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1. ABSTRACT

Some of the recent progress in understanding the behavior of alkalis in concrete is reviewed and discussed. The conversion of alkali sulfate to alkali hydroxide in concrete pore solutions is detailed, and the long-term status of pore solutions illustrated. Reactions with aggregates and with finer particles of various mineral admixtures are considered, as is the influence of calcium on the reaction products. It appears to the writer that the demonstrated great ability of microsilica (silica fume) and perhaps of some slags to remove alkali hydroxide from the pore solution of concrete points the way to reliable prevention of future distress.

Key words: alkali-aggregate reactions, pore solutions, reaction products, silica fume

2. INTRODUCTION

The present introductory lecture is not designed as a formal review of the mechanisms and effects of alkalis in concrete, but rather as a highly specific series of illustrations of current progress in understanding these matters. The focus is on only a few important ideas rather than on broad coverage of the field.

The subject if not new, having been studied on an on-again, off-again basis since the original work of Staton in 1940 /1/. It is a fairly intractable subject for research, since the rate of formation and composition of the reaction product varies so much from place to place even within a particular concrete, as well as with concrete mix design, exposure conditions, and many other variables. Expansion measurements are often substituted for measurements of reaction, but these are not an adequate substitute and provide little insight into the ongoing chemical and physicochemical processes.

There are clearly a variety of alkali-aggregate reactions, rather than a single one. Much of the available information is focussed on reactions in which the susceptible aggregate is some form of disordered silica, most notable opal. But alkali-carbonate reactions are at least as complicated, Poole /2/ listing at least three separate and distinct types of such reactions. Occurrences with more complex rock types such as greywackes, hornfels, etc., are also attracting attention.

All of these have in common the fact that they represent, in the final analysis, responses of individual rock types to exposure to concrete pore solutions that are essentially concentrated alkali hydroxides. Thus the chemistry of the pore solutions provides a common element in all of these problems. In the writer's view it also provides the route to the most efficient and reliable solution of the practical problem of preventing distress in concrete. If the pore solution can be so manipulated as to prevent development of high concentrations of alkali hydroxides during the effective life of the structure, presumably none of the several varieties of alkali-aggregate attack can be expected to occur.

The present lecture thus is focussed on pore solution chemistry and on how

interactions with various substances in concrete may change it, for better or for worse.

3. PORE SOLUTIONS IN THE ABSENCE OF AGGREGATE REACTIONS

The chemistry of pore solutions developed in the absence of reactions with aggregates is important in understanding alkali reactions. It can be studied by expressing such pore solutions from hardened cement paste and quantitatively analyzing these solutions by normal chemical means. The techniques pioneered by Longuet and associates at CERILH /3/ and subsequently developed and applied to a variety of problems in the writer's laboratory are appropriate.

An illustration of the early evolution of the chemistry of the pore solution in what might be considered a typical high-alkali cement paste system is provided in Fig. 1, taken from a recent Ph. D. thesis completed in the writer's laboratory by Penko /4/. The portland cement used was an ASTM Type I cement with an alkali content of 0.91% Na₂O equivalent, with about 2/3 of the total being K₂O, and with 2/3 of both the K₂O and the Na₂O being immediately soluble. The pastes were prepared at a water:cement ratio of 0.50 (a normal concrete water:cement ratio) and were kept sealed to prevent moisture gain or loss.

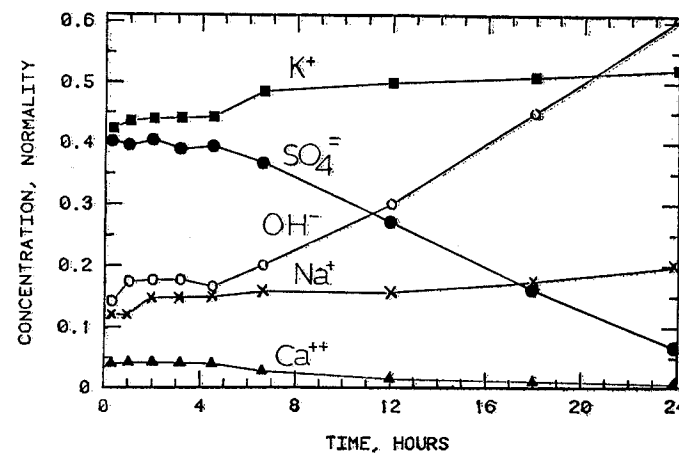


Fig. 1. Concentrations of Calcium, Sodium, Potassium, Sulfate and Hydroxyl Ions in Pore Solutions Expressed From Cement Pastes at Ages Up To 1 Day.

As is usually the case, the ions found in quantifiable amounts were the alkalis (sodium and potassium), calcium, OH⁻, and SO₄²⁻. Silicon, aluminum, and iron-bearing ions were not found in quantifiable amounts.

Calcium ion concentrations are initially on the order of 0.04N and relatively stable for the first few hours; they subsequently decline progressively to about 0.005N by the end of the first day. The alkalis are initially much more concentrated, the levels being about 0.42N for K⁺ and 0.13N for

Na⁺. In contrast with the decline of Ca⁺⁺ ion concentration, the alkali ion concentrations increase with time, first gradually for the first 5 hours or so, then somewhat more rapidly. By the end of the day the levels have reached 0.52N for K⁺ and 0.20N for Na⁺, for a combined alkali ion concentration of 0.72N. This is more than 140 times the Ca⁺⁺ ion concentration.

The anion concentration levels are of great interest. In these data, sulfate is immediately found to be at a very high level of concentration, 0.40N, much higher than that expected from the gypsum solubility product. This level is maintained for about five hours, followed by the start of precipitous decline. At the same time, the OH⁻ ion concentration, which has been reasonably stable at about 0.17N, starts a corresponding precipitous increase. The time at which these complementary responses begin reflect the time at which solid gypsum is exhausted; subsequent ettringite precipitation removes the sulfate from solution without the possibility of its replacement, and OH⁻ ions then are released to the solution to maintain the charge balance. At the end of the day the OH⁻ ion concentration has risen to over 0.60N, the SO₄²⁻ concentration has declined to less than 0.07N. Neither process is quite complete.

The level of SO₄²⁻ subsequently declines to essentially zero in most pastes, and the level of OH⁻ increases to balance that of the combined Na⁺ and K⁺ concentrations. Thus the pore solution is converted essentially to a concentrated alkali hydroxide solution containing little more than a trace (ca. 0.001N) of calcium ions, and much lower concentrations of silica. In the absence of moisture content changes and of reactions with other phases, the level of alkali hydroxide remains stable and reflects the alkali content of the cement and the cement content of the concrete.

An illustration of the long-term state of affairs is provided in the data of Table 1, taken from the thesis of R. S. Barneyback, Jr. /5/. These analyses were made on pore solutions expressed from mortars rather than cement pastes, but the same high-alkali cement was used in the previous illustration, and the same water:cement ratio of 0.50 was maintained. The sand was ASTM C 109 standard Ottawa sand and is essentially pure crystalline quartz in composition.

Table 1.
Analyses of Pore Solutions Expressed
From High-Alkali Cement Mortars

Age, Days	Concentration Equivalents/liter (N)				
	Ca ⁺⁺	Na ⁺	K ⁺	Na ⁺ + K ⁺	OH ⁻
15	0.001	0.22	0.55	0.77	0.73
49	0.002	0.24	0.59	0.83	0.77
70	0.000	0.22	0.57	0.79	0.75
149	0.002	0.23	0.60	0.83	0.80
585	0.000	0.24	0.58	0.82	0.78

It is possible to translate data of this kind to estimates of the mass of Na⁺ AND K⁺ in the pore solution per unit of cement mass. For this purpose the non-evaporable water is determined at each stage and subtracted from the total water per 100 g of cement to estimate the amount of solvent water remaining (in the absence of moisture content changes with the outside). In general the long-term content of alkalis in the pore solution tends to be

about 70 to 80 percent of the alkalis potentially available from the cement as determined from its total chemical analysis,

In practical concretes it is clear that the level of alkali hydroxide in the pore solutions will depend on a number of factors. Obviously, the alkali content of the cement used, the cement content of the concrete, and the amount of mix water used will be primary factors. If the cement has appreciable alkali in solid solution in belite, the completeness of cement hydration in the concrete may be important.

In addition to these "built-in" factors, environmental factors can play an appreciable modifying role. Concrete that dries up will develop high local concentrations of alkali hydroxides, but the residual fluid will be confined to discontinuous interstices within the capillary structure of the material, at least until the concrete is re-wetted. Since drying is usually non-uniform, the concentration of alkali hydroxide may be expected to vary from place to place in a large concrete structure.

Some concretes are relatively permeable, and especially if exposed to leaching conditions in relatively thin sections, may lose a significant portion of their included alkali hydroxide through mass transport in leaching water. This is especially severe for thin laboratory specimens exposed to fog room conditions as is done in many standard tests for alkali-aggregate induced expansion.

On the other hand concretes may develop increased alkali hydroxide concentrations resulting from incorporation of salt from exposure to salt water, salt spray, or salt added in winter to facilitate clearing highways and bridge decks of fallen snow.

So far only "plain" concretes free of reactive constituents have been considered. Obviously, incorporation within concrete of reactive mineral admixtures, i.e. materials like pozzolans, slag, flyashes, or silica fumes may influence the level of alkali hydroxide. They may contribute additional alkalis to supplement those present originally in the cement, or take part in reactions that remove alkali hydroxide from the pore solution and convert them to constituents of solid components. Alkali-bearing chemical admixtures may also contribute to the alkali burden of the pore solution. Certain alkali-bearing aggregate components (feldspars, etc.) may also break down to liberate alkalis to the pore solution.

It is useful for many purposes to be able to estimate the concentration of alkali hydroxide to be expected. In the absence of severe drying or other special circumstances, the pore solution alkali hydroxide concentrations may be expected to vary from about 0.35N for a low alkali cement-bearing concrete of low cement content, to something over 1.0N for a rich concrete made with a high alkali cement at a low water content. Drying may cause portions of concretes to develop local concentrations higher than these. These numbers are to be contrasted with expected calcium hydroxide levels of the order of 0.001N.

4. CALCIUM CONTENT AND NATURE OF ALKALI-SILICA REACTION PRODUCTS

Many years ago Powers and Steinour /6/ hypothesized that alkali reaction products incorporating calcium would tend to be "safe", i.e. non-expanding gels, while products lacking appreciable contents of calcium would be expanding. Research on synthetic gels /7,8/ has indicated that this is an oversimplification; gels lacking calcium vary tremendously in free swelling ability and in ability to expand against restraint, while tested gels with appreciable calcium contents were shown to be swelling in nature. Furthermore, energy-dispersive x-ray and electron probe analyses of expanding gels by various workers indicate the universal presence of calcium as

well as of alkalis in these materials.

The source of the calcium incorporated in these reaction products is not immediately obvious, in view of the very low calcium contents detectable in concrete pore solutions.

Arguments have thus been advanced that the original source of the calcium found incorporated in reaction product gels derive from calcium hydroxide and even C-S-H gel crystals in the vicinity of the alkali-aggregate reaction site. Indeed, it is commonly reported that petrographic examination discloses the diminution or near-disappearance of calcium hydroxide crystals from the vicinity of reacting aggregates. However it is difficult to distinguish whether the gels acquire calcium from diffusion of calcium into the reaction product, or from dissolution of calcium by alkali silica sols moving outward from the site. Regourd et al. /9/ in their electron probe microanalysis of two reacting concretes found that gel near the original reacting aggregates has much lower calcium contents (ca. 15 to 20% as CaO) than gels found in pockets within the cement paste away from the reaction sites (ca. 35 to 40% as CaO). They hypothesized that in the first case the calcium was derived from inward diffusion of calcium released from surrounding lime and C-S-H crystals by alkali silica sol, and that the latter case represented the result of extensive transport of sol through the matrix of lime and C-S-H gel, picking up additional CaO as it impregnated the pre-existing cement paste structure.

A point perhaps worth mentioning in connection with the dissolution of calcium from cement paste constituents by the alkali silica sol has to do with the reason for this "aggressive" /9/ or, according to some authors, "corrosive" nature of the sol. It appears to the writer that this terminology may be misleading, in that it implies a specific chemical attack on the C-S-H gel and calcium hydroxide phases. The attack may simply lie in the less alkaline character of the alkali silica sol, i.e. in pH levels lower than those of the pore solutions normally encountered. The pH range for commercial potassium silicate solutions listed by Weldes and Lange /10/ is only 11.3 to 12.1; for sodium silicate solutions 10.8 to 12.8. These are far below the 13.5 or more calculated for the alkali hydroxide pore solutions normally present in concrete made from high alkali cements, and generally below the level of pure saturated calcium hydroxide (12.45). Thus the alkali silica sol, once formed locally by reaction with the reactive aggregate, may simply cause calcium hydroxide to be locally dissolved in response to the drop in pH and the common ion effect. The calcium is then free to diffuse inward toward the reacting site.

That Ca^{++} ions may diffuse inward into reacting opal grains along with alkali ions has been illustrated by Diamond et al. /11/ in experiments where macroscopic opal cylinders (1 cm. diameter) were immersed into solutions of alkali and calcium hydroxides. Calcium in modest amounts was shown to penetrate about 100 μm into the opal core in 21 days, accompanying the more extensive and faster penetration of alkali (K^+) ions. Here there was little prospect of release of calcium from external C-S-H gel and lime crystals, since the surrounding matrix was a solution of 1N. KOH and free $\text{Ca}(\text{OH})_2$ suspended the pores of an unreactive quartz sand. The solution concentration of $\text{Ca}(\text{OH})_2$, while not measured, was undoubtedly low (on the order of 0.001N), and the $\text{Ca}(\text{OH})_2$ crystals were likely not in close contact with the periphery of the opal.

Recently Kawamura et al. /12/ studied the intrusion of alkalis and of calcium in Beltane opal grains embedded in reacting mortars and confirmed the rapid penetration of alkalis and the somewhat delayed penetration of calcium into the reacting opal grains. Calcium penetration was slow for the first 7 days, but then movement of calcium speeded up and the amount of

calcium moving in after about 14 days was much increased. Coincident with this increase the softened zone detected by microhardness measurements moved inward, but a rim of somewhat harder material started to form around the periphery of the larger opal grains.

In ordinary concretes one would expect the existence of a thin-layer of calcium hydroxide and C-S-H gel in the form of a duplex film /13/ deposited around the surfaces of most aggregate particles. Such a film may be the immediate source of calcium taking part in the earliest portions of the alkali-silica reaction processes.

It has generally been considered that gels resulting from alkali-aggregate reaction were to be thought of as entirely amorphous materials with no fixed chemical composition and certainly no long-range crystalline order. One exception was the crystalline component with an x-ray diffraction peak at 8.6 Å detected some years ago by Buck and Mather /14/ and attributed to an alkali-bearing tricalcium silicate hydrate analogue. At the previous Alkali Conference held in 1981, Regourd et al. /9/ reported the occurrence of a white deposit having a major x-ray peak at 12.3 Å in a concrete containing hornfels aggregate that had been subject to alkali aggregate attack while being maintained at 40° C for a year. More recently a similar phase has been repeatedly detected by van Aardt and Visser /15/ in reacting systems treated at high temperatures (80° C) in the presence of high alkali hydroxide concentrations (ca. 1N or greater). X-ray peaks at 12.6 Å and 3.06 Å have been attributed to a compound of composition $0.25\text{Na}_2\text{O} \cdot 0.8-1.0\text{CaO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$. A second compound with a major spacing at about 16 Å and a composition of $0.33\text{Na}_2\text{O} \cdot 0.67\text{CaO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$ was also reported.

The relevance of these crystalline compounds formed at elevated temperatures to reaction product gel produced in concrete at ordinary temperature was at first not clear. However, subsequently van Aardt and Visser /16/ have reported the formation of the 12.6 Å compound (albeit in poorly crystalline form) in portland cement reacted in 2N NaOH at 22° C for approximately two months. Presumably the silica in this case was derived from the cement itself, rather than from a reactive aggregate. Nevertheless, if this finding is confirmed, the implication is that the normal expanding alkali calcium silica gel in ordinary alkali-silica attack at ambient temperatures may be looked on as an extremely disordered form of the crystalline compound responsible for the 12.6 Å peak. Looked on in this fashion, it is less surprising that almost all reaction product gels whose composition has been examined and reported in the literature have appreciable proportions of calcium present.

5. PORE SOLUTIONS IN THE PRESENCE OF ALKALI SILICA REACTIONS

Pore solutions expressed from mortars undergoing active alkali silica reaction have been analyzed in the writer's laboratory for a number of years. While the specimens used are kept in sealed containers and thus do not necessarily expand at the same rate as mortars exposed to the traditional 100% RH test environment, it has been shown that significant expansions do indeed take place under such conditions /11/.

As indicated previously pore solutions expressed from reacting mortars show significantly reduced concentrations of alkali and hydroxyl ions as compared to companion mortars that are identical except for the absence of reactive aggregate. The reduction is attributed to formation of reaction products which are not mobilized in the pressure expression process used to recover the pore solution. The stoichiometric balance between the alkali ion and the hydroxyl ion concentrations is maintained in the pore solution. Silica is not detected in appreciable concentration, even though locally within the mortar alkali silica sols may be mobile during the reaction

processes. Failure to recover mobile silica may be due in part to the fact that in the absence of a source of external water, i.e. a 100% RH environment, the reaction product tends to be retained in gel form rather than in sol form. Also it may be that the mortar itself may exert a filtering effect on the solutions being expressed through it, with any fluid alkali silica sol being filtered out before the expressed solution emerges. At any rate the solutions recovered are clear and transparent, and only the lowered content of alkali and hydroxyl ions provide indication that the alkali silica reactions are taking place.

The degree of lowering of the alkali and hydroxyl ion concentrations, and the residual level of these concentrations after a steady state has been established naturally vary with the particular system. However, a mortar such as that of Table 1 which contains a near-pessimum amount of Beltane opal in sand sizes (8% by weight of sand or 16% by weight of cement) reduces the concentration of alkali hydroxide from about 0.80N to about 0.35N before reaching essentially steady-state concentration /5/.

6. INFLUENCE OF POZZOLANS, FLY ASH, SLAG, AND SILICA FUME ON ALKALI HYDROXIDE CONCENTRATION LEVELS

Almost since the beginning of investigations on alkali aggregate reactions it has been considered that incorporation of a finely-divided reactive siliceous mineral admixture would be beneficial in reducing the expansion and the distress that would otherwise occur in concrete subject to alkali aggregate attack. It has also been understood that such materials vary widely in effectiveness, and empirical test procedures, such as that of ASTM C 441, have been established for the purpose of qualifying mineral admixtures considered for such use.

Recently there has been a great expansion of interest and activity relating to the use of fly ash, slag, and silica fume in concrete, as attested by a spate of recent international conferences and separately-published reports. The influence of such incorporations on the potential for alkali-aggregate reactions is of considerable interest.

In general it has been assumed that pozzolans and other mineral admixtures reduce the potential for alkali aggregate distress in concrete primarily by their ability to react with the alkalis in the pore solution more quickly than the larger sand-size or coarse-aggregate size reactive aggregates. It is usually considered that the reaction products produced by such reaction are themselves innocuous with respect to causing expansive effects. Thus the mineral admixture pre-empts the alkali hydroxide that would otherwise produce expansive reaction product with the coarser reactive aggregate.

Such a mechanism implies that addition of the mineral admixture results in reducing the alkali hydroxide concentration levels. This may not necessarily occur. Many flyashes and slags contain appreciable percentages of Na_2O and K_2O , and in principal at least, reaction of the glass containing these alkalis could result in augmentation, rather than decrease, of the alkali level in the pore solution. Flyashes may additionally bear readily-soluble coatings of alkali sulfates and occasionally carbonates, the latter stemming from precipitator aids sometimes used to facilitate the effectiveness of electrostatic precipitators in collecting the flyash. These also may augment the alkali hydroxide levels.

It is certainly possible to prepare mortars or pastes containing the specific mineral admixtures under consideration, and after suitable periods of time, express and analyze the pore solutions for comparison with mortars lacking these materials. Thus a definite numerical measure of the effectiveness of the material in reducing alkali hydroxide concentrations can be provided.

A number of such comparisons have been carried out in the writer's laboratory in recent years. Barneyback /5/ for example, found that a commercial finely-ground pozzolan of volcanic origin in widespread use in the southwest US lowered the alkali hydroxide content of the pore solution of mortars like those of Table 1 only to about 0.66N if 10% (by weight of aggregate) was used. If 25% was used a much more effective reduction to about 0.33N occurred.

Several years ago the present writer /17/ published the results of experiments carried out with two Danish flyashes, both of which were low-calcium flyashes compatible with the ASTM Class F designation, used with a Danish cement of relatively modest alkali content (0.7% Na₂O equivalent). Although both flyashes had appreciable alkali contents (2.4 and 3.3% Na₂O equivalent) it was found that neither contributed to the alkali burden of the pore solution; in fact the long-term alkali hydroxide concentration level was found in both cases to be that expected in the absence of any reaction with the pore solution whatsoever, the flyashes seeming to act as inert diluents.

That this is not the case with all flyashes has been illustrated in results secured by Lopez-Flores in the writer's laboratory /18/. Table 2 provides data on the hydroxyl ion concentrations of pore solutions expressed from a portland cement paste (w:c 0.50, cement Na₂O equiv. 0.6%) and two flyash-bearing pastes of the same water:solids content but with 30% of the portland cement replaced by an equal weight of flyash. The examples illustrated are extremes from a set of five different flyashes examined. Flyash C is a high-calcium flyash with a high content of sodium and of sulfate, while flyash D is low-calcium flyash of a relatively high potassium content.

Table 2.
Measured OH⁻ Ion Concentrations of Expressed
Pore Solutions (Equivalents/liter)

Age, Days	Portland Cement Paste	Paste With Flyash D	Paste With Flyash C
1	0.35	0.26	0.68
7	0.43	0.31	0.83
28	0.45	0.28	0.98
90	0.43	0.27	1.04
180	0.41	0.24	0.99

It is evident that incorporation of 30% of flyash D has lowered the alkali burden significantly as compared to that of the portland cement paste; the reduction is somewhat more than would be expected if the flyash were merely acting as an inert diluent, although the marginal effect is relatively small. On the other hand, Flyash C has more than doubled the alkali burden, bringing the long-term hydroxyl ion concentration to 1N, equivalent to a concentration-defined pH of 14. Use of such a flyash would severely increase the likelihood of alkali-aggregate distress in concrete containing any susceptible aggregate. Thus the effect of flyash cannot be assumed to be favorable toward the prevention or mitigation of alkali-related distress, even when large percentages are employed. Flyashes such as flyash C are not uncommon in commercial use, at least in the United States, and of course should be avoided if reactive aggregates are suspected.

Granulated blast furnace slag often contains alkalis, but these do not

appear to contribute to alkali-aggregate distress; in German practice, concretes containing such slags are permitted to have a higher total alkali content than ordinary concretes. The beneficial effects of slag were attributed by Bakker /19/ to reduced alkali ion diffusivity and reduced water permeability in the hydrated slag-cement paste system, rather than to reaction of the slag glass with the pore solution. While direct comparisons of effects of adding slag to cement on pore solution alkalinity of the type illustrated in Table 2 have not been made to the knowledge of the writer, there is indirect evidence available from the results of Longuet et al. /3/. These workers expressed pore solutions from three different portland cement pastes and a slag-cement paste ("CLK"). The former gave OH⁻ ion concentrations ranging from 0.5 to 0.7N after a year; the latter only developed concentrations of the order of 0.13N, suggesting at least the possibility of active reaction of the slag with alkali hydroxides liberated by the cement.

Somewhat beyond the effects produced by the materials so far mentioned is the effect produced by microsilica (silica fume). Recent studies by the present writer /20/ and independently by Page and Vennesland /21/ have shown that this material possesses a remarkable ability to quickly react with and remove alkali hydroxides from cement paste pore solutions, to an extent not achieved by other materials of this nature.

An illustration of the effects produced by even small contents of this active material is provided in Fig. 2, taken from /20/. Fig. 2A shows the concentrations of K⁺ ions found in pore solutions expressed from a moderate alkali portland cement paste (w:c 0.50) and from companion pastes containing 5, 10, and 20% replacements of cement by microsilica. Fig. 2B shows the concentrations of OH⁻ ions determined in the same pastes.

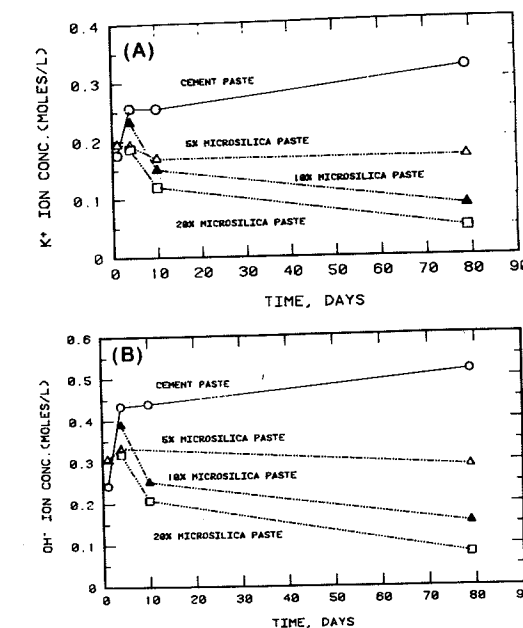


Fig. 2. Concentrations of (A) K⁺ ions and (B) OH⁻ ions found in pore solutions expressed from cement paste and microsilica-bearing pastes at ages up to 79 days.

As expected, the K^+ ion concentration for a given series parallels, and is somewhat less than, the OH^- ion concentration, the difference in each case being approximately the amount of Na^+ in solution. At 79 days the cement paste has an OH^- ion concentration in excess of 0.5N; replacement of only 5% of the cement by an equal weight of microsilica has dropped this level to only 0.3N. A 10% replacement halved this level, and a 20% replacement brought the OH^- ion concentration down to less than 0.1N, i.e. less than 1/5th that of the cement paste. A replacement level of 30% was found to reduce the OH^- ion concentration to 0.016N by 145 days, more than an order of magnitude less than that of the portland cement paste, and indeed less than that corresponding to the pH 12.45 level associated with pure saturated calcium hydroxide.

Substantially similar results were reported by Page and Vennesland /21/. The present writer believes that these results merit close attention with respect to the potential use of microsilica in the prevention of alkali distress in concrete.

7. DISCUSSION

For many years it has been the goal of researchers in alkali-aggregate reaction studies to understand the mechanism of the reaction sufficiently well that an efficient preventative method might be found and recommended for general use.

It appears to the writer that we are nearing that goal.

The argument rests on the simple proposition that there must be some limiting minimum alkali hydroxide concentration developed in concrete pore solutions to initiate and sustain the several alkali-aggregate reactions. It seems that this threshold concentration could readily be established by experiments aimed specifically at its determination. The present writer would be very much surprised if it were less than about 0.25N, a concentration corresponding to a concentration-defined pH of about 13.4.

Judging from the results of Longuet et al. /3/ portland blast-furnace slag cements of high slag content may produce pore solution alkali hydroxide concentrations of the order of 0.13N, comfortably lower than the postulated threshold. Unless additional alkali were provided by the aggregate itself or by other outside sources, it would seem that there is a considerable margin for safety in the use of such materials.

Even more important and exciting in this context is the surprising effect of quite modest dosages of microsilica (silica fume) in sweeping out nearly all of the alkali hydroxides from pore solutions. The speed and completeness with which this apparently can be accomplished is quite remarkable. Apparently the level can readily be reduced, not only to comfortably below the postulated threshold of 0.25N, to values less than 0.02N, more than an order of magnitude lower, if 30% of microsilica is used. While this is perhaps too much for most concretes, treatments of the order of 10% microsilica would be expected to provide reliable protection.

That this is so seems to be confirmed by the practical results obtained in Iceland. According to Asgeirsson /22/ very severe alkali-aggregate problems have been encountered in concrete houses built in Iceland using Icelandic cements which contain exceedingly high alkali contents. Asgeirsson indicated that "Since the Purdue meeting (September 1978) we have resorted entirely to the use of pozzolan or fumed silica condensate blended cements... This appears not to cause any difficulty if cement is replaced by 5% of fumed silica condensate as is now general practice, though a 7% replacement is aimed at. The use of fumed silica condensate from a ferro-silicon plant has provided definite relief for the concrete industry in this

country, since it both cures alkali silica expansion and improves cement strength."

Whether the availability of microsilica and its cost will in the future be such as to support widespread usage as an alkali-aggregate preventative treatment remains to be seen.

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APPLICATION OF QUANTITATIVE EDXA ANALYSES AND MICROHARDNESS MEASUREMENTS
TO THE STUDY OF ALKALI-SILICA REACTION MECHANISMS

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ABSTRACT

The combination of the chemical compositions at a spot in the reacting particle obtained by SEM-EDXA analysis and the microhardness measured at the same spot has a possibility of giving us some informations on the relationship between the progressive inward chemical reaction and the changes in rigidity within the reacting particle. Quantitative EDXA analyses were carried out by using the calibration curves prepared from a series of synthetic sodium-silica, potassium-silica and calcium-sodium-silica gels. The chemical and physico-chemical processes progressing within the reacting opal particles were correlated with the expansion of the corresponding mortar bars made with an opal aggregate. The reactive opal particles embedded in cement paste were found to soften in the vicinity of their periphery with a rapid increase of the alkalies concentration in the region at early ages. The changes in microhardness of the affected portions in the reacting particles brought about by drying also gave us some informations concerning the intrusion of water into the reacting opal particles with time. The EDXA analyses showed that a relatively great amount of calcium moved into the reacting opal particles. An indication that the movement of calcium into the opal particles was always behind the intrusion of the alkalies was also obtained. Explanations for the dependence of expansion on the particle size of the reactive aggregate and for the prevention of the expansion due to alkali-silica reactions by the addition of a fly ash were provided on the basis of the results obtained by the quantitative EDXA analyses. Key Words: EDXA analysis; Microhardness; Expansion; Fly Ash.

1. INTRODUCTION

In relation to the elucidation of alkali-silica reaction mechanisms, usefulness of the application of SEM and EDXA analysis to direct examinations of the progressive inward chemical reaction in a reacting aggregate in concrete has been pointed out by Diamond /1/. Thereafter, a few reports concerning the informations of local chemical compositions in reacting grains in concrete have been presented /2, 3, 4, 5/. On the other hand, there seems to be no research clarifying the local physical changes caused by the intrusion of Na^+ , K^+ , Ca^{++} , OH^- and water into reacting aggregate particles in concrete. A useful technique available for obtaining the informations regarding the mechanical changes of the reacting particles is microhardness test. A combination of the chemical compositions at a spot in the reacting particle obtained by SEM-EDXA analysis and the microhardness measured at the same spot has a possibility of giving us some informations on the relationship between the progressive inward chemical reactions and the changes in rigidity within the reacting particles. In this paper, some explanations for the dependence of expansion on particle size as well as for the mechanisms responsible for the reduction or prevention of deleterious alkali-silica expansion by the addition of fly ash are provided on the basis of the results obtained by the quantitative EDXA analyses being supplemented by the characteristics of microhardness within the particles.