

# 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) the 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) 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 wetted again; (c) silica fume with coarse particles or undispersed agglomerates can induce, rather than prevent ASR distress in certain instances; and (d) 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. © 1997 Elsevier Science Ltd. All rights reserved.*

**Keywords:** ASR, alkali, hydroxides, drying, silica fumes, lithium treatments, problems, paradoxes.

## 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.<sup>1</sup> 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 normally considered that ASR distress is consequent on the effects of the 'ASR reaction', which is almost universally considered to be a reaction between  $\text{OH}^-$  ions in the pore solution and the reactive aggregate components that produces ASR reaction gel. However, recently Wieker *et al.*<sup>2</sup> have proposed an alternate reaction scheme in which, a crystalline hydrous sodium silicate, is formed as an intermediate compound by the reaction of  $\text{OH}^-$  ions on silica. Kanemite is a layer lattice structure similar to expanding clays, and these authors consider that some or all of the ASR expansion may be due to an uptake of water molecules between the silicate layers in this compound. So far at least, there is no confirmation that this expansive crystalline mineral is actually formed in ASR reaction in field concrete. Nevertheless, its possibility adds to the complexities of the ASR reaction, which were complicated enough.

The present paper is aimed at providing some insights into the ASR responses, based on information developed during the course of our research over the last 3 or 4 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 sufficiently complicated that easy assumptions that are often made may turn out to be not correct and at times 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.<sup>3</sup> Alternatively, it has been a 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 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.*,<sup>4</sup> Shayan *et al.*<sup>5</sup> and Yamamoto *et al.*<sup>6</sup>

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  $\text{OH}^-$  ion concentration.<sup>7</sup>

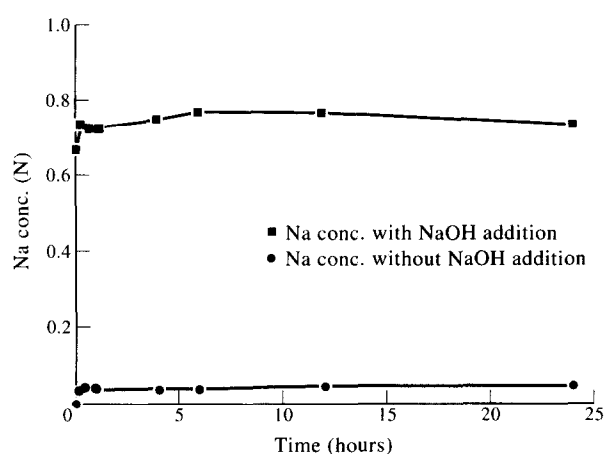
A series of experiments were carried out with w:c 0.485 pastes made with a Type I Portland cement. The particular cement used had a high alkali content (1.14%  $\text{Na}_2\text{O}$  equivalent) and only a moderate sulfate content (2.8%  $\text{SO}_3$ ). One series of pastes was prepared without additional alkali; a second series of pastes was prepared from the same components, but with

$\text{NaOH}$  equivalent to 1%  $\text{Na}_2\text{O}$  in cement pre-dissolved in the mix water. This initial 'mix water' was thus converted to an 0.67 N  $\text{NaOH}$  solution. Hydration was allowed to take place and the mix or pore solutions were filtered or expressed at intervals and analyzed in the usual manner.

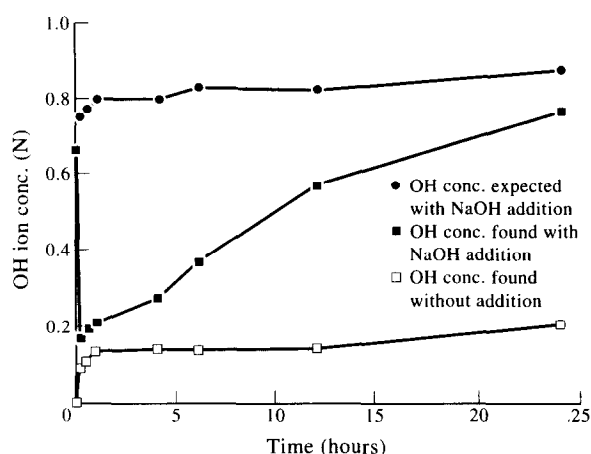
The 'easy' expectation would be that both alkali ion and  $\text{OH}^-$  ion concentrations usually produced by the cement alkalis would be augmented by the concentrations of  $\text{Na}^+$  and  $\text{OH}^-$  ions already dissolved in the mix water. This seems to be true for the  $\text{Na}^+$  ions, but definitely not true for the  $\text{OH}^-$  ions.

Figure 1 provides the  $\text{Na}^+$  ion concentration pattern with time over the first day. It is clear that the added  $\text{Na}^+$ , which much outweighs the  $\text{Na}^+$  produced by the cement, remains in solution. Figure 2 provides three patterns for the corresponding  $\text{OH}^-$  response. The open squares give the actual response for the control cement paste, without  $\text{NaOH}$  addition. The filled circles are the calculated expected  $\text{OH}^-$  response if the  $\text{OH}^-$  ions were to remain in solution as the  $\text{Na}^+$  ions do; that is, the sum of the control  $\text{OH}^-$  concentration plus the  $\text{OH}^-$  concentration present in the mix water of the  $\text{NaOH}$  treated paste. The filled squares provide the actual pattern of  $\text{OH}^-$  ion concentrations found for the  $\text{NaOH}$ -treated paste.

It is found that immediately after mixing (that is, by the time of the first determination at 10 min from the start of mixing), the  $\text{OH}^-$  ion concentration in the mix water had dropped to about 0.32 N. Thus, adding the cement to the mix solution (and mixing) had caused the  $\text{OH}^-$



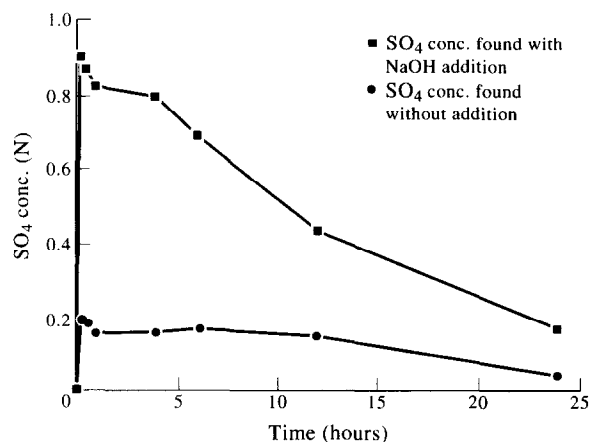
**Fig. 1.**  $\text{Na}^+$  ion concentrations over the first day for control cement paste with no  $\text{NaOH}$  addition and for  $\text{NaOH}$ -treated paste.



**Fig. 2.**  $\text{OH}^-$  ion concentrations over the first day. Open squares: control paste without NaOH addition. Filled circles: expected concentrations, i.e. the sum of the  $\text{OH}^-$  ion concentrations generated by the control paste plus that of the NaOH — containing mix water. Filled squares: actual  $\text{OH}^-$  ion concentrations found in the NaOH-treated paste.

ion concentration to be immediately cut in half. The resulting alkalinity in terms of  $\text{OH}^-$  ion concentration was actually only a little greater than that of the solution in the paste without added NaOH.

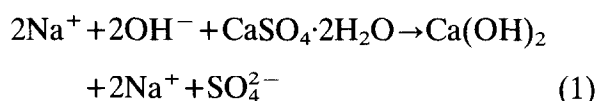
Subsequently the  $\text{OH}^-$  ion concentration in the treated paste increased with time, but it did not reach the 'expected' concentration level in the 1-day period plotted in Fig. 2. Nor did it do so subsequently in the 6 month hydration period examined. If, as stated earlier, the added  $\text{Na}^+$  ions remained in solution, how were the additional cationic charges balanced? The answer is evident from Fig. 3 in which is plotted the  $\text{SO}_4^{2-}$  ion concentrations found for the NaOH-treated and for the control pastes. It is



**Fig. 3.** Comparison of the  $\text{SO}_4^{2-}$  ion concentrations of NaOH-doped and untreated cement pastes found over the first day of hydration.

evident that the addition of the NaOH has resulted in an immediate boost in the concentration of  $\text{SO}_4^{2-}$  ions, rather than the expected boost in the concentration of  $\text{OH}^-$  ions.

It has been shown<sup>7</sup> 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:



The net effect is that gypsum dissolved, calcium hydroxide was precipitated, and sodium and sulfate ions equivalent to the amount of sodium hydroxide introduced were left in solution.

The response is complete if the number of moles of NaOH added is less than the number of moles of gypsum present in the particular cement used. If the NaOH dose exceeds the gypsum content (in molar terms) the excess NaOH would remain in solution as dissolved sodium hydroxide, resulting in an augmentation of the immediate  $\text{OH}^-$  ion concentration proportionate to the excess.

Subsequently, ettringite precipitation removes most (but not all) of the sulfate brought into solution, causing a partial reversion in the solution from  $\text{SO}_4^{2-}$  to  $\text{OH}^-$ . There are both short-term and long-term consequences to these responses. 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, as 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 ettringite content at one day 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'  $\text{SO}_3$  was apparently deposited in some fashion 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  $\text{SO}_4^{2-}$  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,<sup>8</sup> being fed both from sulfate in the pore solution and sulfate feeding to the pore solution 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 of the cement and to the form of sulfate present; to its  $\text{C}_3\text{A}$  content; and to the degree to which the  $\text{C}_3\text{A}$  is available early in the hydration process to form ettringite. These parameters are not normally taken into account in ASR studies.

Thus the apparent paradox associated with the observed immediate drop in  $\text{OH}^-$  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. Adding alkali hydroxide to a low-alkali cement does not seem to be a good way to simulate the effect on ASR of a high 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 deple-

tion of the alkali and of the  $\text{OH}^-$  ion concentrations of the pore solution as the alkali and  $\text{OH}^-$  ions are incorporated into the ASR reaction product gel.<sup>9</sup> 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.<sup>10</sup> The expected concentration (of either  $\text{OH}^-$  or alkali ions) is about 0.7 N per percent  $\text{Na}_2\text{O}$  equivalent in the cement, at w:c 0.5.

Normally, this concentration is reduced as ASR reaction removes alkali hydroxide from the pore solution and incorporates it into ASR gel. 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 in the pores of a given concrete, this fact might be an indication that ASR is occurring in that particular concrete. Furthermore, the extent of depletion might serve as an index of the amount of ASR 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 of the pore solution.

There is a second expectation that might be mentioned, if concrete is allowed to dry out and is then re-wetted. 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 residual pore solutions in the interstices of the pores necessarily increases, but that nothing is precipitated. It is also reasonable to suppose that on rewetting, the pore solution concentrations should return to their original levels, assuming that the amount of water that was lost on drying is replaced by a similar amount of water on rewetting.

If field concrete has dried out appreciably, it is usually not possible to express pore solutions from cores. 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 com-

plete 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 0.1–0.2 N were found, rather than the expected levels of 0.5–0.7 N. 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 from the pore solution to ASR reaction products. Rather, some (or most) of the solute appears to be 'fixed' in 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 it appears that when concrete dries out the dissolved alkali hydroxide does not increase in concentration in the remaining pore solution; rather the concentration appears to decrease substantially.

Detailed investigations into these phenomena were carried out at Purdue University.<sup>11</sup> It was determined that the alkali hydroxide fixation effect takes place on drying with cement paste, so that it is not induced by type of reaction with the aggregate. However, the effect of reduction in alkali hydroxide concentration certainly seems to influence the possibility of ASR subsequent to occurrence of the fixation effect.

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 influence. As indicated in Table 1, it was found that fixation effect is much reduced in the absence of the carbon dioxide of the air.

The pastes listed in Table 1 were allowed to re-equilibrate in sealed moist 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.

**Table 1.** Sum of the concentrations of Na and K ions (N) in pore solutions expressed from various cement pastes

Cement	Continuously sealed (no effect)	Dried in air, then vacuum saturated	Dried in N <sub>2</sub> , 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

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<sup>-</sup> 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 10–20% 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 surface zone concrete due both to reduced volume of pore solution and to reduced OH<sup>-</sup> 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 not seem to increase the potential for further ASR reaction very much, in view of the quasi-permanent reduction in alkali hydroxide level that appears to take place. However, further reaction might be observed after enough time has elapsed to permit alkali hydroxide 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 generally expanding for a long time and the dry or intermittently dry near surface zones generally not expanding as much over time. Thus one would expect to find surface 'shrinkage' cracks, i.e. evidences of differential expansion between the interior and the surface layer. This is certainly a commonly observed phenomenon. It is often explained as a result of carbonation of the surface layer. However, alkali fixation measured in these experimental trials 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 somewhat more permanent effects than ordinarily contemplated, especially if the concrete is not severely cracked. In severely cracked concrete one would expect alkali hydroxide from the interior undried portions to quickly diffuse to the dried and re-wetted exterior zones through the cracks.

#### **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.<sup>12,13</sup> Removal of the alkali hydroxides from the pore solution by the action of silica fume before the alkali hydroxides 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 gel 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<sup>14</sup> 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<sup>15,16</sup> further attest to the practical 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 derived from the superplasticizer remain in solution when the superplasticizer polymer chains are absorbed into the cement hydration products. Depending on dosage, a considerable increase in the  $\text{OH}^-$  ion concentration of the pore solution can be produced,<sup>17</sup> and this increased  $\text{OH}^-$  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 reports like that of Perry and Gillott<sup>18</sup> that sometimes incorporation of silica fume seemed to exacerbate, rather than prevent ASR damage, were mostly ignored.

Against this background, the findings by Bonen and Diamond<sup>19</sup> that a commercial silica fume contained an appreciable content of large siliceous grains (up to 100  $\mu\text{m}$ ) 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.<sup>20</sup> These reaction products appeared to be inert, however, and no evidence of expansion or ASR-like distress was found in this particular paste. However, the paste in question was made with a relatively low alkali cement (0.7%  $\text{Na}_2\text{O}$  equivalent), 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.'

An illustration of these vastly oversized grains found in commercial silica fume is provided in Fig. 4; the particles were sieved from a dry condensed silica fume widely distributed in the United States.

In research being carried out at Purdue University a 'high performance' cement paste was prepared incorporating 10% of the (bulk) silica fume from which the grains depicted in Fig. 4 were sieved, at a water:binder ratio of 0.27. The cement was a low alkali cement and the superplasticizer used was Ca-neutralized rather than Na-neutralized. Despite this, after 7 days of hydration in saturated limewater extensive cracking associated with ASR was observed. Figure 5 provides a typical view. Measurements of the  $\text{K}_2\text{O}$  contents of the coarse reacted silica

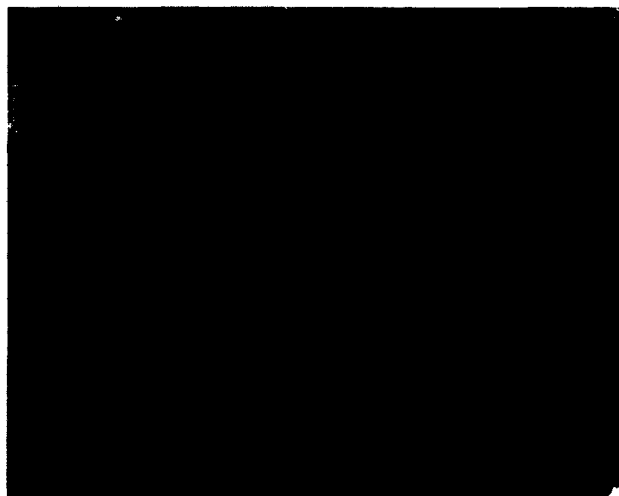


Fig. 4. SEM backscatter micrograph showing separated coarse grains of silica fume sieved from a commercial dry silica fume widely distributed in the U.S.

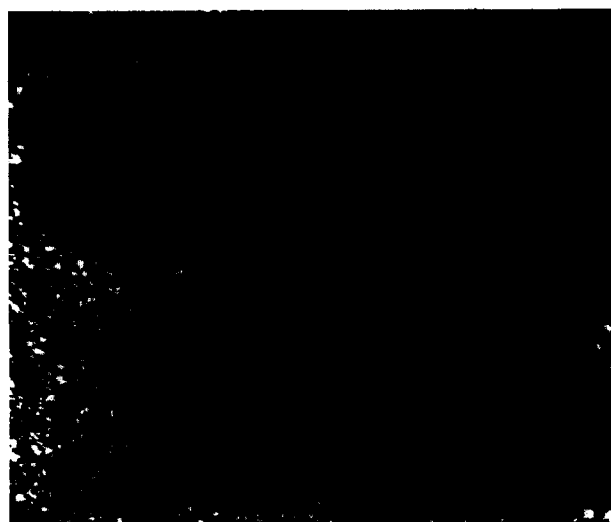


Fig. 5. SEM backscatter view of area in silica-fume bearing 'high performance' paste containing 10% silica fume.

fume grains ranged from 10 to 15%, confirming that ASR was taking place within them.

The extent to which commercial silica fume contains oversize grains has not generally been appreciated or publicized. The 'easy' assumption generally made is that silica fume occurs in discrete particles of the order of 0.1  $\mu\text{m}$  and is, thus, much finer even than cement or fly ash. This idea is illustrated in Fig. 6, taken from a standard concrete textbook.<sup>21</sup> In point of fact, it is increasingly evident from various that many or most dry condensed silica fumes contain significant contents of undispersed and ordinarily undispersable grains of the order of several hundred millimeters. Such grains can indeed

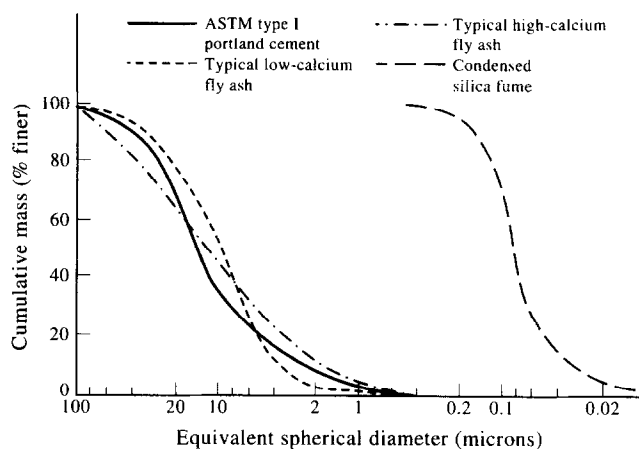


Fig. 6. Comparison of particle size distributions of Portland cement, fly ashes and the supposed particle size distribution of silica fume, after Mehta and Monteiro.

react with alkali hydroxide and may give rise to ASR distress.

This concern was emphasized by the results of Pettersson<sup>22</sup> who found significant contents of 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% Na<sub>2</sub>O equivalent) was used. Exposing this mortar to a concentrated salt solution (1 N 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' described so far might have real-life effects was demonstrated recently by Shayan *et al.*<sup>23</sup> for steam cured concrete. These authors reported that 'densified silica fume aggregates of 40–100  $\mu$ m 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<sup>24</sup> 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 to 800  $\mu$ m 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<sup>25</sup> 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<sup>26</sup> 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.

Figure 7 is a plot of the pore solution concentrations of Li<sup>+</sup>, F<sup>-</sup> and OH<sup>-</sup> ion concentrations over the first day for a w:c 0.485 cement paste to which 1% LiF had been added in solid form, blended with the paste since dissolution in the mix water is not possible. No fluoride was detected in solution at any time, but a substantial fraction of the Li ions rapidly appeared. The Li<sup>+</sup> cations were at first balanced primarily by an excess of SO<sub>4</sub><sup>2-</sup> ions (excess as compared to their concentration in the untreated control paste). However, the usual ettringite formation depleted the SO<sub>4</sub><sup>2-</sup> concentration and after a day or two the Li<sup>+</sup> cations are primarily balanced by OH<sup>-</sup> ions. In

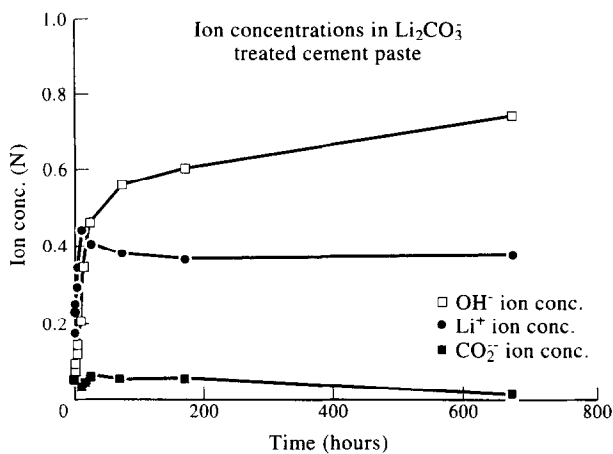


Fig. 7. Concentrations of F<sup>-</sup>, Li<sup>+</sup> and OH<sup>-</sup> found in pore solution of a cement paste incorporating 1% LiF blended mechanically with the portland cement.

effect, the lithium remains in solution primarily as lithium hydroxide.

Similar results were obtained with the slightly less insoluble  $\text{Li}_2\text{CO}_3$ , although here a very small concentration of carbonate ions (about 0.05 N) was found in solution. Thus, LiF and  $\text{Li}_2\text{CO}_3$  act to increase the  $\text{OH}^-$  ion concentration that would normally be produced by the cement. At a high dosage of these salts, the effect produces a much higher  $\text{OH}^-$  ion concentration than would otherwise be present.

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 itself. Thus a major dose of LiF or  $\text{Li}_2\text{CO}_3$  treatment would substantially increase the already high  $\text{OH}^-$  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 immediately increase the  $\text{OH}^-$  ion challenge to the reactive aggregate, without even the necessity of an intervening precipitation step, since lithium hydroxide is a strong and highly soluble base.

However, lithium hydroxide behaves much like sodium hydroxide added to the mix water (i.e. it acts to dissolve cement gypsum and precipitate calcium hydroxide). 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 gets lithium into solution immediately, but it will not increase the early hydroxide ion burden very much, since lithium sulfate rather than lithium hydroxide is what immediately appears in the solution.

Of course, to the extent that the sulfate that enters the solution when LiOH dissolves gypsum is precipitated as ettringite, a partial reversion back to dissolved lithium hydroxide occurs. It appears that at the high dosage levels normally contemplated with lithium treatment for ASR, 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 expected long-term effect of using lithium hydroxide as an admixture is that an increased  $\text{OH}^-$  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 reduces the tendency of the ASR gel to imbibe water and swell. Thus it appears that lithium incorporated into the ASR gel 'gentles' the swelling response. It appears that the greater the proportion of lithium (as against sodium or potassium) incorporated in the gel the less likely that destructive expansion will take place. 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  $\text{OH}^-$  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  $\text{C}_3\text{A}$  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 formation of ettringite could conceivably 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 that: (1) adding alkali hydroxide to cements to raise the alkali level in ASR experiments is a dubious practice, and may cause unexpected consequences; (2) 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) coarse particles or undispersed agglomerates in silica fume may react essentially as ASR reactive aggregate and engender unexpected ASR difficulties; and (4) use of lithium hydroxide or even insoluble lithium salts eventually produces enhanced concentrations of  $\text{OH}^-$  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  $\text{SO}_4^{2-}$  and  $\text{OH}^-$  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.

## ACKNOWLEDGEMENTS

The writer is indebted to Shaode Ong, Daniel Constantiner, David Bonen, Prasad Rangaraju, and other colleagues and former students who

have helped so much in formulating the ideas expressed in this paper.

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