

PORE SOLUTIONS AND ALKALI-AGGREGATE ATTACK

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ABSTRACT

Recent developments in understanding aggressive solutions developed in concrete made with high alkali cements are discussed. It appears that moderately high alkali cements produce pore solutions that become in essence concentrated alkali hydroxide solutions, of concentrations as high as 0.7 M in both total alkalies and hydroxide ions. Calcium ion concentrations in such pore solutions drop to about 0.002 M after a few days. Results of a new extension of Debye-Huckel solution theory to calcium hydroxide in solutions of high ionic strength confirms that these pore solutions are in fact saturated with respect to calcium hydroxide. Experimental results indicating that after a few months the calcium concentration rapidly reduces to undetectable levels are discussed and a tentative explanation advanced. On the basis of this new understanding of pore solution composition it is considered that calcium should not be a significant constituent of the initial reaction product with susceptible aggregates. Recent analytical results appear to confirm that reaction product sols flowing through open cracks radiating from reacted grains pick up most of their calcium from calcium hydroxide crystals encountered by the flowing fluid and lose alkalies to the surrounding paste.

INTRODUCTION

The problem of chemical reactivity of siliceous aggregates in concrete can be studied from many points of view. Regardless of the approach taken, however, it seems necessary that an understanding of the nature of the aggressive solution resident in the pores of the concrete be established, together with a clear idea of the general reaction mechanism. One requires such information both in order to understand the details of the problem, which will vary from case to case with variation in aggregate type, exposure, degree of alkalinity of the cement, etc., and equally important, to be able to properly formulate corrective measures.

A review of some aspects of the alkali-silica reaction problem has recently been published¹, in which the chemistry of the aggressive pore solutions has been discussed. It is the purpose of this presentation to consider additional experimental results and some new extensions of theoretical aspects of the solution chemistry pertinent to the problem. We are concerned here with two specific features: a) the degree to which the pore fluid in concrete made with moderately high alkali cement becomes a concentrated alkali hydroxide solution, and b) the extent and influence of the calcium ion in solution and in the resulting reaction product gel.

PORE SOLUTION COMPOSITION

Obviously, standard chemical methods of analysis can be applied if one wants to know the composition of a given solution, once the solution has been obtained. Unfortunately, in the case of concrete pore solutions,

from 0.85 to 1.04, mostly as potassium oxide; the other was a low alkali slag cement. A set of analyses for the middle alkali cement paste series of these authors is reproduced in Table 1.

Generally, the pertinent results obtained by these workers can be summarized as follows:

a. Alkali ion concentration

For the two higher alkali content cements, the combined concentrations of Na and K ions in the pore solutions was between 0.25 and 0.28 M in five hours, 0.6 to 0.7 M within a week, 0.7 M or slightly higher by 28 days, and fluctuated only slightly thereafter. The third Portland cement yielded a slightly lower peak concentration value of 0.64 M at 28 days, and alkali concentration decayed to slightly over 0.5 M at 1 year.

The peak concentrations found were slightly in excess of the maximum concentration estimated by assuming all of the alkali ions in the cement were dissolved in the water initially present as calculated from the water:cement ratio. The slightly higher concentrations actually found are presumably a reflection of the fact that some water was tied up in solid cement hydration product, and this was not fully compensated for by entry of water from outside the specimens. Nevertheless the figures suggest that essentially all of the alkali ions present in the cement were mobilized in the pore fluid by a month or so.

b. Hydroxide ion concentration

The second important result developed from the data of Longuet et. al.² is that after a few days the hydroxide concentrations in the solutions become substantially equivalent (within a few percent) to the alkali ion concentrations. Thus cement paste pore solutions of the high alkali cements soon became roughly 0.7 M in hydroxide ions. This is about 17 times the concentration of hydroxide ions in pure saturated calcium hydroxide solution, which is only 0.04 M. This points very strongly to the conclusion that $\text{Ca}(\text{OH})_2$ solution is not the agent responsible in any way for alkali attack.

c. Calcium ion concentration

For all of the three moderately high alkali content cement pastes examined by Longuet et. al.² it was established that after a few days the calcium ion concentration dropped to the order of 0.002 to 0.003 M. This approximate level was maintained for periods ranging from a month to three months, whereupon the level of calcium ion in solution dropped below detectable limits and was reported as zero. By six months non of the pastes had any detectable calcium ion in solution.

These data clearly indicate that pore solutions in set cement pastes made from moderately high alkali cements at normal water:cement ratios rapidly achieve, and thereafter maintain the status of concentrated alkali hydroxide solutions; insofar as adding to the hydroxide concentration, the effect of dissolved calcium hydroxide is negligible, and calcium appears to be completely removed from solution after a few months. Presumably similar patterns obtain in concrete exposed to normal environments; in fact, in cases of exposure without access to additional water from the environment the concentration levels of alkali hydroxide in the pore fluid might be even higher.

The data also seem to have important implications with respect to the role of calcium in the alkali-silica reaction both from the point of view of pore solution composition and in terms of the composition of the reaction product gel. These will be treated separately in the remainder of this paper.

CALCIUM HYDROXIDE STATUS OF PORE SOLUTIONS

Among the questions that must be asked in assessing the composition data described above are a) Does the roughly 0.002 to 0.003 M level of calcium found in the pore solutions at intermediate periods from a few days to a few months represent saturation of these solutions with respect to calcium hydroxide, and b) if it does, how and why do the solutions lose their calcium after a few months, in the presence of large volumes of solid calcium hydroxide in the pastes?

The present writer, spurred by these problems, has extended the Debye-Hückel theory treatment of calcium hydroxide solutions of

Greenberg and Copeland³ to permit calculation of the "effective" solubility product constant of calcium hydroxide in solutions of high ionic strength such as those reported by Longuet et. al.². The treatment will shortly be published⁴.

In brief, the equation derived is

$$\log K_{sp}^* = \log K_{sp} - 3B'\mu + 6A\sqrt{\mu} \quad (1)$$

where K_{sp}^* is the "effective" solubility product (in concentration, rather than activity units), K_{sp} is the true thermodynamic solubility product in terms of activities, A and B' are constants in the extended Debye-Hückel equation, and μ is the ionic strength of the solution. $\log K_{sp}$ is taken as -5.15 , A is 0.501 at 20°C , and data taken from the literature on composition of solutions of mixed calcium and alkali hydroxides provided a reasonable fit for B' (which must be determined empirically) at 0.165 .

The data of Longuet et al² are sufficiently complete so that ionic strengths can be estimated for each solution. Typically after a few days these are in the range of 0.6 to 0.7 . These values lead to $\log K_{sp}^*$ values for these solutions of approximately -3.0 .

With K_{sp}^* known, and the hydroxide ion concentration available, one can then establish whether the solution does or does not represent a condition of saturation with respect to $\text{Ca}(\text{OH})_2$ by comparing the "calculated" concentration of calcium ions with that actually found in the solutions. The "calculated" values are obtained from the equation:

$$K_{sp}^* = \text{Conc}_{Ca^{++}} \cdot (\text{Conc}_{OH^-})^2 \quad (2)$$

It turns out that solutions having the ionic strengths and hydroxide concentrations of those actually found for the intermediate periods from a few days to a few months should have calcium ion concentrations of the order of 0.0022 to about 0.0026 M, very close to the levels actually found. Thus the solutions are in fact effectively saturated with respect to calcium hydroxide. Nevertheless, the level of calcium present is roughly 10 fold less than that of "pure" calcium hydroxide solutions which are saturated at roughly 0.02 M in calcium.

This brings up the second feature of the data of Longuet et al.² with respect to calcium, viz. its apparent disappearance from the pore solution after a few months. There seem to be no concurrent changes in concentrations of the other constituents, except a slight increase in the low silica concentrations of some of the solutions. The alkali ion concentrations, the hydroxide ion concentration, and the ionic strength do not appear to have changed.

One can always explain away the disappearance of the calcium as an experimental artifact due to carbonation or some other cause. However, if the effect is real and reproducible by other workers the only explanation the present writer can suggest is that after a few months essentially all of the calcium hydroxide present in solid form may become encapsulated by a coating of silica or a siliceous reaction product so that the calcium hydroxide is effectively out of contact with the pore solution. If this should happen, the solubility characteristics of calcium hydroxide would no longer be pertinent, and the solution will be governed by equilibration with respect to the solubility of the coating

it is the process of acquiring the solution in the first place that constitutes the difficulty. Methods in which pore fluid is swept out of ground concrete or cement paste by adding additional solvent and extracting the resulting solution are not likely to give appropriate assay; there are a number of quasi-soluble compounds present which will be brought into solution to some extent by the extracting solvent, which may not be in solution in the original concrete pore fluid.

The other way to obtain pore fluid is to squeeze it out under pressure. Unfortunately, this has been in the past practical only for very young pastes or concretes, particularly those made at rather unreasonably high water: cement ratios.

The only work known to the writer in which this problem seems to have been overcome is that of Longuet, Burglen, and Zelver², who designed a high pressure apparatus specifically for this task. These workers were able to extract 5 - 10 ml. of pore solution from roughly 300 g specimens of hardened cement paste cast at a uniform water:cement ratio of 0.5 and cured under water for various periods of up to 1 year. The solutions were kept continuously under a nitrogen blanket to prevent carbonation, and were carefully analyzed for essentially all constituents likely to be present. The data provide a picture of the composition of pore solutions and their changes over time which appears to be the best available indication of the status of real concrete pore solutions.

Longuet et. al. reported results on four separate series of pastes made from four different cements. Three of these were moderately high alkali Portland cements with equivalent Na_2O contents ranging only

or of the C-S-H gel. The solubility behavior of C-S-H gel in highly alkaline solutions is not well established, but clearly the calcium concentrations in metastable equilibrium with this phase or with a low C:S ratio coating around lime crystals must be at least an order of magnitude less than those in equilibrium with calcium hydroxide.

Regardless of the ultimate solution to this aspect of the problem, the fact remains that if the data of Longuet et al² are to be regarded as indicative of concrete pore solutions, one would have to expect that during the major portions of the period of reaction between the pore solutions and susceptible siliceous aggregate the calcium concentration of the pore solutions would be at most around 0.002 M, and likely lower after a few months. How then is calcium incorporated into the reaction product gel, and what is the role of this ion with respect to the reaction itself?

ROLE OF CALCIUM IN ALKALI-SILICA REACTION PRODUCT

If the data of Longuet et al² cited are applicable, concrete pore solutions made with reasonably high alkali cement would after a few weeks be 0.7 M in alkali cations and 0.002 M in calcium ions: that is, the ratio of alkali to calcium would be of the order of 350 to 1. Nevertheless, calcium has been reported as a significant constituent of many alkali silica reaction product gels.

In 1961 Idorn⁵ published a compendium of analyses of reaction product gels sampled from the surfaces of affected concretes, some being original data and some from the literature. He divided the eighteen analyses into three categories: "true" alkali-silica gels, lime-alkali-silica gels of low lime content, and lime-alkali-silica gels of high

lime content. Of the 10 analyses in the first group, four had no detectable calcium at all. For present purposes the present writer has split Idorn's first category into completely lime-free and not-quite lime-free groups. The analyses falling into each group were then averaged and re-expressed in terms of ratios of combined Na and K ions to Ca ions, for easy comparison with the solution ratios. The results are as follows:

<u>Category and No. of Analyses</u>	<u>(Na + K)/Ca</u>
Completely lime-free alkali silica gels (four analyses)	infinite
Not-quite lime-free alkali silica gels (six analyses)	33.
lime-alkali-silica gels of low lime content (seven analysis)	7.4
lime-alkali-silica gels of high lime content (two analyses)	1.

It appears that while some of the reaction product gels appear at the surface of the concrete free of calcium, many accumulate calcium, and to a much higher proportion with respect to the alkali ions than is likely to be present in the original pore solution.

Considerable light was shed on the process of accumulation of calcium in the elegant work reported by Knudsen and Thaulow⁶ at the January 1975 meeting of the Transportation Research Board in Washington. These authors prepared thin sections of an opal sandstone-bearing concrete that had reacted severely despite the relatively low alkali content of the cement used (thought to be less than 0.6 percent Na₂O equivalent). In the thin section they found a triangular grain about 5 mm on a side, with cracks radiating from each corner, the cracks being about 20 μm across. They analyzed gel in situ within the cracks

at known and increasing distances from the perimeter of the original opal grain. The technique involved a pioneering use of energy-dispersive x-ray analysis, with a full ZAF correction for each determination.

Eighteen analyses were provided along the three cracks, with distances from the opal grain varying from as little as 10 μm to as much as 5000 μm from the opal grain. The analyses were reported in terms of weight percent of the elements as oxides, with water neglected. For present purposes the data were recalculated in terms of relative mole concentrations of the individual elements, and the ratios of $(\text{Na} + \text{K})/\text{Ca}$ specifically examined. Some of this data is tabulated in Table 2.

None of the points examined show gel that would be classed as either completely lime-free alkali silica gels or even not-quite lime-free alkali silica gels in terms of the classification previously adopted. As indicated in Table 2, the highest ratio of alkali to calcium found was only a little over 5, for the innermost spot on Crack No. 1. In general, the $(\text{Na} + \text{K})/\text{Ca}$ ratios were lower than those tabulated by Idorn⁵, and values as low as 0.25 were recorded. Clearly all of the gel was "lime-alkali silica gel", and much of it would be classed as of high lime content.

One of the important features of the data as emphasized by Knudsen and Thaulow was the fact that as one progressed along any of the cracks the content of calcium in the gel increased progressively, and the content of alkalis decreased. There was no overall correlation with distance from the opal grain independent of which crack one pursued, but along each crack the $(\text{Na} + \text{K})/\text{Ca}$ ratio decreased monotonically.

The implication of this feature is of course the concept that as gel moves down the crack it picks up increasing amounts of calcium from the cement paste it passes near. As Knudsen and Thaulow⁶ pointed out, this feature of their results is in line with the observed depletion of Ca(OH)_2 crystals from the vicinity. Presumably the increased calcium content of the reaction gel reflects accumulation of calcium from these crystals of calcium hydroxide. The problem of explaining how the calcium is "transported" or "diffused" (in the words of Knudsen and Thaulow) into the reaction product gel remains acute, especially in view of the results cited earlier, which indicate that calcium virtually disappears from the pore fluid of high alkali cement products after a few months.

It appears to the present writer that a reasonable working hypothesis lies in recognition of the fact that the reaction product passing down the crack is really a sol rather than a gel during the time it is migrating, and that the sol itself is a very concentrated aggressive fluid. It is likely capable of reacting directly with and dissolving calcium hydroxide crystals as it flows past them along the margins of the crack. Such a hypothesis of the nature of transport of lime is thought by the present writer to be one of the keys to the peculiar behavior encountered in alkali-silica reactions. For example, the strong effect of extra amounts of solid calcium hydroxide intimately intermixed with reactive grains in the early osmotic experiments of Verbeck and Gramlich⁷ which was inexplicable from the point of conventional solution ideas, might very well reflect this kind of behavior. There is one additional point to consider relating

to the analyses of Knudsen and Thaulow. The observed decrease in $(Na + K)/Ca$ ratio comes about not only through increases in the Ca content, but as clearly indicated by the data, also through decreases in the alkali ion content. Thus not only is additional calcium incorporated, as the gel moves down the crack, but alkalies are somehow removed from the reaction product. The content of Si is relatively stable i.e. there is no massive dilution of the gel. Where does the alkali go?

The answer seems to be implicit in additional data recorded by Knudsen and Thaulow but not previously mentioned. They have analyzed spots along a line in the cement paste normal to one of the cracks at roughly 200 μm intervals from the crack center. Apparently some K does diffuse into the paste as far as 800 μm from the centerline of the crack (the crack being less than 20 μm wide). While the concentration at any spot in the paste is low, a significant volume of cement paste is affected. Crude calculations by the present writer suggest that loss of alkali to the surrounding paste is in fact comparable with the observed lowering of the alkali content of the reaction "gel" as it proceeds down the crack.

One final point has already been alluded to but not explained; that is, the relatively low range of the alkali - calcium ratios encountered in the work of Knudsen and Thaulow, compared to many of the gels tabulated by Idorn. The present writer feels that this is possibly related to the fact that the cement actually used to make the reacted concrete examined by Knudsen and Thaulow was, according to these workers, likely to have been a low alkali cement. It seems

likely that in the pore solutions of this concrete the concentration of the alkali ions was not as high, and the concentration of calcium ions not as low, as in the pore solutions of Longuet et. al.², or in typical cases of alkali-silica attack in concrete made from high alkali cement. If this explanation is correct, further work applying the technique of Knudsen and Thaulow to cases of reaction involving concrete made from cements of high alkali contents should produce overall analyses more nearly in line with those tabulated earlier by Idorn.

In summing up these various considerations, it appears to the present writer that they point to the conclusion that calcium is not an important primary constituent of the alkali-aggregate reaction product, particularly with high alkali cements. Indeed the disappearance of calcium from the pore solution after a few months seems to guarantee that this is so. Nevertheless some calcium does seem to be incorporated with most gels; some of this at least occurs when the product pass along cracks as previously described. To the extent that this secondary incorporation occurs after the initial swelling and cracking that is responsible for the distress in concrete, it is unimportant in practical terms.

CONCLUSIONS

Current literature and interpretations by the present writer suggest that:

1. Pore solutions in concrete made from reasonably high alkali cement rapidly become concentrated alkali hydroxide solutions of the order of 0.7 M or more.

2. Calcium concentrations are reduced after a few days to the order of only 0.002 M, and maintained at this level for several months; the level represents saturation with respect to calcium hydroxide in the high ionic strength and high hydroxyl concentration solutions.

3. There is evidence to suggest that even this low level of calcium is reduced to essentially zero after a few months. If so, the explanation likely involves isolation of the calcium hydroxide crystals from the pore solution, presumably by development of a layer of a low-lime calcium silicate around the crystals.

4. Analyses recently reported indicate that as reaction product "gel" moves outward from the reacting grain it increases in calcium content and decreases in alkali content. The calcium probably comes from calcium hydroxide crystals enveloped by the liquified reaction product which is really a sol at this stage. Alkalies are lost to the surrounding cement paste by diffusion.

5. The relative absence of calcium in the original aggressive solution in the pores of the concrete mitigates strongly against the likelihood that calcium plays a significant role in the formation of the original reaction product, which is viewed as the local product of attack of strong alkali hydroxide solution on the siliceous aggregate grains.

ACKNOWLEDGEMENT

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LITERATURE

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TABLE 1

RESULTS OF LONGUET ET AL² ON COMPOSITION OF POLE SOLUTIONS
 EXPRESSED FROM PASTES* MADE FROM CEMENT CPA-2
 (0.99% EQUIV. Na₂O) AND CURED FOR
 VARIOUS PERIODS UNDER WATER

Solution Concentration, Moles/1000 g

<u>Age</u>	<u>Si</u>	<u>SO₃</u>	<u>Ca</u>	<u>Na</u>	<u>K</u>	<u>(Na + K)</u>	<u>OH</u>
5 hours	0.00023	0.082	0.0205	0.0376	0.2238	0.2614	0.129
2 days	0.0010	0.0035	0.0027	0.111	0.468	0.579	0.452
7 days	0.0006	0	0.0023	0.168	0.532	0.700	0.687
28 days	-	0.010	0.0020	0.160	0.534	0.694	0.685
2 months	0.00125	0.0132	0	0.1594	0.628	0.787	0.740
6 months	0.0010	0.0188	0	0.173	0.5186	0.692	0.651
1 year	0.0016	0.015	0	0.137	0.566	0.703	0.670

*W:C = 0.5

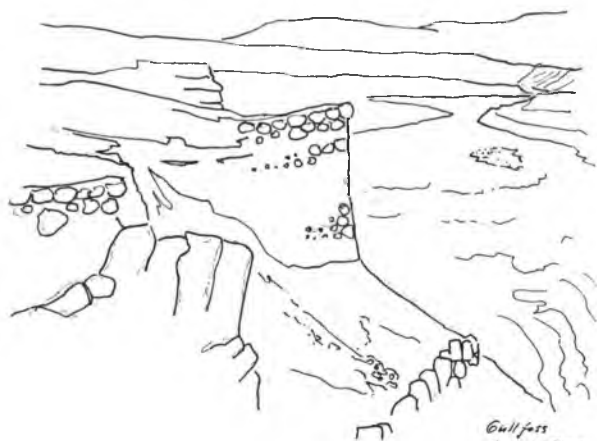
TABLE 2

RESULTS OF KNUDSEN AND THAULOW⁶ RE-EXPRESSED IN
TERMS OF ATOM PERCENTAGES*

Analysis No. and Distance From Grain		Atom Percent*					Ratio (Na+K)/Ca
		Na	K	(Na+K)	Ca	Si	
<u>Along Crack No. 1:</u>							
1-1	(300 μm)	2.6	18.9	(21.5)	4.2	74.4	(5.1)
1-2,1-3**	(370 μm)	2.6	17.6	(20.2)	4.8	75.1	(4.2)
1-4	(490 μm)	2.2	13.0	(15.2)	7.3	70.0	(2.1)
1-5	(1100 μm)	0	13.1	(13.1)	20.8	66.0	(0.63)
1-6	(5000 μm)	1.7	11.2	(12.9)	24.8	62.3	(0.52)
<u>Along Crack No. 2:</u>							
2-1	(30 μm)	5.1	16.6	(21.7)	11.7	66.6	(1.85)
2-2	(50 μm)	3.6	15.0	(18.6)	16.8	64.4	(1.10)
2-3	(70 μm)	4.2	15.4	(19.6)	17.7	62.8	(1.10)
2-4	(90 μm)	2.9	15.6	(17.5)	18.7	62.8	(0.93)
2-5	(660 μm)	3.5	12.2	(15.7)	16.2	68.0	(0.97)
2-6,2-7**	(1000 μm)	2.7	12.3	(15.0)	21.2	63.8	(0.71)
<u>Along Crack No. 3:</u>							
3-1,3-2,3-3**	(100 μm)	5.3	15.1	(20.4)	6.6	72.9	(3.1)
3-4,3-5**	(5000 μm)	0	7.0	(7.0)	27.1	65.8	(0.26)

*Oxygen and H₂O neglected.

**Two or more analyses at the same distance averaged.



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