

A PROSPECTIVE MEASURE FOR THE EXTENT OF ALKALI-SILICA REACTION

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ABSTRACT

Studies of alkali-silica reaction and its effects have been handicapped by the absence of a method of measuring the extent of the chemical reaction itself, as distinguished from measurement of the expansion. Expansion may or may not accompany reaction, depending on various factors. The proposed method involves determination of the alkali contents of pore solutions expressed from mortars in a special pressuring device operated at about 75,000 psi. After appropriate corrections, the reduction in the alkali concentration of pore fluid from reacting mortars as compared with pore fluid from companion mortars free of reactive silica is used to calculate the degree of reaction that has occurred and to estimate the amount of product formed. Illustrative data are provided for reactive mortars made with ground opal and hydrated for periods of up to 70 days.

INTRODUCTION

Interest in alkali-aggregate reactions in concrete is currently at a high level in view of the increased likelihood of deleterious responses stemming from increased levels of alkali contents in many cements and increased usage of marginal aggregates.

One of the major difficulties in understanding the details of alkali-silica reactions has been the inability of research workers to measure the extent and rate of reaction to be expected in a given reactive combination.

Tests of expansions with mortar bars provide appropriate measure of the expansion due to reaction, but not of the reaction itself. It is well known that many combinations of components will react, sometimes extensively, without giving rise to immediate expansion; in some circumstances the expansion does not take place at all. An independent measure of the extent of reaction, separate and distinct from measurements of expansion is clearly needed.

It is the purpose of this paper to present and illustrate progress in the development of such a measure.

BACKGROUND OF METHOD

In principle, most chemical reactions involve the combination of two or more reactants to produce one or more reaction products. The extent of reaction can be assessed by monitoring either the increasing concentration or amount of product or products, or the decreasing concentration or amount of one or more of the reactants.

In alkali-silica reactions the product is an alkali-silica gel of uncertain and variable composition located irregularly in patches within the body of the affected mortar or concrete. It is obviously not feasible to pick out all of these patches to determine the amount of product formed. Of the reactants, it is similarly infeasible to monitor the decrease in amount of reacting siliceous aggregate. Hydroxide ions in solution can be readily monitored, but the presence of a vast reservoir of easily mobilizable hydroxide ions in the form of solid calcium hydroxide disseminated throughout the hydrated cement paste complicates the use of this reactant as an indicator of the progress of the reaction. This leaves measurement of alkali cations, principally K^+ and Na^+ , as the remaining possibility.

Fortunately, use of the alkali for concentration as an indicator of the extent of reaction has several favorable aspects. The alkali ions are readily mobile throughout the affected mortar or concrete, at least while saturated. Thus, while a uniform concentration of these ions throughout the mass cannot be guaranteed, it seems as this should reasonably be the case; if this is so the alkali concentration determined from a sample of pore fluid ought to be reasonably representative. Also, the alkali ions are relatively easy to determine by standard methods, once the solution has been obtained.

However, a number of features preclude the simple approach of using the reduction of alkali ion concentration with time as a measure of the extent of reaction. To begin with, alkali concentrations in mortars isolated from additional water supply increase with time as water is subtracted from the pore fluid by the processes of cement hydration. Secondly, at least in some cements, some of the alkalis are considerably delayed before reaching solution; thus later portions entering solution tend to mask alkali ions being withdrawn from solution by the alkali-silica reaction. Third, there is evidence that some of the alkali ions may enter solid solution within the C-S-H gel of the hydrated cement. Finally, there is the concept that some of the alkali may be "recycled" after reaction with silica, i.e., displaced by calcium to form a more stable calcium alkali silicate.

An approach has been evolved which seems to take care of all of these difficulties except perhaps the last. So far, no method has suggested itself by means of which the amount of "recycled" alkali returned to solution can be monitored. To the extent that this phenomenon occurs, the method illustrated here will underestimate the extent of alkali silica reaction recorded.

The method suggested involves measuring the concentrations of the alkali cations (Na^+ and K^+) in the pore fluid of reacting mortars or concretes and comparing these to corresponding measurements carried out on identical mortars or concretes "blank" with respect to silica that can take part in the reaction. Both measurements are corrected for the increase in concentration due to removal of water for cement hydration. The difference in the adjusted concentrations of alkalis between reacting mixtures and identically exposed "blanks" provides a quantitative index of the alkali consumed in the alkali-silica reaction. Further, an estimate of the amount of reactive silica consumed can be derived if an assumption as to the stoichiometry of the reaction product is made.

The remainder of this paper provides a detailed illustration of the application of this scheme to one series of specimens and of the conclusions that can be drawn from it.

EXPERIMENTAL DETAILS

A series of mortars were prepared using a moderately high-alkali ASTM Type I cement whose composition is given in Table I. "Blank" mortars incorporated cement, ASTM Designation: C 109 standard Ottawa sand, and water, in the weight proportions 1:2:0.5. Reacting mortars incorporated a ground reactive opaline silica ("Beltane opal" from Sonoma County, California) in the proportion of 10 percent by weight of the cement, with a portion of the sand removed so as to provide constant yield of mortar. The opal had been ground in a ball mill to a Blaine fineness of $11,000 \text{ cm}^2/\text{g}$.

The mortar specimens were cured in sealed containers at 20°C for periods from 1/2 hour to 70 days. They were then subjected to pressures

of approximately 75,000 psi in a special pressuring device designed to facilitate extraction and recovery of pore fluid. Yields ranged from ca. 10 ml at early ages to less than 2 ml for more mature specimens, the fluid being collected in a syringe with only minimal exposure to the atmosphere. Details of the apparatus and collection procedure will be published elsewhere. The fluid recovered was immediately analyzed for alkali ions by flame photometry using a Perkin-Elmer Model 503 atomic absorption spectrophotometer flame photometer unit.

ALKALI CONCENTRATION IN "BLANK" MORTARS

From the cement analysis of Table 1 it is calculated that if all of the alkalis were to be dissolved in the mix water the resulting concentrations would be 0.395 N for K^+ ions and 0.193 N for Na^+ ions, for a combined alkali ion concentration of 0.588 N. The concentrations of ions actually found to be present in the pore solutions of the non-reactive "blank" mortars are given in Table 2. The combined "raw" alkali concentration exceeds 0.588 N after about half a day and is very much higher after extended hydration. The effect is clearly due to withdrawal of water as it is incorporated in hydrating cement paste.

Unfortunately the non-evaporable water contents of the present specimens were not measured. In lieu of direct measurements, recourse was had to the "standard" non-evaporable water vs. age curve of Copeland and Kantro (1), and the combined water withdrawn from the pore solution was estimated for each specimen from their w:c 0.5 curve. The combined water was subtracted from the total water to yield an estimate of the residual fluid water at each age. The concentrations of alkali ions found at each stage were then adjusted by multiplying by the quotient of residual water divided by original

water contents. This correction thus eliminates the effect of the removal of the hydration water and yields an equivalent concentration calculated on the basis of the original water content. The results of these calculations are also provided in Table 2.

The data provide some insight into the behavior of alkalis in hydrating cement and concrete not subject to alkali-aggregate reaction. After the first half hour the K^+ ion concentration corrected for hydration water removal was within experimental error of the 0.395 N value expected if all of the potassium is dissolved, indicating that all of the potassium in this cement is readily hydrolyzable. The corrected Na^+ ion concentration was initially only about two-thirds of the corresponding 0.193 N value, although it increases somewhat up to a day. After several days there is a slight but definite decline in the corrected K^+ concentration, and some irregular reduction in Na^+ . We consider that this reduction likely represents slow incorporation of the alkalis into the C-S-H gel; alternatively, some of it may represent reaction with the "non-reactive" quartz sand.

The trend indicated is illustrated in Fig. 1, in which the "corrected" concentrations of combined alkalis are expressed as percentages of the total alkali content provided by the cement, and plotted vs. time. Apparently with this cement about 90 percent of the alkali present is mobilized immediately; the amount in solution increases slightly between half a day and a day; and subsequently there is a gradual reduction to about 80 percent of the total in about two months.

ALKALI CONCENTRATIONS IN REACTING MORTARS

The actual K^+ and Na^+ concentrations found in the solutions expressed from the sealed reactive mortars are given in Table 3, along with the cor-

responding values corrected for the withdrawal of water by cement hydration. The corrected K^+ concentrations are maintained at close to the 0.395 N value for the first half day or so, and then drop steadily and progressively to a low of 0.200 N at 70 days, reflecting the early onset and progress of the alkali-silica reaction. The corresponding Na^+ results are less clearly defined, but appear to show a modest decrease starting at about 4 days.

QUANTITATIVE ASSESSMENT OF EXTENT OF REACTION

The amount of alkali tied up in alkali-silica reaction product, i.e., the desired estimate of the extent of the reaction, is calculated from the difference between the corrected concentrations of the alkalis between "blank" and reacting specimens of a given age. The data are given in Table 4, for each of the alkali ions. The combined tally is re-expressed as a percentage of the total alkali provided by the cement, and plotted against time in Fig. 2.

The results indicate that about 3 percent of the total alkali present has reacted almost immediately; that about 6 percent has reacted by 1 day, about 23 percent by 1 month, and 28 percent by about 2 months. The inset shows the detailed time trend for the first day. Early data can be fitted reasonably well to linear plots on both log time and square root of time plots, but later data depart significantly from the trends.

With an additional assumption about the stoichiometry of the reaction product one can form some idea about the proportion of the reactive silica that has reacted in a given time. Krogh (2) recently summarized published data on analyses of alkali-silica reaction gels. The $(K_2O + Na_2O / SiO_2)$ mole ratios reported range from virtually zero to 0.40; but neglecting four obviously aberrant analyses showing values of 0.06 and below, the average

TABLE 2

ANALYSIS OF ALKALI ION CONCENTRATIONS IN PORE SOLUTIONS EXPRESSED FROM "BLANK" MORTARS

Age	K ⁺ Ion Conc. N		Na ⁺ Ion Conc. N		Na ⁺ +K ⁺ Conc. (Corrected)	Correction Factor*
	Original	"Corrected"	Original	"Corrected"		
1/2 Hour	0.405	0.397*	0.134	0.131	0.528	0.98
1 Hour	0.405	0.389	0.135	0.130	0.519	0.96
3 Hours	0.412	0.395	0.136	0.131	0.526	0.96
6 Hours	0.424	0.399	0.144	0.135	0.534	0.94
14 Hours	0.474	0.427	0.163	0.147	0.574	0.90
27 Hours	0.496	0.396	0.197	0.157	0.553	0.80
4 Days	0.547	0.383	0.201	0.141	0.524	0.70
9 Days	0.532	0.341	0.204	0.131	0.472	0.64
15 Days	0.554	0.344	0.215	0.133	0.477	0.62
49 Days	0.594	0.356	0.242	0.145	0.501	0.60
70 Days	0.575	0.333	0.218	0.126	0.459	0.58

*Corrected for water withdrawal due to hydration of the cement; correction factor for any given age is $\frac{\text{Total Water} - \text{Estimated Non-Evaporable Water}}{\text{Total Water}}$

TABLE 3

ANALYSIS OF ALKALI ION CONCENTRATIONS IN PORE SOLUTIONS EXPRESSED FROM REACTING MORTARS

Age	K ⁺ Ion Conc., N		Na ⁺ Ion Conc., N		Combined (K ⁺ +Na ⁺) Conc., N Corrected*
	Original	Corrected*	Original	Corrected*	
1/2 Hour	0.394	0.386	0.126	0.124	0.510
1 Hour	0.392	0.376	0.123	0.118	0.494
3 Hours	0.394	0.378	0.126	0.121	0.499
6 Hours	0.407	0.383	0.135	0.127	0.510
14 Hours	0.445	0.401	0.148	0.133	0.534
27 Hours	0.454	0.363	0.190	0.152	0.515
4 Days	0.468	0.328	0.173	0.121	0.449
9 Days	0.442	0.283	0.153	0.098	0.381
15 Days	0.447	0.277	0.197	0.122	0.399
49 Days	0.384	0.230	0.186	0.112	0.342
70 Days	0.345	0.200	0.170	0.099	0.299

*For correction factors, see Table 2.

TABLE 4.

DIFFERENCE BETWEEN CORRECTED CONCENTRATIONS
OF "BLANK" AND REACTING MORTARS

<u>Time</u>	<u>Difference in K⁺ Conc., N</u>	<u>Difference in Na⁺ Conc., N</u>	<u>Total Difference N</u>
1/2 Hour	0.011	0.007	0.018
1 Hour	0.013	0.012	0.025
3 Hours	0.017	0.010	0.027
6 Hours	0.016	0.008	0.024
14 Hours	0.026	0.014	0.040
27 Hours	0.033	0.005	0.038
4 Days	0.055	0.020	0.075
9 Days	0.058	0.033	0.091
15 Days	0.067	0.011	0.078
49 Days	0.126	0.033	0.159
70 Days	0.133	0.027	0.160

TABLE 5

CALCULATIONS OF AMOUNTS OF REACTIVE SILICA
CONSUMED IN ALKALI REACTION

<u>Time</u>	<u>*Total Ion Concentration Difference, N</u>	<u>**Calc. No. of Moles of Alkali Ions Reacted per g of Reactive Silica Added to Mortar</u>	<u>***Corresponding No. of Moles of SiO₂ in Reaction Product</u>	<u>Calculated Percentage of the Reactive Silica Added to Mortar that has Reacted</u>
1/2 Hour	0.018	0.000090	0.00072	4.3%
1 Hour	0.025	0.000125	0.00100	6.0
3 Hours	0.027	0.000135	0.00108	6.5
6 Hours	0.024	0.000120	0.00096	5.8
14 Hours	0.040	0.000200	0.00160	9.6
27 Hours	0.038	0.000190	0.00152	9.1
4 Days	0.075	0.000375	0.00300	18.0
9 Days	0.091	0.000455	0.00364	21.9
15 Days	0.078	0.000390	0.00312	18.7
49 Days	0.159	0.000795	0.00636	38.2
70 Days	0.160	0.000800	0.00640	38.5

*Difference in corrected alkali concentrations of "Blank" and "Reacting" Mortars of the same age, from Table 4.

**Reactive silica added at the rate of 10% by weight of cement used, hence ratio is 5 ml of water present per g of reactive silica.

***Assuming $\frac{K + Na}{Si}$ mole ratio is 0.125, corresponding to $\frac{K_2O + Na_2O}{SiO_2}$ mole ratio of 0.25.

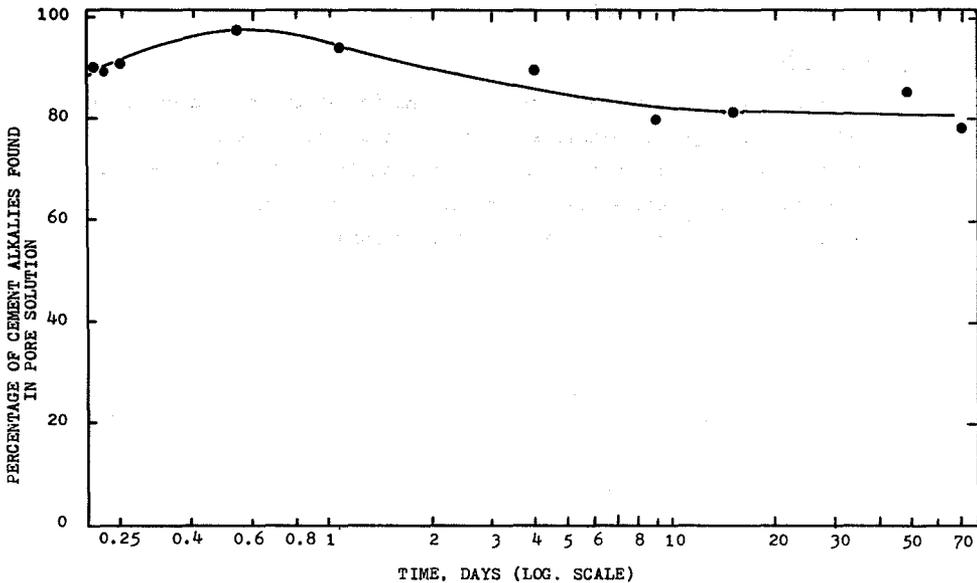


Fig. 1. Combined alkali contents of "blank" mortar pore solutions expressed as percentages of total alkalis present.

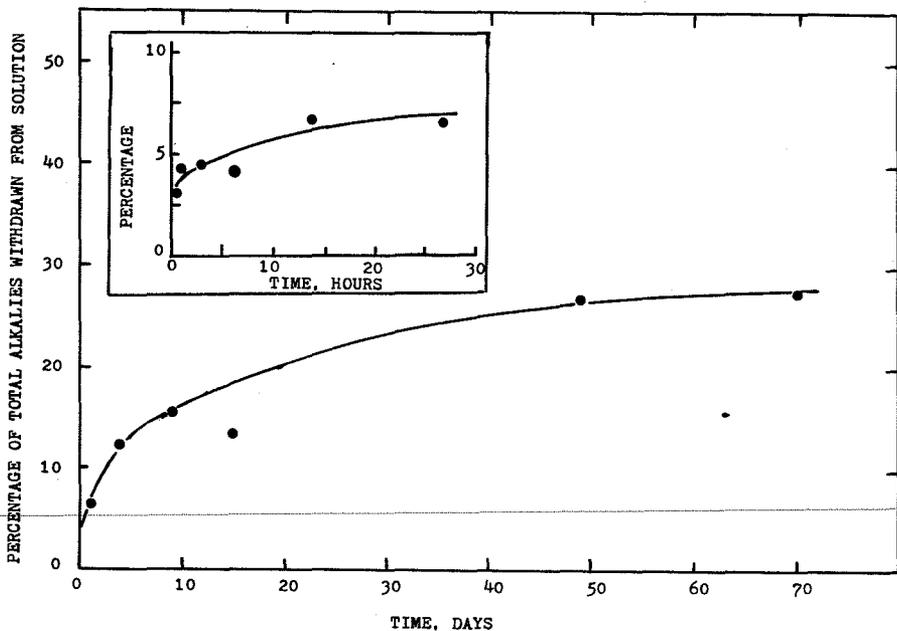


Fig. 2. Calculated percentage of the total alkalis that has been withdrawn from solution as alkali-silica reaction product.

CONTRIBUTION TO DISCUSSION

Dr. D. Hirche

A great problem is to get correct information about the ion exchange of Ca^{++} ions against alkalis in the reaction time. We know that this exchange occurs mainly on the outer surfaces of silica grains. Because of the great surface area (11000 approximately) of the tested opal we have to be careful on this point.