Interface-durability correlations in concrete

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Abstract. The performance of concrete is dictated mostly by the characteristics of the transition zone. Internal bleeding leads to a higher effective water/cement ratio and hence a more open, porous structure at the cement/aggregate interface. Besides, more of AFt, AFm and CH phases and halides, sulphate, alkalis and other admixture components and less of C-S-H are found in this zone. These cause the deterioration of the reinforcing materials like steel, silicious aggregates, glass and natural fibres. The orientation of the crystalline phases parallel to the interface also weakens the mortar. The porosity and related effects are considerably modified by the use of plasticizers, fine pozzolanic additives and reduced water cement ratio. The mechanism of interfacial structure formation and their resulting effects on the reinforcement are discussed together with the possible precautionary measures.

Keywords. Concrete; interface; durability; porosity; admixtures.

1. Introduction

Concrete can be considered as a composite of aggregate particles dispersed in a matrix of hardened cement paste. Therefore, the properties must be governed by the properties of the cement paste, the aggregates and the interface between them. The strength of good concrete ranges between 30 and 40 N mm^{-2} and this value can be doubled if aggregate and cement are carefully chosen, the w/c ratio is reduced and a vigorous compaction is applied (Massazza and Costa 1986). However, this strength of concrete is much lower than that of its two components; i.e. cement paste and aggregate. Cement pastes with w/c = 0·30 can have compressive strength above 100 N mm^{-2} at 28 days curing (Rossler and Odler 1985; Diamond and Gomez-Toledo 1978). On the other hand, good aggregates have strengths more than 200 N mm^{-2} (Massazza and Costa 1986). The lower concrete strength is attributed to the relative weakness of the interface. The same problem is found in paste/reinforcement and paste/fibre systems.

It is not clear as to how much improvement in performance of concrete can be achieved through improvement in bonding. In some cases increase in bond strength may not be desirable. In cases where there are evidences of chemical reaction, how they contribute to bond strength is also to be established.

Though considerable research has been done to improve the properties of cement pastes, aggregates and reinforcing material, very little has been devoted to the understanding and alteration of the interfacial zone. An attempt therefore is made in this communication to analyse the effect of this interfacial zone on the performance of concrete in terms of strength and durability and to highlight the measures required to alter the interfacial characteristics and hence the behaviour of concrete.

2. Transition zone

The structure of the cement paste in the vicinity of the aggregate or fibre, or steel reinforcement surface is distinctly different from that of the bulk, indicating that the process of hydrate formation and crystallization is troubled by their presence (Mindess 1986). However, the detailed structure of the interfacial zone is variable depending on (i) the nature of the cement, (ii) the type of the aggregate, (iii) the presence of admixtures, (iv) the type of reinforcement, and (v) the curing conditions.

The development of transition zone is attributed to the internal bleeding of the paste, which increased the water/solid ratio at the interface, and to the surface effects of the aggregate phase, steel and fibres (James 1991; Monteiro and Mehta 1985, 1986; Skalny and Mindess 1985). This results in a more open, porous structure and consequently more of $Ca(OH)_2$ and ettringite are formed in this region due to the presence of more Ca and SO_4 ions (James 1991). This is schematically represented in figure 1. Such concentration gradient can possibly be found with respect to alkalis and chlorides also, giving rise to reaction with reinforcing steel, glass fibres and silicious aggregates. Thus, a detailed examination of the interface would have far-reaching consequences with respect to corrosion of steel and other metals, deteriorating effects on glass fibre and possibly alkali aggregate reactions.

The calcium hydroxide (portlandite) crystals at the interface are not randomly oriented, but exhibit a preferred orientation parallel to the surface of the aggregate/reinforcement (Barnes *et al* 1979; Grandet and Olliver 1980a; Mindess 1986). The thickness of these crystals is 50–100 μm. It appears that only the first 10–20 μm are significantly different in properties from the bulk cement paste (Grandet *et al* 1980a). However in typical concrete mixes, the volume constituting the interfacial zone represents a significant fraction of the total volume of the cement
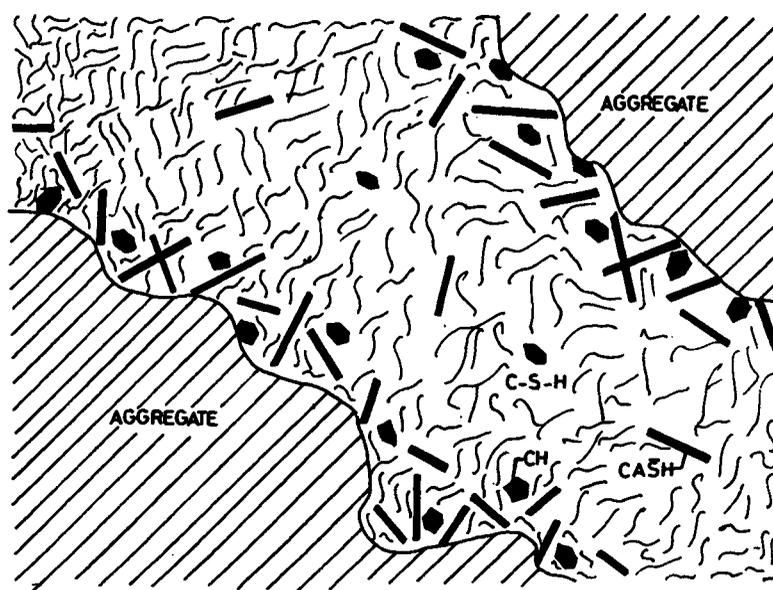

Figure 1.   Cement paste/aggregate interface (schematic).

matrix. The average minimum distance separating two sand grains ranges from 100–75 μm according to mix ratios. Therefore each crack which forms under load is forced to pass through the transition zone (50 μm thick) (Massazza and Costa 1986). Hence most concrete must be affected by the interface, leaving very little room to the development of the bulk cement paste.

Besides the preferred orientation of portlandite the AFt phase content also decreases quickly as the distance from the interface increases for both sulphoaluminates and portland cement (Monteiro and Mehta 1985, 1986). The regular variation in ettringite concentration can be seen from figure 2 (Monteiro and Mehta 1985).

3. Interfacial bond and concrete properties

In the concrete, it is uncertain whether the bond between cement paste and reinforcement is primarily due to mechanical interlocking or some chemical bonding or both. The relative importance of mechanical interlocking, Van der Waals' forces, epitaxial crystal growth phenomena, or other factors in contributing to the bond between the cement paste and either aggregate particles or reinforcement is still not clear. The interfacial zone appears to be the region of highest porosity and lowest strength and hence it represents the weak link in cementitious systems. From available evidences, it appears that the major component of cement aggregate bond is due to mechanical interlocking, perhaps assisted by epitaxial growth of some hydration products on the aggregate surfaces (Mindess 1986).

In the case of bonding between cement paste and steel, there is no evidence of chemical reaction and the bond is entirely mechanical. Regarding the effect of cement-aggregate bond on the strength of concrete, some investigators (Hsu *et al* 1963; Perry and Gillott 1977) find little or no relationship, while there are others (Mindess 1986) who find linear correlations.

Generally, as concrete strength increases, the brittleness of the concrete also increases. Considerable microcracking was reported (Mindess and Diamond 1982) at the cement paste-aggregate interface during loading of concrete. It has been suggested that increasing the bond strength increases the stress level at which extensive microcracking begins (Hsu *et al* 1963; Perry and Gillott 1977). This might in turn explain the increase in brittleness with higher strengths.
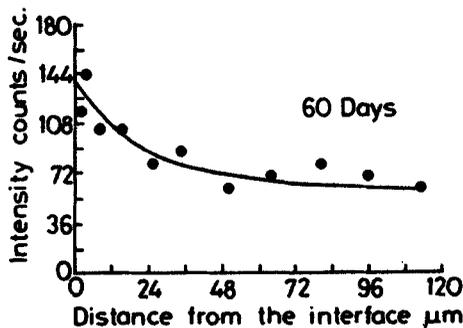

Figure 2. Variation of ettringite concentration with the distance from outerface.

Increase in ductility of concrete can be achieved by incorporating fibres into the mix. In the practical range of fibre-reinforced concrete, the fibres failed by pull-out rather than by fracture (Bentur *et al* 1985b). Here the fibre-matrix bond controls the apparent ductility.

3.1   *Cement aggregate interface*

There is a higher concentration of CH and AFt phases at the cement aggregate interface than in the bulk cement paste. There are three different descriptions of the region of higher CH concentration: (i) There is a duplex film at the interface: plates of CH-oriented parallel to the interface surface and backed by C-S-H (Barnes *et al* 1979; Monteiro *et al* 1985). (ii) There is a definite layer of oriented CH crystals on the surface of the aggregate, but without C-S-H backing (Skalny and Mindess 1985; Cojeaud *et al* 1980). (iii) There is only a localized increase in CH crystals, but with no preferred orientations (Struble and Mindess 1983). These two layers form only on unreactive aggregates and four different layers are detected on the reactive ones (Langton and Roy 1980). There is general agreement that the portlandite crystals are preferably arranged with *c*-axis perpendicular to the interface (Barnes *et al* 1978, 1979; Grandet and Olliver 1980b). However it may be mentioned that well-defined hexagonal crystals are unusual at the interface (Monteiro *et al* 1985).

At the early stages of cement hydration relatively large (10–30 μm) and well-formed crystals, with *c*-axis roughly parallel to the interface, are developed in the wide space available. In old pastes, however, stacked plates are noticed in the residual pores with its *c*-axis roughly normal to the interface (Massazza and Costa 1986). A parameter called 'orientation index' is defined in the literature which gives a measure of the preferred orientation (Carles–Gibergues *et al* 1982). The value of this index varies with distance of the paste from interface (figure 3) up to about 40 μm, which is the orientation limit (Grandet *et al* 1980b). The thickness of the transition zone depends only on the thickness of the liquid film that initially wetted the aggregate and does not change with time. The orientation limit varies as the *w/c* ratio increases. The preferential orientation of portlandite increases with *w/c* ratio up to 0·33 and then decreases. However, the orientation index increased beyond 180 days owing to crystallization of additional portlandite (Massazza and Costa 1986). It would be interesting to note how the orientation index varies for different aggregates.
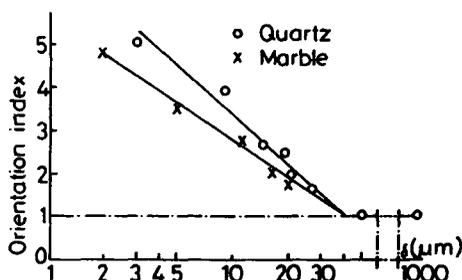

Figure 3.   Variation of orientation index with distance from the interface for quartz and marble.

The orientation of CH crystals is affected by aggregate roughness, the formation of aluminate hydrates and ettringite, low w/c ratios and extremely short setting times. Generally the characteristics of the transition zone are fixed during the period preceding setting.

3.2 *Cement steel interface*

The cement steel interface is mostly similar to the cement aggregate interface. The salient features are (Bentur *et al* 1985; Pinchin and Tabor 1978); (a) 1–2 μm thick duplex film in contact with reinforcement; (b) 10–30 μm thick layer largely occupied by relatively massive CH crystals, and (c) a highly porous layer parallel to the interface.

If the steel is oxidized, disordered crystals of portlandite deposit on the surface modified by corrosion (Arligiue *et al* 1985). After a day's curing the orientation index is rather low, 1·7 and there are also C-S-H layers on the steel apart from the portlandite layer. Ettringite is also reported to be found in higher concentration in the open space at the steel cement interface (Pinchin and Tabor 1978).

The strength of steel cement interface increases with w/c ratio and the fracture surface is usually of the cement paste-steel interface. The frequency of such failures was 73·3% for mild steel and 80·3% for stainless steel, after 7 days of curing. The corresponding values for copper and brass are 3·3 and 3·2% respectively (Page *et al* 1978; Khalaf and Page 1979). This indicates the existence of better adhesion likely of chemical origin. This can be seen from figure 4.

In the C_3A hydration, the nature of product changes depending on the metal used (Tashiro and Ueoka 1981). Cubic hydrate C_3AH_6 is formed on iron and
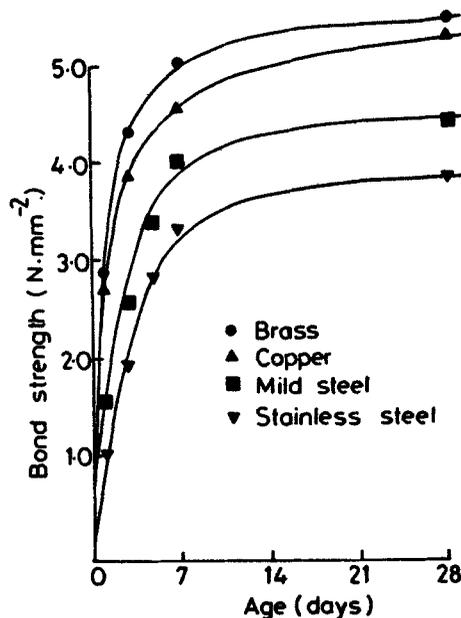

Figure 4. Variation of cement/metal bond strength with time, for brass, copper, mild steel and stainless steel.

copper wires, while hexagonal aluminates C_3AH_{13} and C_2AH_8 together with cubic C_3AH_6 are observed on zinc wires. How the metal affects the formation of these different phases is still not known.

3.3 *Cement fibre interface*

The tensile strength and toughness of cementitious products are usually enhanced by strengthening the matrix with fibres. The most known and common fibre is asbestos. However, other fibres (both natural and artificial) like glass, resin, carbon, cellulose and steel have also been used recently. The practical advantages of incorporating fibres into cementitious composites are however limited by the low fibre volume that can be included owing to workability requirements (Nayeb Hasemi and Cohen 1985).

The applications of fibre-reinforced cement products were, however, limited mainly because the properties of some fibre-reinforced composites deteriorated with time. An important, though not exclusive, cause of this behaviour seems to be the changes occurring at the matrix-fibre interface (Barthos 1981; Massazza and Costa 1986). A great deal of research has already been carried out to understand the mechanism through which fibres reinforce the cement paste and contribute to the composite properties. The properties critically depend on the stress transfer mechanism between reinforcement and matrix, which in turn depends on the interfacial properties. The tensile strength is increased by strengthening the interfacial bond of the fibre-reinforced composites. Nevertheless a strong bond causes brittleness (Barthos 1981). A weaker bond can also offer several advantages. The most common method to determine the bond strength is the pull-out test, which allows the average bond strength to be calculated (Akers and Garrett 1983).

The technical advantages obtained by fibres suggest preparation of mineral fibres different from the traditional ones and with better performance.

3.3a *Asbestos fibre*: These fibres have high strength and resistance to fire and chemical attack and their easy wetting facilitates dispersion in water and adhesion to cement paste. Unlike aggregate and steel reinforcement, no enrichment in portlandite was observed at the asbestos fibre-cement paste interface (Akers and Garrett 1983). Though isolated portlandite crystals are noticed on the fibres they do not create structurally weaker areas. A thin layer of CSH is found to stick to the fibres pulled out from the cement matrix, indicating that the bond between fibre and matrix is higher than the matrix cohesion (Massazza and Costa 1986; Mindess 1986).

3.3b *Steel fibres*: As in the case of aggregate and steel, the steel fibre cement interface has a composition, pore structure and morphology which are different from that of the bulk cement matrix. The $Ca(OH)_2$ percentage and the preferential orientation decreases with distance from the fibre (Page 1982). The interface region which can extend as far as $100\,\mu m$ contains 20–40% $Ca(OH)_2$ in excess of that in the bulk cement paste (Pinchin and Tabor 1978).

There is no chemical bond between steel fibre and cement matrix, as no trace of cement paste was observed on the fibre after debonding. The pull-out failure of steel fibre-reinforced cement material occurs at much lower loads than those required for

fibre breaking. In this context, use of some surface chemical treatments and covering the fibre with other materials, to increase interfacial bond, and fibre deformation to improve the mechanical anchorage are suggested (Khalaf *et al* 1980). The bond strength increases from stainless steel to mild steel. The use of brass-coated steel instead of mild steel fibres improves the composite rupture work by an order of magnitude.

3.3c *Glass fibres*: In glass fibre-reinforced cement, the interface plays a primary role in determining the properties. The interfacial region, in general, is very porous again due to higher w/c ratio. However there is still disagreement regarding the existence of a duplex film at the interface (Barnes *et al* 1978). The contact with the glass fibre strands and matrix is not continuous due to the many voids in the cement matrix at the interface (Stucke and Majumdar 1976; Massazza and Costa 1986). Preferential precipitation of $Ca(OH)_2$ is observed on glass fibre strands. These crystals form, with time, a dense layer with a strong axis normal to the longitudinal axis of fibres. After 5 years, the glass fibres are mostly wound with portlandite. There are large platy crystals of $Ca(OH)_2$, at the filament surface, along with clusters of C-S-H and occasional long needles of ettringite, when the spacing between the filaments making up the fiber is large ($> 10\ \mu$m) (Mindess 1986). When this space is small ($< 3\ \mu$m), no cement grain penetrates into this space and hence no hydration product is found here (Bentur and Diamond 1984). The clean fibre surface of the glass threads pulled out is thus an index of the adhesive failure.

Although glass-reinforced cements show excellent mechanical properties, their uses are limited as the properties deteriorate with time. This is attributed to the fibre strength reduction owing to the strong alkalinity of the cement paste. This is noticed for both common glass and special alkali-resistant glass. However the same phenomenon, though to a lesser extent, was observed in supersulphated and aluminous cements which are known to be less basic. Hence, it may be more appropriate to conclude that the environment created by cement involves the glass fibres in some chemical reactions (Massazza and Costa 1986; Sing and Majumdar 1985). Addition of pozzolanic material improves the behaviour of glass fibres (both borosilicate and zirconia glass) in cement matrix.

3.3d *Polypropylene fibres*: The bond between the fibre and cement paste is reported to be low, $0.1\ N\ mm^{-2}$. But this is probably an underestimated value, since a portion of the filament surface does not come into contact with the cement paste and therefore does not participate in bond (Watton and Majumdar 1975; Dave and Ellis 1979). However, these fibres have high tensile strength and rupture elongation and good chemical resistance and are not affected by moisture.

3.3e *Natural organic fibres*. The organic fibres are found to be firmly anchored to the cement matrix. The wetting of lignocellulosic fibre-reinforced cements reduces the flexural strength by 10–20% (20–40% with respect to dry samples) and increases the material toughness (Anonian *et al* 1979; Mindess and Bentur 1982; Coutts and Kighty 1984). The observed phenomenon is explained with two models:

In dry environment, organic fibres are strong and brittle and are firmly bound to the cement matrix. Hence the composite strength is high but the toughness is low (Mai *et al* 1983). In a wet environment, however, these fibres become ductile and

stretching and unravelling, and hence are pulled out more easily. Therefore they produce a strength decrease and a toughness increase.

The wooden fibre cement paste bond is also affected by the variation in the hydrogen bonds and hydroxide bridges. In dry environment the hydrogen bonds and the hydroxide bridges are active and contribute to high strength. However, the increased fibre stiffness reduces toughness. In wet environment, on the other hand, the hydrogen bonds are destroyed by the water molecules penetrating between the two materials (Coutts 1984). Here the fibres become more ductile and expand increasing the maximum pull-out length.

Banana fibre reinforcement up to 8 weight percentage can produce composite products with flextural strength values of about 20 MPa which is adequate for building applications (Coutts 1990). However the fracture toughness is low (< 1.0 kJ m^{-2}) and therefore the material would be prone to failure by impact. This should hence be used in situations where due consideration has been given to this aspect.

4. Chemical reactions at the interface and durability

Many chemical reactions can occur between reinforcement and cement paste at the interface and they can either improve or worsen the bond between the two components depending on the case. Among the particularly studied positive reactions are those involving C_3A (or CA) present in the cement with the calcite in the calcarious aggregate (Grandet *et al* 1980a–c), and those involving $Ca(OH)_2$ formed by the hydration of cement and finely-divided reactive aggregates like silica fume, fly ash, rice husk ash and blast furnace slag. The reactions that worsen the interfacial bond and thus the behaviour of the structure are those involving the corrosion of metal reinforcement, alkali silica reaction and deterioration of glass and natural fibres.

4.1 *Reactions of calcareous aggregates*

At the portland cement paste calcite interface carboaluminate hydrate (C_3ACaCO_3 $11H_2O$) is formed with time as early as three days and its concentration in the paste decreases as the distance from the interface increases (figure 5) (Grandet *et al* 1980). Its formation is also decreased by low w/c ratio. The mechanism of its formation is analogous to that due to the action of the atmospheric carbon dioxide. The formation of this phase in filler cement system is accompanied by the disappearance of 20–25% calcite (Cojeaud *et al* 1980).

The presence of carboaluminate instead of hexagonal calcium aluminate hydrates at the calcareous aggregate aluminous cement interface is advantageous to these mortars and concrete, since they show no strength decrease related to the hexagonal aluminate conversion to the cubic form (Cussino and Negro 1980). Conversely, the strength retrogression is not hindered if the filler is silicious, since silicates do not react with aluminates. Chemical bond is also formed between aluminous cement and aluminous aggregates, where the interface cannot visibly be distinguished after about 45 days. Here only the X-ray image analysis enables the boundary of the two components to be distinguished (Massazza and Costa 1986).
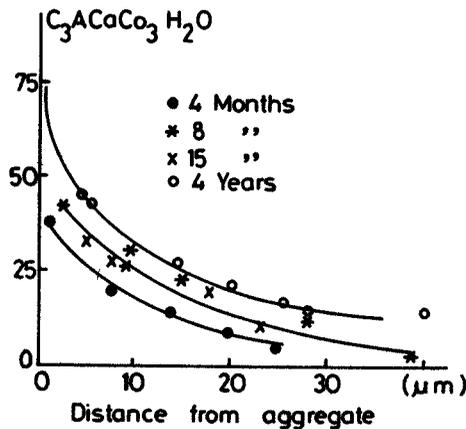
Figure 5. Variation of carboaluminate hydrate with distance from the aggregate interface at different periods of hydration.

The reaction of calcium carbonate with aluminates also prevents ettringite monosulphate transformation. Dolomite behaves like calcium carbonate, while magnesite and quartz causes no reaction.

At the cement calcarious aggregate interface, aluminate hydrates react with marble corroding its surface. Portlandite crystallization on this rough surface reduces the regularity of the crystal growth. Addition of up to 2% finely subdivided CH to cement gives portlandite, crystallizing from solution, nuclei from where the crystals can grow in all directions. This reduces the amounts of portlandite deposited on the aggregate surface, increasing the mechanical properties of the mortar.

4.2 Reactions of silicious aggregates

There is no evidence of chemical reaction between quartz and cement paste at room temperature (Massazza and Pezzuoli 1980). By mixing cement with seven different powdered materials, viz. quartz, microcline, albite, anorthite, horneblende, augite and olivine) it was found that the first four materials react with the cement paste while the other three remain inactive. The reaction of paste solutions with aggregate is accelerated if curing occurs at elevated temperatures and even quartz surface is attacked if the reaction is carried out under hydrothermal conditions.

A reaction considered harmful to concrete is that occurring between the silicious aggregates (e.g. Opal, Chalcedony, Glasses etc) and the alkalis present in the cement pore solution (Perry and Gillott 1983). This causes expansion and cracks in concrete indicating decrease in the interfacial bond strength. The variation in interfacial bond strength of mortars on polished reactive aggregates is given in figure 6.

Reactions between aggregate, which were usually considered as not dangerous, like gneiss and mica schist, and cement paste leading to deterioration in concrete properties are also reported. Kaolinite and hydromica are found at the interface in contact with aggregate grains, while a gel of sodium calcium silicate is noticed at the paste side.
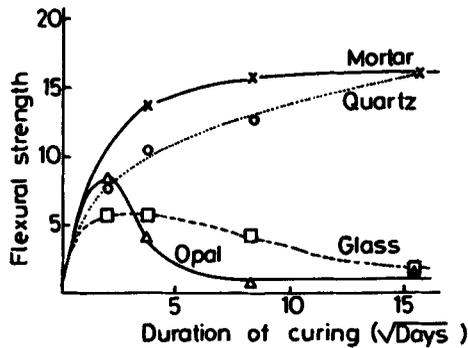
Figure 6. Variation of interfacial bond strength of various aggregates.

Table 1. Analysis of pore solutions expressed from high alkali cement mortars.

Age	Concentration	Equivalent/litre		
Days	Ca^{2+}	Na^{2+}	K^+	OH^-
15	0·001	0·22	0·55	0·73
49	0·002	0·22	0·59	0·77
70	0·000	0·24	0·57	0·75
149	0·002	0·23	0·60	0·80
585	0·000	0·24	0·58	0·78

In concrete-containing aggregates belonging to the serpentine group, the formation of brucite resulted in a discontinuity between paste and aggregate. This causes deterioration of the properties of the concrete.

The decrease in the aggregate-cement paste bond strength cannot always be attributed to alkali-aggregate reactions (Perry and Gillott 1983). At quartzite-cement interface the presence of dark spots was noticed, which is due to the migration of iron from aggregate. Here the formation of iron hydroxide gel or alkaline calcium silicate hydrate or both may be responsible for the decrease in strength. Also for natural sand aggregates containing quartz diorites, the surface was covered with a film of reactive Opal produced by slow natural weathering. Here only a decohesion of bond between grains and cement paste was observed.

The cement pore liquid after one or two days of hydration contains concentrated solution of alkaline hydroxides with only traces of calcium (0·001 N) (Turriziani 1986). The alkali content of the pore liquid reaches 70–80% of the alkali in the cement, in the long term, in the absence of severe drying out or other special circumstances (Diamond 1986). The concentrations of alkalis in the pore liquid of the concrete under normal circumstances vary from 0·35 N to more than 1 N depending on the alkali content of the cement and water content (table 1).

Use of low alkali cement, controlling the total quantity of alkalis in concrete mix and use of fine pozzolanic materials are known to reduce the alkali silica reactions. The main technical advantage of this is a decreased permeability. The improvement is due to the denser, microporous structure with low capillary porosity developed for the blended cement pastes (Roy 1987). Generally if the hydrated cement paste does not contain pores $>1320\,\text{Å}$, the coefficient of permeability remains insignificantly low.

4.3 *Reactions of microaggregates*

In cements containing slag, fly ash, silica fume, rice husk ash etc the paste aggregate transition zone is smaller and the orientation index lower compared to portland cement aggregate interface. The pozzolana grains (at least the larger ones) act as microaggregates around which the portlandite and ettringite are preferentially crystallized, due to local increase in w/c ratio (Massazza and Costa 1986; Roy 1987; James and Subba Rao 1986). Thus, the amount of portlandite crystals available on the larger aggregate is less and hence, the orientation index does not change with curing. The fine pozzolana particles react with lime giving normal hydration products. This is a positive effect since the amount of free lime formed during cement is reduced (James and Subba Rao 1987, 1988). The alkalis also react with microaggregates (pozzolana grains) but does not cause expansion. If the reactive microaggregate contains Fe_2O_3, Al_2O_3 and CaO (e.g. fly ash and slag) it reacts with cement paste constituents forming compounds which do not absorb water. Hence no increase in volume and consequent expansion is noticed when fine pozzolanic materials are used.

Cement pastes containing silica fume has a much lower transition zone and orientation index than pure portland cement pastes. $Ca(OH)_2$ disappears with time except at the aggregate, where it remains longer as an oriented crystal film. Thus the pozzolanic addition changes the interface in the long term, besides increasing strength and eliminating the discontinuities caused by the portlandite crystals.

4.4 *Reactions of metal interface*

Copper and brass reinforcements undergo chemical reactions at the interface increasing the cement metal bond. Formation of $Zn(OH)_2$ occurs at the interface between the cement paste and the zinc covering the galvenised steel. This delays the setting considerably and the normal setting and hardening proceeds only when $Zn(OH)_2$ is removed by subsequent reactions. $Ca(OH)_2$ reacts with $Zn(OH)_2$ to give calcium hydroxyzincate, which improves the cement paste galvanized steel bond. When $CaCl_2$ is available zinc hydroxychloride is formed instead of zinc hydroxide, and hence $CaCl_2$ addition does not accelerate the setting and hardening near the galvanized reinforcement. With time the zinc hydroxychloride too is converted to calcium hydroxyzincate (Khalaf and Page 1979; Tashiro and Ueoka 1981). The concrete reinforcing steel in alkaline cement paste pore solution ($pH = 13.5$) is covered with an oxide layer which protects the metal from corrosion (Thomas 1987). Other reactions appear to be absent and the bond between the two components remains weak. By replacing mild steel by steel also the situation does not change. Covering the reinforcing bars' with resin has lately been suggested to prevent corrosion under aggressive conditions.

5. Conclusions

The transition zone and the interfacial bond characteristics have a significant role in determining the properties of all cementitious composites. In modern concrete, interfaces involving cement paste and aggregate, fibre, reinforcing steel or their

combinations, are important in determining the mechanical properties and durability of the structure. Selection of appropriate cement reinforcement (or aggregate or fibre) combinations, surface modification of reinforcement, use of admixtures and changing the curing conditions are suggested to increase the interfacial bond strength and alter the chemistry and morphology of the transition zone.

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