup>	-	180x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>
4	-	162x10 <sup>-4</sup>	-	185x10 <sup>-4</sup>	-	210x10 <sup>-4</sup>	-	185x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>
8	-	190x10 <sup>-4</sup>	-	212x10 <sup>-4</sup>	-	210x10 <sup>-4</sup>	-	185x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>	-	167x10 <sup>-4</sup>



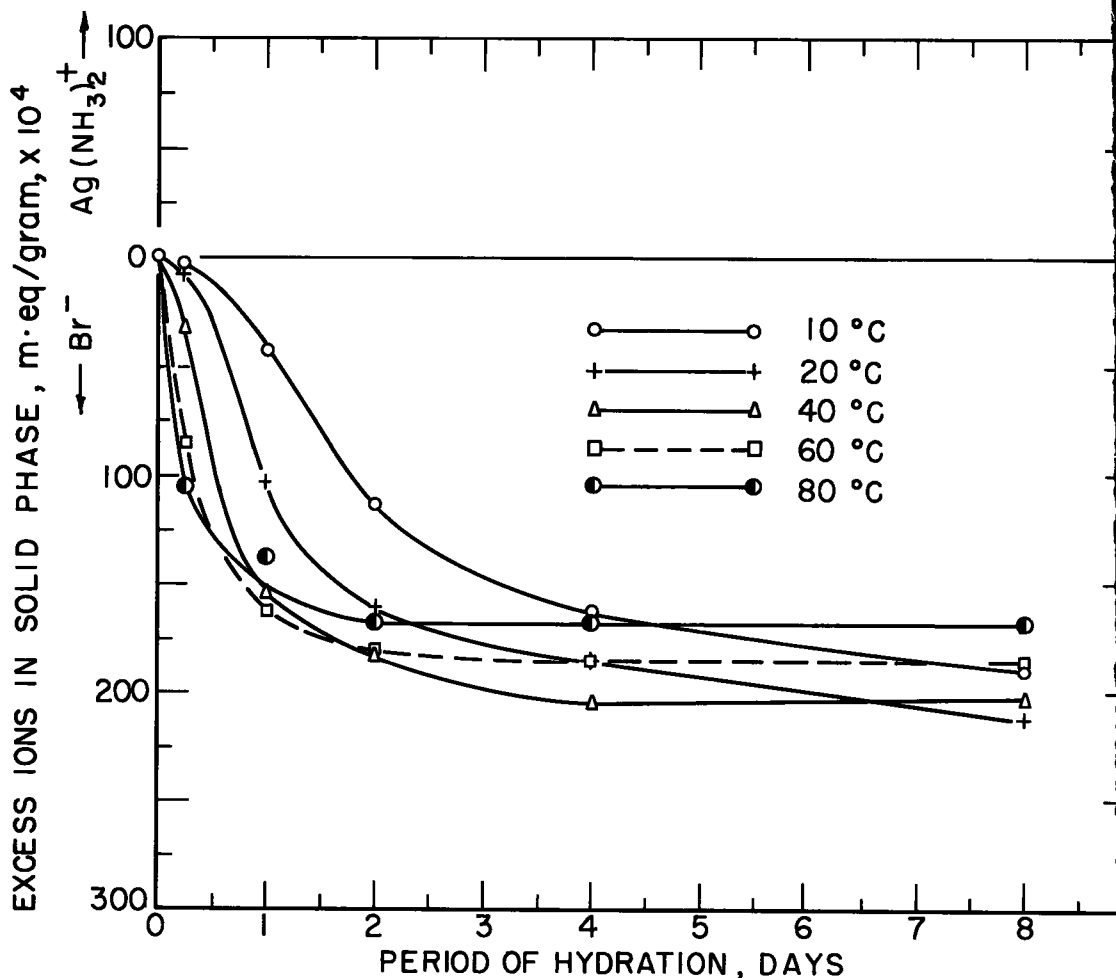


Figure 8. Ionic charge on a low alkali cement after various periods of hydration at different temperatures. (Ten gram samples hydrated in 50 ml of distilled water with sufficient agitation to prevent setting). Data Table 4.

ble to explain the quantitative swelling phenomena in cements during hydration by the Donnan 'membrane equilibria' existing in the cement-water systems, just as the corresponding phenomena in gelatin-water mixtures are explained."

A study was made by means of the interferometric procedure to determine the swelling and reduction in swelling of hydrated cement pastes on their exposure to solutions of various pH values. Special cement<sup>6</sup> specimens were fabricated by compressing the water cement mixture (0.1 part water to 1.0 part cement) at a pressure of 10,000 psi. After curing in water at atmospheric pressure for 7 days the specimens were hard and dense and could be cut and polished sufficiently flat to show acceptable interference fringes under the Pulfrich interferometer.

The expected severe attack on hydrated cement caused by high acid (pH 2) solutions is shown in Figure 13, curve B. Curve A, Figure 13, illustrates the marked swelling which occurs over the range from pH 4 to 11.8 measured immediately after the sample is removed from the solution. Curve B, Figure 13, shows the same specimen treated as above and then dried in air for 24 hours before the measurements are made. Note that the swelling is more completely reversible at the higher pH values. The swelling

<sup>6</sup>Unless otherwise designated the cement used throughout this paper is the type II low alkali of Table 3.

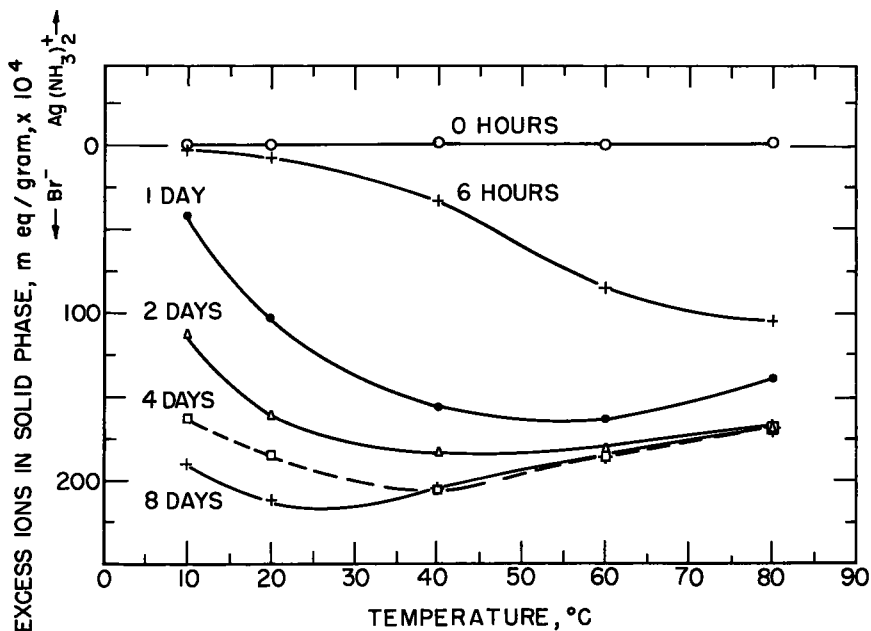


Figure 9. Ionic charge on a low alkali cement as a function of temperature for different periods of hydration. (Ten gram samples hydrated in 50 ml of distilled water with sufficient agitation to prevent setting). Data Table 4.

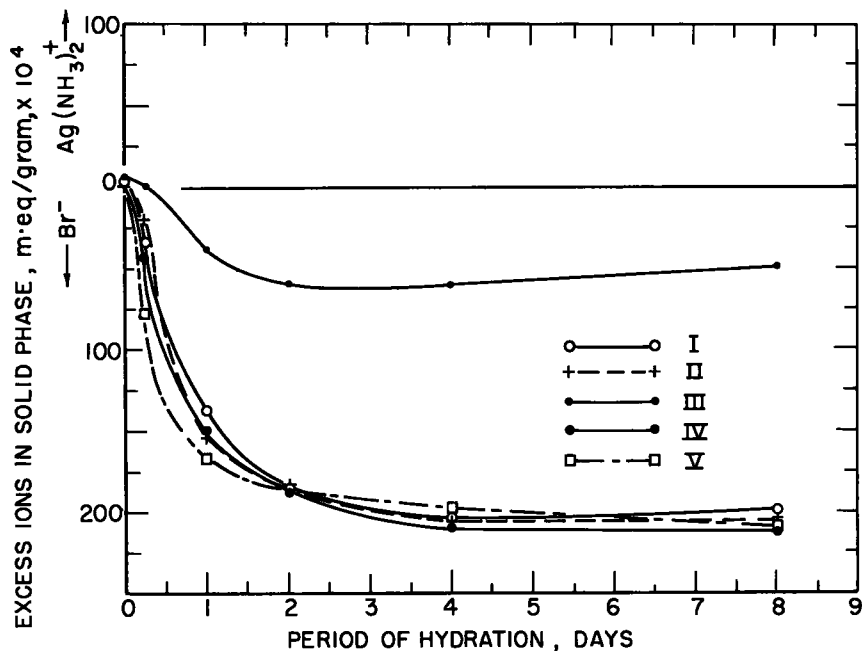


Figure 10. Ionic charge on five types of portland cement after various periods of hydration at 40 deg C. (Samples hydrated in 50 ml of distilled water with sufficient agitation to prevent setting).



TABLE 5

EXCESS IONIC CHARGE RETAINED BY 5 TYPES OF PORTLAND CEMENT DURING HYDRATION AT 40°C,  
USING  $\text{Ag}(\text{NH}_3)_2^+$  AND  $\text{Br}^-$  AS THE INDICATOR IONS

Hydration		Type I				Type II				Type III				Type IV				Type V			
Time	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	
Days	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g
0	$3 \times 10^{-4}$	—	$< 1.2 \times 10^{-4}$	—	$6.2 \times 10^{-4}$	—	$< 1 \times 10^{-4}$	—	$< 1 \times 10^{-4}$	—	$< 1 \times 10^{-4}$	—	$< 1 \times 10^{-4}$	—	$< 1 \times 10^{-4}$	—	$< 1 \times 10^{-4}$	—	$< 1 \times 10^{-4}$	—	$< 1 \times 10^{-4}$
¼	—	$33 \times 10^{-4}$	—	$20 \times 10^{-4}$	—	$20 \times 10^{-4}$	—	$1.2 \times 10^{-4}$	—	—	—	—	—	—	—	—	—	—	—	—	$78 \times 10^{-4}$
1	—	$137 \times 10^{-4}$	—	$155 \times 10^{-4}$	—	$155 \times 10^{-4}$	—	$37 \times 10^{-4}$	—	—	—	—	—	—	—	—	—	—	—	—	$162 \times 10^{-4}$
2	—	$187 \times 10^{-4}$	—	$182 \times 10^{-4}$	—	$182 \times 10^{-4}$	—	$60 \times 10^{-4}$	—	—	—	—	—	—	—	—	—	—	—	—	$187 \times 10^{-4}$
4	—	$203 \times 10^{-4}$	—	$205 \times 10^{-4}$	—	$205 \times 10^{-4}$	—	$59 \times 10^{-4}$	—	—	—	—	—	—	—	—	—	—	—	—	$199 \times 10^{-4}$
8	—	$198 \times 10^{-4}$	—	$203 \times 10^{-4}$	—	$203 \times 10^{-4}$	—	$49 \times 10^{-4}$	—	—	—	—	—	—	—	—	—	—	—	—	$210 \times 10^{-4}$

Excess ions retained within the solid phase by 5 types of cement after hydration at 40°C

TABLE 6

EXCESS IONIC CHARGE RETAINED BY HIGH ALUMINA CEMENT UPON HYDRATION AT VARIOUS TEMPERATURES  
USING  $\text{Ag}(\text{NH}_3)_2^+$  AND  $\text{Br}^-$  AS THE INDICATOR IONS

Hydration		20°C				30°C				40°C				60°C				80°C					
Time	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	Ag <sup>+</sup>	Br <sup>-</sup>	
Days	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g	m. eq/g
0	$2.5 \times 10^{-4}$	—	$2.5 \times 10^{-4}$	—	$2.5 \times 10^{-4}$	—	$2.5 \times 10^{-4}$	—	$2.5 \times 10^{-4}$	—	$2.5 \times 10^{-4}$	—	$2.5 \times 10^{-4}$	—	$2.5 \times 10^{-4}$	—	$2.5 \times 10^{-4}$	—	$2.5 \times 10^{-4}$	—	$2.5 \times 10^{-4}$	—	$2.5 \times 10^{-4}$
¼	—	$87 \times 10^{-4}$	—	$75 \times 10^{-4}$	—	$63 \times 10^{-3}$	—	$53 \times 10^{-3}$	—	$53 \times 10^{-3}$	—	$330 \times 10^{-3}$	—	$330 \times 10^{-3}$	—	$330 \times 10^{-3}$	—	$330 \times 10^{-3}$	—	$330 \times 10^{-3}$	—	$575 \times 10^{-4}$	—
1	—	$133 \times 10^{-4}$	—	$160 \times 10^{-4}$	—	$125 \times 10^{-4}$	—	$340 \times 10^{-4}$	—	$340 \times 10^{-4}$	—	$750 \times 10^{-4}$	—	$750 \times 10^{-4}$	—	$750 \times 10^{-4}$	—	$750 \times 10^{-4}$	—	$750 \times 10^{-4}$	—	$465 \times 10^{-4}$	—
2	—	$185 \times 10^{-4}$	—	$70 \times 10^{-4}$	—	$340 \times 10^{-4}$	—	$480 \times 10^{-4}$	—	$480 \times 10^{-4}$	—	$700 \times 10^{-4}$	—	$700 \times 10^{-4}$	—	$700 \times 10^{-4}$	—	$700 \times 10^{-4}$	—	$700 \times 10^{-4}$	—	$450 \times 10^{-4}$	—
4	—	$115 \times 10^{-4}$	—	$5 \times 10^{-4}$	—	$470 \times 10^{-4}$	—	$575 \times 10^{-4}$	—	$575 \times 10^{-4}$	—	$575 \times 10^{-4}$	—	$575 \times 10^{-4}$	—	$575 \times 10^{-4}$	—	$575 \times 10^{-4}$	—	$575 \times 10^{-4}$	—	$390 \times 10^{-4}$	—
8	—	$65 \times 10^{-4}$	—	$48 \times 10^{-4}$	—	$380 \times 10^{-4}$	—	$560 \times 10^{-4}$	—	$560 \times 10^{-4}$	—	$425 \times 10^{-4}$	—	$425 \times 10^{-4}$	—	$425 \times 10^{-4}$	—	$425 \times 10^{-4}$	—	$425 \times 10^{-4}$	—	$250 \times 10^{-4}$	—

Excess ions retained within the solid phase after hydration at the following temperatures

10 gram sample hydrated in 50 ml. distilled water with sufficient agitation to prevent setting.

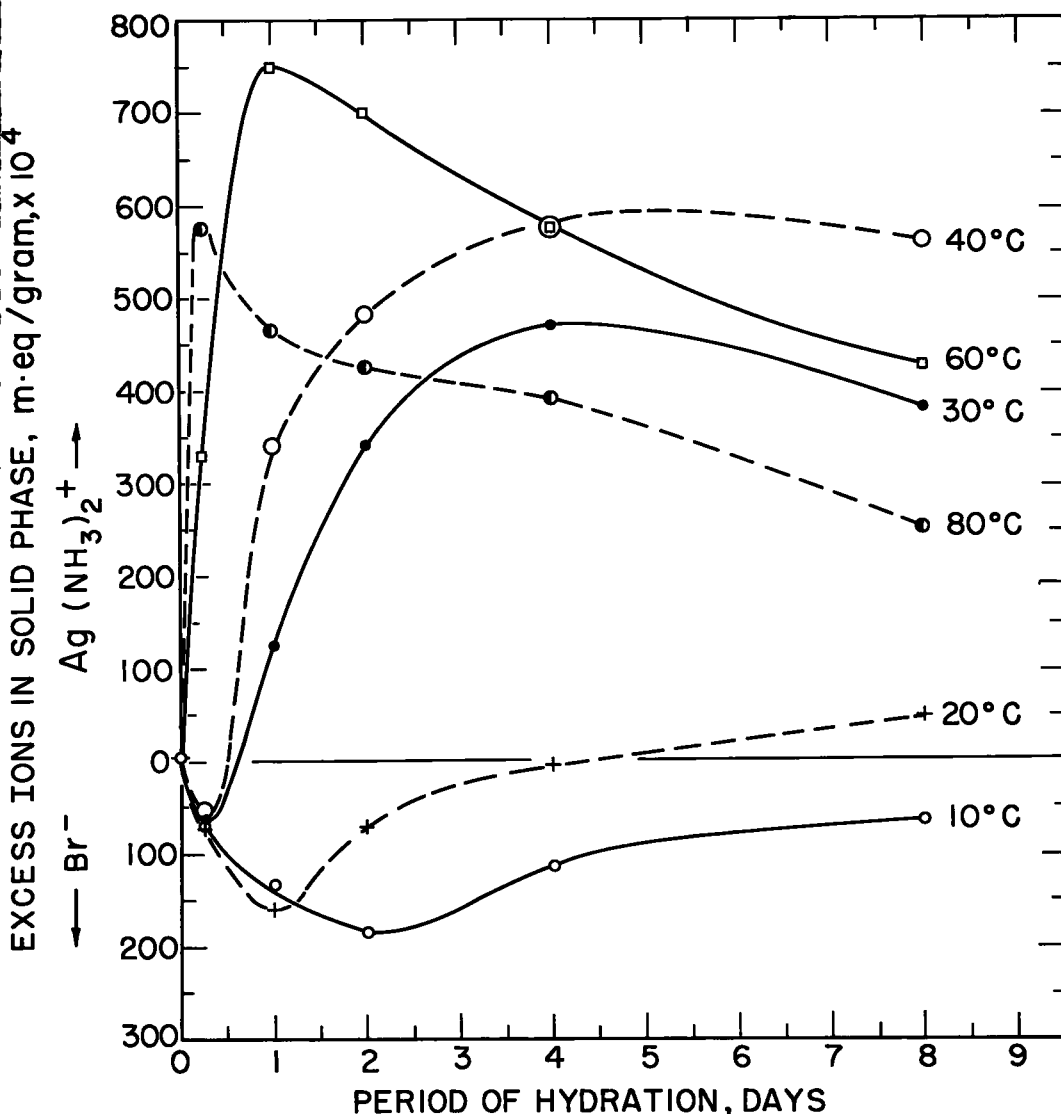


Figure 11. Ionic charge on a high alumina cement after various periods of hydration at different temperatures. (Ten gram samples hydrated in 50 ml of distilled water with sufficient agitation to prevent setting). Data Table 6.

and the subsequent reduction in swelling of this hydrated cement is much greater than for any other substance tested by this method.

It has been demonstrated (6) that the swelling of certain glasses in acid solution is caused by the uneven distribution of migratable ions brought about by an excess negative ionic charge on the silicate. This effect may also be one of the contributing factors in the swelling of hydrated cement. However, in contrast to glasses which swell because of a non-migratable negative charge, the excess positive charge (discussed in the preceding section) is the determining factor in portland cement.

The positive non-migratable ionic charge on hydrated portland cement is also in accord with the fact that the attack on Pyrex is more rapid in the settling cement sludge than in the supernatant liquid and also with the higher pH values measured in the sludge.

Non-Expansion with Certain Aggregates

In previous work it was noted that several glasses (barium crown glass BaC 572, fiber glass type E, medium flint glass F620 and borosilicate crown glass BSC 517) were quite reactive by the interferometric test but failed to show serious expansion up to a period of 240 days when used in mortar bars. Therefore, these and other glasses were also tested for any Donnan membrane equilibria effects and the results compared with those obtained on portland cement.

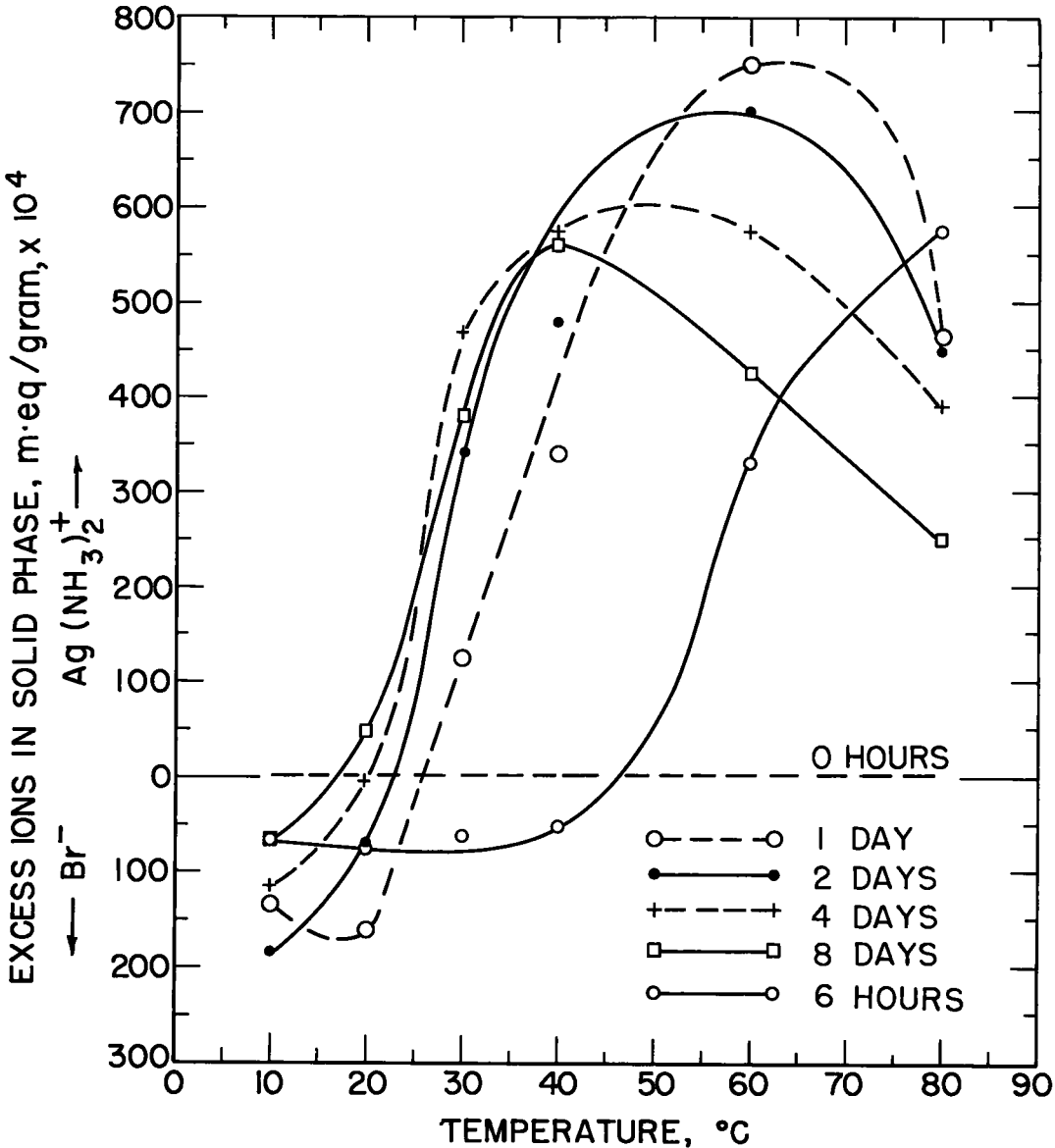


Figure 12. Ionic charge on hydrating high alumina cement as a function of temperature for different periods of hydration. (Ten gram samples hydrated in 50 ml of distilled water with sufficient agitation to prevent setting). Data Table 6.

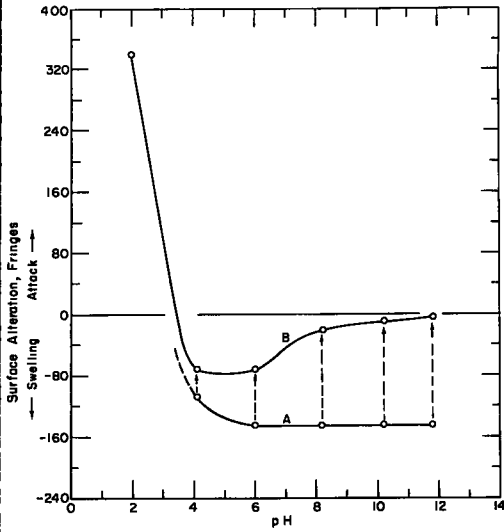


Figure 13. Chemical durability (surface alteration) of hydrated cement over an extended pH range at 80 deg C.

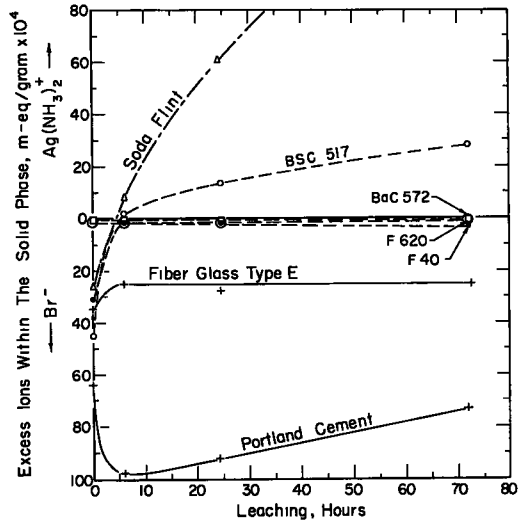


Figure 14. Excess positive  $[(Ag(NH_3)_2)^+]$  or negative  $[Br^-]$  ions retained by the samples after various periods of leaching in distilled water.

In Figure 14 is plotted the excess  $Ag(NH_3)_2^+$  or  $Br^-$  ion held by the different glasses after the various periods of leaching. It may be noted that in the very early stages of leaching they have a positive ionic charge (shown by the concentration of negative  $Br^-$  ions) or are nearly neutral. This positive charge rapidly decreases on leaching or, as in the case of the BSC 517 and soda flint, the charge is actually reversed after 6 hours treatment. On comparing these curves with those illustrating the expansion of mortar bars containing these glasses in Figure 15, it appears, with the exception of F620, that the glasses which retain their positive charge show little harmful expansion when subjected to the standard mortar bar test.

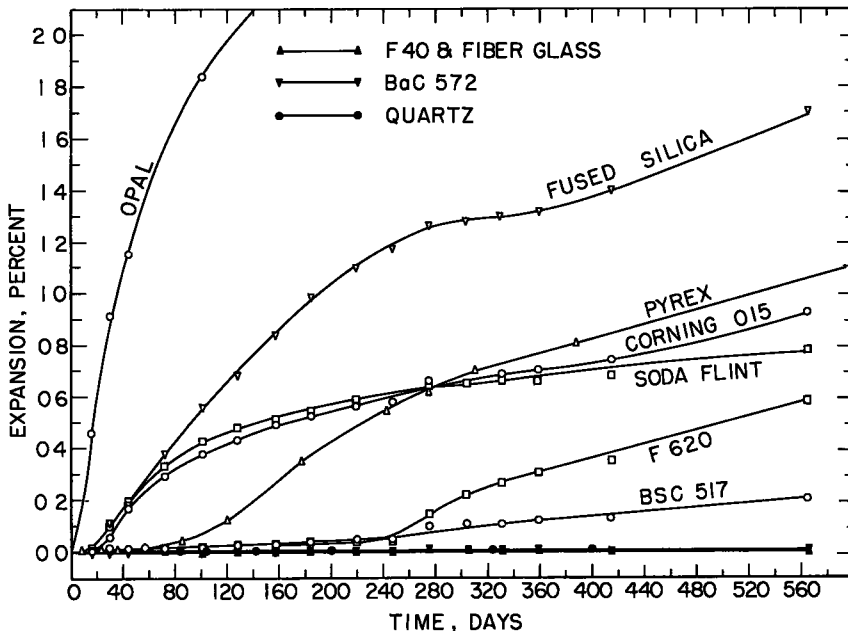


Figure 15. Expansion of mortar bars in which 6 percent of the Ottawa sand was replaced by various natural and synthetic aggregates. Aged over water at 100 deg F.

## SUMMARY

1. The inhibiting effect of calcium hydroxide on the alkali-aggregate reaction is illustrated by the fact that the rate of attack of sodium hydroxide plus calcium hydroxide on opal is about  $\frac{1}{5}$  that of sodium hydroxide solution alone.
2. Sodium hydroxide is shown to cause swelling of opal in the absence of any cement paste membrane.
3. Aggregates are more rapidly attacked in settling cement sludge than in aqueous extracts from the same cement because the pH of the sludge is higher than that of the aqueous extract.
4. The swelling of set portland cement pastes was demonstrated by means of the interferometer procedure. This swelling was accompanied by the uneven distribution of migratable ions in accordance with the Donnan membrane theory.
5. The portland cement pastes tested are shown to carry an excess positive and the high alumina cement pastes an excess negative ionic charge after hydration.
6. Tests indicate that certain glasses (which are re-active by the interferometric procedure) when used in mortar bars cause little harmful expansion, or greatly layed expansion. The fact that these glasses carry an excess positive ionic charge similar to the positive charge on portland cement may be a contributing factor in the delayed expansion caused by these glasses.

## REFERENCES

1. Stanton, Thomas E., "Expansion of Concrete Through Reaction Between Cement and Aggregate." Proc., ASCE 66, 1781-1811 (1940).
2. Vivian, H. E., A. R. Alderman, A. J. Gaskin, and R. H. Jones, "Studies in Cement Aggregate Reaction." Bulletin Nos. 229 and 256, Commonwealth Scientific and Industrial Research Organization, Australia (1950).
3. Hansen, W. C., "Studies Relating to the Mechanism by which the Alkali-Aggregate Reaction Produces Expansion in Concrete." Proc. ACI 40, 213-227 (1944).
4. Lerch, William, "Studies of some Methods of Avoiding the Expansion and Pattern Cracking Associated with the Alkali-Aggregate Reaction," ASTM Symposium on use of pozzolanic materials in mortars and concretes, Special Technical Publication No. 99, (1950).
5. Pike, Robert G., Donald Hubbard and Herbert Insley, "Mechanisms of Alkali-Aggregate Reaction." Proc. ACI 52, 13-34, (1955).
6. Hubbard, Donald and Richard G. Goldman, "Heterogeneous Equilibria at the Glass Electrode-Solution Interface." J. Research NBS 48, 428-36 (1952) RP 2333.
7. Hester, J. A. and O. F. Smith, "Alkali Aggregate Phase of Chemical Reactivity in Concrete," Highway Research Board, Proc. 32, 306-12, (1953).
8. Powers, T. C. and H. H. Steinour, "An Interpretation of Published Research on the Alkali Aggregate Reaction." Proc. ACI 51, 497 and 785 (1955).
9. Verbeck, George and Charles Gramlich, "Osmotic Studies and Hypothesis Concerning Alkali-Aggregate Reaction." Proc. ASTM 55, 1110-28 (1955).
10. Kalousek, George L., "Discussion of Paper by Hansen." Proc. ACI 15, 228 (1944).
11. Parsons, W. H. and H. Insley, "Aggregate Reaction with Cement Alkalies." Proc. ACI 44, 625-632 (1948).
12. Britton, H. T. S., "Hydrogen Ions," I, 3rd ed., p. 313, D. Van Nostrand Co., New York, N. Y., (1943).
13. Bates, Roger G., "Electrometric pH Determinations." (Theory and Practice) p. 197, John Wiley and Sons, Inc., New York, N. Y. (1954).
14. Jenny, H., T. R. Nielse, N. T. Coleman, D. E. Williams, "Concerning the Measurement of pH, Ion Activities and Membrane Potentials in Colloidal Systems," Science 112, 164 (1950).
15. Federal Specification SS-C-158.
16. Bogue, R. H., "The Chemistry of Portland Cement." 2nd ed. pp. 24-5, Reinhold Publ Corp., New York (1955).
17. Unpublished data.

18. Wells, Lansing S. , "Reaction of Water on Calcium Aluminates." J. Research, NBS, pp. 951-1009 (Dec. 1928) RP34.
19. Assarsson, Gunnar, "Die Reaktion zwischen Tonerdezement und Wasser," Sveriges Geologiska Undersakn, Ser. C. No. 379, Vol. 27, No. 4, 22-60 (1933).
20. Wells, Lansing S. and E. T. Carlson, "The Hydration of Aluminous Cements and Its Relation to the Phase Equilibria in the System Lime-Alumina-Water." J. Research, NBS 57, 335-353 (1956) RP 2723.
21. Michaelis, W. , "Ueber die Wasserbindung der Hydraulischen Bindemittel." Protokoll des Vereins Deutscher Portlandzement-Fabrikanten. 22, 148-62 (1899).
22. Eitel, Wilhelm, "The Physical Chemistry of the Silicates." p. 1219, Univ. of Chicago Press, Chicago, Ill. (1954).
23. Lea, F.M. and G.H. Desch, "The Chemistry of Cement and Concrete." p. 172 Edward Arnold and Co. , London (1935).
24. Powers, T. C. and T. L. Brownyard, "Studies of the Physical Properties of Hardened Portland Cement Paste." Proc. ACI 43 582-95 (1947).

# Pressures Developed in Cement Pastes and Mortars by the Alkali-Aggregate Reaction\*

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Measurements with a special pressure cell, using an SR-4 strain gage as the sensitive element, show that the alkali-aggregate reaction in cement pastes and mortars may develop pressures in excess of 2,000 psi.

● IN HIS DISCUSSION of the alkali-aggregate problem, Hansen (1) showed that the cement paste could act as an osmotic membrane across which hydrostatic pressures might arise to cause the disintegration known to occur with high alkali cement and opaline aggregates (2). Also McConnell and co-workers (3) measured pressures in excess of 550 psi, using a neat cement disc as an osmotic membrane and water glass (38 percent sodium silicate,  $\text{Na}_2\text{O}$  to  $\text{SiO}_2$  ratio of 0.30) as the solution. This pressure is of the same order of magnitude as the tensile strength of concrete and could perhaps cause the observed disintegration. However, at higher concentrations of electrolyte (which form at the surface of pure opal (3, p. 123) one might expect much higher pressures such as were found in the following tests.

## APPARATUS AND PROCEDURE

The pressures developed were measured with a special pressure cell turned from a solid piece of cold rolled steel (Fig. 1). An SR-4 type AB-3 strain gage wrapped in a spiral around the outside acted as the sensitive element. Because of the difficulty of removing the cement mixtures a new cell was required for each test.

In order to calibrate the device the cap on the cell was replaced by a special plate drilled and tapped to take a  $\frac{1}{4}$  inch nipple. Oil was then pumped in under known pressures varying from 50 to 2,000 psi. The response observed on the SR-4 strain gage was linear and acceptably reproducible when the hydrostatic pressure was repeatedly cycled.

In an actual test the cement paste or mortar was packed into the cell with a  $\frac{1}{4}$  inch diameter rod. The mortar was struck off flush with the surface of the flange and the cell sealed with a steel plate so that no moisture could be lost or gained. An initial pressure reading (shown on the curves as zero psi) was immediately taken which gave an indication of from 250 to 750 psi pressure above that of the empty cell. Increase or decrease in pressure was then read on the strain indicator every few hours at the start of the test, and later at intervals of several days.

The cause of the initial pressure mentioned above is not known. However, several possibilities may be advanced, the most probable of which is that the mortar is tightly packed in the cell which thus makes possible the negative pressures indicated later in the paper. Second, stresses may be set up when tightening the screws in the cell cap to close the cell, particularly if a grain of sand or other foreign matter becomes lodged under the cap.

Several different mixtures were tested: (a) A cement paste, using 100 g of high-alkali cement (1.10 percent  $\text{NaO}$ , 0.09 percent  $\text{K}_2\text{O}$ ) with 25 cc water, and 4 g of opal from Carson City, Nev. (analysis in Table 1) sized between No. 16 and No. 20 (US standard) sieves. (b) A similar paste using low-alkali cement (0.00 percent  $\text{NaO}$ , 0.29 percent  $\text{K}_2\text{O}$ ). (c) Mortar made with 100 g of low-alkali cement, 40 cc water and 200 g graded Ottawa sand. (d) A mortar similar to No. 3 using a high alkali cement. (e) A mortar similar to No. 4 with 6 percent of the sand replaced by opal sized between No. 50 and No. 100 (US standard) sieves.

\*Presented at the open meeting of the Committee on Durability of Concrete—Chemical Aspects; January 8, 1957.

## RESULTS AND DISCUSSION

The results of five typical tests are shown in Figure 2. Pressures measured in comparable tests differed from those shown by about 25 percent. The highest pressures (about 2,100 psi) were obtained in about 140 days using a paste of high-alkali cement and opal. The development of this high pressure in a closed system is compatible with the facts that  $\text{Na}^+$  and water are known to migrate through the cement paste (4) and that their reaction with opal can cause an increase in the volume of the opal in excess of 300 percent (5). The control sample using low-alkali cement and opal showed no appreciable pressure over the same period.

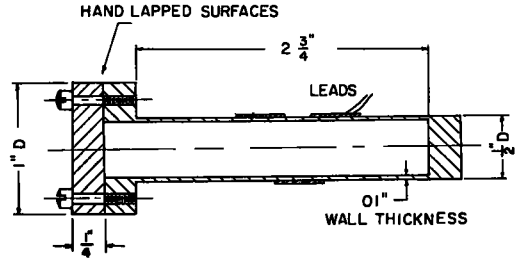


Figure 1. Cell used to measure pressures developed by the alkali-aggregate reaction material is CR steel.

Mortars made with high-alkali cement, and using opal as 6 percent of the aggregate, also developed considerable pressure: about 400 psi in 190 days. The three compositions which did not contain both high-alkali cement and opal developed only low pressures.

In the course of this investigation it seemed desirable to determine if creep in the metal of the cell was a significant factor after prolonged pressures. A cell which had indicated a pressure in excess of 1,700 psi over a period of 142 days was opened and, without disturbing the cement, placed in a vacuum desiccator. After evaporation had

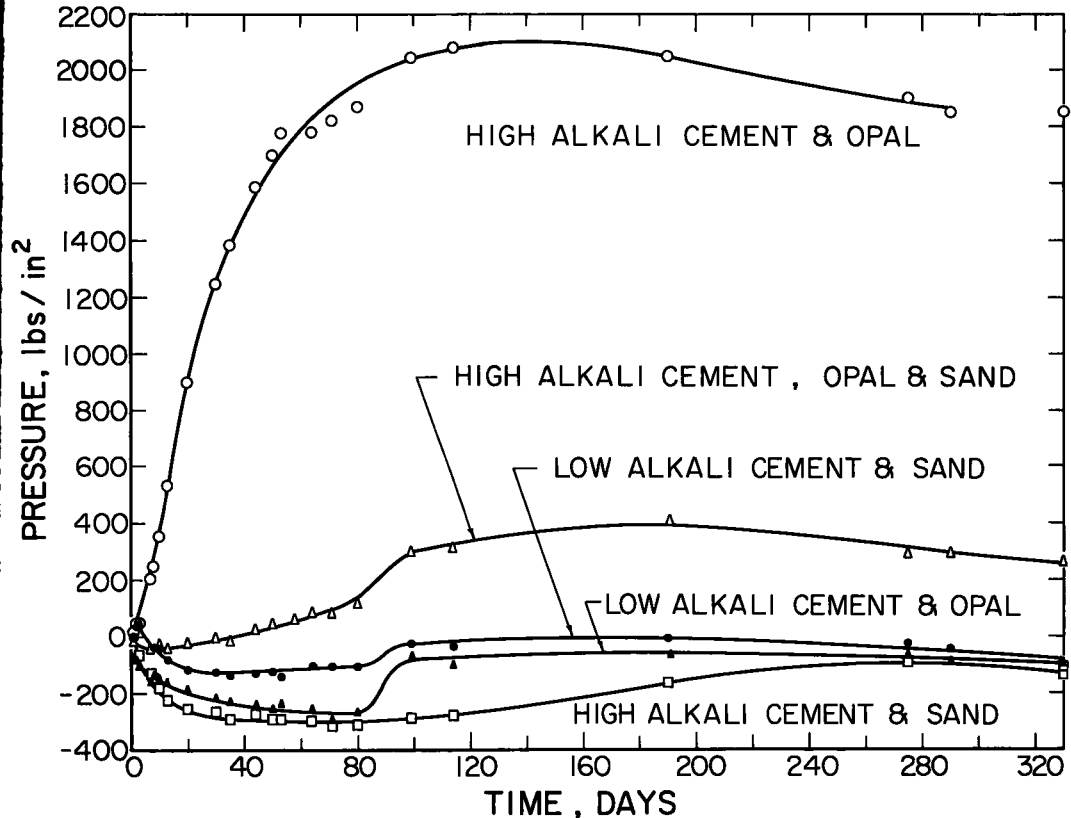


Figure 2. Pressures developed by the alkali-aggregate reaction over a period of 320 days.



continued for 60 days the indicated pressure dropped to less than 70 psi signifying the absence of any excessive creep in the gage. This drop in pressure also indicates that there had been no permanent volume increase caused by reaction or by recrystallization in the mortar and strongly suggests that the pressures developed in the cell are due to osmotic forces generated in the vicinity of the reactive aggregate.

The cell was originally packed under considerable positive pressure. The "negative pressure" indicated by the curves at early ages for all mixtures except that developing the highest pressure is attributed to the shrinkage which is known to occur during hydration of cements (6).

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#### REFERENCES

1. Hansen, W. C., "Studies Relating to the Mechanism by Which the Alkali-Aggregate Reaction Produces Expansion in Concrete." Proc. ACI 40 213-227 (1944).
2. Stanton, Thomas E., "Expansion of Concrete Through Reaction Between Cement and Aggregate." Proc., ASCE 66, 1781-1811 (1940).
3. McConnell, D., R. C. Mielenz, W. Y. Holland, and K. T. Greene, "Cement-Aggregate Reaction in Concrete." Proc., ACI 44, 93-128 (1947).
4. Vivian, H. E., "Studies in Cement-Aggregate Reaction, II. The Effect of Alkali Movement in Hardened Mortar." Council for Scientific and Industrial Research, Bulletin No. 229, 47-54 (1947).
5. Pike, Robert G., Donald Hubbard, and Herbert Insley, "Mechanisms of Alkali-Aggregate Reaction." Proc. ACI 52, 13-34 (1955).
6. Bogue, R. H., "The Chemistry of Portland Cement." 2nd ed. p. 623, Reinhold Pub. Corp., New York (1955).

TABLE 1 — ANALYSIS OF OPALS<sup>a</sup>

Item	Percent
Loss on ignition (1, 100 C)	5.32
HF residue	4.30
SiO <sub>2</sub> (by difference)	90.38
Fe <sub>2</sub> O <sub>3</sub> <sup>b</sup>	0.54
Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	2.72

<sup>a</sup>Analysis by E. B. Clark of the National Bureau of Standards.

<sup>b</sup>The HF residue was fused and dissolved and "R<sub>2</sub>O<sub>3</sub>" precipitated with NH<sub>4</sub>OH and ignited. The Fe<sub>2</sub>O<sub>3</sub> was determined in the ignited precipitate and the remainder of the R<sub>2</sub>O<sub>3</sub> assumed to be Al<sub>2</sub>O<sub>3</sub>.

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