

THE INFLUENCE OF ALKALI-SILICA REACTIVITY
ON THE DEVELOPMENT OF TENSILE BOND STRENGTH

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ABSTRACT

The results of cement/aggregate tensile bond strength measurements are discussed in terms of the development of cement adhesion to reactive and unreactive aggregates, their temperature dependence and the alkali content of cement.

The results show that both temperature and alkalis have a marked effect on the adhesion to reactive aggregates and determine the stage at which the reactions begin to destroy further development of bond strength. It is concluded that failure at the contact in certain cases may be due to the development of a zone of weakness in the paste immediately adjacent to the interface, rather than failure at the interface itself.

Introduction

The mechanisms of paste strength development and the development of aggregate/cement adhesion appear to be areas which have not been as extensively researched as for example have the problems of hydration chemistry. And yet in many cases the bond between aggregate and cement paste forms the weakest link in the overall strength of a concrete and therefore plays an important part in the final strength of finished concrete units.

F. M. Lea¹ in *The Chemistry of Cement and Concrete* has reviewed the main ideas on aggregate/cement bond strength and suggests that the factors affecting bond strength are as follows:-

1. Surface Rugosity - keying to the aggregate surface.
2. Epitaxial Growth - the growth of cement hydrates aligned to crystallite lattice directions in the aggregate.
3. The enhanced cement hydration reaction rates due to increased crystal nucleation at the interface.
4. Variations in water/cement ratio at the interface leading to microscopic variations in paste strength.
5. Van der Waals forces acting across the interface.

Considering these various factors it could reasonably be supposed that factor 1 would be important although it should be noted that Alexander et al.² after numerous experiments suggested that there is little evidence to support the view that deep pits and extensive interlocking are required at the interface before high tensile bond strength can develop. Factor 2 may also be important in that calcium silicate hydrates may well develop in alignment with silicic lattices. This is also supported by Alexander et al.² who, in another series of experiments found that the modulus of rupture of the aggregate/cement bond was directly related to the silica content of silicic rocks used as aggregate in his experiments. These first two, and also factors 3, 4 and 5 can play a part in modifying overall strength but to these must be added another factor, that of chemical reactivity of the aggregate surface. Many types of aggregate have been reported as being reactive. Particularly important in this category are opal, trypidite, cristobolite and chalcedonic, glassy and cryptocrystalline rocks. These materials may be reactive because their silica is crystallographically disordered, as is opal, or alternatively they may be microcrystalline or microporous with a large internal surface

area available for reaction. Perhaps even pure crystal quartz should be classed as reactive in that it is soluble in alkalis at high values of pH. This factor was stressed by Alexander² who suggested that even materials such as basalt, become reactive if finely divided and that this form of pozzolanic activity, occurring at the surface of siliceous fillers, probably also determines the characteristics of bond between normal siliceous aggregates and portland cement paste.

Experimental Procedures

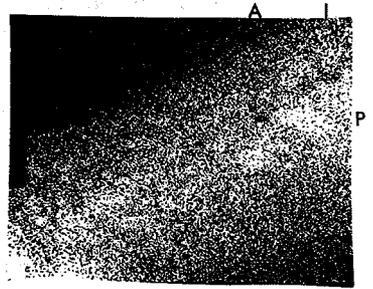
The effects of reactive siliceous aggregates on bonding can be conveniently studied in the laboratory by examining cement and aggregate combinations with a scanning electron probe microanalyser. Pieces of opal and quartz were embedded in a medium alkali portland cement (0.71 Na₂O equivalent) with a 0.25 water/cement ratio, cured at 50°C. These specimens were then sectioned and polished in order to investigate the movement of ions at the aggregate/cement interface after a 24 hour storage period. Movement of ions is easily demonstrated with known alkali-silica reactive aggregate materials³ but has not been reported in unreactive materials such as quartz. The effects of alkali-silica reaction with these specimens are illustrated in the series of photomicrographs in figure 1. These show the distribution of Na, Si, and Ca near the opal and quartz interfaces with the cement.

In these photomicrographs the sensitivity of the instrument has been varied in order to show the variations in concentration of each element and therefore although each photomicrograph gives a visual indication of the elemental concentration over each sample, the relationships between the photographs can only be considered in relative terms.

Scanning electron micrographs for iron show the expected random scatter with small local concentrations indicating the positions of ferrite phases. In figures 1 and 2 photographs I and II show local concentrations of sodium, which appears as a broad band in the cement paste about 100 microns from the interface with the opal. Photographs VII and VIII show the sodium and silica distributions for opal, but after storage for 240 hours at 50°C. Photographs III and IV are of the silica distribution and show an apparent infiltration of silicon into the cement possibly as a mobile gel produced during the 50°C curing process. The distribution of calcium is shown in photographs V and VI. These provide some evidence to show that calcium migrates into the reactive opal

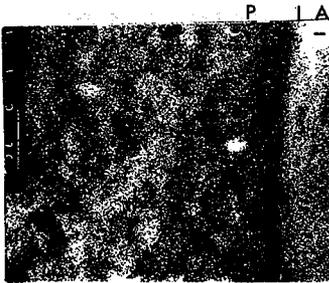


P I A

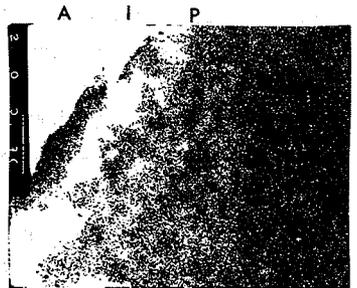


II

Sodium distribution at a Quartz(I), and opal interface(II)
50C, 24 Hours.



P I A



A I P

III

IV

Silicon distribution at a Quartz(III), and Opal interface(IV)
50C, 24 Hours.

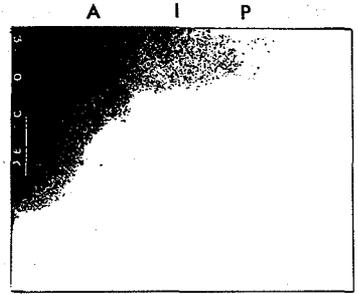
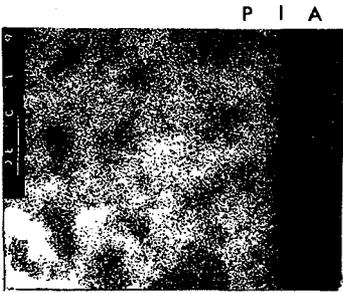
P: Paste

A: Aggregate

I: Interface

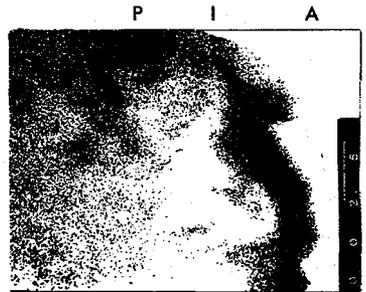
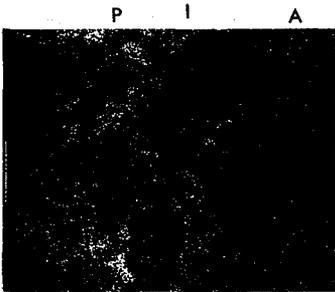
Elemental distributions at cement/aggregate interfaces.

Fig 1



V VI

Calcium distribution at a Quartz(V) and Opal interface(VI),
50C, 24 Hours.



VII VIII

Sodium(VII) and Silicon(VIII) distributions across an opal
interface 50C, 240 Hours.

Elemental distributions at cement/aggregate interfaces.

Fig 2

with a decrease in concentration in the paste adjacent to the interface. This effect may be due to the rapid reaction of Ca(OH)_2 with silica to produce calcium silicate hydrate gels which act as barriers to further calcium migration to the interface as has been suggested by Lea¹.

The apparent modifications to the cement and aggregate chemistry during these early hydration reactions near the interface might be expected to have an effect on the cement/aggregate bond strength. In order to investigate possible changes in tensile bond strength a series of experiments were devised to study the variation in bond strength with temperature of curing, and to follow the reactive process in terms of its effect on tensile bond strength.

25mm diameter discs of opal and quartz aggregate were mounted on metal holders with araldite. The bonding surface of the disc was polished and freshly prepared cement paste with its holder cast directly onto this surface. Each specimen was moist cured for 2 hours and then stored under water at various controlled temperatures. At appropriate intervals the specimens were removed from storage and tested to failure totally immersed in water in a special jig.

The first series of test results were obtained using Brazilian rock crystal quartz and a pure low cristobolite opal and a medium alkali cement (0.71 Na_2O) with a slightly higher K_2O than Na_2O content. These results are reproduced in Figure 3. The lower 3 lines which are for opaline interfaces show that at first the bond strength increases rapidly, but before 20 hours at both 50°C and 75°C the curves level out because of the formation of an alkali-silica gel reaction product at the interface. At 30°C this effect takes 25 hours. Further increases in bond strength at 30°C and 50°C are cancelled out by the hygroscopic nature of the gel itself which after 48 hours can exert enough pressure to begin forcing the aggregate away from the cement. Strength then decreases until at approximately 66 hours the gel becomes fluid enough to ooze out of the specimen when bond strength begins to build up again. The subsequent increase in strength is probably due to a localised build up of further gel only at the more reactive sites on the interface while over the rest of the surface of the aggregate the cement is still in good bond contact. The results for curing at 75°C would appear to support this since no recovery is observed indicating that the whole area of the interface is reactive at this temperature.

Comparison of these three sets of results with those obtained with quartz shows that the effect of having a reactive aggregate becomes apparent at about 15 hours. The strength curves for quartz at 30°C and 50°C differ in that the higher curing temperature gives a lower overall strength after 15 hours. This effect may be explained by the observations of Neville⁴ concerning compressive strengths of concretes cured at various temperatures. These results suggested that the rapid hydration at high temperature tends to produce a more porous concrete with incipient flaws which will give rise to early low tensile strengths.

The results indicated in the graph figure 4 were produced using a high alkali cement with a 1.10 Na₂O equivalent and similar K₂O, Na₂O contents. Comparison of the results for opal in figures 3 and 4 clearly show the effect of high alkalis in the cement, and the increased temperature effects produced with such a cement. These effects are most probably the result of increased alkali reactivity resulting from the higher alkali contents.

Conclusions

It is clear from these results that alkali-silica reactivity has a major effect on cement/aggregate bonding. Kennedy and Mather⁵ have commented on the beneficial effect of mild alkali-silica reactions in 1953 improving bond strength for cherts from Treat Island, Maine. The work of Alexander, Wardlow and Gilbert² on the contact zone between cement and "inert" aggregates has shown that microhardness results are lower in the cement at the interface than elsewhere.

1965
The results of this present investigation clearly show tensile bond strengths for both opal and quartz to be similar in the early stages of the curing of a concrete after which the strength of the reactive aggregate bond falls off, while that for quartz only levels off. The photomicrographs taken at an early stage in the curing of the experimental specimens show an increase in alkalis near the interface and this increase according to Alexander and Davis⁷, McCoy and Eshenour⁸, 1968 Alexander⁹ should reduce paste strength. 1960

1959
The anomaly of an increase in strength at the interface, combined with a reported decrease in microhardness in the adjacent paste is a

difficult one to resolve. Presumably it must be a matter of degree of operation of both processes. If reaction is very mild then the strength increase due to reactivity may supercede the effect of increased concentration of alkalis in the paste at the interface. If however, reaction is more pronounced, but at a time before any gel stages are reached, the paste failure will override any increase in bond strength at the interface.

The graphs in this paper may indicate this in that the high alkali cement has produced a concentration of alkali in the paste such that although surface bonding of the aggregate to the paste may be excellent, lack of intergranular adhesion in the contact zone produces an early failure.

The graphs, figures 3 and 4 seem to indicate that tensile bond strengths are temperature dependent although Alexander, Wardlow and Gilbert⁶ suggested that bond strength may be independent of temperature under certain conditions. In the light of these experiments perhaps this should be modified in that bond strength is independent of curing temperature providing the aggregate shows no surface chemical reactivity with cement paste.

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increase in strength at interface

agg.

paste

2 equal

microhardness lower strength

tensile strength similar early stage; levels off falls off later stage

reaction could vary strength due to reactivity supercedes the effect of concentration of alk.

reaction pronounced before gel stages high alkali paste failure

concentration of alkali \rightarrow good bond but inter granular adhesion in contact zone poor

tensile bond \rightarrow dependent on t^0
 if alkali reactive material strength is dependent on t^0
 if alkali reactive \rightarrow strength dependence

