

ALKALI-CARBONATE REACTIONS IN CONCRETE

by Dr A B Poole*

SYNOPSIS

Certain types of carbonate aggregate will react with alkalis from the cement paste in concretes. At least three types of reaction have been identified. One, which involves fine grained dolomitic limestone aggregate, has been shown to cause deleterious expansion in concrete. Detailed experimental studies using electron probe micro-analysis show how ion concentration maxima develop and migrate through the reacting zones with time. The modification of ionic concentrations in the cement paste pore fluids have also been investigated by this technique to show how changes in Na^+ and OH^- ions modify the reaction rate. Scanning electron microscopy has been used to study the solution and crystallisation of phases in the reacting zones and to investigate the role of the interstitial clay in producing the expansive and disruptive features of the reaction.

SAMEVATTING

Sekere tipes karbonaat-aggregaat sal met alkalië uit die sementbry in beton reageer. Minstens drie tipes reaksie is geïdentifiseer. Een, waarby fynkorrelrige dolomitiese kalksteen betrokke is, is uitgewys as die oorsaak van vernietigende uitsetting in beton. Gedetailleerde eksperimentele ondersoek, waarin van mikrosonde ontleding gebruik gemaak is, toon hoe ionkonsentrasie ontwikkel en met verloop van tyd deur die reaktiewe sones beweeg. Die wysiging van ionkonsentrasie in die sementbryporievloeistowwe is ook dmv hierdie tegniek ondersoek om aan te toon hoe veranderinge in Na^+ en OH^- ione die reaksietempo wysig. Aftaselektronmikroskopie is gebruik om die oplossing en kristallisering van fases in die reaksiesones te bestudeer en die rol van die tussenruimtelike klei te ondersoek wat die uitset- en verbrokkelingskenmerke van die reaksie veroorsaak.

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the alkali-siliceous rock reaction, seemingly to indicate different types of reaction mechanism. He asked Prof Gillott whether he still believed it was the phyllosilicates that caused expansion with rock types such as greywackes, hornfelses and phyllites, and whether he would use the term alkali-silicate reaction specifically for this mechanism. If so he asked would this signify a different reaction to the one for which Dr Grattan-Bellew used the term alkali-siliceous rock reaction in his papers. He added that in their work on the Malmesbury Group of rocks NBRI researchers had been unable to prove that it was the phyllosilicates that caused the expansion in concrete.

Prof J Gillott (University of Calgary, Canada) replied that when he had suggested that the phyllosilicates were a significant factor in the expansion mechanism in Nova Scotia, much of the work had been quite new and he had felt then that the exfoliation that had been observed was probably significant in so far as the expansive mechanism was concerned. He still thought that it might be the case because he had observed this type of reaction in other rocks of this type, from other places, but had always to bear in mind that it was quite possible that it was the fine-grained quartz or other forms of silica in the rock that were the major factors in the mechanism of expansion. Nova Scotian rocks were metamorphic and the quartz might well show strain and certainly was fine-grained. All fine-grained silica was to some extent soluble in alkaline solution and so gel products might be formed and presumably could perform in much the same way as they did from more reactive forms of silica such as opal. He had suggested that the alkali-aggregate reaction should be subdivided into more than one category because he thought that in addition to the possibility that there was a different mechanism in rocks of this sort, there were significant differences between the way in which those rocks had behaved and what he had called the classical alkali-silica reaction. He felt it was convenient to have more than one 'general sack category' for alkali-aggregate reactions. As to whether the phyllosilicates contributed to expansion, he thought they did, but had always recognised the possibility that they were not the major cause. Possibly it was indeed the fine-grained quartz which was the principal cause of expansion, but either way he still thought it was useful to have more than one class of alkali-aggregate reaction and whether the term alkali-silicate was adopted for rocks of this kind or whether one referred merely to siliceous rock did not matter greatly. What did matter was that it was convenient to be able to categorise the reactions.

Dr L Dolar-Mantuani (Ontario, Canada) claimed that she was the originator of the term alkali-siliceous rock reaction, and said that she had introduced it because she needed a wider term than alkali-silica reaction (which she said referred to the reaction of alkalis with the metastable silica minerals and volcanic glasses) to include rocks such as quartzite, granite, granodiorite and gneiss. There was no doubt that with the greywackes and argillites of the Canadian shield, there was a silica reaction in which plenty of gel formed. The grey-

wackes that occurred in the Appalachians were different in that as a result of hydrothermal action vermiculite had been formed. However, despite the fact that the vermiculite may exfoliate, she could not see why there should be a different reaction with the cement alkalis.

Dr P E Grattan-Bellew (NRC, Ottawa, Canada) said he did not think that there was a fundamental difference in the mechanism of the classical alkali-silica reaction and the reaction mechanism of the slowly expanding siliceous rocks.

He was not entirely satisfied with the term 'siliceous' but it had been used by Dr L Dolar-Mantuani and he hesitated to coin yet another new definition.

He thought it would be much better to use the term 'slowly expanding silica reaction' in place of siliceous aggregate reaction.

The reason for needing a second definition at all was that the siliceous aggregates such as greywacke, some quartzites, quartz biotite and gneiss, which showed this reaction expanded much more slowly than the classical alkali-silica aggregates and this fact was very important in testing.

In the case of the classical alkali-silica reaction a test could be done in 36 days, or at most 3 months, but if one ran such a test on a slowly expanding silica aggregate for only 3 months one would conclude (incorrectly) that they were non-expansive.

He believed that in both reactions the mechanism was the same but that it showed up in different ways.

In the classical alkali-silica reaction

- the opal was first attacked by the alkali and swelled (expanded)
- the opal then started to dissolve and shrank
- the 'gel'-impregnated pores in the concrete absorbed water and swelled creating internal pressure which resulted in the expansion of the concrete.

In the slowly expanding silica aggregates (e.g. hornfels)

- the grain boundary region between the quartz grains where there was a high concentration of defects, and hence high free energy, was attacked by alkali and started to dissolve
- this resulted in the expansion of the aggregate either through the release of stress or through the 'gel' impregnating the pores in rock as for the classical reaction.

The expansion of concrete might be due to both the expansion of aggregate and to a mechanism similar to (c). The difference was that in this case only a small part of the SiO_2 that occurred around the grain boundaries was soluble and available to form 'gel'.

1. INTRODUCTION

Deterioration of concrete resulting from the reaction between sodium and potassium hydroxides released from the cement and certain types of silicious aggregates was first described by Stanton¹ in 1940 and has since been the subject of much research. A different type of reaction involving the inter-action between cement alkalis and dolomitic limestone aggregate was recognised and reported by Swenson² in 1957. This reaction is quite distinct from the alkali-silica reaction in that no expansive gel reaction product is formed though the disruptive deterioration of the concrete can be quite severe as is indicated by the description of a section of sidewalk given by Swenson in 1957. 'Excessive expansion had closed the joints and cracking had occurred within six months of placing. The cracks defined roughly hexagonal areas 2 to 3 inches across and extended deeply into the concrete, being clearly distinguishable from surface crazing.' Since these original observations were made at Kingston, Ontario, Canada, many other cases of alkali-carbonate reactivity in concretes have been reported from many parts of the world. These include areas in the USA reported by Newlon and Sherwood³, Axon and Lind⁴, Welp and De Young⁵, Hadley⁶ and others, Iraq, reported by Alsinawi and Murad⁷, and Bahrain by Hussen⁸. Various types of alkali-carbonate reaction have also been reported though not all of them appear to be expansive or deleterious. They may be classified into the following broad groups principally according to the type of reaction rim or reaction products they produce.

a) Carbonate reactions with calcitic limestone. Dark reaction rims develop in the margin of the limestone aggregate particles. These rims are more soluble in hydrochloric acid than the interior of the particle⁹.

b) Reactions involving dolomitic limestones characterised by distinct reaction rims within the aggregate. Etching with hydrochloric acid shows that both rim zones and interior of the particles dissolve at the same rate.

c) Reactions involving fine grained dolomitic limestone containing interstitial calcite and clay. This reaction produces a distinct dedolomitized rim^{10, 11}. Etching of reacted particles with dilute acid clearly shows up a reaction rim at the margin which in the majority of cases reported is enriched in silica.

In addition to the above groups numerous cases have been reported where alkali-silica and alkali-carbonate reactions occur together in a concrete which contains the appropriate aggregate materials. Examples of this combination of reactions were reported by Mather, Buck and Luke⁹ and have recently been observed in samples of distressed concrete from structures in SW England where reactive silicious fine aggregate and Devonian dolomitic coarse aggregate have been used in the concrete.

2. REACTION INVOLVING NONDOLOMITIC LIMESTONE

Cores of concrete containing limestone coarse aggregate from structures in Kansas and Nebraska have been reported by Buck and Dolch¹² as exhibiting reaction rims between 0.5 and 1 mm wide. The limestones were fine-grained and contained little or no dolomite and had a low acid insoluble fraction. The rims were dark and lay just within the margin of affected aggregate particles. Treatment with dilute hydrochloric acid showed them to be more soluble than the interior of the aggregate particles.

Laboratory tests by Buck and Dolch showed that this reaction phenomenon could be produced in 30 days under laboratory conditions of 50 °C, 100 per cent relative humidity using aggregate from the same source as that in the concrete. The reaction did not appear to be dependant on the alkali content of the cement used in the test concretes and very little change in chemical composition or the mineralogy could be detected in the reaction zone. Buck and Dolch reported X-ray diffraction studies which appear to indicate an increase in crystalline calcium hydroxide within the reaction zone. These hexagonal tabular crystals exhibited strong preferred orientation with their major surfaces parallel to the surface of the aggregate particle. Buck and Dolch postulated that the observed rim reaction was due to an attack on the carbonate rock by alkali solutions from the cement paste which converts some calcium carbonate into calcium hydroxide at the aggregate/cement interface. They further conclude that the reaction may improve the bond strength between limestone aggregate and cement in concretes.

The preferential development of calcium hydroxide at cement/aggregate interfaces in concretes has been reported by other workers, Barnes, Diamond and Dolch¹³ present evidence for a duplex layer development adjacent to the aggregate. This consists of an orientated layer of calcium hydroxide adjacent to the aggregate with an outer layer of calcium silicate hydrate gels. The tendency for calcium hydroxide to form preferentially at aggregate/cement interfaces is well documented and may relate to the water film that can develop around the aggregate particle during the manufacture of the concrete. The frequent development of relatively large calcium hydroxide crystals close to the interface supports this suggestion. An example of this hydroxide layer is shown in the scanning electron micrograph Figure 1, page 2, where a particularly thick layer of calcium hydroxide has developed round a small quartz grain and a microcrack (bright white line) has formed at the hydroxide cement paste interface. Figure 2, page 2, shows a similar rim development but in this case the calcium hydroxide is forming round a carbonate aggregate fragment. Work done by Hussen⁸ showed white rims to develop on both limestone and dolomite aggregate fragments in experimental mortar bars kept at 50 °C and 100 per cent relative humidity. Detailed examination of these rims failed

Since these rims are shown to be chemically inactive it is probable that physical phenomena provide a better explanation of the rim development and microcracking. Cement paste has a coefficient of linear expansion in the range 12 to 20×10^{-6} and this is not dissimilar to the coefficients for many aggregates in common use. Calcite however has expansions that lie outside these limits and depending on the crystallographic orientation the coefficients of linear expansion are $-4,5 \times 10^{-6}$ and 24×10^{-6} , this suggests that stresses will be induced at cement/aggregate interfaces of concretes made with limestone aggregate because of temperature changes. Where daily temperature fluctuation is high for example in Middle Eastern countries which can have a day/night variation of as much as 20°C the differential expansions between limestone aggregate and cement paste may produce stresses sufficient to cause microcracking at the interface and hence reduce the strength of the cement/aggregate bond. An alternative or contributory cause of microcracking at the interface could be volume changes resulting from differential moisture movement in the cement paste and aggregates due to wetting and drying cycles to which a concrete can be subjected.

These mechanisms acting singly or more probably acting together could give rise to the microcracks observed in the white rims. The white colouration could also be explained as resulting from this microcracking, but whether the white rims described here are similar to the rims described by Buck and Dolch remains uncertain. However, it is possible that calcium hydroxide could develop within physically induced microcracks in the rim zones and hence explain the observations made by Buck and Dolch. The increased reactivity of these rims when treated with acids may merely

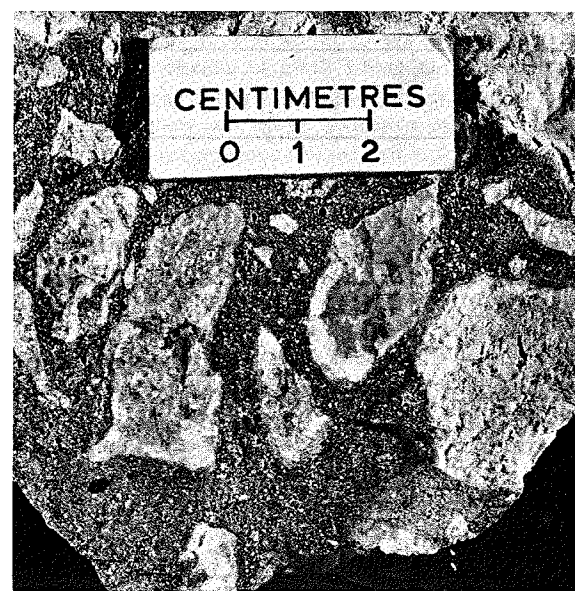


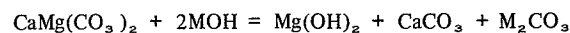
FIGURE 5: A broken portion of concrete from Libya which exhibits well developed dedolomitized rims.

reflect the increased permeability and surface area available for attack resulting from the microcracking. Colouration of the rims might easily arise through the ingress of coloured contaminants.

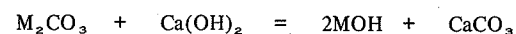
3. ALKALI REACTIONS WITH DOLOMITIC AGGREGATES

It is generally recognised that dolomitic rocks of appropriate texture can produce reaction rims when used as aggregates in concrete. The reactions which produce various types of rim are considered by Hadley⁶ and others to be closely related and principally dependant on rock type. There are reported examples of aggregates with positive, negative and neutral rims developed by treatment with dilute acids. This difference in rim solubility appears to be associated with the concentration of silica in the rim zone of the aggregate. Thus it is possible to subdivide this type of alkali-carbonate reactivity into reactions which do not produce a silicified rim zone (group 2 of the initial list) and reactions where silicification of the rim is a feature (group 3 of the initial list). The first group usually involves fine grained porous dolomites (Figure 5) containing little impurity, while the second typically consists of rocks which are less pure and contain both interstitial clay and calcite. The Kingston dolomitic limestones described by Gillot¹⁴ provide a classic example of this type of reactive dolomite which produces deleterious expansion in concretes. Mineralogically the Kingston dolomites vary from horizon to horizon but the dolomite is of the non-ideal metastable type with an enlarged unit cell owing to the incorporation of excess calcium in the lattice. The principal clays are illite and chlorite.

Both groups are believed to react with alkalis from the cement paste in a similar way. Hadley⁶ has proposed that the reaction proceeds in two stages which may be expressed as follows:



and



where M may represent Na, K or Li.

Thus the process is essentially one of dedolomitization together with the production of brucite and regeneration of alkali hydroxide. The observed increase in the concentration of silica in the rim zone is explained by Hadley as owing to silicate ions in solution reacting with the brucite. Hadley also suggests that the alkali carbonate which forms diffuses into the cement paste to react with the calcium sulphoaluminate hydrates to form calcium carboaluminate hydrate thus releasing sulphate ions which diffuse back into the cement paste 'ahead of the advancing carbonate front while the alkalis are regenerated and diffuse again into the rock'.

In a recent paper (Poole and Sotiropoulos)¹⁵ an attempt was made to examine this process in greater detail using

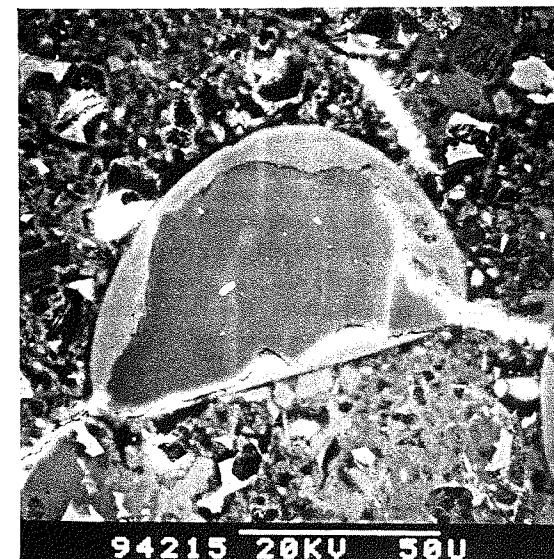


FIGURE 1: Calcium hydroxide developed round a small grain or quartz aggregate in 4 year old concrete.

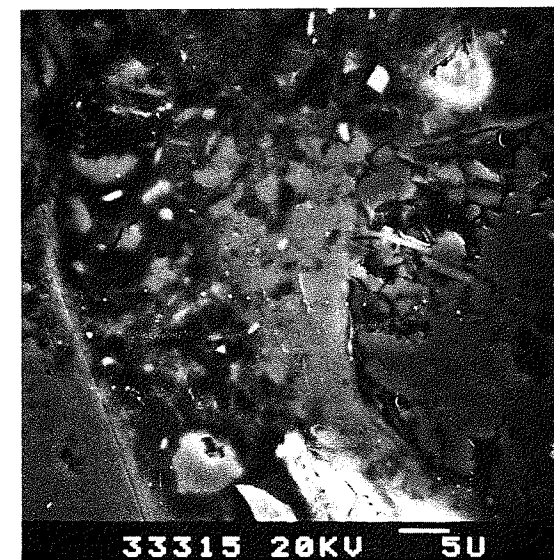


FIGURE 2: The calcium hydroxide layer at a cement/limestone aggregate interface in 4 year old concrete.

to show any mineralogical changes though treatment with dilute acid showed the rim zones to be slightly more soluble than the interior as was the case with the rims described by Buck and Dolch.

More careful detailed study of the aggregates with white rims using the petrographic microscope show them to be typical of limestones and dolomites which have mosaic texture and a grain size between $0,05$ and $0,17$ mm. The rim zone itself contains a series of microcracks running parallel to the margins of the aggregate particle. An ex-

ample of a white rim developed in a dolomitic limestone is illustrated in Figure 3. Figure 4 is a photomicrograph showing the development of microcracks along its margin.



FIGURE 3: The development of a white rim at the margin of a dolomitic limestone aggregate particle.



FIGURE 4: A petrographic thin section micrograph showing microcracks developed in the rim zone.

above but were wider than those developed in the unmodified samples as is shown in Tables 2 and 3.

The development of brucite associated with these reaction zones was observed in the petrographic thin sections and confirmed using infrared spectrophotometry. The formation of brucite has been noted by Hadley and others but an interesting feature of these experimental specimens was the development of brucite well away from the rim reaction zones. Brucite was identified in the cement paste beyond zones B and C and also in the centres of aggregate particles, though it was also present in small amounts in zone B which is largely composed of calcite.

4. ELECTRON PROBE MICROANALYSIS STUDY

The details of the complex reaction rims described above are difficult to study by normal chemical techniques because of the small scale of the zones. This problem was partly overcome by Hadley¹¹ who used a lathe to turn off successive shells of material from a cylindrical specimen containing a central cylinder of reactive rock. The electron probe microanalyser provides an easier method of obtaining detailed chemical information on this scale. Queen Mary College has been fortunate in recently acquiring a Hitachi S450 scanning electron microscope to which a Link Systems 860 energy dispersive system has been fitted. The microscope has been modified to allow fully ZAF corrected quantitative analyses to be made from polished thin sections. This instrument was used to make spot analyses of petrographic thin sections of the specimens described above. These analyses were made along traverses across the reaction rim zones from the hydrated cement paste on the one side through to unmodified aggregate material.

The detailed analytical results for well over one hundred spot analyses are being published elsewhere^{15, 16}. These analyses show that for the specimens which do not contain additions, initially zone A within the aggregate contains a concentration maxima of alkali which gradually moves inwards across this zone and gradually dissipates. The analyses also show that silicon develops a maxima within this zone and that magnesium is reduced in the zone while calcium increases markedly. Zone B in the cement paste adjacent to the interface widens with time but its calcium concentration remains fairly constant. Magnesium concentration is generally higher than in the unaltered cement paste, however, it is at a maximum close to the interface with the dolomite and shows a drop in concentration outwards across the zone. Alkali concentrations are low in zone B by comparison with zone A but after about four months storage alkalis develop a small concentration maxima which moves across the zone with time. Zone C diminishes with time as zone B increases. Although magnesium concentrations are very low in this zone a minor concentration peak does develop within the zone. It is most marked in specimens stored for six months but appears to diminish in older specimens. A small concentration maxima for alkali is initially present in this zone, but after about four months appears to migrate out of zone C and into zone B though this effect may be partly due to the

widening of zone B with time. There is also a high silicon concentration in zone C compared with zone B. These observations are illustrated diagrammatically in Figure 7, page 6, together with a diagrammatic indication of the change in reaction rim widths with time. An important feature of this diagram is the indication of multiple concentration fronts for alkalis, silicon and magnesium and their apparent migration with time.

Similar summary diagrams Figures 8 and 9, page 6, are used to illustrate the analytical results obtained for the specimens which contain additional alkali as NaOH and the sodium chloride addition. Comparison of the diagrams shows that in these cases concentration fronts develop in a similar manner to those shown in Figure 7. However, as has already been shown, the addition of alkali or sodium chloride causes a widening of the reaction rims and there is some evidence to suggest that the concentration fronts migrate across the zones more rapidly with time in specimens containing additional alkali and less rapidly in specimens containing sodium chloride. As indicated in the diagrams, the concentration maxima are not always clearly developed and in some cases, notably the older specimens containing additional alkali, the maxima form broad and diffuse zones. Differences in the development of silicon concentration fronts are apparent when Figure 7 is compared with 8 and 9. The development of high silicon concentrations in zone B for specimens with added hydroxide or chloride contrasts with the simple system illustrated by Figure 7. This difference is difficult to explain but perhaps a silicon maxima may be present in zone B in the unmodified specimens though not in concentrations sufficient to be observed. Although this data is largely confined to the reaction rim zones, chemical and mineralogical evidence indicates that magnesium ions migrate beyond these zones both into the aggregate and out into the surrounding cement paste. The chloride ions in those specimens containing added sodium chloride do not appear to be significantly associated with the reaction zones and are typically in higher concentration in the hydrated cement paste away from the site of reaction.

5. THE ALKALI-DOLomite REACTION MECHANISM

The data given above clearly support the hypothesis that the reaction broadly follows the equations proposed by Hadley with a subsidiary reaction involving silicon and the regeneration of alkali hydroxide as suggested by Hadley. The sites of the reactions can be more clearly defined as a result of the petrographic and the electron probe microanalytical work. Zone A in the aggregate is clearly the area from which magnesium ions are being removed, they diffuse both further into the aggregate and out into the cement paste. Silicon and OH ions enter this zone, but the magnesium and OH ions precipitate as brucite predominantly outside the reaction area. The silicon, however, may react with the brucite as it forms in Zone A as is postulated by Hadley⁶. Zone B is the principal area where calcite is precipitated and where sodium hydroxide may be regenerated according to Hadley's second equation.

electron probe microanalytical techniques. Two dolomite samples from Bahrain, numbers 13 and 19, were selected for study. Some details of these samples is given in Table 1 below:

TABLE 1 : Data for samples 13 and 19

	Sample 13	Sample 19
Water absorption (BS 812), %	10,0	2,0
Relative densities	2,15	2,68
Average grain size, mm	0,01	0,025
Mass % CaO	29,66	30,25
Mass % MgO	21,57	21,85
Acid insoluble residue, %	0,92	0,49

Fragments from these rocks between 2,5 and 5 mm diameter were used with quartz sand in a 1:1 mix with cement and with a water/cement ratio of 0,35 to make mortar specimens which were stored over water at 50 °C. The cement used had an alkali equivalent of 0,62. These specimens had sections cut from them for examination at a series of time intervals of up to 300 days.

Petrographic examination of cut surfaces and petrographic thin sections showed that in favourable cases three distinct zones can be distinguished at the cement/dolomite interface (Figure 6).

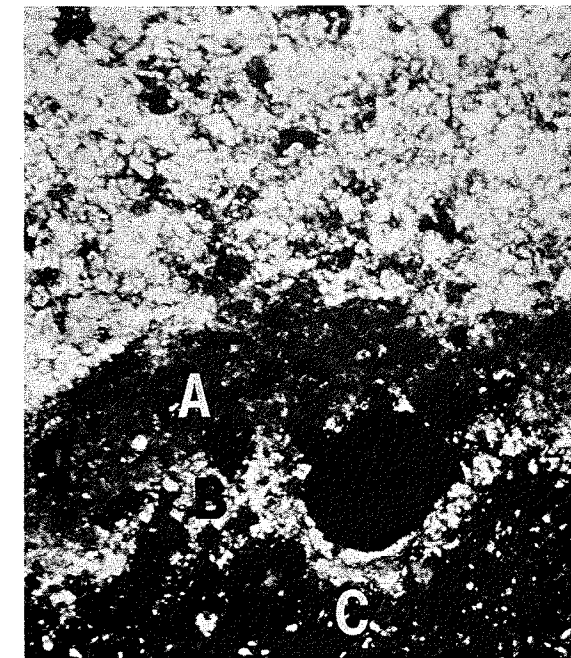


FIGURE 6: A photomicrograph of the 3 zones in the reaction rim at the cement/dolomite interface. Plane polarised light width of photomicrograph 1,1 mm.

Zone A: a dark zone extending inwards from the margin of the aggregate with an irregular and gradational inner margin.

Zone B: a light zone in the cement paste immediately adjacent to the aggregate which is only present round some of the grains.

Zone C: a dark zone beyond zone B in the cement paste which has a gradational outer margin.

These complex marginal zones were found to increase in width with time and that the more porous finer grained sample 13 had the wider more complex rim. After 300 days the total rim width (A + B + C) gave an average value of 335 μm and 245 μm for samples 13 and 19 respectively. It was also observed that for sample 13 zone B gradually widened with time at the expense of zone C. It was also noted in a separate experiment that rim widths were temperature dependant and that after a 40-day storage period sample 19 had rim widths which were 15 and 20 μm at 20 °C and 35 and 43 μm at 50 °C for the zone A and zones B + C respectively.

Parallel sets of specimens containing reactive dolomite were also prepared containing in one series an additional 2 per cent sodium hydroxide and in a second 2 per cent sodium chloride. These additions were made in order to study the effect of increased alkali on the cement/dolomite reaction and the effect of salt contamination of the specimens since salt contamination of concretes in Middle Eastern Countries is sometimes a major problem. Petrographic examination of these specimens showed that the features of the reaction rims were similar to those described

TABLE 2 : Sample 13 mean width of reaction rims (A + B + C) in μm against specimen age

Time in days	60	120	180	240	300
Unmodified samples	294	289	323	318	335
Samples with 2% NaOH	370	518	546	576	540
Samples with 2% NaCl	420	362	411	475	427

TABLE 3 : Sample 19 mean width of reaction rims (A + B + C) in μm against specimen age

Time in days	60	120	180	240	300
Unmodified samples	100	138	142	122	122
Samples with 2% NaOH	310	316	227	256	353
Samples with 2% NaCl	199	264	298	134	231

This zone widens with time as magnesium is removed from zone A. It is noted that additional calcite must form in zone A nevertheless this zone appears to become more porous with time. Zone C is the region where hydroxide may be forming at the expense of calcium sulphoaluminate hydrates and where silicon is reacting with brucite.

It is clear from comparison of the three series of specimens that additional alkali increases the reaction rate. The possible differences in the speed of migration of the alkali concentration fronts through the reaction zones may be explained by variation in pH between cement pore fluids containing chloride ions and those with hydroxyl ions only. An alternative explanation may be that the solubility of magnesium is lower in alkali solutions containing chloride ions than in alkali hydroxide solution alone.

6. THE EXPANSION MECHANISM

It is clear that microcracking at the margins of carbonate aggregates in cement, the 'Group 1' type of reaction may be expected to reduce the bond strength between the cement and aggregate and hence possibly reduce the strength of concretes made with certain types of carbonate

aggregate. The loss in bond strength may, however, be mitigated in that it is likely that the microcracks may be 'healed' by the formation of additional calcium hydroxide and it seems possible that such a healing effect could eventually even strengthen the bond between the cement and the aggregate.

The dedolomitization reaction described above does not in itself produce reaction products which would give rise to expansion and cracking of concretes. In the cases where deleterious expansion has occurred a common factor concerning the dolomitic aggregate involved is that it contains clay either as intergranular material or as inclusions within the carbonate crystallites. The explanation put forward by Gillot and others suggests that as the dedolomitization reaction proceeds clay particles in the reaction zone in the aggregate become exposed to hydrous solutions for the first time. The uptake of hydroxyl ions by the clay is sufficient to cause the expansion and disruption observed even though the clays may not be swelling types. The dolomites from Bahrain used in this study although reactive do not produce excessive expansive disruption of concrete and this is probably because their clay content is low.

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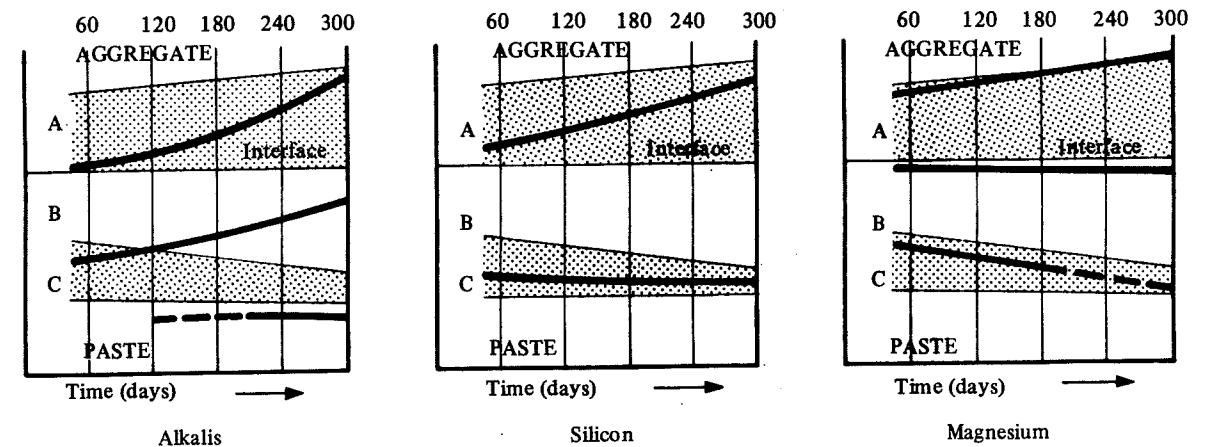


FIGURE 7 : Diagrammatic representation of ion concentration fronts near the dolomite/cement interface and their change with time. Sodium equivalent of specimens, 0,62 per cent

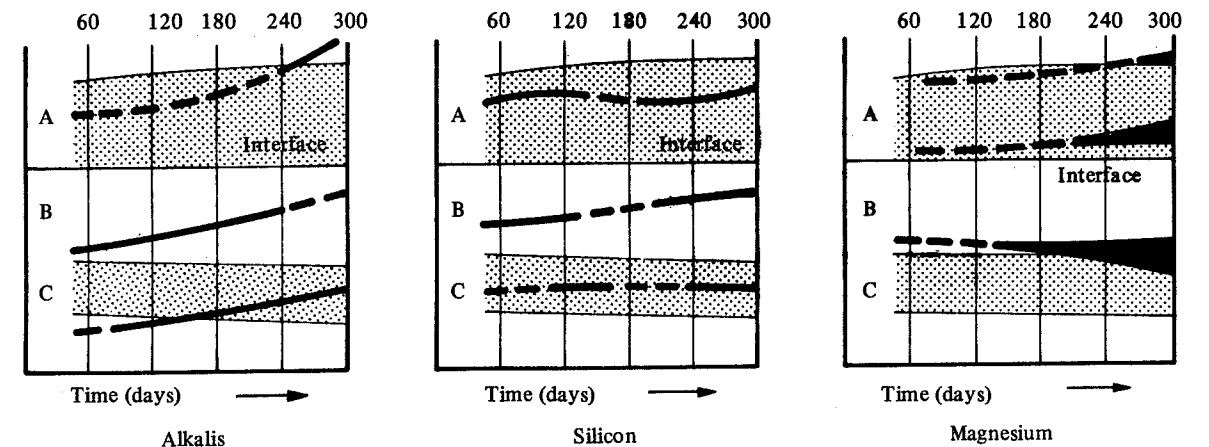


FIGURE 8 : Diagrammatic representation of ion concentration fronts near the dolomite/cement interface and their change with time. Specimens contain 2 per cent additional NaOH

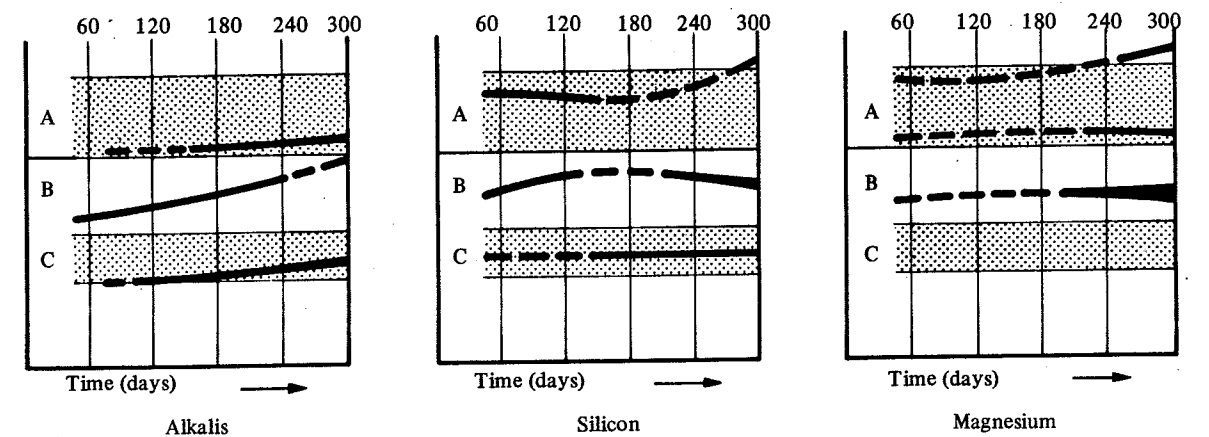


FIGURE 9 : Diagrammatic representation of ion concentration fronts near the dolomite/cement interface and their change with time. Specimens contain 2 per cent additional NaCl

DISCUSSION

Mr R T L Allen (C & CA, London) asked whether, in cases where alkali-carbonate reaction was combined with alkali-silica reaction, the former contributed significantly to the damage to the concrete.

Dr A Poole replied that mixed reactions which involved both alkali-silica and alkali-carbonate reaction had been frequently reported and his own reading of those papers was that in most reported cases, and all the cases he had had personal experience with, the alkali-carbonate reaction was insignificant in comparison with the alkali-silica reaction. The most recent case he had heard of was at the transformer station where a Devonian dolomitic limestone had been used as coarse aggregate. They had been told that it was the flinty fine aggregate, that was producing the alkali-silica reaction, but K Mather, A Moore and he had all observed the small white reaction rims on the dolomitic coarse aggregate. Whether they were really type 1 due, perhaps to thermal movement, or whether they were type 2 or 3 was in doubt. They were certainly dolomites and though they did not seem significantly expansive, could still be type 2.

Dr I Sims (Messrs Sandberg, London) asked whether Dr Poole had observed any short contractions during the rock cylinder tests on Arabian Gulf dolomites, prior to the one-year expansions mentioned. If so, could he suggest any reason for this behaviour.

Dr Poole said there was a certain irregularity at the start of the measurements including a small contraction in some cases. He speculated that material was perhaps being extracted from this much more porous material. Thereafter a slightly irregular expansion did take place. He referred to some electron-micrographs of aggregates of both Kingston limestone, from Ontario and Bahrainian limestone. In the latter, one could see clay particles of 1 or 2 μm diameter. In the Kingston limestone, they were obviously rather smaller and at that level of magnification both rocks appeared to be micro-porous as might be expected, and were not significantly different. However, looking at the reactive margin in the two cases, the Bahrainian rocks showed a very rugged reactive margin whereas the Kingston dolomites, at the two-month period, were not showing much reaction.