

CONTINUING STUDIES OF ALKALI-AGGREGATE REACTIONS IN CONCRETE

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SYNOPSIS

Studies are continuing into the nature of the different forms of the alkali-aggregate reaction. No general agreement exists as to the detailed nature of the expansive mechanisms.

Alkali is known to react internally with opaline silica because of its microporous nature whereas reaction at the external surface is thought to be relatively more important in the case of quartz. A combination of Fourier shape and surface texture analysis, microscopy and osmotic studies is being used to obtain information on the relative importance of these two forms of alkaline attack on silica.

Analytical methods are much more rapid than dimensional change tests and it is hoped that a better understanding of the expansion mechanism will lead to more certain recognition of potentially alkali expansive aggregates.

SAMEVATTING

Ondersoeke in verband met die aard van verskillende vorme van die alkali-aggregaatreaksie word voortgesit. Daar bestaan geen algemene ooreenkoms ten opsigte van die gedetailleerde aard van uitsetmeganismes nie.

Dit is bekend dat alkali intern met opaalsilika reageer as gevolg van die mikroporieuse aard; reaksie op die eksterne oppervlak, daarenteen, word in die geval van kwarts as van relatief groter belang beskou. 'n Kombinasie van Fourier-vorm- en -oppervlaktekstuurontleding, mikroskopie en osmotiese ondersoeke word gebruik om inligting aangaande die relatiewe belang van hierdie twee vorms van alkali-aanval op silika te bekom.

Analitiese metodes is baie vinniger as dimensionele veranderingstoetse en daar word vertrou dat 'n beter begrip van die uitset meganisme tot 'n sekerder herkenning van potensiële alkali-uitsetbare aggregate sal lei.

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1. INTRODUCTION

The continuing dramatic increase in the price of fuel has accelerated the predicted trend towards the manufacture of cement with increased alkali content. This has resulted from the increased use of more energy-efficient dry process kilns even though bypass systems can be constructed which make possible alkali reduction. Environmental protection, use of coal-fired kilns and difficulties in obtaining raw materials of low alkali content have significantly affected this trend. This has led to increased interest in the influence of alkalis on clinkering reactions in the kiln, on cement hydration and in the role played in the alkali-aggregate reaction. Durability problems from this cause in portland cement concrete are expected to increase as, among other things, the alkali content of cement goes up, and as quality materials close to urban centres become depleted and the use of marginal aggregates increases. Remedial techniques and more rapid and reliable methods for the recognition of potentially alkali-expansive aggregates are therefore of interest. Analytical methods are much more rapid than dimensional change tests and a better understanding of the mechanism of the reaction should lead to more reliable identification of deleterious aggregates.

Durability problems and the influence of alkalis on the properties of portland cement and concrete have been reviewed in numerous publications (Brotschi and Mehta¹; Diamond^{2 · 3}; Gillott^{4 · 5}; Jawed and Skalny^{6 · 7}) and in the proceedings of the four symposia on this topic. It is the object of the present paper to describe some recent studies of the behaviour of various forms of silica in strong sodium hydroxide solution.

2. NATURE OF SAMPLES

Three forms of silica were chosen for comparative studies. These were opal, strained quartzite and quartz (rock crystal).

The opal was a non-precious, light brown variety from Mexico which displays conchoidal fracture. It appeared isotropic under the petrographic microscope; when examined on the scanning electron microscope fracture surfaces showed a very fine 'rounded' texture with no visible pore space or evidence of organic remains (Figs 1a & b, page 2). X-ray diffraction analysis showed that the material was relatively well crystallized compared to other opals (Jones et al[®]) and the polymorphic form was cristobalite (Fig 2, page 3).

The quartzite, which came from the Appalachian region of Eastern Canada, was observed in a hand specimen to be a medium grained rock displaying lineation and iron staining. Under the petrographic microscope the quartz crystals showed elongation (\sim 0,5 mm x 1,0 mm) and strain extinction.

The rock crystal was from Hot Springs, Arkansas, USA; the quartz crystals exceeded 1 cm, showed no strain or iron staining and few impurities. The samples of opal and rock crystal were obtained from Ward's Natural Science Establishment, Inc, and the quartzite was supplied by the Department of Geology, University of Calgary.

3. EXPERIMENTAL METHODS

Changes in shape, texture and crystallinity of the silica samples as a function of time in NaOH at 38 $^{\circ}$ C were studied. Shape and texture were investigated microscopically by light optical and electron optical methods and mathematically by the Fourier method. Mineralogical composition, crystallinity and crystallite size were determined by x-ray diffraction; dimensional change was studied with an osmotic cell.

The silica samples were crushed with pestle and mortar to pass #16 and be retained on # 50 mesh sieves, then washed and stored at 38 $^{\circ}$ C in a dry atmosphere. For Fourier analysis samples of 100 grains each were obtained from the crushed aggregate by 'riffling'. This entailed splitting the complete 'population' a number of times to obtain samples of the desired size. For light and electron microscopic examination grains of each silica type were randomly chosen from the same crushed aggregate from which the samples for numerical shape testing were taken; similar material was used for the studies of dimensional change characteristics. Samples for x-ray diffraction analysis were also taken from the same crushed aggregate and ground for 30 minutes in methanol to give a suitably fine powder.

The concentration of the sodium hydroxide (NaOH) used as the aggressive solution was 1,6 M calculated from a hypothetical consideration of the free water and available alkali in a concrete. Assuming that concrete is made with a water/ cement ratio of 0,5 and uses a cement of 1,1% Na₂0 equivalent alkali content, then the saturated mature concrete would have a pore solution concentration of 50 g Na₂0/litre if 55% of the water is involved in cement hydration and 100% of the alkali is dissolved. In practice hydration rate, free water evaporation and rate of alkali solubility will cause variations in the concentration and the solution. The concentration calculated using these assumptions probably represents an extreme case.

(a) Light microscopy. Photographs of the grains of silica were taken in transmitted light using a Leitz orthoplan microscope. They were then put in petri dishes containing 10 ml of 1,6 M NaOH and stored above a water bath maintained at 38 °C. Photographs of the treated grains were taken at regular intervals in order to provide direct comparisons with the numerical data. It was found that it was most practical to photograph the grains while still in the solution since the washing and drving of single grains was a difficult operation likely to cause damage to the delicate opal particles. In order for the grains to be photographed while immersed it was necessary to use a much larger ratio of alkali to silica than in the tests for Fourier analysis of shape change. Since the solution will take much longer to become saturated in silica it is assumed that this is a more aggressive test. The grains illustrated in Fig 3 (page 4) show changes in shape typical of other grains of the same silica type.





FIG 2 : X-ray diffractograms of opal

Opal grains were translucent when untreated. After only a few hours in sodium hydroxide they became white and opaque if removed from the solution and allowed to dry slightly. Upon returning to the solution they again became translucent. If removed after several days, drying caused marked shrinkage, the dimensions of the grains decreasing by about 25%. The drying shrinkage seemed not to alter gross shape but internal micro-structural change was evidently implied.

A majority of the grains studied were constantly immersed in sodium hydroxide to prevent possible damage by mishandling. Features of the attack on the opal grains are typified by the grain in Fig 3a to 3d. It can be seen that:

- Gross shape was maintained over 28 days; (i)
- Some rounding of corners took place; (ii)
- (iii) The relief of the grain became extremely low, ie its refractive index came closer to that of water:
- (iv) Surface overgrowth formed at between one and two weeks. This is presumably caused by outgrowth of gel products rather than precipitation of silica from the solution since the concentration of silica in solution was below the level of saturation* under the conditions of the experiment;
- The surface overgrowth was not stable. The area of (v) reaction product visible on the righthand side of the

grain in Fig 3c disappeared by the fourth week (Fig 3d). At four weeks the grain also showed some signs of general disintegration; the surface became diffused and was apparently severely pitted. Other grains developed large cracks at this age and it is likely that the grains used for shape analysis would have developed this distress earlier due to the cyclic wetting and drying they underwent.

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The quartz and quartzite grains were studied microscopically for 3 months. In no case was shape change, growth of reaction products or loss of relief observed (Fig 3e to 3h). This was not unexpected in the case of the quartz crystals but it was hoped that some change may have been scen in the quartzite. The crystals were severely strained and as shown in the Figure, some of the grains were highly textured with numerous asperities. Nonetheless the quartz crystals, though strained, were relatively large (0,5 x 1,0 mm) and possibly this factor was of paramount importance on the time-scale of the experiments.

(b) Electron microscopy. Fragments of each of the minerals were mounted on stainless steel stubs using epoxy resin adhesive. All were metalized with aluminum and viewed in a Cambridge S-150 scanning electron microscope. A series of micrographs were taken, each at progressively higher magnification, to aid in relocation (Gillott ''). Following initial viewing the samples were placed in 1,6 M sodium hydroxide for a few seconds to remove the aluminium coating and then in another container of the same solution and stored at 38 °C. For subsequent study each stub was removed from its container, washed in gently circulating deionized water for eight hours (with 4 changes of water) then dried before being metalized once more and viewed in the microscope. Air drying caused severe shrinkage and some cracking of the opal fragments so other specimens were either freeze dried or critical point dried from water (Gillott¹¹). Similar distress was not noted in the quartz or quartzite fragments and it was assumed that air drying did not harm them.

Opal samples, prior to treatment, showed a fine 'spheroidal' microtexture on glassy surfaces and coarser microtextural detail at conchoidal fractures (Fig 1a, b). Following 7 days treatment in 1,6 M Na0H solution at 38 ^OC conchoidal fracture lines were still present and relatively coarse features could be relocated. Change in the microstructure of the opal was however so extreme that at high magnification original areas could not be recognized. The surface of air dried specimens appeared composed of a mass of small closely packed platelets (Fig 1c).

Opal samples were delicate and readily cut by a knife after alkali treatment and as mentioned air drying caused marked shrinkage. Freeze drying and critical point drying produced negligible shrinkage. Samples prepared by both methods were found to be microfibrous (Fig 1d, e) and quite different in appearance from the air dried material. An area of overgrowth, presumably of the same type as that seen in the light micrographs of opal, was also found to have a microfibrous texture (Fig 1f). Although very similar the



Untreated opal



Opal after 1 week in 1,6N NaOH (air dried) (c)



Opal after 1 week in 1,6N NaOH (fractured sur-(e) face, critical-point dried)



Untreated opal (b)



Opal after 1 week in 1,6N NaOH (freeze dried) (d)



Overgrowth on opal after 1 week in 1,6N NaOH (freeze dried)

FIGURE 1 : Scanning electron micrographs of untreated and alkali-treated opal

(f)

fibrous texture is finer in the original fragment than in the overgrowth. The fibrous nature of the material is reminiscent of lussatite, fibrous cristobalite found in association with opal and chalcedony (Frondel¹²). It is not known whether the fibrous microstructure is formed during reaction with sodium hydroxide or whether the fibres are original, being exposed by the alkali, which has an etching effect, removing a more highly reactive silica cement in which the more crystalline fibres were embedded. Etching of opal using hydrofluoric acid resulted in a microtexture resembling the conchoidal fracture lines in the untreated samples. Elemental analysis using an energy dispersive x-ray analysis system shows very low sodium content in the fibres - of the order of 0,5 - 3 per cent; the small cross-section of the fibres precludes accurate analysis and so no corrections were made for matrix effects. It was found that varying the method of sample preparation resulted in further differences in appearance of the sample surface at high magnification. Platelets and delicate foils were observed not unlike textures shown by Diamond¹³ in synthetic silica gels.

Samples of alkali-reacted opal, which had been freeze-dried. were gently crushed and disaggregated in a solution of water and alcohol. Drops of the dilute suspension were deposited on grids used for transmission electron microscopy and allowed to air-dry. Transmission electron micrographs confirmed the fibrous nature of the material and showed that some of the fibres appeared to be 'hollow' suggesting a tubular morphology (Fig 4). The significance of features of this sort on electron micrographs of fibrous minerals has been discussed in the literature (Whittaker and Zussman¹⁴). The suggestion has been made that the appearance may not result from a hollow fibre but could arise from diffraction contrast effects associated with differences in crystallographic orientation in different parts of the fibre. In the case of some of the serpentine minerals high resolution electron micrographs of cross-sections of the fibres have been used to answer the question. Some of the fibres of the alkali-treated opal appear 'solid' but others are very similar to micrographs of tubular minerals.



FIG 4 : Transmission electron micrograph of freeze dried alkali-treated opal 1270Å

No changes could be detected by scanning electron microscopy using area relocation in either the quartz or quartzite samples after 4 weeks in sodium hydroxide even though fine asperities were visible on some surfaces. As all forms of silica are soluble at high pH, and rate of solution increases with temperature (Krauskopf⁹) the lack of change indicates that insufficient time was allowed for significant dissolution of even the strained quartz. Evidently the rate is very slow.

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(c) The Fourier method. A Fourier series may be used to express the shape and texture of a grain and this principle was developed into a method of shape analysis by Ehrlich and Weinberg¹⁵. Shape was defined as the intersection with a plane of the maximum projected area of a grain. Coordinates on the grain outline are recorded by a digitizer with respect to an arbitrary internal or external origin. Fourier coefficients are calculated at each harmonic number by a computer programme. From the amplitude coefficients various other coefficients have been calculated to express grain shape and surface texture. Shape may be expressed as one numerical value, T, the total roughness, which is the sum of the shape contribution factor, P_c , and the surface texture contribution factor, T_c, (Czarnecka and Gillott¹⁶). There are various methods for comparing the results obtained for different samples or samples subjected to different treatments.

In the present work the outlines of grains to be digitized were traced from the magnified image on the screen of a Vickers projection microscope. About 100 images per hour could be prepared by this method. Outlines of grains were traced prior to treatment and the same grains were repeatedly traced after increasing periods of immersion in 1,6 M Na0H at 38 $^{\circ}$ C to maximum ages of 1 month; data at ages of 3 months and 6 months are to be recorded.

The traced grain outlines were digitized using a Tektronix automatic digitizing tablet operating on-line to the University of Calgary Honeywell Multics system. The tablet was capable of locating a pencil type probe and providing its rectangular coordinates to an accuracy of \pm 0,125 mm on each axis. A Fourier series was calculated for each grain periphery from the rectangular coordinate data using a computer program written at the University of Calgary. The number of harmonic terms in the Fourier series is an operator selected variable. Following tests on series of 'artificial' shapes it was decided that 15 harmonics would provide a sufficiently accurate description of the opal and quartz grains while 20 harmonics was chosen for the more textured quartzite grains.

Data were analyzed by various methods. It was found that the quartzite grains were rather rounder but more textured than the opal or quartz. After 28 days in NaOH the quartz and quartzite particles showed no statistically significant evidence of change in shape. For opal, changes in shape coefficients, although significant in some cases, lacked any consistent trends and were thus difficult to interpret. It was believed that this resulted from the complex micro-



(a) Untreated opal



(b) Opal after 1 week in 1,6N NaOH



(c) Opal after 2 weeks in 1,6N NaOH



(d) Opal after 4 weeks in 1,6N NaOH





(f) Quartzite after 1 week in 1,6N NaOH



(g) Quartzite after 4 weeks in 1,6N NaOH





1 mm

FIGURE 3 : Optical micrographs of opal and quartzite

chambers are filled with sodium hydroxide solution. Therefore reaction between sodium hydroxide and silica takes place in only one chamber while the other provides a source of fresh sodium hydroxide solution. Nominal capacity of each chamber was 20 ml. Flow between the chambers and total expansion of the system was measured using capillary tubes inserted through the top opening in each chamber.

The membrane was made from a very high water/cement ratio cement paste (w/c = 0,7) in order to achieve high flow rates and rapid completion of reactions. The paste was moist cured for 15 days, after demolding at 24 hours, then sawn and ground to a thickness suitable for use as membranes. The membrane was stored in a dry atmosphere prior to use to prevent hydration and reduction of permeability. It is very unlikely that this cement paste was truly semipermeable but it was capable of maintaining the maximum difference between fluid levels in the capillary tubes for long periods of time and proved a satisfactory membrane in practice. It is probable that sodium and hydroxyl ions could migrate freely through the membrane in response to changes in concentration since even silica gel moved into the silica-free chamber after 3 to 4 weeks of reaction.

Degassed, 1,6 M sodium hydroxide was placed in each chamber of the assembled cell and the cell was then placed in a desiccator under vacuum to saturate the cement paste membrane. The silica was vacuum saturated with water to avoid the possibility of either apparent volume reduction as air held in pore spaces was displaced or of protection of parts of the silica surface by trapped air. Silica could not be saturated with sodium hydroxide as the procedure takes several hours and dimensional changes at early stages of reaction would not have been measurable. After degassing, both the cell and the water-saturated silica were placed



in a water bath at 38 °C until temperature equilibrium had been reached (at least 12 hours was usually allowed since the plexiglass cell was found to have considerable thermal inertia). Once equilibrium had been reached the surface dried silica was added to one chamber of the cell, the capillary tubes were fitted and fluid level readings begun immediately. Levels in the capillaries were read using a cathetometer. Readings were taken periodically until the flow rate between the cells had decreased sufficiently for an asymptote to be estimated or until the meniscus went off-scale.

Capillary tubes were calibrated with mercury to ascertain their bore. Their volume per unit length was found by using a precision syringe. Volumes of liquid flowing between the chambers of the cell and absolute expansion of the system could then be calculated. These were found as percentages of the original specific volume of silica.

Neither quartz nor quartzite produced measurable volume changes after 28 days; that is, less than an estimated experimental error of 0,25% of original silica volume. In both cases 3 g silica to 40 ml sodium hydroxide was used. A three month test of quartzite is being undertaken at present with the cell sealed with epoxy resin to prevent possible leakage.

Opal was found to be strongly expansive and the test was repeated with a number of different alkali/aggregate proportions. Fluid volume was constant at 40 ml. Results are shown in graphical form in Figs 6 and 7. The volume of fluid imbibed by the opal (Fig 6) increased at a consistent rate for any one test but that rate was not the same at any two different alkali:silica ratios. The sample with lowest silica to alkali ratio (0,5 SiO₂:1,0 Na₂O) showed a relatively low rate of imbibition in comparison to other samples but imbibition continued for a longer time. With increase in relative proportion of silica there was an increase in rate but decrease in imbibition. If one arbitrarily selects a time of 250 hours one finds that there is a maximum in the rate of flow at about 3,0 in the ratio of grams opal:grams Na₂O; this peak is reminiscent of the pessimum found when using the mortar bar test (Fig 7).



alkali ratios

structural changes observed microscopically. Outgrowth and subsequent dissolution of reaction products are believed partly responsible.

(d) X-ray diffraction. X-ray diffraction patterns of the different forms of silica were recorded on a Philips diffractometer and Nonius Guinier camera. The quartz sample, ground to a size at which sharp diffraction maxima were recorded, was used as a standard for comparison of the other samples.

The quartzite, though composed of strained quartz, showed only a small amount of line broadening. The opal was composed of a-cristobalite which, when compared with results published by Jones et al^a, was found to be relatively well crystallized (Fig 2). Diffractograms of the total sample showed little decrease in crystallinity or increase in line breadth after 3 weeks immersion in 1,6 M NaOH at



38 °C. Microscopic examination had indicated that some grains altered more rapidly than others. Altered grains are lighter than unaltered or only slightly altered grains so following treatment in alkali some of the opal was fractionated by gravity separation. X-ray diffraction photographs of this material taken on the Guinier camera showed decrease in crystallinity but no peak shifts or new crystalline phases were detected. The breadth of various diffraction lines was measured and the size of the crystallites in the opal was found by use of the Scherrer equation to be between 50 and 75 Å.

(e) Dimensional change. A two chambered cell (Fig 5), the design of which was based on a sketch published by Verbeck and Gramlich¹⁷, was used to investigate dimensional change behaviour in the three forms of silica. In the cell the two chambers are divided by a cement paste membrane. Silica is placed in only one chamber while both

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4. DISCUSSION

The present work is a continuation of studies of alkaliaggregate reactions which have progressed in many laboratories for over 40 years. There is general agreement that osmosis is the driving force in the alkali-silica reaction. This requires preferential diffusion of water into the reactive particles of silica with increase in volume and generation of swelling pressure. It is also believed that the silica need not be separated from the alkaline solution by a secondary semipermeable membrane such as cement paste and that expansive forces are produced while the silica particles remain essentially solid. With time the hydroxyl ion from the alkaline solution causes sufficient breakdown of the silica structure for fluid gels to form; these migrate through cracks and sufficiently large pore spaces and appear in pockets and at the surface of affected concrete. Differences of reactivity of different forms of silica are attributed to differences in crystallinity, internal surface area, composition, etc. Many details of the reaction mechanism such as the cause of the pessimum, the role of pozzolans and the influence of various cations (eg Li, Na, K, Ca) remain unclear.

The studies with the optical microscope in the present work confirm former ideas concerning the progress of the reaction between opaline silica and alkali. The decrease in refractive index implies movement of moisture into the grain, gel-like reaction products form at the surface and grains eventually crack and disintegrate. The observations with the scanning electron microscope of the relatively rapid development of a microfibrous texture appear not to have been previously described in studies of alkali-silica reaction, though occurrence of fibrous silica of natural origin (lussatite - fibrous cristobalite; chalcedony-fibrous quartz) is well documented.

Studies with the osmotic cell yielded a curve of rate of flow similar in form to that obtained with mortar bars in that a pessimum occurs. The curve showing total flow is however quite different and suggests that the maximum expansion should occur for small amounts of opal. Presumably rate of flow is more closely connected with expansion than total flow under the conditions of a mortar bar test.

In recent articles the growth mechanism in 'silicate gardens' and in the hydration of portland cement has been discussed (Double et al¹⁸; Double and Hellawell¹⁹). These authors propose a two-stage process in which initially an envelope of colloidal gel forms surrounding a reacting particle followed by secondary growth of fibres. In the postulated sequence moisture migrates through the envelope in response to the concentration gradient. The gel functions as a semi-permeable membrane so osmotic pressure builds up within the envelope. When its tensile strength is exceeded at points of weakness jets are ejected into the surrounding solution where reaction occurs with precipitation of tubular fibrils. Growth of the fibrous tubes continues until they narrow down and close because driving pressure decreases or viscous drag increases. Fibres within the grains of the alkali-treated opal are similar (though finer) to those in the over-growth. Thus while the inner fibres could have a natural origin similar to those in lussatite, etc, the external fibres at least must be a growth feature resulting from reaction with the alkali.

The transmission electron micrographs suggest a tubular morphology for the fibrous alkali-reaction products of opal. If this is confirmed by future work it seems not unlikely that growth mechanisms in 'silicate gardens', in portland cement and in the alkali-opal reaction may well be similar. Certainly the proposed osmotic effects resemble ideas which have been discussed for many years concerning the expansive mechanism of alkali-silica reaction and the fibrous morphology of the freeze dried and super critical dried alkali-reacted opal and its products reinforce the suggested connection.

5. CONCLUSIONS

(a) External morphology does not provide an accurate guide to aggregate reactivity in alkali. Changes on internal surfaces have preponderant effects in reactive minerals such as opal. Despite the mathematical precision possible with the Fourier method, changes in the shape of materials such as quartzite are too slow to be measurable on a relatively short time scale. It is therefore unlikely that this approach will lead to a rapid method for recognition of alkaliexpansive aggregates.

(b) Alteration of quartz and quartzite samples during the period of the investigation was not observed by microscopic methods. Opal was found to undergo a microstructural change from smooth and glassy in the fracture surface to microfibrous within a relatively short period (less than 1 week) in the presence of sodium hydroxide solution. Careful specimen preparation using freeze- or critical point-drying was essential to avoid damage to the fibrous opal structure.

(c) It was shown by x-ray diffraction that the crystallinity of the opal was reduced by reaction with sodium hydroxide but that the original cristobalite did not alter to another crystal form.

(d) Studies with an 'osmotic cell' show that flow becomes negligible once solution ion concentration reaches a certain level although the solution is still strongly basic at this concentration. Continued increase in volume was noted for the alkali solution/silica system after flow had ceased.

(d) Attention is drawn to the fibrous structures described in the literature in 'silicate gardens' and the possibility of related growth mechanisms is discussed in the light of the fibrous, and possibly tubular, structures observed in alkali-reacted opal.

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DISCUSSION

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Dr P E Grattan-Bellew (NRC, Ottawa, Canada) referring to the quartzite containing strained quartz which had been exposed to 1,6 M NaOH and which had not expanded after three months treatment asked whether it was possible that Prof Gillott had not waited long enough and should have treated it for six months or more. He said they had found that rocks such as quartzites were 'slow expanders'.

Prof J E Gillott admitted that this was quite possible. However, the reason they had not done so was because if one had to wait that long, it would not be much use as a means of rapid analysis.

Dr Ian Sims (Messrs Sandberg, London) asked whether their results with strained quartz suggested that considerable caution should be exercised in extrapolating experimental results obtained from opal aggregates to cover other more realistic aggregate materials.

Prof J E Gillott agreed and said that he had a suspicion that people like himself tended to like working with opaline materials because, of course, something happened in a reasonable length of time and whether one was really justified in going from these results to a rock such as a metamorphic quartzite, was something which was, in a way, slightly bothersome. There was a tendency to do this, and perhaps they were right, but he had misgivings about it.

Mr D A St John (DSIR, New Zealand) asked whether Prof Gillott would comment further on the textural change which occurred in opal exposed to sodium hydroxide. One started out with a clear opal grain and within a week its microscopic optical texture had changed quite dramatically. What mineralogical changes would he think were causing the optical changes. Prof J E Gillott thought that moisture and alkaline solutions entered the micro-pore system and that the changes were, at least, in part caused by a fall in the refractive index. Certainly, one could tell from the ease with which one could see the grain boundary that there had been a marked decrease in the refractive index. The authors thought that this was probably due to the imbibition of water and obviously the penetration of alkali into the grain.

Dr P E Grattan-Bellew wondered whether some of the fibres or tubules could be growing from the actual pores within the opal and asked whether the pore size distribution of the opal had been measured before work began.

Prof J E Gillott said they had not measured pore size distribution. They had, in fact, wondered whether the material had been fibrous to begin with, in other words something like fibrous cristobalite (lussatite) and whether they were simply dissolving away some phase which was between the fibres and in effect doing a 'glorified etch technique' leaving a fibrous structure which was original to the type of opal that they happened to be working with. For that reason they had examined the outgrowth material which was certainly not part of the original grain although it had also shown a similar fibrous morphology. When they had done the transmission electron microscope work they had been surprised to find that at least some of the fibres looked as though they might be hollow, and resembled the phenomena described by Double et al¹⁰ and Double and Hellawel¹⁹ in their growth experiments.

Dr P E Grattan-Bellew re-emphasised that as the opal began to dissolve, it would probably dissolve in the pores whereupon the uptake of moisture by the presumably gel-like material in the pores would force it out and one might get the kind of texture that had been observed. It would be interesting to see if the diameter of those fibres or tubules was approximately the same as that of the pores.

