

ALKALI SILICA REACTIONS - SOME PARADOXES

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ABSTRACT

This paper provides an exposition of several special chemically-related areas of ASR that have been actively investigated in the past few years. It was found that (a) addition of alkali hydroxide to cement to simulate cement of higher alkali contents in laboratory studies has unexpected consequences that may jeopardize the validity of interpretations made, (b) that partial drying of concrete may cause practically irreversible fixation of the alkali hydroxide in the pore solution, an effect which would appear to render further ASR problematical for a long time even if the concrete is again wetted, (c) that silica fume with coarse particles or undispersed agglomerates can induce, rather than prevent ASR distress in certain instances, and (d) that lithium-based treatments for ASR commonly result in lithium being retained in the pore solution as lithium hydroxide; the addition to hydroxide concentration over that produced by cement alkalis may pose an augmented challenge to any reactive aggregates in the concrete. It was also indicated that some treatments may induce long-term retention of sulfate ions in the pore solution, posing a risk for possible delayed ettringite formation.

INTRODUCTION

Research on alkali aggregate reaction problems continues at a substantial rate, as does the pace of additions to technical literature. Several years ago the writer compiled an annotated bibliography of papers on alkali silica reaction (Diamond, 1992). Approximately 1300 papers were found to have been published between 1939 and 1991 that were pertinent enough to be included. ASR papers published since 1991 surely number many hundreds.

While some observers suggest that this extensive research effort is not really justified by the magnitude of the ASR problem, the present writer demurs. It seems to him that there has recently been enhanced awareness of ASR problems in the general concrete community and a growing appreciation of the magnitude of the economic losses being engendered. Along with this increased awareness of the challenge posed by ASR, there is a corresponding need for a better appreciation of the complexities of the problem.

It is well understood that ASR distress is consequent on the effects of the ASR reaction, which is fundamentally a reaction between OH^- ions in the pore solution and the reactive aggregate components. However, the complexities of the reaction, and especially of the factors governing the OH^- ion concentration in the pore solution under various circumstances are not very well appreciated.

The present paper is aimed at providing some insights into the complexities of these responses, based on information developed during the course of our research over the last three or four years.

All of the examples chosen display elements of paradox of one kind or another. These paradoxical aspects have been emphasized to make the point that chemical responses in concrete are complicated. Easy assumptions often made turn out to be not correct, and at times can be seriously misleading.

PARADOX: ADDING SODIUM HYDROXIDE TO RAISE THE ALKALI LEVEL OF CEMENTS RAISES THE SULFATE LEVEL OF THE PORE SOLUTION INSTEAD OF THE HYDROXIDE LEVEL

Researchers investigating the effects of varying the cement alkali content on specific manifestations of the ASR response in the laboratory have generally used one of two alternatives. One is to assemble a suite of cements of varying alkali content, and accept the fact that the cements will vary in many respects other than the desired variation in alkali content. This approach was used, for example by Struble and Diamond (1985). Alternatively, it has been popular and accepted practice to select a base cement, often of relatively low alkali content, and enhance its alkali content in progressively increasing steps by pre-dissolving increasing amounts of sodium or potassium hydroxide in the mix water. This option has the perceived advantage of permitting comparisons of the effects of increasing alkali contents without the complications associated with concomitant variations in other characteristics of the cement. This alternative has been followed by, for example, Poole et al. (1986), Shayan et al. (1986) and Yamamoto et al. (1986).

The validity of this alternative is assumed to be based on the well-established fact that cement alkalis eventually appear in the pore solution as alkali hydroxide. Thus it is assumed that adding the alkali directly as the hydroxide would not change things materially.

It appears that this assumption is in error. Paradoxical as it seems, laboratory investigation has shown that if sodium hydroxide is dissolved in the mix water prior to the addition of the cement, when the cement is added, instead of an increase a precipitous reduction takes place in the OH^- ion concentration (Ong and Diamond, 1993).

A series of experiments were carried out with w:c 0.485 pastes made with a Type I portland cement. The particular cement used had a high alkali content (1.14% Na_2O equiv.) and only a moderate sulfate content (2.8% SO_3). One series of pastes was prepared without additional alkali; a second series of pastes was prepared from the same components, but with NaOH equivalent to 1% Na_2O in cement pre-dissolved in the mix water. Hydration was allowed to take place and the mix or pore solutions were filtered or expressed at intervals and analyzed in the usual manner.

The expectation would be that both alkali ion and OH^- ion concentrations usually produced by the cement alkalis would be augmented by the concentrations of Na^+ and OH^- ions already dissolved in the mix water.

Immediately prior to mixing the OH^- ion concentration in the mix water containing dissolved NaOH was 0.67N. Immediately after mixing (that is, by the time of the first determination at 10 minutes from the start of mixing), the OH^- ion concentration had dropped to about 0.32N, i.e. adding the cement (and mixing) had caused the OH^- ion concentration to be cut in half. The resulting alkalinity in terms of OH^- ion concentration was actually only a little greater than that of the solution in the paste without added NaOH.

On the other hand, the expected concentration of Na^+ ions was found in the pore solution of the NaOH-doped cement.

A comparison of further determinations of OH^- ion concentrations over the first 24 hours is given in Fig. 1. It displays three separate OH^- ion concentration curves. The curve marked by open squares indicates the OH^- ion concentration pattern over time for the control paste without NaOH treatment. The curve marked by filled circles is the "expected concentration" curve, i.e. the sum of the OH^- ion concentration actually found in the control paste at each age and the 0.67N OH^- ion concentration of the NaOH-doped mix water. The curve marked by filled squares represents the actual OH^- ion concentrations found over time in the NaOH-treated paste.

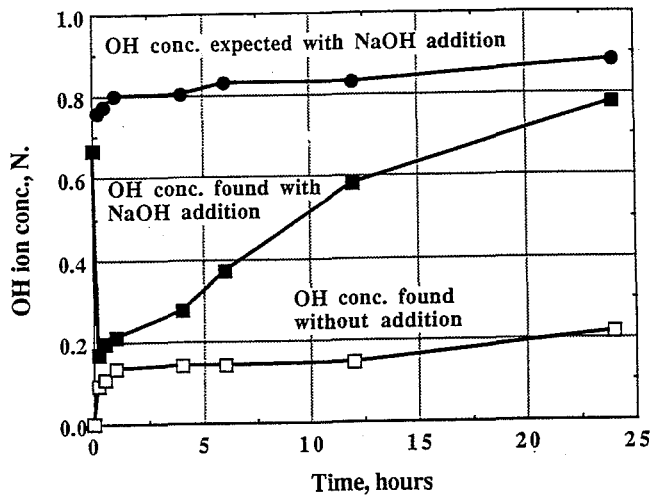


Fig. 1. Comparison of the OH^- ion concentrations of NaOH-doped and untreated cement pastes found over the first day of hydration. The closed circles represent the sums of the concentrations present without NaOH addition and the initial NaOH concentration of the mix water.

As mentioned, the first OH^- concentration found in the treated paste represents a major reduction from the OH^- ion concentration of the mix water. Subsequently the OH^- ion concentration in the treated paste increased with time, but it did not reach the "expected" concentration level in the 1-day period plotted in Fig. 1. Nor did it do so subsequently in the six-month hydration period examined.

If, as stated earlier, the added Na^+ ions remained in solution, how were the additional cationic charges balanced? The answer is evident from Fig. 2.

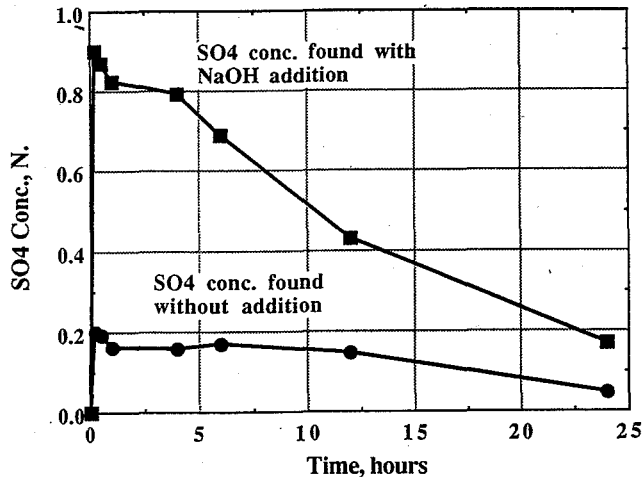
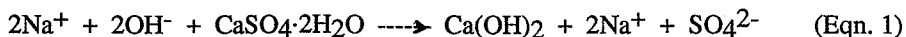


Fig. 2. Comparison of the SO_4^{2-} ion concentrations of NaOH-doped and untreated cement pastes found over the first day of hydration.

In Fig. 2 I have plotted the SO_4^{2-} ion concentrations found for the NaOH-treated and for the control pastes. It is evident that the addition of the NaOH has resulted in an immediate boost in the concentration of SO_4^{2-} ions, rather than the expected boost in the concentration of OH^- ions.

It has been shown (Ong and Diamond, 1993) that these responses are due to an almost immediate reaction between the dissolved sodium hydroxide and the gypsum (or hemihydrate) of the cement. The reaction results in dissolution of the gypsum and precipitation of calcium hydroxide, according to the equation:



If the number of moles of NaOH added is less than the number of moles of gypsum present in the particular cement used, all of the added NaOH may be converted to the equivalent amount of dissolved Na_2SO_4 . If the alkali hydroxide dose exceeds the gypsum content in molar terms, the excess NaOH would remain in solution as the hydroxide.

There are both short-term and long-term consequences of this response.

One short term consequence is that the hydrating cement undergoes its early hydration in a solution that is much different than normal, in particular, one with a very high concentration of sodium ions. Despite the accompanying higher concentration of dissolved sulfate, it appears that the rate of ettringite formation is much reduced. In the experiment described above, the ettringite content at the end of the first day in the *untreated* paste (determined by DSC) corresponded stoichiometrically to about 90% of the total sulfate present; only a little sulfate remained in the pore solution. In contrast, in the *NaOH-treated paste*, the 1-day ettringite content corresponded to only a little over 30% of the total sulfate. Another 25% was found in the pore solution. No monosulfate was detected by DSC, and the "missing" SO_3 was apparently deposited within the calcium silicate hydrate of the hydrated cement paste.

The longer term consequences are complicated as well. In the normal hydration sequence in cement pastes, alkali sulfate brought into the pore solution from the cement is converted to alkali hydroxide as sulfate is withdrawn from solution by ettringite formation. This process is usually completed by the end of the first day. Alkali sulfate produced by the gypsum dissolution reaction of Eqn. 1, could be similarly converted back to alkali hydroxide, to the extent that ettringite is formed. However, it appears this reconversion process is limited. We have examined several different cement pastes, and in all of them significant contents of SO_4^{2-} ions remain in the pore solution indefinitely. It also appears that some of the sulfate is indefinitely sequestered by the CSH.

This means that the full expected effect of the adding alkali hydroxide on ASR initiation is not felt, even after an indefinite period. It also means that delayed ettringite formation may come about (Diamond and Ong, 1994), being fed both from sulfate in the pore solution and sulfate feeding to it from within the CSH. DEF itself can lead to expansion which may be mistaken for ASR-induced expansions, or expansion due to the two causes acting conjointly may come about.

To understand the response in a given case, attention must be paid to factors such as the sulfate content and the form of sulfate present in the particular cement, and to its C_3A content; and the degree to which the C_3A is available early in the hydration process. These parameters are not normally taken into account in ASR studies.

Thus the apparent paradox associated with the observed immediate drop in OH^- ion concentration when cement is added to alkali hydroxide - doped mix water has a satisfactory explanation. However both short and long-term consequences of such treatment lead to unexpected complications. It does not seem to be a good way to simulate the effect on ASR of having a higher alkali cement.

PARADOX : PARTIAL DRYING REDUCES, RATHER THAN INCREASES, PORE SOLUTION CONCENTRATION OF ALKALI HYDROXIDES

Early in our research on ASR it became evident that the formation of ASR gel involves a depletion of the alkali and of the OH^- ion concentrations of the pore solution as the alkali and OH^- ions are incorporated into the ASR reaction product gel (Diamond and Barneyback, 1976).

There is a general relationship between the long-term level of alkali hydroxide to be expected in concrete pore solutions and the alkali content of the cement, in the absence of perturbing factors (Diamond, 1989). The expected concentration (of either OH^- or alkali ions) is about 0.7N per percent Na_2O equiv. in the cement, at w:c 0.5.

Naturally, this concentration is reduced by any ASR reaction that takes place.

It is certainly possible to express and analyze pore solutions from field concrete.

One might suppose that if a much lower than expected concentration is found, this fact might provide an indication that ASR is occurring in that particular concrete. Furthermore, the extent of depletion might be serve as an index of the amount of reaction that has taken place.

In the author's experience, this generalization seems to be valid for pore solutions expressed from cores taken from wet concrete that have been maintained in the wet state prior to expression.

There is a second expectation that might be mentioned. Concrete pore solutions are primarily solutions of potassium and sodium hydroxides. Both extremely soluble substances. Accordingly, it is reasonable to suppose that when concrete starts to dry out, the concentrations of these dissolved substances in the remaining pore solution necessarily increases, but that nothing is precipitated. It is also reasonable to suppose that on rewetting, the concentrations should return to their original levels, assuming that the amount of water lost on drying is replaced by an identical amount of water on rewetting.

It is usually not possible to express pore solutions from field concrete that has dried out. However, various means can be used for re-wetting such concrete to permit expression of pore solution.

In our experience, this may be done most expeditiously by a vacuum saturation method such as is used to saturate concrete specimens for the well-known "rapid chloride permeability" test. (ASTM C 1202). The procedure results in essentially complete resaturation of dry concrete in a few hours.

However, paradoxically, the writer has found that pore solution expressed from such re-saturated concrete typically show very low alkali hydroxide concentrations. In extreme cases alkali hydroxide concentrations of the order of only 0.1N to 0.2N were found, rather than the expected levels of 0.5 to 0.7N. This was true even after correction had been made for alkali hydroxide lost to the reservoir water in the vacuum saturation process.

Most of the concretes so examined showed no obvious symptoms of ASR reaction. Accordingly, the low content of alkali hydroxide found in the pore solution did not seem to be caused by the transfer of alkali hydroxide to ASR reaction products.

Rather, some (or most) of the solute appears to be "fixed" by the drying process and will not re-dissolve when the replacement water is introduced into the concrete by vacuum saturation.

The paradox here is that when concrete dries out the dissolved alkali hydroxide does not increase in concentration in the remaining pore solution; rather it appears to decrease substantially.

Detailed investigations into these phenomena were carried out at Purdue University (Constantiner, 1994). It was determined that a similar alkali hydroxide fixation effect takes place on drying with cement paste, so that the effect is not induced by possible reaction with aggregate. It does, however, influence the possibility of ASR after the fixation has occurred.

Comparative studies were carried out of the fixation effect resulting from drying in a slowly moving air stream controlled at 42% RH, and drying in a similar stream of high purity nitrogen gas, the latter treatment being essentially free of the possibility of carbon dioxide effects. As indicated in Table 1, it was found that fixation is much reduced in the absence of the carbon dioxide of the air.

Table 1.
Sum of the Concentrations of Na and K Ions (N.) In Pore Solutions
Expressed From Various Cement Pastes

Cement	Continuously sealed	Dried in air, then vacuum saturated	Dried in N ₂ , then vacuum saturated
A	0.46	0.25	0.43
B	0.57	0.27	0.51
C	0.80	0.46	0.69
D	1.01	0.55	0.84
E	0.97	0.43	0.70

The pastes listed in Table 1 were allowed to equilibrate in sealed storage for approximately one week after the vacuum resaturation. Corrections were made for the alkali lost to the vacuum saturating water, and for the slight difference between the water content of the continuously sealed specimens and the slightly higher water content of the vacuum saturated specimens.

It is apparent from Table 1 that the fixation effect is enhanced by or is somehow associated with carbonation. However, alkali hydroxide fixation on drying does not require the degree of carbonation that is necessary to produce a color change in the usual phenolphthalein test. The pore solutions recovered after resaturation are still highly alkaline, even though of somewhat reduced pH. Furthermore, the OH⁻ ion concentrations found were in balance with the alkali cation concentrations.

Long term re-equilibration under saturated conditions after vacuum saturation eventually produces a partial return of some of the "fixed" alkali hydroxide to solution. Recoveries of the order of 10 to 20 % of the amount fixed were observed following post-saturation equilibration periods of about 4 months in sealed storage.

The possible consequences of this fixation effect with respect to ASR is obviously of interest. Usually only near-surface layers of field concrete dry out under normal atmospheric conditions. As drying proceeds and water is evaporated from the pore solution, it appears that this drying effect might kick in and alkali hydroxide concentration in the remaining pore liquid actually decrease despite the reduced volume of pore solution left. Thus the potential for ASR likely diminishes in the dried concrete due both to reduced pore solution content and availability, and to reduced OH⁻ ion concentration in whatever solution is left in the interstices of the concrete pores. It would be likely that ongoing ASR would stop. Rewetting these dried out near-surface layers would seem to have comparatively little effect on the potential for further ASR reaction, in view of the quasi-permanent reduction in alkali hydroxide level that appears to take place. However, some effect might be observed after enough time has elapsed to permit some alkali to diffuse back from deeper zones of undried concrete.

Meanwhile, in the deeper zones any ongoing ASR reaction might be expected to continue until the local concentration of alkali hydroxide is reduced to below some critical level. This reduction would take place as a consequence of both the ASR itself, and because of diffusion of alkali hydroxide toward the outside layers.

The overall effect to be expected would thus be differential expansion, with the interior expanding and the dry or intermittently dry near surface zones generally not expanding. Thus one would expect to find surface "shrinkage" cracks. This is certainly a commonly observed phenomenon, often explained as a result of carbonation of the

surface layer. However the alkali fixation effect does not seem to require extensive carbonation, and may be more directly involved.

One of the standard treatments often prescribed for the amelioration of ASR distress is to attempt to dry out the structure to the extent possible. It is usually considered that this has only temporary benefit, and that when the concrete is eventually subject to rewetting, further ASR to be expected. It would appear from the present considerations that drying may produce more permanent effects than ordinarily contemplated.

PARADOX: SILICA FUME CAN INDUCE ASR RATHER THAN MITIGATING IT

Over a period of the last decade silica fume or microsilica has become established as a useful (albeit expensive) component to incorporate into concrete, particularly if high performance is desired. Used with an appropriate dosage of superplasticizer, silica fume functions to reduce the water demand. A combination of this effect and the well-known filler effect associated with the very fine particles permits the development of much stronger, less porous, and presumably more durable concrete.

The effects of silica fume on ASR have generally been considered to be favorable. Many years ago it was established that silica fume acts to reduce the alkali hydroxide content of the pore solution (Diamond, 1983, Page and Vennesland, 1983). Removal of the alkali hydroxides from the pore solution before they can react with aggregates is obviously beneficial in terms of ASR. Furthermore, silica fume is known to function as an extremely efficient pozzolan, reducing or even eliminating the calcium hydroxide normally formed by cement hydration. Many studies have shown calcium hydroxide needs to be present to "stabilize" the ASR gel. Lacking access to calcium hydroxide, the ASR reaction product tends to be too fluid to exert much mechanical effect, and in extreme cases, it may simply dissolve into the pore solution.

On a practical level, silica fume has been incorporated into Icelandic cement since 1979 to mitigate the effects of severe ASR taking place in that country. According to Olafsson (1992), this incorporation has been highly effective, and no cases of ASR damage have been found in Icelandic structures built since this practice began.

Recent experimental results (Shayan 1995, Langley et al. 1995) further attest to the benefits of silica fume in preventing ASR.

On the other hand, silica fume is often used with superplasticizer. If the sulfonate groups of the usual sulfonated superplasticizers are neutralized by alkali, as is commonly the case, the alkali ions remain in solution indefinitely, while the polymer chains are absorbed into the cement hydration products. Depending on dosage, a considerable increase in the OH^- ion concentration of the pore solution can be produced (Matsukawa and Diamond, 1991), and this increased OH^- ion concentration necessarily results in a further challenge to any potentially reactive aggregates present.

Nevertheless, in view of the generally favorable reports on silica fume effects on ASR, scattered early indications like that of Perry and Gillott (1985) that sometimes incorporation of silica fume seemed to exasperate, rather than prevent ASR damage, were mostly ignored.

Against this background, the findings by Bonen and Diamond (1992a) that a commercial silica fume contained an appreciable content of large siliceous grains (up to 100 μm) were disturbing. In examinations of a 1-year old cement paste incorporating this silica fume, the authors showed that both potassium and calcium ions were able to invade these large silica fume particles, converting them to hydrous alkali calcium silicates (Bonen and Diamond, 1992b). They appeared to be inert, however, and no evidence of expansion or ASR distress was found in this particular paste.

However the paste in question was made with a relatively low alkali cement (0.7 % Na_2O equiv.), and no superplasticizer was used. Accordingly the alkali burden was relatively low. The writers concluded that "the reaction product here was not of the

expansive alkali aggregate reaction gel category, although such products might be produced with cements of higher alkali contents."

This concern was emphasized by the results of Pettersson (1992) who found coarse undispersed grains in a granulated silica fume. The silica fume was incorporated into mortar at a 10% replacement level, and a high alkali cement (1.1% Na₂O equiv.) was used. Exposing this mortar to a concentrated salt solution (1N NaCl, saturated with respect to calcium hydroxide) produced large expansions. Typical ASR cracking, and evidences of ASR gel developing from the coarse grains were clearly described by Pettersson. No expansion or cracking was found with similar mortars made with "dispersed" silica fume.

That these laboratory curiosities might have real-life effects was demonstrated recently by Shayan et al. (1994) for steam cured concrete. These authors reported that "densified silica fume aggregates of 40 - 100 μm in size persisted in the concrete, and in the presence of high alkali levels acted like reactive aggregates." While such effects might be passed off as somehow being induced by steam curing, Marusin and Shotwell (1995) recently reported a similar occurrence taking place in cast-in-place (not steam cured) concrete in a newly renovated parking structure. The alkali content of the cement was not known; the aggregate was primarily expanded shale. The concrete exhibited severe cracking after only a few months of service. Marusin and Shotwell reported that "the lumps of silica fume (from 100 μm to 800 μm in size) were observed to react like reactive aggregates with cement alkalis to form the silica gel (ASR) associated with expansion that leads to cracking of the concrete." Apparently the reaction occurred early in the age of the concrete, when it was particularly vulnerable to tensile cracking.

The lesson is clear. Paradoxical though it may be, silica fume in concrete does not *always* prevent ASR distress; sometimes it can induce ASR distress. In particular, oversized, undispersed grains can respond in concrete much as any alkali reactive aggregate would, and react to generate expansive ASR gel if the alkali hydroxide concentration is high enough. Thus it appears that the existence of significant contents of coarse grains or undispersed (and possible undispersable) agglomerates in some commercial silica fumes may constitute an unexpected hazard.

PARADOX: LITHIUM TREATMENT FOR ASR USUALLY INVOLVES INCREASING THE HYDROXIDE ION CHALLENGE TO THE REACTIVE AGGREGATE IN THE CONCRETE

It has been known for many years that lithium incorporated in concrete has a significant beneficial effect in reducing or eliminating the expansive and cracking effects associated with ASR. There is a major effort currently underway to develop and commercialize both lithium-based admixtures and lithium based ameliorative treatments for concrete already undergoing ASR. A workshop was held on this subject at the Building Research Establishment in the U. K. in April 1995.

While various reports have confirmed the effectiveness of lithium treatments in preventing ASR damage, especially when used at high dosage levels, there have been comparatively few studies aimed at elucidating the mechanisms involved.

The very early laboratory results of McCoy and Caldwell (1951) suggested that the nature of the anion accompanying the lithium was not particularly important. Even almost insoluble lithium salts, such as lithium fluoride, seemed to be beneficial. Research carried out at Purdue University (Ong, 1993) indicated that such salts, while not very soluble in water, dissolve quickly in cement mixes. The mechanism seemed to involve precipitation of the even more insoluble calcium salt of the anion concerned (e. g. fluoride, carbonate, etc.). The calcium involved is derived from the cement gypsum, calcium sulfate being a much more soluble salt than the calcium fluoride or calcium carbonate.

Ong found that the lithium cation remains behind in solution and is balanced first by sulfate. Subsequently (over the course of a day or so) most or all of the sulfate may be precipitated in ettringite formation, and to the extent that this happens the lithium in solution remains behind as dissolved lithium hydroxide.

Fig. 3 provides a plot of the OH^- ion concentrations developed in a w:c 0.485 paste hydrated at room temperature, in which a 1% addition of LiF by weight of the cement was incorporated by mixing with the cement prior to adding the water. Shown for comparison is the pattern of OH^- ion concentration developed by an otherwise identical "control" paste that received no lithium treatment. The eventual difference in OH^- ion concentration is very close to the concentration of Li^+ that eventually appears in the solution (0.38N at 672 hours, i.e. 28 days).

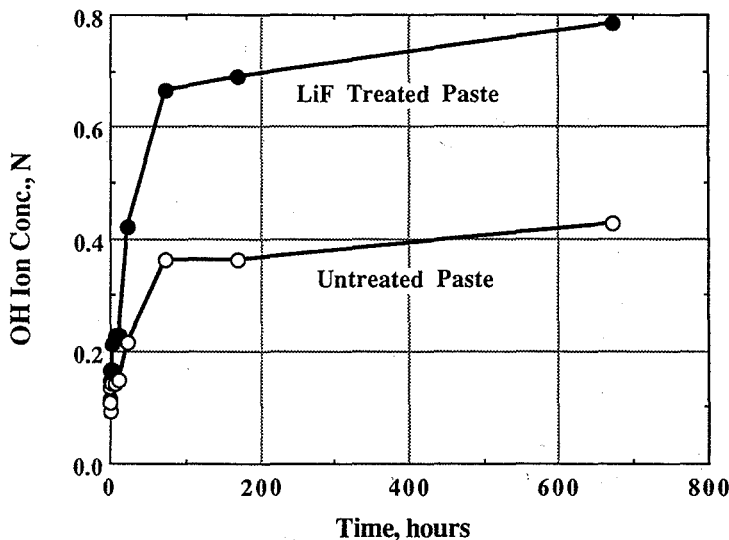


Fig. 3. Comparison of OH^- ion concentrations developed in 1% LiF-treated and in untreated cement pastes.

Similar results were obtained with Li_2CO_3 .

Thus, LiF and Li_2CO_3 act to increase the OH^- ion concentration that would normally be produced by the cement. At a high lithium dosage, this effect may produce a major OH^- ion concentration increase.

Since lithium treatment is expensive, it presumably would be applied only to those concretes at high risk of ASR. Such concretes would already be expected to develop high concentrations of hydroxide ions, based on the high alkali content of the cement used. Thus a major dose of LiF or Li_2CO_3 treatment would substantially increase the *already* high OH^- ion concentration that would be produced by the cement alone. Paradoxically, such treatment thus increases the "challenge" to potentially reactive aggregate in the concrete at the same time that it strives to mitigate the ASR effects.

Actually lithium hydroxide itself may be used as the lithium admixture. At first glance this would be expected to increase the OH^- ion challenge to the reactive aggregate, without even the necessity of an intervening precipitation step.

However, when dissolved in water, lithium hydroxide is a strong base, presumably equivalent to sodium or potassium hydroxide in OH^- ion activity at a given concentration.

As such, lithium hydroxide incorporated in the mix water acts to dissolve cement gypsum and precipitate calcium hydroxide exactly as indicated previously for sodium hydroxide (Eqn. 1). This converts some or all of the added lithium hydroxide to lithium sulfate (depending on whether the dosage used exceeds the gypsum content on a molar basis). Thus a further paradox emerges - adding lithium as lithium hydroxide may not increase the *early* hydroxide ion burden very much, since lithium sulfate rather than lithium hydroxide appears in the solution.

To predict what would happen in a given case one needs to consider the dosage applied in relation to the gypsum content of the cement.

There is another facet of cement composition that must also be considered, specifically the C₃A content and its availability. To the extent that the sulfate that quickly enters the solution as a result of adding LiOH to the mix water is quickly precipitated as ettringite, a partial reversion back to dissolved lithium hydroxide occurs. It appears that at the dosage levels normally contemplated and with typical cements, short-term ettringite precipitation is insufficient to cause complete reversion of the sulfate to hydroxide, and both sulfate and hydroxide continue to be present in the pore solution indefinitely.

Thus the long-term effect of incorporating lithium as lithium hydroxide is that some increase in the OH⁻ ion burden will result, but the increased concentration level will not be as great as would be calculated from the amount of LiOH added. The difference persists as dissolved sulfate.

The ameliorative effect produced by lithium appears to involve the incorporation of lithium into the ASR reaction product gel, specifically the effect that lithium seems to have in reducing tendency of the ASR gel to imbibe water and swell. It appears that lithium "gentles" the swelling response; the greater the proportion of lithium (as against sodium or potassium) actually present in the reaction product the less likely it seems to be to cause distress. High lithium dosage appears to be necessary to get sufficient lithium taken up by the gel. It appears that this can overcome the concomitant increase in OH⁻ ion challenge.

However, there is yet another factor to consider in assessing the effects of lithium hydroxide treatment. The presence of significant concentrations of sulfate remaining in the pore solution may produce a side effect that has been previously mentioned. To the degree that the cement C₃A is not all readily available but is only slowly exposed to solution by progressive cement hydration, the sulfate in solution may react to produce ettringite long after the concrete has hardened. This delayed ettringite could produce expansion and cracking, even in the absence of ASR-induced distress.

This is probably not a practical concern with most cements, but it points out the need to establish pertinent characteristics of the particular cement to be used with lithium treatment. Lithium treatments can cause side effects in the pattern of cement hydration that need to be evaluated for the particular cement and for the form and dosage level of the lithium treatment contemplated.

CONCLUSIONS

A number of lessons emerge from consideration of the several paradoxes discussed in this report.

Specifically, it has been pointed out (1), that adding alkali hydroxide to cements to raise the alkali level in ASR experiments is a dubious practice, and may cause unexpected consequences, (2) that alkali hydroxide in pore solutions may be substantially "fixed" when concrete is dried to modest RH values, and that such fixation, once accomplished, may provide permanent benefit, (3) that coarse particles or undispersed agglomerates in silica fume may react essentially as ASR reactive aggregate and engender unexpected ASR difficulties, and (4) that use of lithium may result in greatly enhanced concentrations of OH⁻ ions in concrete pore solutions, thus rendering the desired ASR amelioration effects more difficult.

A general theme runs through the various topics discussed. It is simply that the internal workings of concrete are complicated, and are influenced in sometimes unexpected ways by admixtures and chemical treatments.

As a final consideration, there seems to be an overall reciprocity in effects various factors exert on anion concentrations, i.e. concentrations of SO_4^{2-} and OH^- in concrete pore solutions. Only the latter is important in ASR, but the former is extremely important in cases where DEF is possible. In view of the various instances where symptoms of the two problems occur in the same concrete, pertinent attention should be paid to the effects of various factors on both.

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