

# Source of the Non-Migratable Ionic Charges Developed by Portland and High-Alumina Cements During Hydration

ROBERT G. PIKE AND DONALD HUBBARD,  
*National Bureau of Standards, Washington, D. C.*

The nature of the non-migratable ionic charges characteristic of some of the major and minor constituents of hydrated portland and high-alumina cements has been investigated. Using  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{Br}^-$  as indicator ions it was found that mono-calcium silicate hydrate ( $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ , or  $\text{CSH}(\text{B})$ ), the major constituent of hydrated portland cements, possessed a non-migratable negative ionic charge, whereas  $\text{Ca}(\text{OH})_2$ , always present in abundance in the hydrating cement, possessed a positive ionic charge. Treating  $\text{CSH}(\text{B})$  with saturated aqueous  $\text{Ca}(\text{OH})_2$  solution resulted in a positive ionic charge on the resulting  $\text{CSH}(\text{B})$ - $\text{Ca}(\text{OH})_2$  complex, similar to that found for hydrated portland cements.

For the high-alumina cements (Lumnite, Ciment Fondu, and Alcoa) the non-migratable ionic charges on the hydrated products (which are dependent on the time and particularly sensitive to the temperature of hydration) were found also to correlate qualitatively with the calcium aluminate hydrates known to exist over certain temperature ranges. In addition, a superimposed characteristic was apparently contributed by the small percentage of calcium sulfide present.

• **PORTLAND CEMENTS** during their period of hydration behave as non-migratable positive ionic charges, whereas the high-alumina cement "Lumnite," after developing an early positive charge, reverses to an imposingly large negative one (1). Typical curves illustrating the non-migratable ionic characteristics of five types of portland cement and Lumnite, based on data from an earlier publication (1), are shown in Figure 1 for the hydration temperature of 40 C.

The present investigation was undertaken to ascertain, if possible, the source of these non-migratable ionic charges, by a study of the ionic characteristics, of a few of the known major and minor constituents of hydrated cements. It was initiated by the suggestion in the previous paper (1) that aggregates with a positive ionic charge similar to the positive ionic charge on hydrated cements might be a contributing factor in the delayed alkali-

aggregate expansion of mortar bars containing those aggregates.

## EXPERIMENTAL

### Materials

In this investigation five portland cements (types I, II, III, IV, and V) (2) and three high-alumina cements (Lumnite, Ciment Fondu and Alcoa) were studied. The analyses are given in Table 1.

The individual constituents (see Tables 2 and 3) of the portland and aluminous cements studied were as follows:

1.  $\text{Al}(\text{OH})_3$  precipitated and filtered at pH 7.8 as suggested by Duval (3).
2. Reagent grade  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .
3.  $\text{Ca}(\text{OH})_2$  made by hydrating reagent grade  $\text{CaO}$ .
4.  $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$  ( $\text{CSH}(\text{B})$ )<sup>1</sup> made

<sup>1</sup> All symbols in this paper are as defined by Bogue (4).

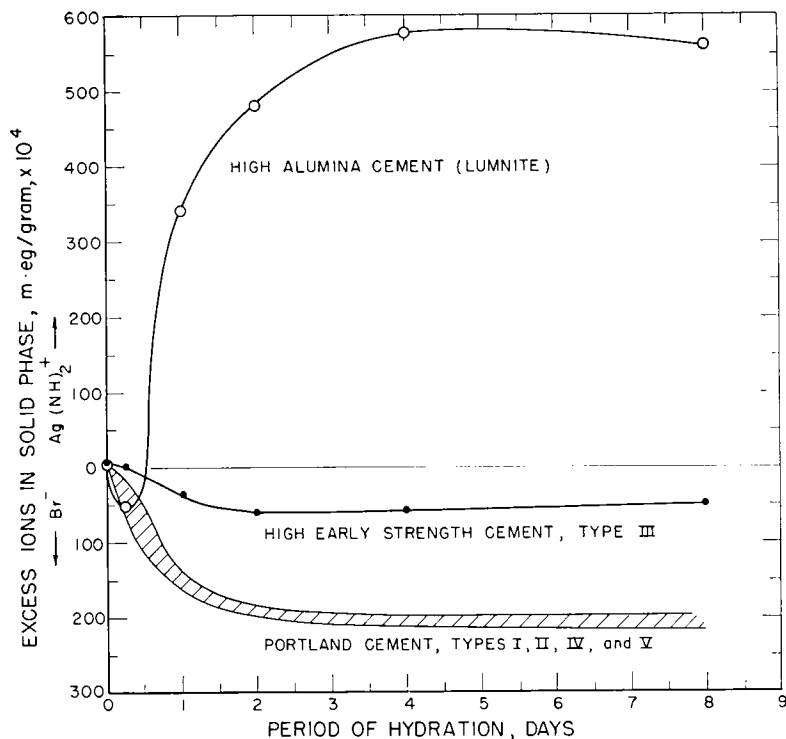


Figure 1. Comparison of the ionic charge characteristics of high-alumina cement (Lumnite) and five types of portland cement during hydration at 40 C. (Retention of  $\text{Br}^-$  indicates a positive charge on the cement; retention of  $\text{Ag}(\text{NH}_3)_2^+$  indicates a negative charge in the cement.)

by autoclaving reagent grade  $\text{CaO}$  and silica gel for 50 days at 135 C.

5.  $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$  ( $\text{C}_3\text{S}_2\text{H}_3$ ) prepared by mixing reagent grade  $\text{CaO}$  and silica gel in proper proportions and autoclaving for 52 days at 135 C, then drying over  $\text{Mg}(\text{ClO}_4)_2$  in a vacuum.

6.  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 30\text{H}_2\text{O}$  ( $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot \text{H}_{30}$ ) made as follows: 8.7 g of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  in 4 l of water and 4 l of saturated lime solution were added simultaneously to 1 l of water at the rate of 1 l of each per hour. The precipitate was then washed by suspension in alcohol and ether and dried in laboratory air for 4 days.

7.  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  ( $\text{C}_4\text{AF}$ ) prepared by burning stoichiometric amounts of reagent grade constituents then grinding in a ball mill, gaging with water, and burning a second time. The product was identified by petrographic methods, and

analysis showed about 4 percent ferrous iron and 0.5 percent  $\text{SiO}_2$ , the latter probably introduced by the ball mill.

8.  $\text{Al}_2\text{O}_3$ , reagent grade alpha alumina.

9.  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$  ( $\text{CAH}_{10}$ ) made by shaking for 1 hr 20 g of  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  (CA) in 1 l of water and filtering through a Buchner funnel. The filtrate was then diluted with 100 cc of saturated  $\text{Ca}(\text{OH})_2$ , cooled and left for several days at 1 C until sufficient precipitate was formed.

10.  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  (CA) prepared by repeated heating at 1,500 C and grinding of stoichiometric amounts of  $\text{CaCO}_3$  and gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ).

11.  $\text{CaS}$ , reagent grade calcium sulfide.

12.  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$  ( $\text{C}_2\text{AH}_8$ ) prepared as described by Wells, Clarke and McMurdie (5).

13.  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  ( $\text{C}_3\text{AH}_6$ ) and

TABLE 1  
CHEMICAL ANALYSIS AND COMPOUND COMPOSITION OF FIVE PORTLAND AND THREE ALUMINOUS CEMENTS

Type	Function	Constituent (%)												Compound Composition (%)				Fineness <sup>a</sup> (cm <sup>2</sup> /g)				
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	F <sub>2</sub> O	CaO	SO <sub>3</sub>	MgO	Loss	Insol.	Na <sub>2</sub> O	K <sub>2</sub> O	StO <sub>2</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	S		C <sub>2</sub> A	C <sub>3</sub> S	C <sub>4</sub> S	C <sub>1</sub> A,F
(a) PORTLAND CEMENTS																						
I	General use	20.2	7.0	2.6	—	62.7	2.1	3.0	1.1	0.4	0.38	0.88	0.38	—	—	—	—	14	45	24	8	3,410
II <sup>b, c</sup>	Moderate heat of hydration	22.6	4.5	3.2	—	65.1	1.7	1.2	1.5	0.2	0.0	0.29	—	—	—	—	—	6	54	24	10	3,410
III	High early strength	23.5	3.8	2.9	—	65.5	2.2	0.8	1.4	0.0	0.23 <sup>d</sup>	0.10	—	—	—	—	—	4	55	26	9	3,960
IV <sup>e</sup>	Low heat of hydration	23.2	5.2	4.1	—	63.2	1.8	1.0	0.9	0.0	0.15	0.39	0.14	—	—	—	—	7	36	40	12	3,430
V	Sulfate resisting	24.6	3.6	2.5	—	65.0	1.4	1.8	0.8	0.1	0.12	0.30	0.07	—	—	—	—	5	46	36	8	3,380
(b) HIGH-ALUMINA CEMENTS																						
Lumnite		8.6	42.7	4.3	6.2	36.8	0.3	0.8	0.1	1.7 <sup>e</sup>	—	—	—	0.4	—	—	0.25	—	—	—	—	—
Ciment Fondu		4.2	37.0	10.6	4.85	37.4	—	1.01	—	7.7 <sup>e</sup>	—	—	—	4.0	0.001	0.00	0.02	—	—	—	—	—
Alcoa		0.0	81.3	0.18	0.13	17.4	—	0.58	—	— <sup>e</sup>	—	—	—	0.0	0.001	0.00	0.01	—	—	—	—	—

<sup>a</sup> Air permeability.

<sup>b</sup> Low alkali.

<sup>c</sup> Types II and IV do not meet specifications for compound composition.

<sup>d</sup> Total alkalinity as Na<sub>2</sub>O.

<sup>e</sup> Insolubles determined in accordance with Fed. Spec. SS-C-158c. Alcoa did not respond to specified treatment; colloidal particles formed passed through extremely dense filter paper.

$3\text{CaO} \cdot \text{Al}_2\text{O}_3$  ( $\text{C}_3\text{A}$ ) prepared according to Thorvaldson, *et al.* (6).

14.  $\text{C}_4\text{AH}_{13}$  prepared according to the general procedure described by Wells *et al.* (5). However, microscopic examination showed considerable amounts of  $\text{C}_3\text{AH}_6$ .

### Methods

The nature and semi-quantitative magnitude of the non-migratable ionic charge present on the hydrated cement, and on the synthesized constituent cement compounds, were determined by using  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{Br}^-$  as the indicator ions (1, 7). The hydrated specimens were treated with 50 ml of full-strength aqueous ammonia solution saturated with  $\text{AgBr}$ . This procedure was adopted after experience indicated that any non-migratable ionic charges characteristic of the hydrated cement would necessarily cause an uneven distribution of the migratable  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{Br}^-$  ions between the solid and ambient liquid phases (1). The excess  $\text{Ag}(\text{NH}_3)_2^+$  or  $\text{Br}^-$  ions appearing in the liquid phase were determined potentiometrically after acidifying with  $\text{H}_2\text{SO}_4$ , using the  $\text{Ag}-\text{AgBr}$  and the glass electrodes as indicator and reference electrodes, respectively. The retention of  $\text{Br}^-$  ion indicates a positive charge on the cement and, conversely, retention of  $\text{Ag}(\text{NH}_3)_2^+$  ion indicates a negative charge on the solid sample.

The acceptability of this procedure is dependent on the validity of a few broad assumptions: First, that the solubilities of the specimens remain essentially the same in the full-strength aqueous ammonia, having an alkalinity near pH 13, as in the saturated and supersaturated  $\text{Ca}(\text{OH})_2$  aqueous solutions with values greater than pH 12.4 (8). Evidence from glass-electrode voltage departures and the chemical durability of silicate glasses in full-strength ammonia lend a considerable degree of confidence in this assumption (9, 10). Furthermore, ammonium hydroxide is reported to have no effect on concrete (11). Second, that no compounds of  $\text{Ag}^+$  or  $\text{Br}^-$  are formed with

the hydrated constituents of cement which are less soluble than  $\text{AgBr}$ ; or more correctly stated, that no compounds of  $\text{Ag}^+$  or  $\text{Br}^-$  are formed which have a smaller solubility product than  $S_{\text{AgBr}} = 6.4 \times 10^{-13}$  (12). Third, that the heterogeneous equilibria considerations derived by Donnan (13) are valid. Fourth, that "adsorption" in the conventional sense contributes little or nothing toward the uneven distribution of migratable ions.

The last assumption may be justified as follows: Consider adsorption on any typical colloidal particle such as  $\text{Ag}$  suspended in a saturated solution of  $\text{Ag}(\text{NH}_3)_2 \text{Br}$  in full-strength ammonia.  $\text{Br}^-$  ions will be preferentially oriented toward the  $\text{Ag}$  particle with  $\text{Ag}(\text{NH}_3)_2^+$  ions left in the solution but with their field of motion restricted to the thin film of solution wetting the particle. The volume of this film will be measured by the surface area of the particle and the average distance that the  $\text{Ag}(\text{NH}_3)_2^+$  ions are free to travel from the anchored negatively charged  $\text{Br}^-$  ions. Although there will be a greater concentration of  $\text{AgBr}$  in the film immediately surrounding the  $\text{Ag}$  particle than in the ambient solution,  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{Br}^-$  will be present in equal numbers here and also in the solution far removed from the surface of the particle (14). Thus, when the solution is acidified and titrated, no excess of either ion would be indicated.

## RESULTS AND DISCUSSION

### Portland Cement

In Table 2 are listed the excess indicator ions retained within the solid phase of major and minor constituents of hydrated portland cement. Also listed are the ionic charges found for the five types of portland cement after 4 days of hydration, in which an equilibrium or near-equilibrium state appears to have been attained (Fig. 1, also (1)). Inspection of these data reveals that the hydrated portland cements have a large positive ionic charge (about  $200 \text{ meq/g} \times 10^{-4}$ ), whereas calcium silicate hydrate, the major

TABLE 2  
IONIC CHARGES ON HYDRATED PORTLAND CEMENTS AND ON SOME OF THE HYDRATED MAJOR AND MINOR CONSTITUENTS

Name	Compound	Formula	Symbol	Distrib. of Migratable Ions in Inner Phase (meq/g $\times 10^{-4}$ )		Ionic Charge	Remarks	Ref.
				Excess Br <sup>-</sup>	Excess Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>			
Tetracalcium aluminat hydrate		4CaO·Al <sub>2</sub> O <sub>3</sub> ·13H <sub>2</sub> O	C <sub>4</sub> AH <sub>13</sub>	11	—	Pos.	Major constituent	(20)
Gypsum		CaSO <sub>4</sub> ·2H <sub>2</sub> O	—	29	19	Neg.	Not generally present	(20)
Calcium hydroxide		Ca(OH) <sub>2</sub>	—	—	—	Pos.	Major constituent, always in surplus	(20)
Calcium silicate hydrate		CaO·SiO <sub>2</sub> ·H <sub>2</sub> O <sup>a</sup>	CSH(B)	75	349	Neg.	Major constituent	(20)
Calcium silicate hydrate, treated with saturated Ca(OH) <sub>2</sub> solution				—	—	Pos.	Treated 20 min. with saturated Ca(OH) <sub>2</sub> prepared from CaO	—
Afwillite		3CaO·2SiO <sub>2</sub> ·3H <sub>2</sub> O	C <sub>3</sub> S <sub>2</sub> H <sub>3</sub>	63	—	Pos.	Existence in cement doubtful	(20)
Calcium sulfo-aluminate		3CaO·Al <sub>2</sub> O <sub>3</sub> ·	C <sub>3</sub> A·	—	—	Neg.	Minor constituent	(20)
Calcium aluminoferrite		4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub>	3CaSO <sub>4</sub> ·H <sub>30</sub>	—	35	Neg.	Present in unhydrated cements	(20)
Calcium aluminoferrite, hydrated		Unknown	C <sub>4</sub> AF	620	1	Neutral	Considerable change in appearance after 4-day hydration at 40°C	(20)
5 types of portland cement after 4-day hydration at 40°C			Type I #9 b II III #103 IV #107 V #116	203 205 59 210 199	— — — — —	Pos. Pos. Pos. Pos. Pos.	General use Mod. heat of hardening High early strength Low-heat Sulfate-resisting	(15, p. 15) (1, Table 5)

<sup>a</sup> CaO:SiO<sub>2</sub> range 1:1 to 3:2; H<sub>2</sub>O:SiO<sub>2</sub> range 1:1 to 5:2 (2, p. 509) (15).

<sup>b</sup> These numbers refer to identifications in the Bureau of Standards' long-term cement test program (unpubl. data).

constituent of hydrated portland cements carries an even larger (about  $350 \text{ meq/g} \times 10^{-4}$ ) negative ionic charge. Thus, one is faced with an anomaly at the very outset, which, however, can be readily interpreted.

Mono-calcium silicate hydrate, CSH(B), the chief constituent of hydrated portland cement, carries a large negative ionic charge of  $349 \times 10^{-4} \text{ meq/g}$  (Table 2). As CSH(B) behaves as a non-migratable negative ion during the hydration period, it necessarily causes an uneven distribution of all migratable ions in the system. Of the positive ions in hydrating cement,  $\text{Ca}^{++}$  is always present in abundance, so that the  $\text{Ca}^{++}$  concentration in the CSH(B) phase must be greater than in the outer aqueous phase in accord with the fundamental concepts of the Donnan membrane equilibria (13). As the outer phase is already saturated with respect to  $\text{Ca}(\text{OH})_2$ ,<sup>2</sup> the inner phase becomes supersaturated, and  $\text{Ca}(\text{OH})_2$  will necessarily precipitate in and on the CSH(B).<sup>3</sup> But solid  $\text{Ca}(\text{OH})_2$  has been shown to have a positive ionic charge (Table 2), so that hydrated portland cements, although consisting largely of negatively charged CSH(B), should appear to be positive, as shown in Figure 1 and Table 2. (Since this manuscript was submitted for publication other articles (22, 23, 24) illustrating this type of reversal and ionic charge on cement have been brought to the attention of the authors.) To test the acceptability of this picture, a 1-g sample of CSH(B) was treated with 50 ml of saturated  $\text{Ca}(\text{OH})_2$  solution prepared from quicklime ( $\text{CaO}$ ). The large negative ionic charge on the CSH(B) was replaced by a substantial positive charge, as shown in Table 2. The magnitude of this final positive charge apparently is dictated by such factors as particle size, time of exposure and the availability of  $\text{Ca}(\text{OH})_2$ .

The only other material carrying any significant charge is the hydration product of  $\text{C}_4\text{AF}$  which has a positive charge of  $620 \times 10^{-4} \text{ meq/g}$  (Table 2). It is possible that this hydration product contributes materially to the positive charge found on the portland cements, although the presence of  $\text{C}_4\text{AF}$  hydrate as such in portland cements has not been substantiated.

The mutual neutralization of these oppositely charged ionic species and the subsequent continued hydration, crystal growth, and reaction, undoubtedly plays a dominant role in the setting of portland cements.

If the foregoing experiment gives a correct, or partially correct, interpretation of the source of the positive ionic charge exhibited by hydrated portland cement, the removal of lime or  $\text{Ca}^{++}$  from the hydrated cement should reverse the ionic charge from a large positive to a substantially negative charge. In order to ascertain the validity of this reasoning, 10-g samples of portland cement, after four days of hydration at 40 C (see Fig. 1), were extracted with water in a Soxhlet reflux condenser for various periods of time. As shown in Figure 2, there is indeed a substantial change from a positive to a negative charge on the removal of  $\text{Ca}^{++}$ .

A possible explanation is offered for the marked difference in magnitude of the ionic charge reported for the type III cement compared with the other four types of portland cement shown in Figure 1 and Table 2. There is little in the chemical analysis of the type III (high early strength) cement to distinguish it from the other four types (Table 1). However, a marked difference exists in the fineness of the unhydrated samples. This finer grind should make available a greater portion of the negatively charged CSH(B) in the hydrated cement and thereby decrease the ratio of available positive to negative ions. However, before such a conclusion can be accepted, additional experiments should be made on one cement at different particle sizes.

<sup>2</sup> Hydrating cement is known to be supersaturated with respect to  $\text{Ca}(\text{OH})_2$  in the early stages of setting, which serves further to accentuate the conditions as outlined.

<sup>3</sup> This "sorption" complex could readily account for the confusion of compositions ( $\text{CaO}:\text{SiO}_2:\text{H}_2\text{O}$  ratios) ascribed to hydrated calcium silicates (footnote (a), Table 2).

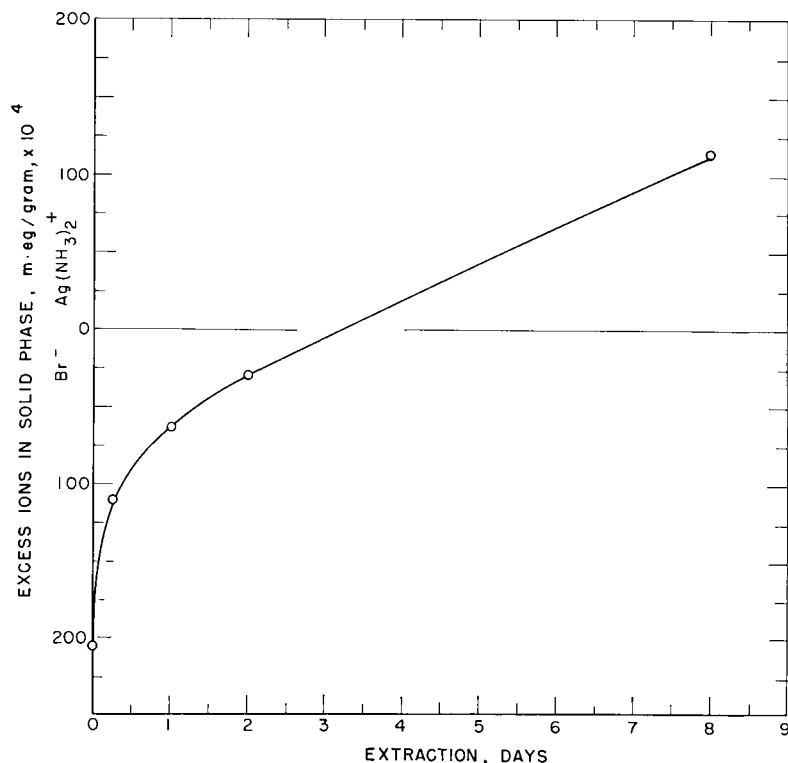


Figure 2. Reversal of ionic charge on hydrated portland cement brought about by leaching with water in Soxhlet reflux condenser.

### High-Alumina Cements

*Lumnite.* The nature and magnitude of the ionic charge exhibited during hydration of the high-alumina cement, Lumnite, is dependent on the duration of the hydration period, and highly sensitive to the temperature at which hydration takes place (Fig. 3 and Table 4). To rationalize these data for the ionic charge on this hydrating cement, it is necessary to examine the ionic charge characteristic of various lime-alumina hydrates known to exist at different temperatures. The results are listed in Table 3. (Although there is not complete agreement as to the presence or absence in aluminous cements of some of these compounds, they are included here for completeness.)

Mono-calcium aluminate (CA), which is present in unhydrated cement and persists in the core of partially hydrated

grains, adequately accounts for the small initial negative charge exhibited by the unhydrated cement (Table 3). During the initial stages of hydration, especially at 10 C and 20 C, the major constituent, mono-calcium aluminate hydrate ( $\text{CAH}_{10}$ ), and any small amount of  $\text{Al}(\text{OH})_3$  present, can readily account for the positive ionic charge which appears early on the hydrating cement (Fig. 3 and Table 3).

The negative charges which appear during hydration at higher temperatures can be partially attributed to dicalcium aluminate hydrate ( $\text{C}_2\text{AH}_8$ ), a constituent identified at 35 C, and tricalcium aluminate hydrate ( $\text{C}_3\text{AH}_6$ ), the major stable constituent above 35 C (16). Both of these hydrates carry a small negative ionic charge (Table 3). However, the small charge on these compounds would appear to be inadequate to account for

TABLE 3  
IONIC CHARGE FOR SOME OF THE MAJOR AND MINOR CONSTITUENTS OF HIGH-ALUMINA CEMENTS

Name	Formula	Symbol	Distrib. of Migratable Ions in Inner Phase (meq/g $\times 10^{-4}$ )			Remarks	Ref.
			Excess Br <sup>-</sup>	Excess Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Ionic Charge		
Hydrated alumina gel	Al(OH) <sub>3</sub>	—	127	—	Pos.	Product of the hydration reaction	(16)
Alumina (aluminum oxide ignited powder)	Al <sub>2</sub> O <sub>3</sub> (alpha)	A	—	32	Neg.	Present in Alcoa cement	(18)
Monocalcium aluminate hydrate	CaO · Al <sub>2</sub> O <sub>3</sub> · 10H <sub>2</sub> O	CAH <sub>10</sub>	1,190	—	Pos.	Major constituent in hyd. aluminous cements below 35°C	(16)
Monocalcium aluminate	CaO · Al <sub>2</sub> O <sub>3</sub>	CA	—	12	Neg.	Present in unhydrated aluminous cement	(16)
Calcium sulfide	CaS	—	—	110	Neg.	Probably present as a minor constituent in some aluminous cements	—
Dicalcium aluminate hydrate	2CaO · Al <sub>2</sub> O <sub>3</sub> · 8H <sub>2</sub> O	C <sub>2</sub> AH <sub>8</sub>	—	17	Neg.	Identified in hydrated aluminous cement at 35°C	(16)
Tricalcium aluminate hydrate	3CaO · Al <sub>2</sub> O <sub>3</sub> · 6H <sub>2</sub> O	C <sub>3</sub> AH <sub>6</sub>	—	10	Neg.	Major stable constituent of hydrated aluminous cement above 35°C	(16)
Tricalcium aluminate	3CaO · Al <sub>2</sub> O <sub>3</sub>	CA <sub>3</sub>	297	—	Pos.	Not usually present in aluminous cements	(19)

the magnitude of the negative ionic charges shown in Figure 3 at the elevated temperatures.

Some of the high-alumina cements contain small percentages of sulfide, presumably calcium sulfide. This material appears to have a moderately large non-migratable negative ionic charge (Table 3). This apparent charge can be attributed to two possible factors; first, a true negative ionic charge possessed by the CaS precipitate, and second, any CaS which dissolves in the liquid phase during the test. The dissolved CaS upon acidifying prior to the potentiometric titration will precipitate Ag<sub>2</sub>S with the liberation of Br<sup>-</sup> ions, which will be added to the negative charge for the CaS. It should also be noted that the solubility product of  $1.6 \times 10^{-49}$  for Ag<sub>2</sub>S is much smaller than that of  $6.4 \times 10^{-13}$  for AgBr. Both of these factors would tend to augment the magnitude of the negative ionic charge appearing on hydrated Lumnite cement.

An additional experiment to eliminate (oxidize) the sulfide from the Lumnite cement by heating to 700°C in air resulted in the cement, after hydration and leaching, having a small positive ionic charge of  $12 \times 10^{-4}$  meq/g after 24 hr (Fig. 4B) compared with a negative ionic charge of  $163 \times 10^{-4}$  for the same cement when untreated (Fig. 4A). Although the shift is in the expected direction, the interpretation should be accepted with reservations because the cement was obviously altered in other respects than oxidation of the sulfide. For example, the resulting hydrated cement was a deep red in color.

*Ciment Fondu.* To ascertain if the ionic characteristics of hydrated Lumnite cement were unique, another high-alumina cement (Ciment Fondu) was investigated for a similar hydration-temperature series. Comparison of the results (Table 5 and Fig. 5) with Figure 3 reveals that the curves for these two high-alumina cements, although quantitatively different, possess essentially the same features.

*Alcoa Cement.* Alcoa, another high-



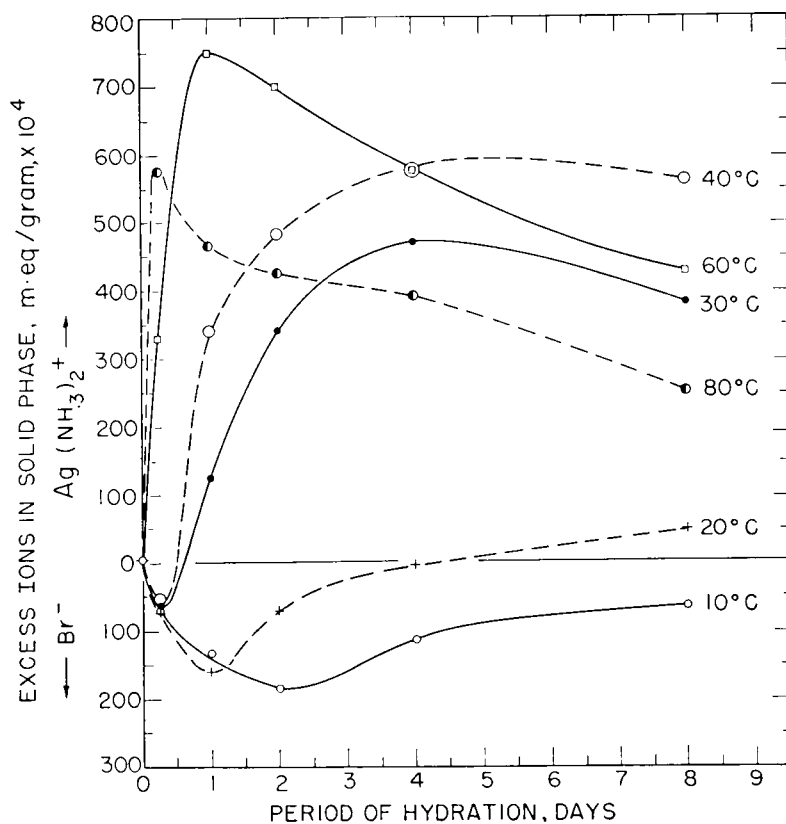


Figure 3. Ionic charge on high-alumina cement (Lumnite) after various periods of hydration at different temperatures (10-g samples, hydrated in 50 ml of distilled water with sufficient agitation to prevent setting).

TABLE 4  
IONIC CHARGE ON LUMNITE CEMENT AFTER VARIOUS PERIODS OF HYDRATION AT DIFFERENT TEMPERATURES USING  $\text{Ag}(\text{NH}_3)_2^+$  AND  $\text{Br}^-$  AS THE INDICATOR IONS

Hydra- tion Period (days)	Excess Ions Retained in the Solid Phase After Hydration ( $\text{meq/g} \times 10^{-4}$ )									
	10 C		20 C		30 C		40 C		60 C <sup>a</sup>	80 C <sup>a</sup>
	$\text{Ag}^+$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Ag}^+$
0	2.5	—	2.5	—	2.5	—	2.5	—	2.5	2.5
1/4	—	67	—	75	—	63	—	53	330	575
1	—	133	—	160	125	—	340	—	750	465
2	—	185	—	70	340	—	480	—	700	450
4	—	115	—	5	470	—	575	—	575	390
8	—	65	48	—	380	—	550	—	425	250

<sup>a</sup> No  $\text{Br}^-$ .

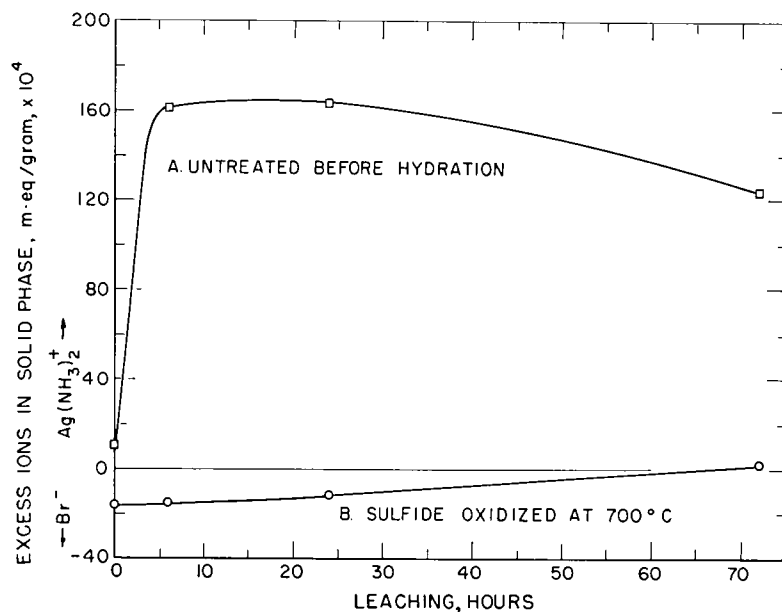


Figure 4. Comparison of treated and untreated set Lumnite cement leached at 80°C to illustrate decrease in negative ionic charge on the set cement caused by oxidation of contained sulfides.

TABLE 5  
IONIC CHARGE ON CEMENT FONDU AFTER VARIOUS PERIODS OF HYDRATION AT DIFFERENT TEMPERATURES USING  $\text{Ag}(\text{NH}_3)_2^+$  AND  $\text{Br}^-$  AS THE INDICATOR IONS

Hydra- tion Period (days)	Excess Ions Retained in the Solid Phase After Hydration ( $\text{meq/g} \times 10^{-4}$ )									
	10 C <sup>a</sup>		20 C <sup>a</sup>		30 C		40 C		60 C	
	$\text{Br}^-$	$\text{Br}^-$	$\text{Br}^-$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Br}^-$
0	5	5	—	5	—	5	—	5	—	5
1/4	237	96	—	98	—	120	267	—	637	—
1	320	300	—	95	320	—	560	—	537	—
2	280	147	137	—	510	—	387	—	320	—
4	267	127	225	—	487	—	287	—	99	—
8	287	154	187	—	390	—	175	—	47	—

<sup>a</sup> No  $\text{Ag}^+$ .

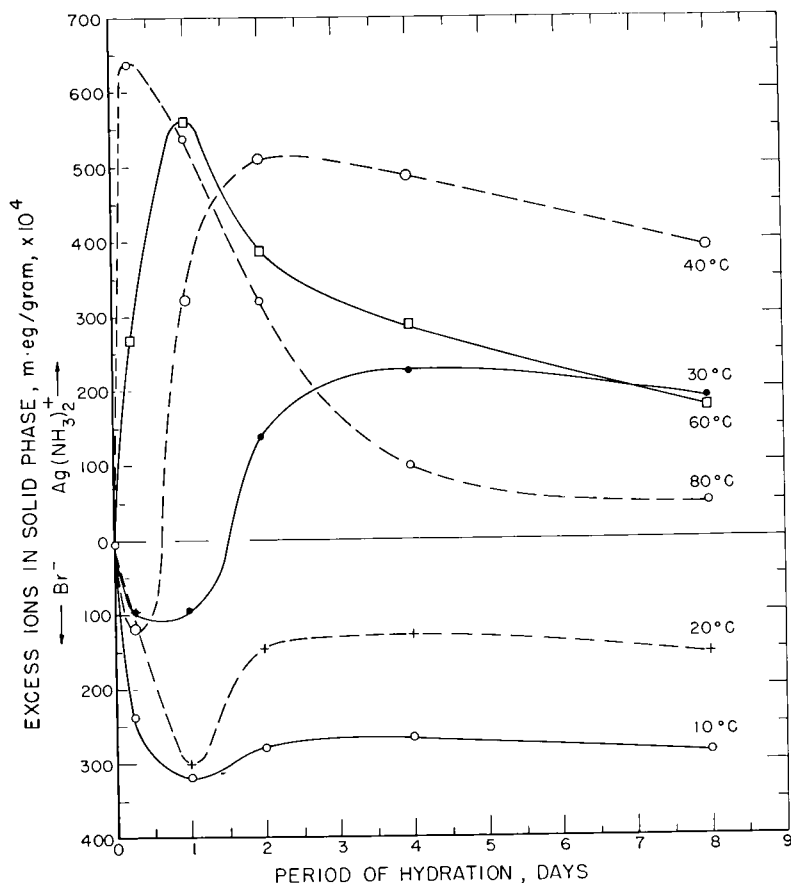


Figure 5. Ionic charge on high-alumina cement (Ciment Fondu) after various periods of hydration at different temperatures (10-g samples, hydrated in 50 ml of distilled water with sufficient agitation to prevent setting).

alumina cement, but one having a composition markedly different from Lum-nite and Ciment Fondu (Table 1), also seems to reflect the ionic charge dictated by the constituent compounds known to be present or known to be formed during hydration at various temperatures (Table 6 and Fig. 6). These data show the ionic charge acquired by the cement during hydration for a series of temperatures ranging from 10 C to 80 C. The negative ionic charge found for the unhydrated cement can be attributed to CA and to alpha alumina, each of which has been identified as being present (17, 18) and which have been found to carry a small negative ionic charge (Table 3). Within

6 hr of hydration the charge on the cement became positive, which is in accord with the positive ionic charges found on  $\text{CAH}_{10}$ , the stable hydrate below 25 C, and on  $\text{Al}(\text{OH})_3$ . Concerning the conspicuous change in magnitude of the ionic charge for the 10 C and 20 C hydration curves between the first and second day, and equally conspicuous change in appearance and texture of the cement paste was observed during this period. Furthermore, the appearance and other characteristics of the solid phase for the 10 C and 20 C hydration temperatures were entirely different from those for the 40 C and higher temperatures.

For the curves at the higher tempera-

TABLE 6  
IONIC CHARGE ON ALCOA CEMENT AFTER VARIOUS PERIODS OF HYDRATION AT DIFFERENT TEMPERATURES USING  $\text{Ag}(\text{NH}_3)_2^+$  AND  $\text{Br}^-$  AS THE INDICATOR IONS

Hydra- tion Period (days)	Excess Ions Retained in the Solid Phase After Hydration ( $\text{meq/g} \times 10^{-4}$ )											
	10 C		20 C		30 C		40 C		60 C		80 C	
	$\text{Ag}^+$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Br}^-$	$\text{Ag}^+$	$\text{Br}^-$
0	21	—	21	—	21	—	21	—	21	—	21	—
$\frac{1}{4}$	—	6	—	37	—	25	—	38	—	73	—	145
1	—	43	—	126	—	65	—	75	—	112	—	210
2	—	450	—	410	—	87	—	90	—	112	—	60
4	—	410	—	387	—	112	—	32	—	42	—	0.0
8	—	330	—	360	—	62	—	15	—	42	3	—

tures, the resulting ionic charge seems to be caused by a competition between the small negative charges of  $\text{C}_2\text{AH}_8$ , and  $\text{C}_3\text{AH}_6$ , and the positively-charged  $\text{Al}(\text{OH})_3$  (Table 3) produced during the formation of these hydrates from CA.

As the Alcoa cement contains little or no sulfide sulfur, it lends some support to the reason offered for the displacement of Curves A and B (Fig. 4). By the same reasoning, it also appears that the rapid drop, particularly at high temperatures, in the negative charge shown by Lumnite and Ciment Fondu (Figs. 3 and 5) may be caused by oxidation of the sulfides.

However, this decrease in charge may also be due to other causes (such as increase in size of the hydrated crystals, with its attendant reduction in effective surface).

A comparison of the three high-alumina cements after 4 days of hydration is shown in Figure 7. Although the curves for these cements are appreciably different, they all illustrate strikingly the change in ionic characteristics accompanying the transition from  $\text{CAH}_{10}$  (the hydrate formed at low temperatures) to the higher temperature forms  $\text{C}_2\text{AH}_8$  and  $\text{C}_3\text{AH}_6$ .

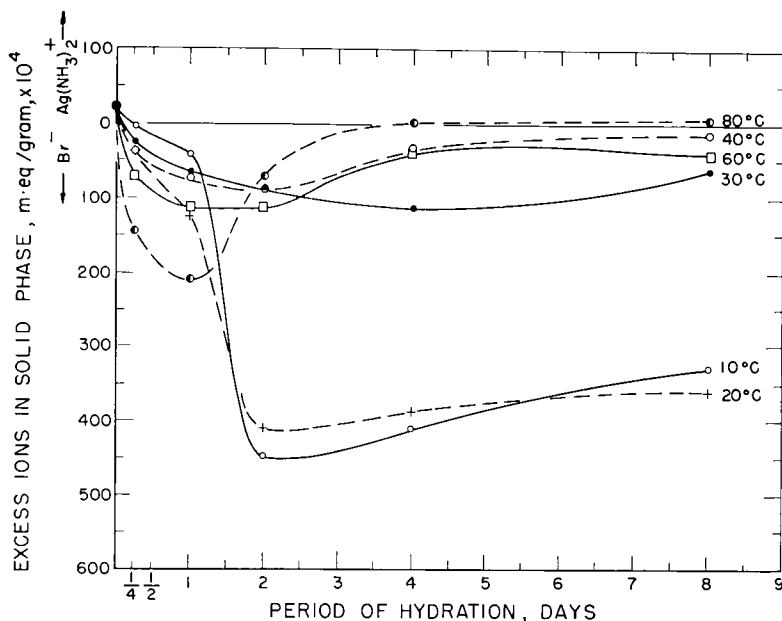


Figure 6. Ionic charge on high-alumina cement (Alcoa) after various periods of hydration at different temperatures (10-g samples, hydrated in 50 ml of distilled water with sufficient agitation to prevent setting).

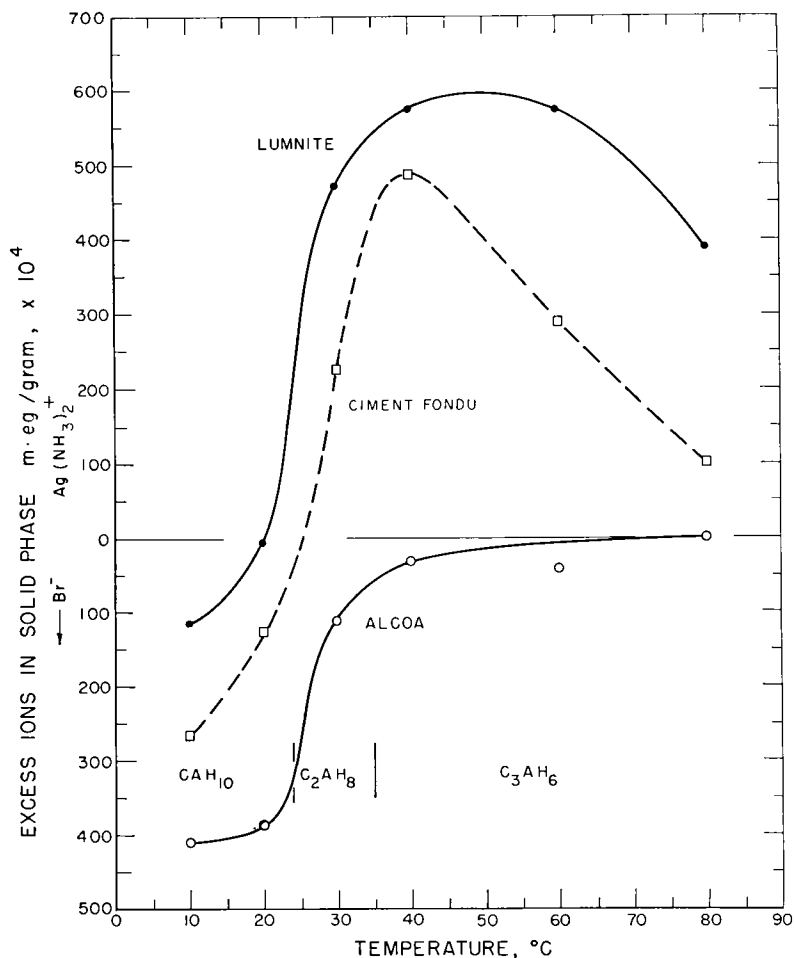


Figure 7. Ionic charge exhibited by Lumnite, Ciment Fondu and Alcoa cements after 4 days of hydration at different temperatures, illustrating the change in ionic characteristics accompanying the transition from  $CAH_{10}$  (the hydrate formed at low temperatures) to the higher temperature forms  $C_2AH_8$  and  $C_3AH_6$ .

#### SUMMARY AND CONCLUSIONS

Although the data obtained in this investigation are of a predominantly qualitative nature, they appear to offer an acceptable picture of some of the major factors responsible for the non-migratable ionic charges characteristic of portland and high-alumina cements during hydration.

For the portland cements, the excess  $Ca(OH)_2$  available during hydration, with its positive ionic charge, seems to be the major determinant. This positive non-migratable ionic charge predomi-

nates although the major constituent of hydrated cement (*viz.*, mono-calcium silicate,  $CSH(B)$ ) possesses a large negative ionic charge. The very small ionic charge shown on the cement in the unhydrated state agrees with the data of Ernsberger and France (21) obtained by their electrophoretic procedure.

The non-migratable ionic charges characteristic of the high-alumina cements (Lumnite, Ciment Fondu and Alcoa) during hydration also correlate qualitatively with the ionic charges characteristic of the major constituents (cal-

cium aluminate hydrates) stable at various temperatures of hydration. Typical of these are  $\text{Al}(\text{OH})_3$  and  $\text{CAH}_{10}$ , both with positive ionic charges and both stable below 25 C. In contrast to this behavior both  $\text{C}_2\text{AH}_8$ , a hydrate identified at 35 C, and  $\text{C}_3\text{AH}_6$ , a hydrate stable above 35 C, have a weak non-migratable negative ionic charge. The presence of CaS in Lumnite and Ciment Fondu may displace the ionic charge for the hydrated cements toward a high negative value.

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