

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.¹

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

¹ 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 ^a	BaC 572 ^b	BSC 517 ^b	F 620 ^b	Soda-Flint ^b	Pyrex ^c	Fiber-Glass ^d Type E	Li ₂ O-SiO ₂ ^b Glass	F-40 ^b	Opal ^e	Opal ^f
Na ₂ O	22	0.4	8.4	3.6	20	3.8					
K ₂ O		7.7	11.8	5.2		0.4					
Li ₂ O								23.9			
CaO	6						16.0				
BaO		30.8							30		
PbO				45.1	20						
ZnO		7.2	0.5								
B ₂ O ₃		3.6	12.4			12.9	9.5				
As ₂ O ₃		0.2	0.5	0.5							
Sb ₂ O ₃		0.4									
SiO ₂	72	49.7	66.4	45.6	60	80.5	55.0	76.1	50	93.09	90.38
Al ₂ O ₃						2.2	14.5			0.87	2.72
Fe ₂ O ₃										0.11	0.54
MgO							5.0				
Ign. Loss										5.40	5.32
HF Res. ^g										1.51	4.30
TiO ₂									20		

^aMacInnes, D. A. and Dole, M., "The Behavior of Glass Electrodes of Different Compositions" Jour. Am. Chem. Soc., Vol. 52, p. 29, (1930).

^bCompositions of batch material.

^cPhillips, C. J., "Glass, the Miracle Maker," p. 47, Pitman Pub. Corp., New York.

^dO'Leary, M. J. and Hubbard, D., "Some Properties of a Glass Used in Paper Manufacture" Jour. Research NBS, Vol. 55, (1955) RP 2599.

^eSelected clear pieces, used in interferometer flats.

^fRun-of-mine grade, used in expansion bars.

^gThe HF residue was fused and dissolved, and "R₂O₃" precipitated with NH₄OH and ignited. The Fe₂O₃ was determined in the ignited precipitate and the remainder of the R₂O₃ assumed to be Al₂O₃.

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(NH₃)₂Br 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 H₂SO₄ in order to precipitate and eliminate any adsorbed AgBr. The excess Ag⁺ or Br⁻ 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,

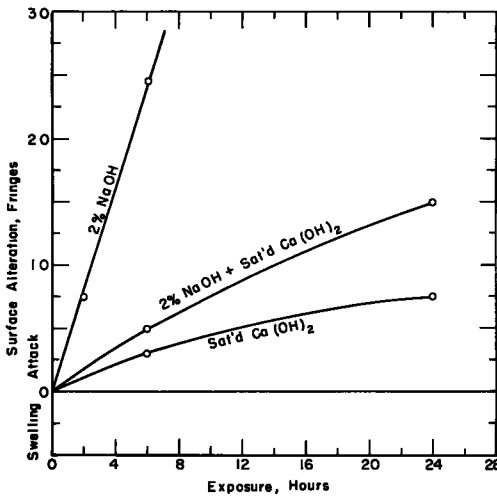


Figure 1. Chemical durability (surface alteration) of barium crown glass 572 illustrating the inhibiting effect of saturated calcium hydroxide solution when added to a 2 percent solution of sodium hydroxide. Exposure at 80 deg C.

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.

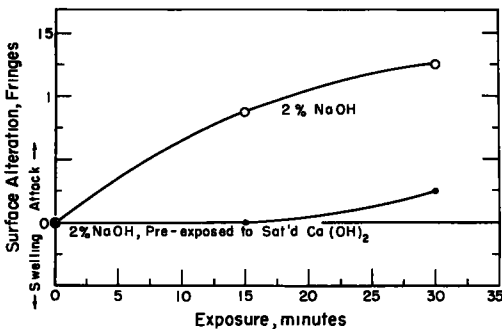


Figure 2. Chemical durability (surface alteration) of opal in 2 percent sodium hydroxide at 80 deg C. One sample untreated and one pre-exposed to saturated calcium hydroxide solution for 6 hours at room temperature.

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^e) 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 buffer² 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.

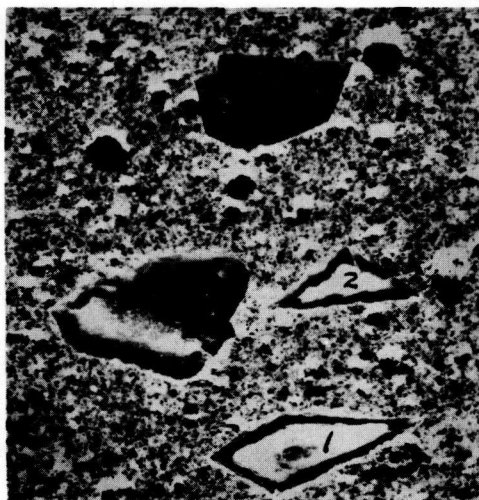


Figure 3. Polished section of opal in high-alkali cement. Note particularly the angular grains (No. 1 and 2) showing reaction in the center portion (soft and white) and the dark (apparently unreacted) outer edge about 50 microns in thickness (Reproduced from Ref. 5).

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 OH^- ions in the sludge

² Britton-Robinson Universal Buffers (12).

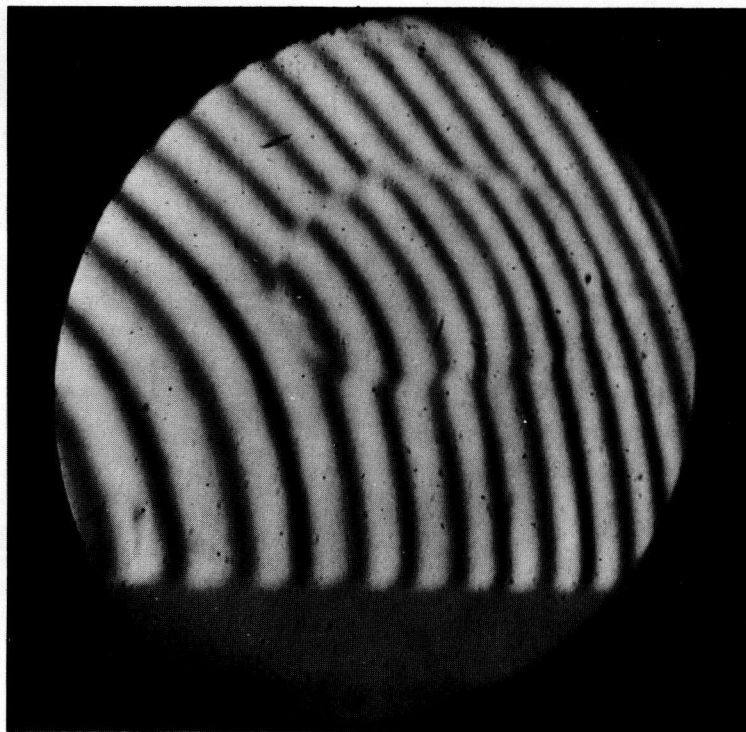


Figure 4A. Interferometric pattern showing swelling on a $\text{Li}_2\text{O-SiO}_2$ glass caused by a drop of buffer at pH 2 in 24 hours.

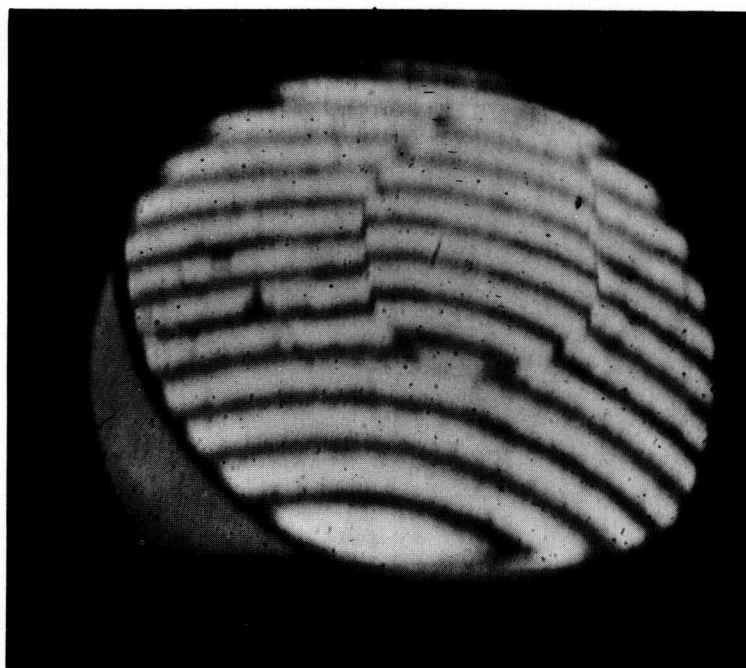


Figure 4B. Interferometric pattern showing swelling on a $\text{Li}_2\text{O-SiO}_2$ glass caused by a drop of saturated calcium hydroxide solution in 48 hours.

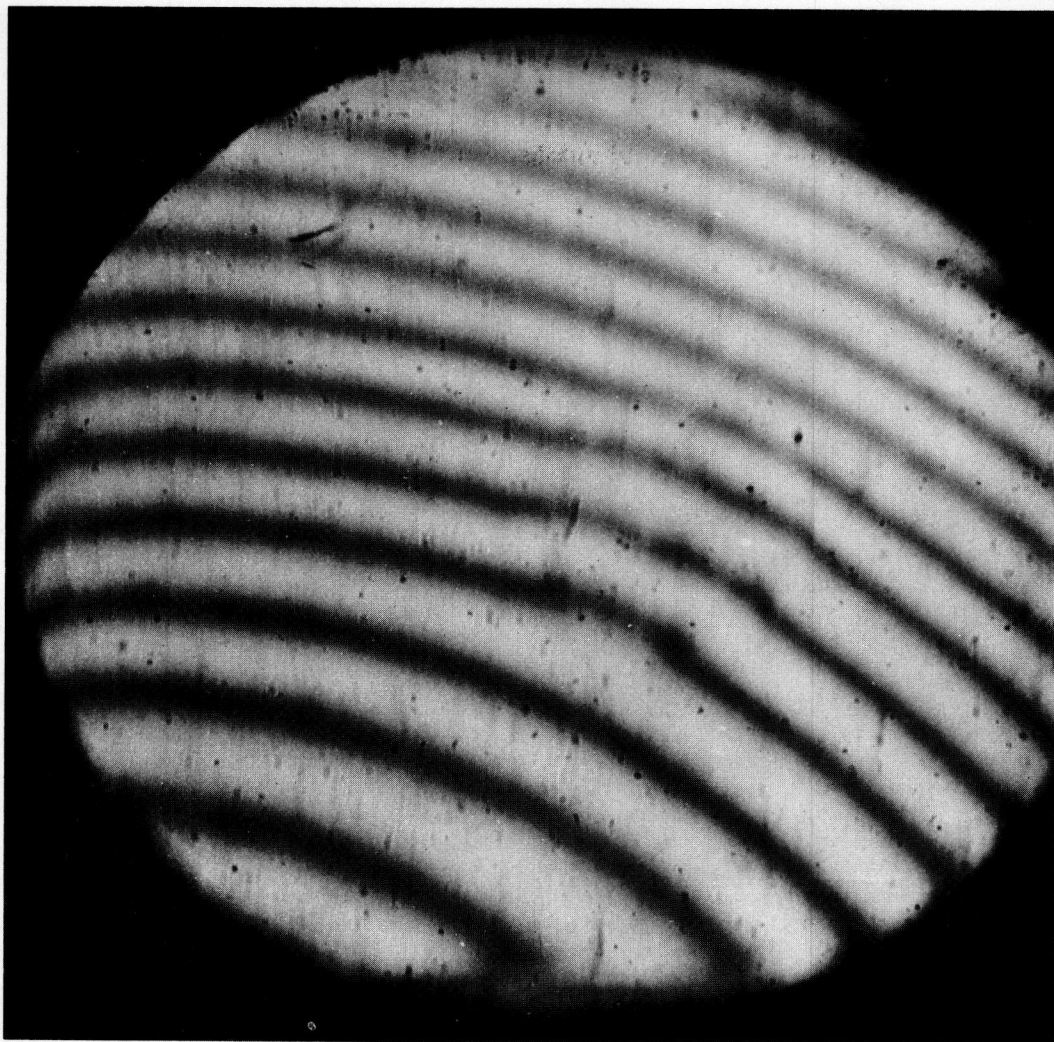


Figure 4C. Interferometric pattern showing swelling on a $\text{Li}_2\text{O-SiO}_2$ glass caused by a drop of a 2 percent solution of sodium hydroxide in 48 hours.

phase than in the supernatant liquid. This increased concentration of 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 Pontoppidan³ and it appears that there is as much evidence for a positive as for a negative charge on hydrated portland cement.⁴

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

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

⁴ 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)).

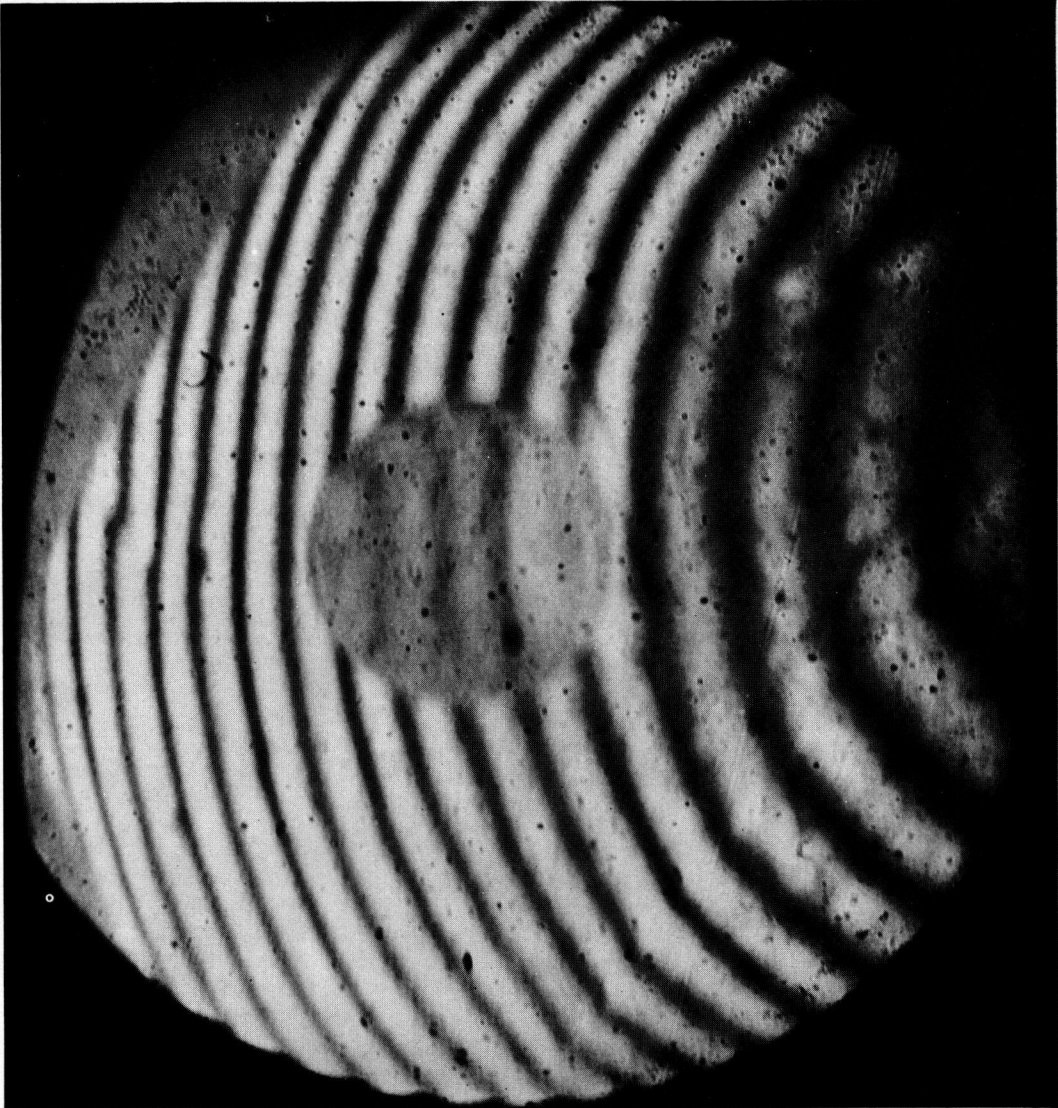


Figure 4D. Interferometric pattern on opal showing swelling caused by a drop of a 2 percent solution of sodium hydroxide in 6 hours.

Figure 7 as a function of leaching time.⁵ 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 13×10^{-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.

⁵ 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^a

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

^a 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-

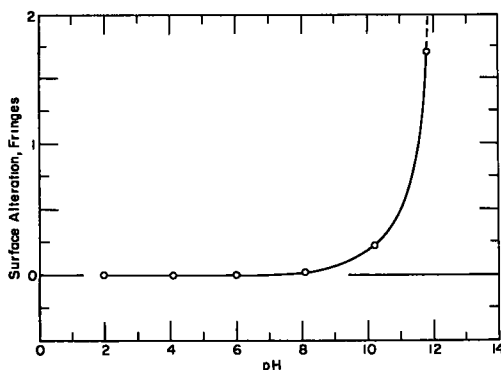


Figure 5. Chemical durability (surface alteration) of Pyrex over pH range from 2 to 11.8. Exposure 6 hours at 80 deg C.

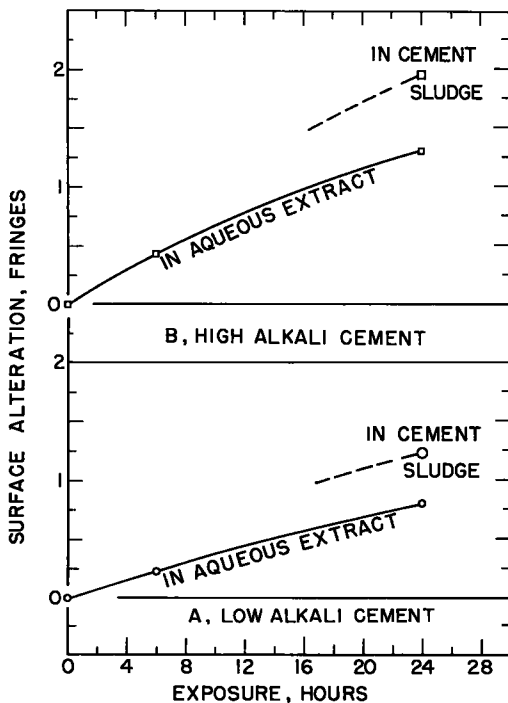


Figure 6. A. Chemical durability (surface alteration) of Pyrex in aqueous extracts from a high alkali cement compared with durability in the settling cement sludge. Exposure at 80 deg C. B. Chemical durability (surface alteration) of Pyrex in aqueous extracts from a low alkali cement compared with durability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

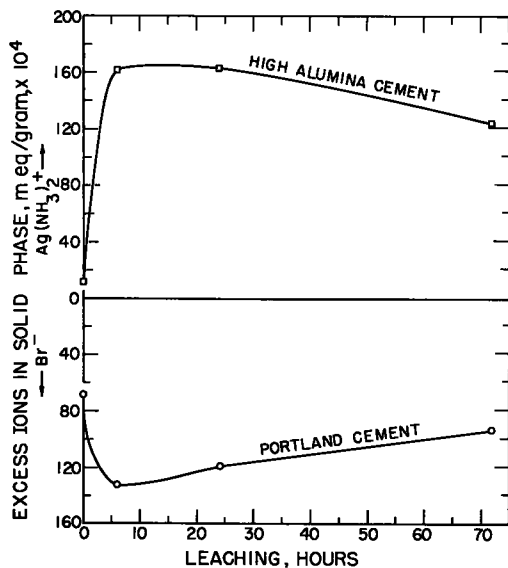


Figure 7. Ionic charge (or the uneven distribution of migratable ions [$\text{Ag}(\text{NH}_3)_2^+$ and Br^-] between the solid and liquid phases) on portland and alumina cements after leaching in distilled water. Cement samples hydrated 7 days at 25 deg C. before leaching.

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 ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	MgO	Loss	Insol.	Na ₂ O	K ₂ O	CaSO ₄	Li ₂ O	SrO	Fineness Air Permeability
														am ² /g
							Percent							
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	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		0.15		3410
Type III #103	23.5	3.3	2.9	65.5	2.2	0.8	1.4	0.0			0.01		0.10	3960
Type IV #107	23.2	5.2	4.1	63.2	1.8	1.0	0.9	0.0	0.15	0.39			0.14	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	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(NH₃)₂⁺ AND Br⁻ AS THE INDICATOR IONS

Hydration 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	Ag+	Br-	Ag+	Br-	Ag+	Br-	Ag+	Br-	Ag+	Br-
0	<1.2x10 ⁻⁴	—	<1.2x10 ⁻⁴	—	<1.2x10 ⁻⁴	—	<1.2x10 ⁻⁴	—	<1.2x10 ⁻⁴	—
¼	—	2x10 ⁻⁴	—	7x10 ⁻⁴	—	32x10 ⁻⁴	—	85x10 ⁻⁴	—	103x10 ⁻⁴
1	—	42x10 ⁻⁴	—	102x10 ⁻⁴	—	155x10 ⁻⁴	—	162x10 ⁻⁴	—	137x10 ⁻⁴
2	—	112x10 ⁻⁴	—	160x10 ⁻⁴	—	182x10 ⁻⁴	—	180x10 ⁻⁴	—	167x10 ⁻⁴
4	—	162x10 ⁻⁴	—	185x10 ⁻⁴	—	210x10 ⁻⁴	—	185x10 ⁻⁴	—	167x10 ⁻⁴
8	—	190x10 ⁻⁴	—	212x10 ⁻⁴	—	—	—	185x10 ⁻⁴	—	167x10 ⁻⁴

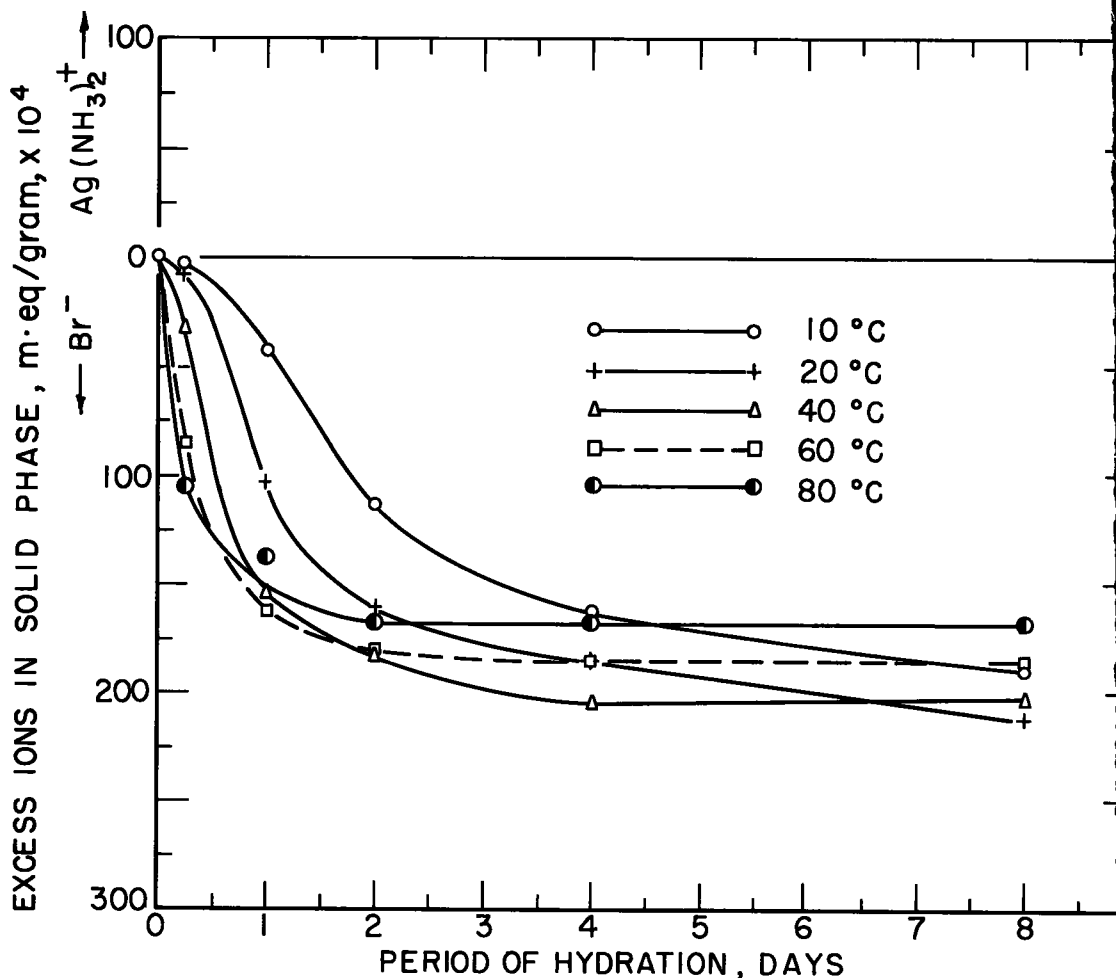


Figure 8. Ionic charge on a low alkali cement after various periods of hydration at different temperatures. (Ten gram samples hydrated in 50 ml of distilled water with sufficient agitation to prevent setting). Data Table 4.

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 cement⁶ 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

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

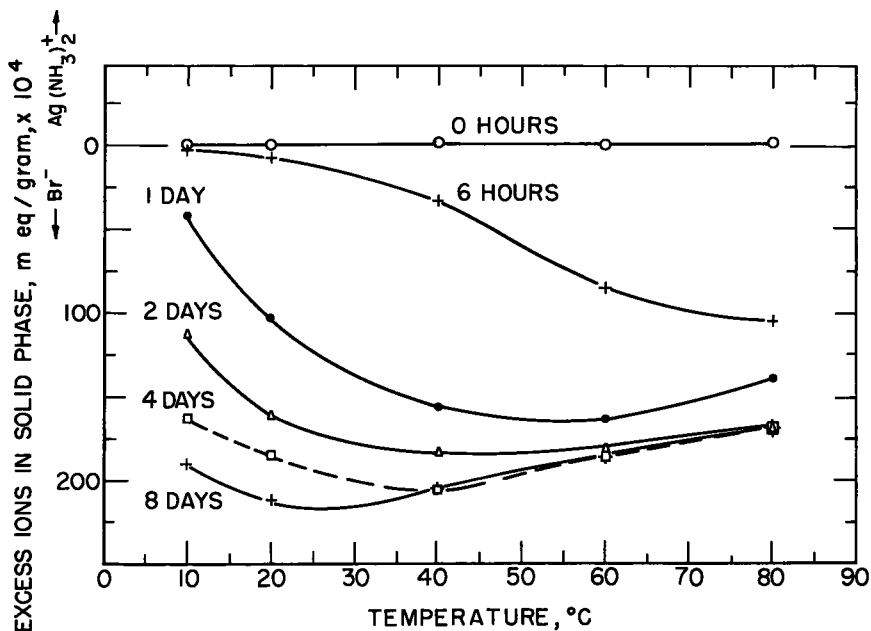


Figure 9. Ionic charge on a low alkali cement as a function of temperature for different periods of hydration. (Ten gram samples hydrated in 50 ml of distilled water with sufficient agitation to prevent setting). Data Table 4.

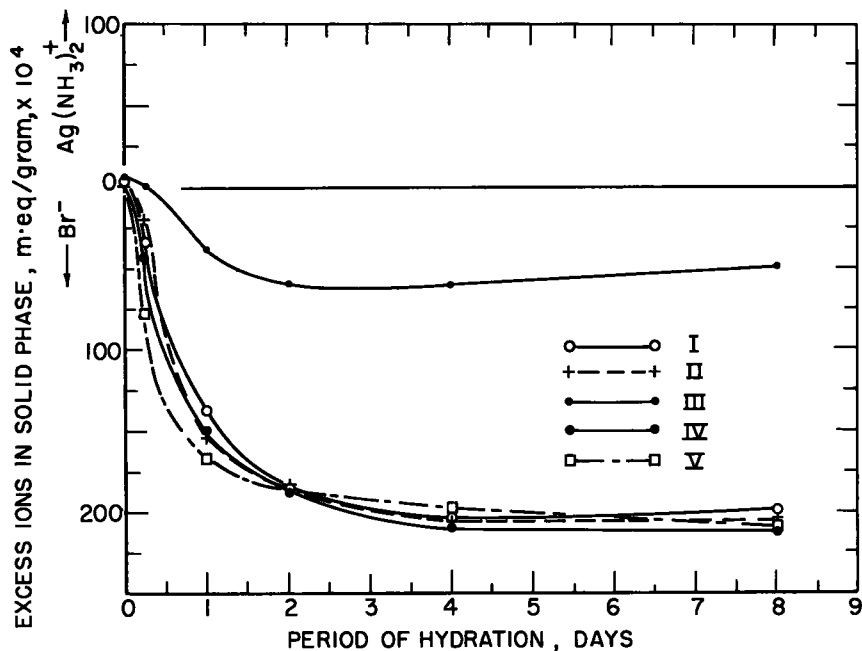


Figure 10. Ionic charge on five types of portland cement after various periods of hydration at 40 deg C. (Samples hydrated in 50 ml of distilled water with sufficient agitation to prevent setting).

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 Br^- AS THE INDICATOR IONS

Excess ions retained within the solid phase by 5 types of cement after hydration at 40°C										
Hydration Time	#9 Type I		Type II		#103 Type III		#107 Type IV		#116 Type V	
	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-
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
0	3×10^{-4}	—	$< 1.2 \times 10^{-4}$	—	6.2×10^{-4}	—	$< 1 \times 10^{-4}$	—	$< 1 \times 10^{-4}$	—
¼	—	33×10^{-4}	—	20×10^{-4}	$< 1.2 \times 10^{-4}$	—	—	43×10^{-4}	—	78×10^{-4}
1	—	137×10^{-4}	—	155×10^{-4}	—	37×10^{-4}	—	150×10^{-4}	—	162×10^{-4}
2	—	187×10^{-4}	—	182×10^{-4}	—	60×10^{-4}	—	187×10^{-4}	—	187×10^{-4}
4	—	203×10^{-4}	—	205×10^{-4}	—	59×10^{-4}	—	210×10^{-4}	—	199×10^{-4}
8	—	199×10^{-4}	—	203×10^{-4}	—	49×10^{-4}	—	212×10^{-4}	—	210×10^{-4}

TABLE 6
EXCESS IONIC CHARGE RETAINED BY HIGH ALUMINA CEMENT UPON HYDRATION AT VARIOUS TEMPERATURES
USING $\text{Ag}(\text{NH}_3)_2^+$ AND Br^- AS THE INDICATOR IONS

Excess ions retained within the solid phase after hydration at the following temperatures												
Hydration Time	10° C		20° C		30° C		40° C		60° C		80° C	
	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-
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
0	2.5×10^{-4}	—	2.5×10^{-4}	—	2.5×10^{-4}	—	2.5×10^{-4}	—	2.5×10^{-4}	—	2.5×10^{-4}	—
¼	—	67×10^{-4}	—	75×10^{-4}	—	63×10^{-3}	—	53×10^{-3}	330×10^{-3}	—	575×10^{-4}	—
1	—	133×10^{-4}	—	160×10^{-4}	125×10^{-4}	—	340×10^{-4}	—	750×10^{-4}	—	465×10^{-4}	—
2	—	185×10^{-4}	—	70×10^{-4}	340×10^{-4}	—	480×10^{-4}	—	700×10^{-4}	—	450×10^{-4}	—
4	—	115×10^{-4}	—	5×10^{-4}	470×10^{-4}	—	575×10^{-4}	—	575×10^{-4}	—	390×10^{-4}	—
8	—	65×10^{-4}	48×10^{-4}	—	380×10^{-4}	—	560×10^{-4}	—	425×10^{-4}	—	250×10^{-4}	—

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

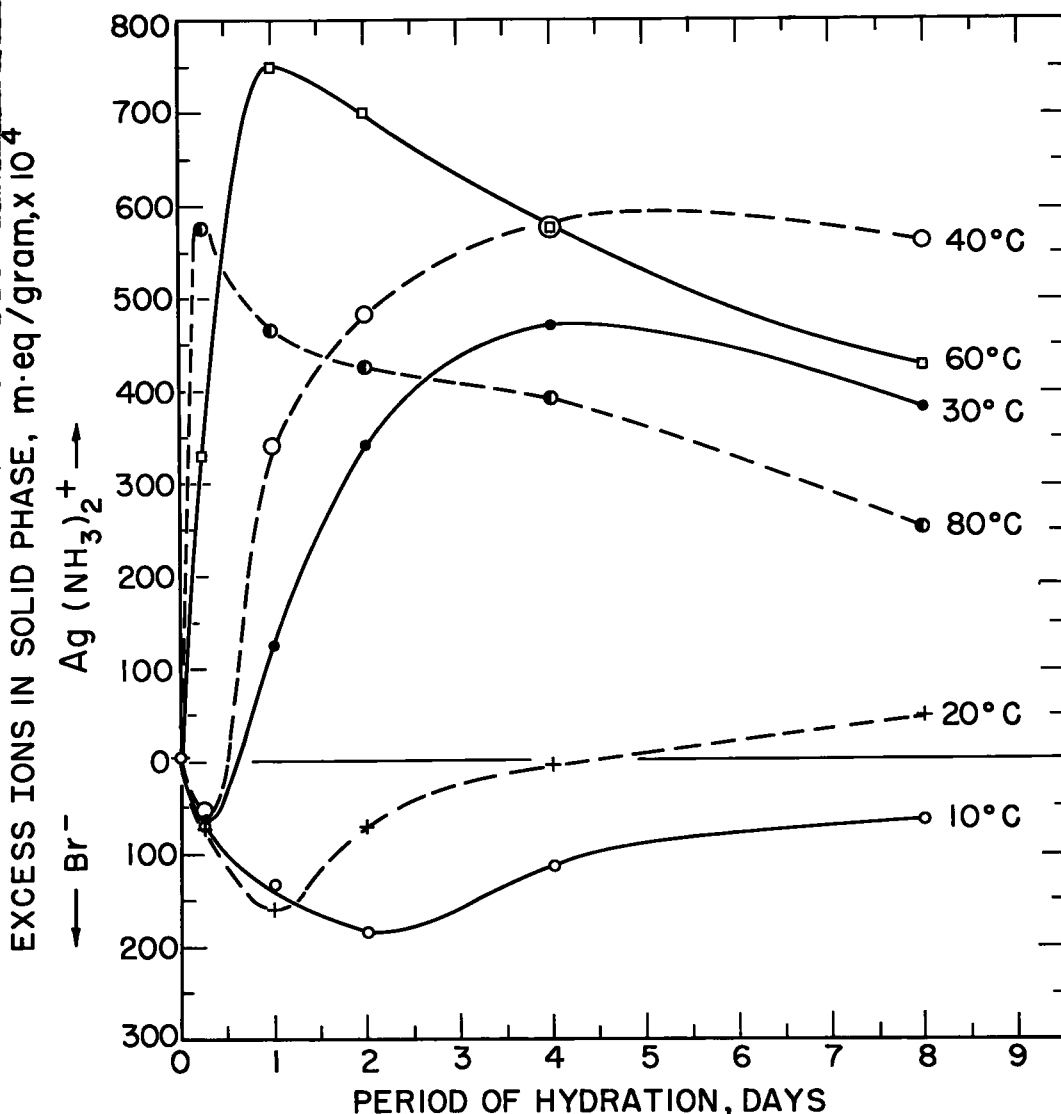


Figure 11. Ionic charge on a high alumina cement after various periods of hydration at different temperatures. (Ten gram samples hydrated in 50 ml of distilled water with sufficient agitation to prevent setting). Data Table 6.

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.

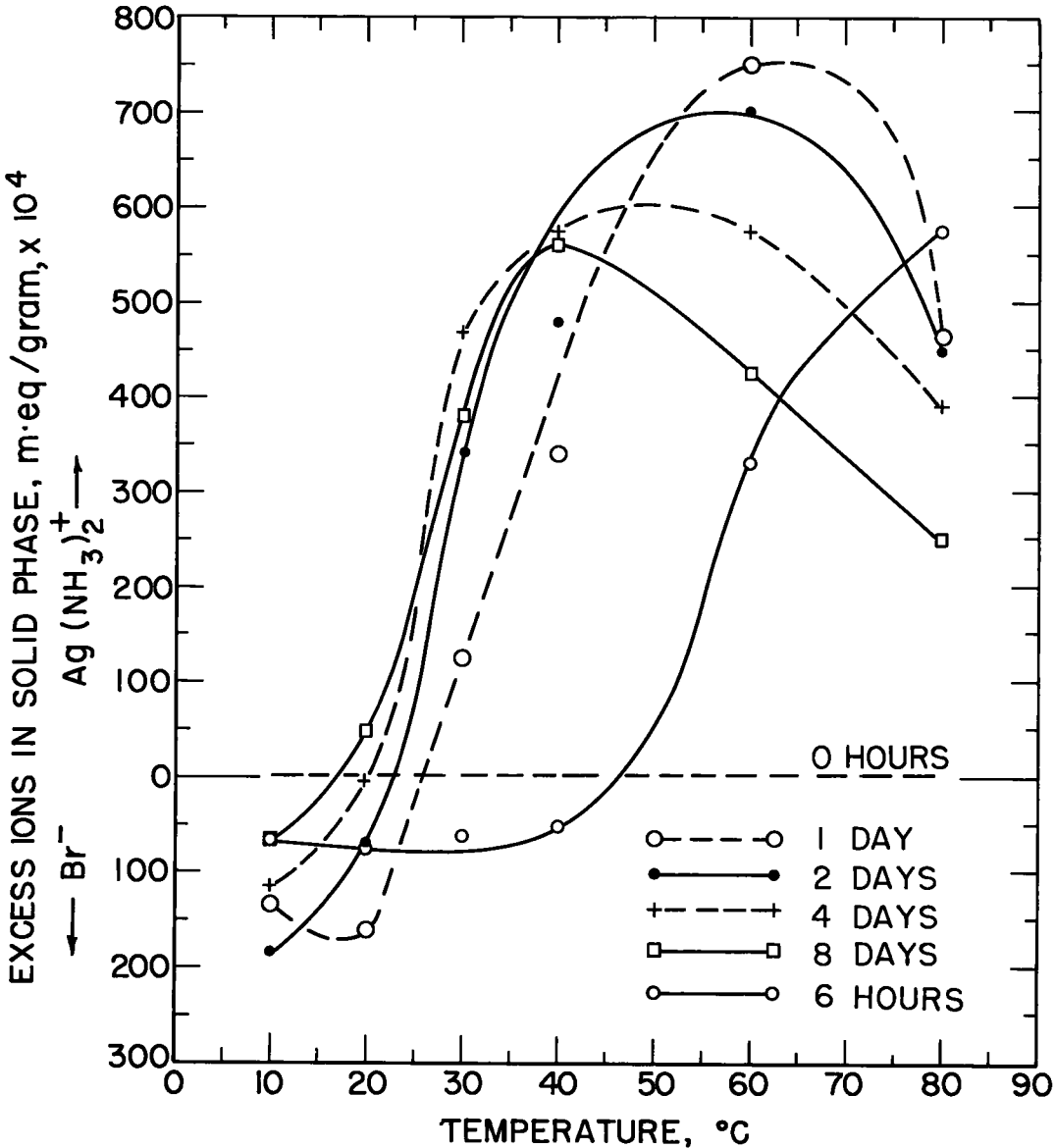


Figure 12. Ionic charge on hydrating high alumina cement as a function of temperature for different periods of hydration. (Ten gram samples hydrated in 50 ml of distilled water with sufficient agitation to prevent setting). Data Table 6.

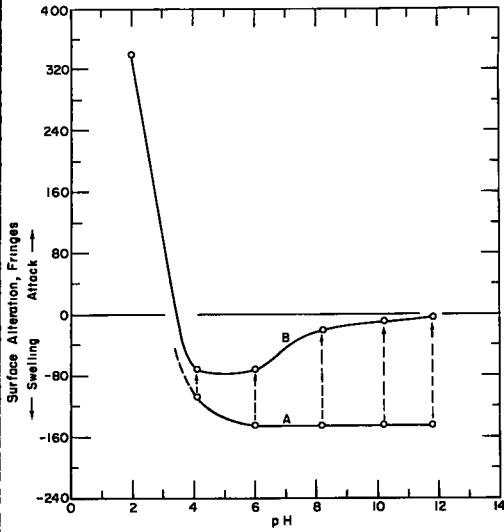


Figure 13. Chemical durability (surface alteration) of hydrated cement over an extended pH range at 80 deg C.

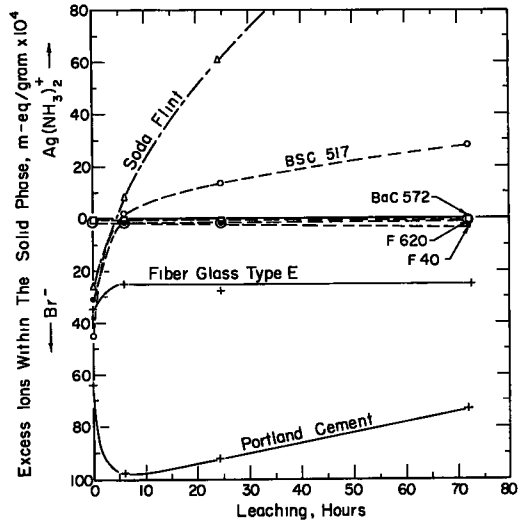


Figure 14. Excess positive $[(Ag(NH_3)_2)^+]$ or negative $[Br^-]$ ions retained by the samples after various periods of leaching in distilled water.

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.

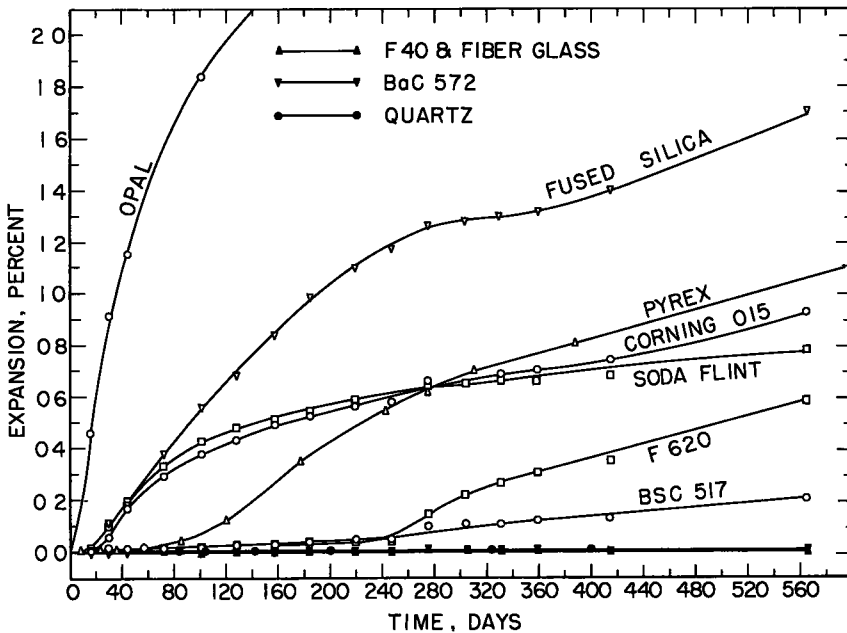


Figure 15. Expansion of mortar bars in which 6 percent of the Ottawa sand was replaced by various natural and synthetic aggregates. Aged over water at 100 deg F.

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.

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