

# ON THE PHYSICS AND CHEMISTRY OF ALKALI-SILICA REACTIONS

by Prof Sidney Diamond\*, R S Barneyback, Jr, and L J Struble

### SYNOPSIS

The philosophy underlying recent research on alkali-silica reactions at Purdue University is reviewed and illustrations of recent results are provided. It has been possible to follow the kinetics of the chemical reaction between dissolved alkalis and opal in mortars by monitoring the rate at which alkalis are removed from the pore solutions of reacting mortars. Studies of the expansion behaviour of synthetic alkali silica gels under controlled conditions were carried out and show no obvious correlation to chemical composition. The alkali reaction in mortars was found to produce changes in the appearance of opal grains documentable by the use of a scanning electron microscope.

# SAMEVATTING

Die onderliggende filosofie van onlangse navorsing oor alkali-silikareaksies aan die Universiteit van Purdue word voorsien. Dit was moontlik om die kinetika van die chemiese reaksie tussen opgeloste alkalië en opaal in mortel te volg deur die spoed waarteen alkalië uit die porie-oplossings van reagerende mortel verwyder word, te monitor. Ondersoek is gedoen oor die uitsetgedrag van sintetiese alkali-silikajelsoorte in beheerde toestande en geen duidelike korrelasie is met chemiese samestelling gevind nie. Dit blyk dat alkali-reaksie in mortel veranderinge in die voorkoms van opaalkorrels teweegbring wat deur middel van 'n aftaselektronmikroskoop gedokumenteer kan word.

# S252/22

Conference on alkali-aggregate reaction in concrete Cape Town - South Africa March 30 - April 3, 1981

Secretariat: NBRI of the CSIR PO Box 395, Pretoria 0001, South Africa Telephone (012) 86-9211 Telegrams Navorsbou Telex SA 3-630

Konferensie oor alkali-aggregaat-reaksie in beton Kaapstad - Suid-Afrika 30 Maart - 3 April, 1981

Sekretariaat: NBNI van die WNNR Posbus 395, Pretoria 0001, Suid-Afrika Telefoon (012) 86-9211 Telegramme Navorsbou Teleks SA 3-630

\* School of Civil Engineering, Purdue University, West Lafayette, Indiana, USA.

Mr H E Vivian made the point that the sealing of structures was not usually particularly effective because it was not longlasting. He reiterated that there was a huge quantity of potentially water-soluble lime in the cement which had the habit of going into solution and being deposited as an efflorescent layer on the surface. This tended to creep and cover the surface and what had started off as, say, a water repellant silicone surface now became a hydrophillic surface through which water would go quite readily. Incidentally he added, silicones were 'damp proofers' rather than 'water proofers' because water, even under a very slight head of pressure, would pass through the membrane.

Mr W A Schoon, (Liebenberg & Stander Consulting Engineers, Cape Town) drew the attention of the conference to Dr Idorn's suggestion that early microcracks in concrete might significantly affect the course of the alkali-aggregate reaction. The British code of practice for the design of water retaining structures, BS 5337, he said, recognised the problems of early thermal cracking and provided limited guidelines for taking these effects into account. However this and some other codes still recommended a minimum cement content which was higher than that normally applicable to medium strength concrete where fairly good quality aggregates were available. He said that his own views agreed with those of Mr Flanagan, and asked him to comment on this apparent anomaly. Mr Schoon went on to ask Dr Idorn what practical measures he would recommend apart from reducing the heat of hydration by reducing the cement content, to minimise early thermal cracking taking into account the reuse of form work.

Mr J C Flanagan replied that he thought the specifications were misguided because it was the water/cement ratio that really controlled durability and permeability. He felt that by reducing the cement content, provided one did not change the water/cement ratio, one improved the concrete. A higher cement content meant more heat of hydration and possibly a very high early strength which did not enable stresses to be taken up by creep. In general, he added, high cement contents per se were not a good thing.

Dr G Idorn stressed that he had brought in temperature as a parameter in order to emphasise the difference between how

research on the alkali-aggregate reaction was carried out, and how things were done in practice. This had been his main point. If he were to go into detail about how calculations of the heat of hydration were applied, how the dissemination of heat was calculated, how these things were monitored and the stresses which followed were measured, it would have necessitated a separate paper. He mentioned that the very early properties of hardening concrete at temperatures other than 20 °C, and under temperature gradients, were not very well known and further complicated the problem. To answer the question in full, he would need to go into specific detail with the questioner.

Dr D E Davis added that when BS 5337 on water retaining structures had first come out, South Africans had been a bit worried about the high cement content specified and had discovered that by using medium to good quality aggregates they could obtain the necessary water/cement ratio with a considerably lower cement content than had been suggested in the UK.

Mr C J Semmelink, (NITRR, South Africa) asked Prof Diamond if in the light of the fact that alkalis were dissolved virtually immediately in the mixing water, whether it would not be advantageous to draw off as much of this water as possible, for example by a vacuum process, after the concrete had been poured.

Prof S Diamond said he though it would. By the completion of normal mixing, he thought that at least the sulphate portion of the alkalis would be completely dissolved and if one could remove this solution it would significantly reduce the alkali burden of the concrete once it had hardened.

Dr P E Grattan-Bellew, (NRC, Canada) added that in practice he did not think that the vacuum process could remove the alkalis. The pattern slabs which he had previously referred to, were often prepared using a vacuum process. After casting, a vacuum was applied to suck the water out, but it did not seem to be very successful in preventing alkali aggregate attack. One might be simply increasing the alkali concentration.

# 1. INTRODUCTION

The general features of the alkali-silica reaction in Portland cement concrete have been understood for a number of years. Our recent research in this area at Purdue University has been focussed on attempts to develop a closer understanding of the physics and chemistry of the reaction and expansion processes that occur. Among other things, we have tried to develop methods to assess the kinetics of the alkali-silica reaction process per se, independently of whether or not expansion is taking place; with attempts to develop an understanding of the relationship between the chemical composition and other characteristics of the reaction product gels and their capacity to sorb water and swell; and with study of the local microstructural and chemical changes taking place at the sites of the reacting aggregate grains. Details of some of this work have been described in the MS thesis of L J Struble<sup>1</sup> and in the prospective PhD thesis of R S Barneyback. The present paper provides only a few illustrations of the findings so far accumulated.

### 2. BASIS OF THE PRESENT RESEARCH

The present work rests on several specific underlying concepts that are worth discussing in some detail.

The first general idea is that alkali silica distress in concrete results from processes of chemical and physical reaction that are separable into two distinct stages:

(I) Chemical reaction to produce the reaction product gel, usually taking place within the boundary of the reacting aggregate.

(II) Physical or physicochemical sorption of fluid by this gel, which may in turn produce local swelling at the site of the affected grain. If this swelling is long continued, overall expansion and cracking in the affected areas may follow.

The second process naturally occurs only after the first is well underway, if not indeed completed.

The second premise underlying this research is that the Stage (I) reaction, being a purely chemical one, can be followed by purely chemical means. We consider that it is a heterogeneous solid-solution reaction that takes place between the solid reactive aggregate grains and the pore solution within the mortar or concrete. The kinetics of a heterogeneous chemical reaction between a solid and a dissolved substance may be followed by measuring any one of the following: (a) the rate of disappearance of the solid, (b) the rate of removal of the dissolved reactant from solution, or (c) the rate of accumulation of reaction product. In this case the solid is usually amorphous or badlycrystallized silica surrounded by well crystallized silica and other aggregate material and cemented in place, and the reaction product is an amorphous gel being developed within a cemented matrix. Neither seems well suited to analytical assessment. Thus we have concentrated on the remaining alternative, that is, measurement of the rate at which dissolved alkali hydroxide is removed from the pore solution. This is done by expressing small volumes of pore solution from reacting mortars at suitable intervals by use of special equipment designed for the purpose, and analyzing the expressed pore solutions by normal chemical means.

The third concept underlying our research is that of conducting experiments which attempt to duplicate the Stage (II) processes under controlled experimental conditions so as to develop information on the relationship between the composition and other characteristics of the gel and the extent of sorption, swelling, and expansion pressure development that may take place. Because of the seeming impossibility of removing sufficient amounts of homogeneous gel from reacting mortar or concrete, these studies to date have been carried out on gels prepared outside of concrete, by the reaction of alkali hydroxide with silica sols followed by concentration to gel form.

The fourth premise is that information obtainable by the examination of physical and chemical changes taking place at individual reacting grains in reacting mortars is likely to be helpful in understanding the details of the processes occurring. We are continuing to study such changes by scanning electron microscopy and energy-dispersive x-ray analysis of local areas as time and facilities permit.

#### 3. KINETICS OF ALKALI SILICA CHEMICAL REACTION AS MEASURED BY PORE SOLUTION CONCENTRATION CHANGES

For several years equipment has been available that enables the investigation of changes in the composition of pore solutions in cement pastes and mortars as cement hydration and other reactions proceed. This is done by expressing pore solutions from replicate specimens of paste or mortar at progressively increasing ages, and analyzing these expressed pore solutions chemically. The results of a series of such determinations were published by Diamond and Barneyback<sup>2</sup> several years ago and in the interim a number of additional experiments have been carried out.

These, and similar results by others on cement pastes, have established that after a day or two pore solutions contain alkali hydroxides derived from the cement alkalis, and very little else. Calcium concentrations fall to the order of 0,001M, and only trace or negligible concentrations of sulphate, aluminium, silica, or iron ions remain in solution (although at somewhat later ages some sulphate reappears). The alkali hydroxides reach combined concentrations of the order of 0,5 to 1,0M.

In sealed pastes or mortars not subject to ingress or egress of water, the alkali hydroxide concentration levels vary with (a) the alkali content of the cement, (b) the rate at which the cement alkalis are readily mobilized, (c) the water:cement ratio, and (d) the progress of cement hydration. The last mentioned influences the alkali hydroxide



3

It is seen in Figure 2 that for the present mortars there is a brief induction period followed by rapid reaction consuming about 25 per cent of the alkalis by the end of the first three days. Subsequently the chemical reaction slows and a steady state seems to be reached after somewhat more than 35 per cent of the alkalis have reacted. This requires about a month or so at 20 °C with these mortars.

# 4. EFFECT OF TEMPERATURE ON **REACTION KINETICS**

One generally expects that increasing the temperature will increase the rate of chemical reaction. To investigate the influence of temperature elevation on the present reaction, mortars of the same composition were prepared in an identical manner, but after the first day of hydration they were transferred to a controlled temperature chamber maintained at 40 °C instead of continuing at the 20 °C preparation temperature. Changes in the velocity of reaction resulting from this increased temperature are indicated in the results of Figure 3. In this figure the time axis is plotted on a scale proportionate to the square root of the number of days, strictly to facilitate the presentation of the data.

The comparison of the 40 °C results with those obtained at 20 °C shows that, as expected, the chemical reaction which we identify as Stage (I) of the alkali silica reaction process is greatly speeded up at the higher temperature. It appears that after exposure to 40 °C temperature for 2 days (3 days total time) the reaction had proceeded further than after 30 days at 20 °C. In fact, the reaction had reached apparent completion. The residual concentration of alkali in the pore solution would seem large enough to generate further reaction product, but it does not appear to \_ do so, even after a year of additional aging. The implication seems to be that all of the susceptible aggregate that is capable of reacting under these conditions has already reacted by the end of the 3 days. As indicated by Gutteridge and Hobbs<sup>3</sup> Beltane opal seems to be a complex of several varieties of quasi-amorphous silica of varying solubility in strong alkali solution, plus associated insoluble





impurities. Thus it appears likely that only a portion of the aggregate is capable of reacting with cement alkalis in mortars, even at 40 °C.

### 5. COMPARISON OF THE VELOCITIES OF CHEMICAL REACTION AND OF EXPANSION

It seems exceedingly difficult to develop specific means of monitoring the Stage (II) sorption and expansion process within mortars, other than relying on external measurements of the total expansion. However, it appeared to us that the usual methods of measuring the expansion of mortar bars exposed to nominally 100 per cent RH atmospheres were not adequate. Reproducibility problems. difficulties in maintaining local atmospheric saturation with water vapor, uncontrolled drip and leaching losses of alkalis from the exposed mortar bars, and the strong effects of the size and shape of specimens all provide difficulties.

To overcome these problems a system was developed by R S Barneyback in which short mortar cylinders, identical in all respects to the specimens from which pore solutions are expressed, are incorporated into thin, extremely flexible butyl rubber jackets. These prevent water ingress or egress while providing only miniscule resistance to expansive stresses. The specimens were provided with the means for accurately measuring length changes, and were kept at 20  $^{\circ}$ C and at 40  $^{\circ}$ C, with length measurements being made at these temperatures at appropriate intervals. Companion mortars were made for expression of pore solutions in a manner identical to the measurements already described. The mortar mix design was identical to that of the previously-mentioned mortars except that the cement used had a significantly lower alkali content, 0,90 per cent Na<sub>2</sub>O equivalent.

By this means the data were made available for a direct comparison of the velocities of the chemical reaction process of Stage (I) and the physicochemical processes of Stage (II) insofar as they are reflected in expansion measurements. The results, for both 20  $^{\circ}C$  and 40  $^{\circ}C$ , are provided in Figure 4, (page 4), again with the time axis proportionate to the square root of the number of days.

It is instructive first to compare the 20 °C reaction and expansion curves. With these mortars, reaction at 20 °C is somewhat more brisk than with the mortars of Figure 3, with significant alkali removal accomplished within 2 days. Expansion here lags much behind reaction, being negligible for the first week or ten days. Subsequently the expansion process takes hold, and expansion proceeds at a comparatively slow rate for a long time, substantially longer than a year at the minimum. It should be recalled that these are sealed specimens, and difficulties of water sorption from the outside are not involved here.

It was previously indicated that raising the temperature to 40 °C accelerates the chemical reaction. This is also evident in Figure 4, although the acceleration seems less pronounced than was recorded for the more alkaline mortars of Figure 2.

concentration indirectly by removing solvent water from the pore solution and combining it into cement hydration product, thus concentrating the alkali hydroxide. Some uptake of alkalis into cement hydration product occurs, but only to a modest extent.

If reactive aggregate is present and alkali silica reaction occurs, the effect of this reaction is to transfer some of the alkali from the solution to solid reaction products, thus causing a reduction in the pore solution concentration. This reduction is naturally superimposed on any other concentration changes that may be taking place.

It is possible to assess the extent of the alkali silica reaction by comparing concentrations developed in two series of mortars identical in all respects except that one contains reactive aggregate and the other does not. The reduction in alkali concentration resulting from the alkali silica reaction is thus obtained.

To be meaningful as indices of reaction, the comparisons must be made in such a way that the concentrationreducing effect of ion movement out of the pore solution is being tallied independently of the concentrating effect of solvent binding by cement hydration. We do this by measuring the non-evaporable water content of the control mortar at each stage, and use it to adjust the observed pore solution concentration to what it would be if that amount of bound water were restored to the pore solution. This places all concentration expressions on an identical basis, that of the original water content. In these calculations the implicit assumption is made that the non-evaporable water content of the reacting mortar is the same as that of the control mortar companion; that is, that the alkali-silica reaction does not significantly influence the cement hydration process.

The kind of results usually obtained by this method of investigation are illustrated in Figure 1. In this figure



FIGURE 1 : Comparison of the combined alkali concentrations (adjusted for bound water) of reacting and of control mortars as functions of time at 20 °C.

are plotted data obtained by R S Barneyback for two companion mortar series, the control mortars containing only quartz sand, the reacting mortars an 8 per cent replacement of quartz sand with sand-sized Beltane opal. A very high alkali cement was used (1,31 per cent Na<sub>2</sub>O equivalent), the water: cement ratio was 0,50, and the total sand:cement ratio was 2,0. Three trends are plotted: (a) the combined concentrations of the alkalis (Na<sup>+</sup> + K<sup>+</sup>), after adjustment for bound water, in the control mortars, (b) the corresponding results for the reacting mortars, and (c) the difference between the two at each stage. The difference curve provides an indication of the progressive removal of alkalis from the pore solution of the reacting mortar.

It is possible to gain more specific insight into the course of the alkali-silica reaction by running what corresponds to a mass balance analysis on the alkalis in the system. Calculation indicates that the total cement alkali burden completely dissolved in the mix water would yield a combined alkali concentration of 0,845M. Measured pore solution concentrations, after adjustment for bound water. may be compared directly to this maximum level, so as to determine the proportion of the total alkalis present in solution at a given stage. It is seen that the pore solutions of the control mortars contain alkali contents corresponding to slightly more than 70 per cent of the total alkalis starting as early as the first reported measurement at one-half day. This general level is maintained indefinitely, with some variation from sample to sample.

By an extension of this procedure one can calculate what fraction of the total alkalis is being removed from the pore solution in the reacting mortars. This is done by dividing each of the values for the 'difference curve' of Figure 1 by the reference level of 0,845M. The resulting curve is shown in Figure 2, and provides a direct measure, over time, of the chemical reaction parameter with respect to the alkalis.









35

2

After preparation the gels were chemically analyzed and characterized by various means. As soon as possible thereafter specimens were placed in a test system allowing free access to water through a membrane. The resulting expansion under a free swelling condition, ie in the absence of superincumbent loading, was experimentally recorded. 5

In companion experiments replicate gel specimens were similarly exposed to water, but the gels were confined by a piston loaded with just sufficient mechanical force to prevent swelling, the loading being adjusted as needed during the course of a run. The loading pressure was monitored continuously to provide a measure of swelling pressure development by the gel.

In both types of experiment water, rather than simulated pore solution, was the fluid used.

Some of the gels, and others which were not tested in the swelling and swelling-pressure trials, were used as specimens for equilibrium water vapour sorption studies carried out in desiccators in the usual manner, except that the gels were not dried prior to exposure of replicate specimens to the different RH environments.



gels. Arrows mark initial moisture content. Gel compositions are as follows: (a)  $Na_2O:SiO_2 0.08$ (b) Na<sub>2</sub>O:SiO<sub>2</sub> 0,22 (c)  $Na_2O:SiO_2 0.59$ 

All of the gels except one yielded sorption isotherms of the usual BET Type II variety. Figure 5 illustrates the general range of isotherms obtained. It was found that, as expected, the more silicic gels tended to have lower water vapour sorption isotherms, the more sodic ones higher isotherms. The two calcium-bearing gels tested, both of intermediate sodic character, were intermediate in water sorption behaviour as well, no special influence of the calcium being apparent.

This general agreement with expectation was not found with the results of the free swelling tests. Of the eight soda-silica gels tested in this manner, five showed expansions of less than 4 per cent, constituting a clearly lowswelling group. The other three gels showed free swelling expansion of roughly 60 to 80 per cent, clearly in a different category. Most of the gels, including two of the three high swelling ones, started to swell almost immediately on exposure to water and had stopped expanding within periods of a few minutes to a few hours. In contrast the other high expansion gel swelled gradually and progressively over a period of 3 days, after which, with no equilibrium in sight, the test had to be abandoned. Three of the swelling curves, illustrating the variations in behaviour encountered, are reproduced in Figure 6.

The unexpected feature of the results was the lack of clear correlation between the expansion behaviour on free swelling and the sodic or siliceous character of the gel. The three gels in the high swelling group ranged in soda: silica mole ratio from 0,27 to 0,53; the five low swelling gels from 0,28 to 0,46, an almost complete overlap in range. Nor was the initial water content of the gels a clear cut deciding factor, the low swelling group containing gels with initial water contents both higher and lower than the high swelling group.



FIGURE 6 : Free swelling expansions of several synthetic alkali silica gels. Gel compositions are as follows: (d) Na<sub>2</sub>O:SiO<sub>2</sub> 0,53 (e) Na<sub>2</sub>O:SiO<sub>2</sub> 0,27 (f) Na<sub>2</sub>O:SiO<sub>2</sub> 0,30



Temperature elevation would also presumably accelerate the internal re-distribution of pore solution that must be taking place in the expansion process in these sealed specimens. The 40 °C expansion curve shows much less of an induction period than the corresponding 20 °C curve in Figure 4, noticeable expansion occurring by the second day. Nevertheless even at 40 °C it is clear that expansion lags significantly behind the chemical reaction curve.

At later ages expansion at 40 °C seems to slow markedly. and after a few months it falls behind that occurring at 20 °C. Thus the initial effect of accelerating the expansion process is not maintained in the long run, and the eventual effect of exposure to the higher temperature is to significantly reduce long term expansion. This negative effect of temperature elevation has been confirmed for a variety of specimen configurations.

The data of Figure 4 showing the separation in time between the chemical response and the expansion response of sealed identical mortars seems to us to provide excellent confirmation of the idea that the alkali silica response in fact can be separated into Stage (I) and Stage (II) processes as assumed throughout this work.

These results are of interest in another context as well. It has generally been assumed that the Stage (II) response involves the sorption of water from outside the specimen. Mortar bar testing, and practical advice given by consultants to owners of affected structures to keep external water away from their structures as much as possible, both reflect this assumption. However, the present results indicate that expansion may be produced in the complete absence of such water. Thus the fluid being sorbed by the gel in the present experiments must be pore solution, and the swelling

20 °C and at 40 °C

a consequence of redistribution of pore solution within the affected body. This is a concept suggested by French<sup>4</sup>. However, the observed lack of change of alkali concentrations of expressed pore solutions during the period involved must mean that the flow into the swelling gel is mass flow of both water and dissolved species, without discrimination or chromatographic effect.

#### PHYSICAL RESPONSES OF ALKALI SILICA 6. GELS TO WATER

The classical 'pessimum proportion response' in alkali aggregate reaction studies is usually interpreted as reflecting the different swelling capabilities of gels of different chemical composition, formed in response to different amounts of reactive aggregate being placed in contact with a given level of alkali derived from a constant cement dosage. The composition of the gel formed, especially its ratio of alkali to silica, is thought to influence its capacity for water sorption and swelling. Highly siliceous gels have been thought to have only limited ability to sorb water and swell, while highly alkaline gels, particularly those rich in soda, have been considered to become too fluid after only a little water uptake to be able to continue exerting much swelling pressure. The influence of calcium in gels has been much debated.

In an attempt to provide experimental data relating to this question a series of synthetic gels was prepared and studied by L J Struble. These were mostly soda-silica gels, but a few contained calcium as well. The gels were prepared by mixing various proportions of sodium hydroxide solution (sometimes containing calcium hydroxide) with freshly prepared silicic acid, and then concentrating the resulting sol by vacuum evaporation until the gel produced became too stiff for further mechanical stirring.

It should be pointed out that the time period involved in these swelling pressure tests is much shorter than the time over which mortars usually expand, as indicated, for example, in Figure 4. Mortar expansions involve sustained swelling pressure development active over periods of the order of months, rather than the hours recorded here.

# 7. DIRECT EXAMINATION OF REACTING AGGREGATE GRAINS

A useful technique for investigating details of the alkali aggregate reaction is that of examining the actual sites involved by means of scanning electron microscopy (SEM). supplemented by local chemical information derived from energy dispersive x-ray analysis (EDXA). An example of the sort of results that have been obtained in our limited studies of this sort is provided below.

The reactive mortar examined in this illustration contained 10 per cent of sand-sized Danish opal as a replacement for an equal weight of quartz sand, and was prepared with a moderately high alkali cement. The mortar was cured at room temperature for 33 days and then dried and prepared for SEM investigation. Significant expansion and some cracking had occurred by this time.

It was easy to differentiate reacted opal grains from quartz sand grains on the surfaces being examined by their appearance, by potassium content, and by visible cracking. An indication of the overall appearance of a fractured reacted opal grain is provided in Figure 8. An approximate outline of the grain has been drawn in ink. Within the grain (area 'A') one can see that extensive fracture has occurred in consequence of reaction, swelling, shrinkage on drying, and perhaps of the overall fracturing in sample preparation.

Figure 9 provides additional detail of the area of the left hand portion of Figure 8. The large vertical crack is not the left boundary of the opal grain; rather it repre-

FIGURE 9 : Detail of the left-hand portion of Figure 8.

sents a crack occurring entirely within the grain and parallel to and about 3 um to the right of the true boundary. Note the close contact and apparently good bonding of the outer portion of the opal grain to the cement paste (area 'B'). It is worth observing that the horizontal crack of about 1 um in width through the cement paste is an extension of the much larger crack through the opal grain, suggesting that this horizontal crack was originally a swelling crack rather than an artifact produced by drying.

Figure 10 provides a detailed view of the residual reacted opal grain portion to the left of the 'A' marking in Figure 8. This area is reasonably flat and smooth, and it is possible to get a fairly good idea of variations in local chemical composition from count rate ratios taken along its length. The nine numbered spots represent individual sites where 100-second EDXA spectra were obtained, using a stationary beam, an exciting voltage of 25 KeV, and a beam current of approximately, 2,6 x 10<sup>-10</sup> amperes. The count data (above background), and count rate ratios of potassium and calcium to silica are provided in Table 1, (page 8).

The results confirm that spot No 1 is clearly within the cement paste matrix and not in the reacted opal grain. No potassium is detected, and the Ca:Si count ratio is 5,6, indicative of C-S-H gel and some Ca(OH), within the excited volume. The other odd analysis in the set is that for spot 7, where examination of the figure indicates the presence of an adventitious white particle, presumably of C-S-H gel, lying on the surface of the reacted opal grain. The remaining 7 spots provide a consistent series of analyses and are thought to be properly indicative of the compositional variations within the reacted grain.

It is apparent from the data of Table 1 that potassium has spread from the pore solution surrounding the grain into the grain and become fixed, leaving an approximately uniform potassium content from the boundary at spot 2 to the upper end of the flat area at spot 9. The observed potassium level indicated by a K:Si count ratio of approximately 0,02 is low, but potassium here is supplemented by



FIGURE 10: Area of grain subjected to analysis by EDXA, showing individual spots analyzed.

The two calcium-bearing gels tested had low to intermediate swelling capacity, one yielding an expansion of about 3 per cent, the other a substantial value of about 8 per cent.

A further unexpected effect in these tests was the discovery of a pronounced aging effect. All of the gels were initially tested within a few days after preparation. One relatively highly sodic gel (soda:silica mole ratio 0,42) was retested after four months storage at room temperature in a sealed container. After aging, the gel changed in character from a high expansion gel (63 per cent expansion) to a practically inert gel (less than 2 per cent expansion). The effect seemed not to be due to solidification on aging, since the aged specimen was described as 'fluid' after completion of the free swelling trial.

The exact interpretation of these results is still open to question, but it is clear that the free swelling behaviour of alkali silica gels is more complex and less directly related to chemical composition than had previously been assumed.

The results of the swelling pressure measurement trials were also not as expected, and these lead to further complications in interpretation.

In most of these trials a steady-state pressure equilibration was reached within a few minutes and maintained thereafter. A few gels started to shrink after some period of time and the pressure had to be accordingly reduced to maintain constant dimensions. In some cases progressively increasing swelling tendency required progressively increasing levels of applied pressure to prevent expansion, in one instance for as long as 24 hours. In some instances this progressive increase in pressure required to prevent swelling lasted only for a few hours, after which sudden shrinkage occurred,



(h)  $Na_2O:SiO_2 0,30$ 

(i)  $Na_2O:SiO_2 0,42$ 

indicating that some sudden structural rearrangement had taken place within the gel structure. In a few instances the gel suddenly became so fluid that it immediately leaked through the membrane confining it, thus terminating the test.

Several characteristic swelling pressure curves are illustrated in Figure 7.

The maximum values of swelling pressure attained, like the free swelling expansion results previously discussed, fell into two distinct categories. Three of the gels were clearly high swelling pressure generators, yielding maximum measured pressures between 2 MPa and approximately 11 MPa. The remainder developed pressures of less than 0,5 MPa. However, only two of the three gels that showed high expansion in the free swelling test also developed high swelling pressures. In fact, the gel yielding the highest free swell expansion (82 per cent) developed only a modest 0,4 MPa swelling pressure, and conversely, a gel that had one of the lowest expansions on free swell testing (1,7 per cent) developed the highest measured swelling pressure, almost 11 MPa. These gels of contrasting behaviour had similar compositions, the former having a soda:silica mole ratio of 0,27, the latter 0,34.

Again, there seemed to be no clear correlation between the soda:silica ratio and behaviour, an almost complete overlap existing between the compositions of the gels falling into the 'high pressure' and 'low pressure' groups. However, there is some indication that gels of soda:silica ratios just over 0,32 tend to be high swell pressure gels.

The two calcium-bearing gels tested were again modestly active in behaviour, developing maximum swelling pressures of 0,5 and 0,3 MPa, respectively. These values, though modest in comparison with those developed by the gels of the high pressure group, were higher than the swelling pressures developed by four of the eight purely soda:silica gels tested.



FIGURE 8 : Scanning electron micrograph of residual reacted opal grain in 33-day old reacting mortar.



#### CONCLUSIONS 8.

(a) It is possible to follow the kinetics of the chemical reaction between dissolved alkalis and reactive aggregates in mortars by monitoring the rate at which alkalis are withdrawn from the pore solutions.

(b) The chemical reaction is much more rapid at 40  $^{\circ}C$ than at 20 °C and in one series of mortars tested it was found to reach equilibrium by the third day.

(c) Mortar specimens sealed in butyl rubber jackets to prevent either entry or evaporation of water were found to expand in the normal manner. Thus expansion is not necessarily dependent on external water being supplied. but may occur in consequence of the sorption of pore solution into reaction product gels without the external entry of additional fluid. Such sorption does not change the concentration levels of alkali hydroxide; consequently, it must involve mass flow of pore fluid into the gel without discrimination between solute and solvent.

(d) Expansion (in the absence of external water) significantly lags behind the chemical reaction, both at ordinary (20  $^{\circ}$ C) and at elevated temperature (40  $^{\circ}$ C), confirming the separability of the two processes.

(e) Expansion at elevated temperature (40 °C) is initially accelerated as compared to expansion at ordinary temperature (20 °C), but it subsequently slows down and falls below the ordinary temperature response, leading to a net negative temperature effect on long-term expansions.

(f) Water vapour sorption isotherms for synthetic soda: silica gels show an expected general reaction between water affinity and sodic character of the gel. Gels containing calcium were not significantly different from soda: silica gels without calcium in the type and level of water sorption encountered.

Expansions of synthetic soda:silica gels on exposure (g) to water under free swelling conditions were either very high (of the order of 60 to 80 per cent) or quite low (less than 4 per cent), with no clear correlation to soda: silica ratio. Calcium-containing gels expanded modestly.

(h) Measured swelling pressure responses of the synthetic soda: silica gels also fell into two classes: a few gels capable of exerting high swelling pressure (4 to about 11 MPa), and the remainder exerting swelling pressures of less than 0,5 MPa. Again there was no clear correlation with chemical composition, although there was some indication that gels of soda: silica just over 0,3 tend to develop high swelling pressure.

(i) Gels showing large free swelling expansions did not necessarily develop high swelling pressures. The gel exhibiting the highest expansion developed only negligible pressure, and the gel exhibiting by far the highest swelling pressure exhibited only modest expansion on free swelling exposure.

(j) The calcium-bearing gels tested exhibited modest, though significant swelling pressures, higher than many of the purely soda: silica gels.

(k) Observations of opal grains in reacted mortars by scanning electron microscopy can be used to document the physical changes that have occurred.

(1) Spot analyses of reacted opal grains by energydispersive x-ray analysis indicate the rapid penetration of potassium completely through sand-sized aggregate grains within a few weeks. Such analyses also indicate the penetration of calcium, although it is concentrated primarily around the perimeter of the grains.

# ACKNOWLEDGEMENTS

Most of the work reported here was carried out with support from the National Science Foundation (ENG 77-09166) and from the US Department of Energy (EM-78-S-02-5027). The writers thank W L Dolch for extensive discussions, Janet Lovell for technical assistance, and Arnon Bentur for special assistance in the design and assembly of the apparatus for the testing of free swelling expansions and swelling pressures.

Spot No.	Counts, K	Counts, Si	Counts, Ca	Count Ratio	Coun Ratio
1*	0	16782	94125	0	5,61
2	1877	87710	12394	0,0214	0,14
3	1979	94670	1510	0,0209	0,01
4	1448	71918	574	0,0201	0,00
5	1392	63150	350	0,0220	0,00
6	1321	61490	374	0,0214	0,00
7**	876	54062	15745	0,0162	0,308
8	1432	64501	545	0,0222	0,008
9	1640	74033	723	0,0221	0.010

\*\* Spot near surface cement gel particle

an unknown but probably significant content of sodium, an element not detected by this instrument. Calcium has also penetrated through the grain, but is concentrated near the boundaries; thus the Ca:Si count ratio drops from 0,14 at spot 2 near the boundary to 0,016 at spot 3, to the order of 0,006 near the center of the grain.

These data are reminiscent of results reported by Poole<sup>5</sup> for mortars containing large tabular inclusions of opal. and of results on simulated mortars secured by the firstnamed author some years ago at the Concrete Research Laboratory, Karlstrup, Denmark. In these experiments opal cylinders 1 cm in diameter were machined from a solid block of opal and sealed into a container surrounded by a mixed bed of quartz sand grains and solid calcium hydroxide crystals into which had been added enough 1M potassium hydroxide solution to fill the pores. After an appropriate period the specimens were disassembled and the opal cylinder fractured to expose a cross section for examination. The results of EDXA examinations made at intervals from the periphery to the centre of the cross section for a 21-day old specimen are plotted as K:Si and Ca:Si count ratios in Figure 11. It is apparent that under these conditions calcium is in fact mobilized inward to some extent. but potassium ions are mobilized inward and fixed much more extensively and in substantially greater proportions.

The movement of calcium into reacting silica grains is particularly interesting in view of the very low calcium concentrations in the pore solutions. It may be that calcium entry into reacting siliceous aggregates is by a process of surface diffusion as originally postulated by Powers and Steinour<sup>6</sup> many years ago.

# TABLE 1 : EDXA spot analysis results for the spots indicated in Figure 10





Mr M P Brandt, (NBRI, Pretoria) said that the authors had shown in their Figure 1 that the alkali concentration in the pore solutions of the control mortar had maintained the same general level from  $\frac{1}{2}$  day to 30 days. (According to Prof Diamond's text this level is maintained indefinitely. Editor.) Was this the active alkali, he asked, and what percentage did it represent of the acid soluble (total) alkali content of a cement?

Prof S Diamond said that the figures on the graph represented the percentage of the total alkali content of the cement. So what they had in the control mortars, at least at any given time as shown on the graphs, was the percentage of, for all practical purposes, all the alkali brought into the sytem by the cement. (For the control mortar this was about 70 per cent of the total alkali content. Editor.) No alkali was contributed by any component of the aggregate and since the system was sealed they had good control over it. In a practical situation, of course, alkali might be introduced from various sources and this made things 'much more difficult'.

Mr M P Brandt said he had been interested to see in one of the slides that Prof Diamond had shown that the pH of the pore solution had become constant after, if he had read the graph correctly, about 30 to 40 days, and went on to say that he had adapted the ASTM C311 test to determine the available alkalis for different cements. For some cements it was the same as the total alkali or the acid soluble alkali content, but for others it was less and compared with the water soluble alkali content, the available alkali content was more. To him it was interesting to note that there was some comparison between the available alkalis of cements and the concentration of the alkalis in the pore solutions of the control mortar. In other words it was less than the total alkali content of the cement. He asked Prof Diamond the whereabouts of those alkalis which were not present in the pore solution.

Prof Diamond said he was not sure of the exact basis on which it had been decided what portion of the alkalis were 'available' and what were not. If he remembered correctly, the test for fly-ash involved its ability to react with lime, which really had no relevance to the system that was under discussion. He thought it was rather an arbitrary distinction.

# DISCUSSION

11

He thought that all the alkalis in cements that were reacting would eventually pass into solution and, if there were nothing else for them to react with, they would remain in solution, except for a small amount of sodium and potassium that would find its way into the hydrating cement gel. Some of this was deposited in solid solution in the CSH, perhaps another hydrated species, although not very much. To summarise he thought that almost all of the alkalis in cement, would, in time, dissolve and become 'available' in the system.

Mr M P Brandt explained that the determination of the available alkalis in cements was done without the addition of lime. With regard to Prof Diamond's comment that all the alkalis in a cement would eventually pass into solution he said this might be true but the fact was that a cement with a high total alkali content but with low available alkali content did not give expansion with Malmesbury aggregate after 500 days. (The available alkali content is the amount of alkali extracted when 7 g of cement is mixed with 10 ml of distilled water and kept at 38  $^{\circ}$ C for 28 days. Editor.)

Mr R Rimmer, (Engineer, City Health Department, Johannesburg) asked whether Prof Diamond could explain the difference between the time taken for the gel expansion to take place, which was of the order of hours, and the time taken for this expansion to manifest itself in a concrete structure, which was of the order of years.

Prof S Diamond replied that if one studied the expansion of synthetic gels in free swelling tests or in swell-pressure tests, it took a matter of hours or days. The gel had ready access to water and responded very quickly. In the expansion measurements that he had shown for mortars, the period was of the order of days, weeks and months and, in one case, of more than a year, despite the fact that there was no water entering from the outside. What had been going on was that there had been a redistribution of fluid within the mortar. Swelling of the affected gel might take longer if the fluid involved had to work its way through reasonably tight pores. Prof Diamond thought that the time scale involved depended not on how long it took the gel to 'want to swell', but on how long it took to get the fluid to the gel. In other words it was a transport problem that limited the rate at which expansion took place rather than the mechanical problem of getting the gel to swell when fluid was available.

- 1. STRUBLE L J Swell and other properties of synthetic alkali silica gels, MS Thesis, School of Civil Engineering, Purdue University, 1979.
- 2. DIAMOND S and BARNEYBACK R S, JI A prospective measure for the extent of alkali-silica reaction, in 'The effects of alkalis on the properties of concrete'. A B Poole, ed, Cement and Concrete Assn, London, 1976.
- 3. GUTTERIDGE W A and HOBBS D W Some chemical and physical properties of Beltane opal rock and its gelatinous alkali silica reaction product, Cem Concr Res 10 1830194, 1980.

#### REFERENCES

FRENCH W J The role of solvent migration in 4. alkali-silica reactivity, in 'The effects of alkalis on the properties of concrete'. A B Poole, ed, Cement and Concrete Assn, London, 1976. POOLE A B Electron probe microanalyses of 5. reaction zones at cement/opal interfaces, in 'The effects of alkalis on the properties of concrete'. A B Poole, ed, Cement and Concrete Assn, London, 1976. POWERS T C and STEINOUR H H An interpre-6. tation of some published researches on the alkali aggregate reaction, part 2. A hypothesis concerning safe and unsafe reactions with reactive silica in concrete, J Amer Concr Inst Proc V 51, 1955.

10