Stellingen

"The Cement Paste-Aggregate Interfacial Zone in Concrete"

J.A. Larbi

1.

In normaal beton is de overgangszone tussen de bulk cementsteen en de toeslagmaterialen de meest poreuze component; het kan beschouwd worden als een 'zwakke schakel' in beton. (Dit proefschrift).

2.


3.


4.

De bibliotheek van de Faculteit der Civiele Techniek te Dafit vertoont twee hinderlijke fouten: (i) veel belangrijke boeken en tijdschriften zijn permanent afwezig; (ii) er is geen kopieerpapier beschikbaar om kopieën te maken, zodat het "even" lenen van tijdschriften en boeken, met het idee om kopieën te maken, maanden in beslag kan nemen.

5.

In de academische publicatiecultuur zou enige zelfcensuur, wat betreft het laten verschijnen van negenoog gelijkvloeiende artikelen, de informatiestroom inkrampen, maar zeker niet beperken.

6.

De doorsnee civiel-ingenieur is nog te weinig bekend met de toepassingsmogelijkheden van het materiaalkundige onderzoek in zijn vakgebied.
7.
Ervaring heeft een onmiskenbare invloed op de ontwikkeling van de intelligentie.

8.
De kennis van de eigenschappen van materialen en de microstructuur van compo- sietmaterialen zoals glasvezel versterkt beton, zou van groot nut zijn voor het modelleren van composiet constructies.

9.
'Open grenzen 1992' zal de mogelijkheden verruimen, niet het gezichtsveld.

10.
Bureaucratie kan gezien worden als een geccepteerd en alledaags verschijnsel, totdat men het tegenkomt in het buitenland.
The Cement Paste-Aggregate Interfacial Zone in Concrete

Joseph Aduamoah Larbi
The Cement Paste-Aggregate Interfacial Zone In Concrete

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof. drs. P.A. Schenck,
in het openbaar te verdedigen ten overstaan van een commissie aangewezen door het College van Dekanen
op 3 september 1991, te 14.00 uur.

door

Joseph Aduamoah Larbi

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Dit proefschrift is goedgekeurd door de promotor
Prof. Dr. J.M.J.M. Bijen


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Samenvatting

In dit proefschrift zijn de resultaten neergelegd van een onderzoek naar de microstructuur van de overgangszone tussen toeslagmateriaal in beton. De betekenis ervan voor de eigenschappen van beton is geëvalueerd.

De microstructurele kenmerken van de overgangszone tussen portlandcementsteen en toeslagmateriaal verschillen aanzienlijk met die van de bulk cementsteen matrix. De zone is minder compact dan de bulk cementsteen matrix en bevat een groter aandeel calciumhydroxide. De calciumhydroxidekristallen vertonen een voorkeursoriëntatie, zodanig dat hun c-as in het algemeen loodrecht staan op het oppervlak van het toeslagmateriaal. Deze textuur van calciumhydroxide treedt echter niet op in de buurt van alle toeslagmateriaalkorrels; bij sommige toeslagmateriaalkorrels is er geen of nauwelijks kristallijn calciumhydroxide aanwezig. In de overgangszone zijn tevens meer microscheuren aanwezig dan in de bulk matrix. De richting van de meeste scheuren loopt langs de cementsteen-toeslagmateriaal overgang en langs de (zwakke) breukvlakken van de calciumhydroxide kristallen. De cement hydratatieproducten in de buurt van de toeslagmateriaalkorrels zijn zwak met elkaar en met het toeslagmateriaal verbonden. De hardheid van de overgangszone is geringer in vergelijking met de toeslagmateriaalkorrels en met de bulk cementsteen. De overgangszone is tevens de meest poreuze component van beton. Aldus kan in normaal beton de overgangszone tussen de bulk cementsteen en de toeslagmateriaalkorrels beschouwd worden als een ‘zwakke schakel’. In het algemeen is de overgangszone circa 50 µm dik, terwijl deze ongeveer 30 tot 50% van het totale volume van de cementsteen in het beton inneemt.

De vorming van het ‘zwakke overgangsgebied’ in portlandcement beton is het resultaat van twee effecten. Ten eerste is er micro-ontmenging, dat als gevolg heeft dat de concentratie van water rond het toeslagmateriaal relatief hoog is. Ten tweede treedt een inefficiënte stapeling van cementdeeltjes (gem. diameter 10-30 µm) op, bekend als het ‘wandezelfect’, wat er toe leidt dat minder cementdeeltjes bij het oppervlak van het toeslagmateriaal kunnen komen. Deze twee effecten zijn het gevolg van de eigenschappen van een ‘vers’ mengsel. Na zetting van het beton en bij het begin van het uitharden is het gebied bij het toeslagmateriaaloppervlak nagenoeg vrij van cementdeeltjes en gevuld met water. Dit veroorzaakt het ontstaan van met porier watergevulde microporiën (locale gebieden met een hogere water-cement factor) in de nabijheid van toeslagmateriaal. Naarmate het cement hydratatieproces vordert zal deze overgangszone niet effectief gevuld worden met cementachtige reactieproducten vanwege de eigenschappen van het cement reactieproces: reactieproducten precipiteren aan het oppervlak van cementdeeltjes. Hierdoor ontstaat een meer open en porueuze structuur dan in de bulk cementsteen. Tevens zal, dankzij de lokaal hogere water-cement factor in de overgangszone en het grote aantal porieruimten, het transport van Ca²⁺ ionen van de bulk matrix naar de overgangszone vergemakkelijkt worden; ook zijn de kristallisatieconditions er gunstiger dan in de bulk cementsteen. Aldus zullen in de nabijheid van toeslagmaterialen, (semi)kristallijke hydratatieproducten, met name calciumhydroxide en ettringiet, gevormd worden.

Ofschoon de overgangszone poruezer is dan de bulk portlandcementsteen, speelt deze slechts een kleine rol bij het transport van vloeistoffen (water), waterdamp en ionen in beton. Het onderzoek heeft aangetoond dat het transport van ionen en water in beton voornamelijk bepaald wordt door de bulk matrix, de enige continue fase in beton. In mindere mate wordt het vloeistoftransport beïnvloed door de porueze overgangszone.

Goede kwaliteit puzzolane en latent hydraulische toeslagmaterialen, zoals vliegas, silica fume, metakaolinit en hoogovenslak, kunnen samen met portlandcement gebruikt
worden om de structuur van de overgangszone te verbeteren. Daarnaast kunnen compo-
siet cementen, zoals hoogovencement (≈ 70 massa % slek) en portlandvliegascement
(≈ 20 massa % vliegas) worden toegepast om de zwakke overgangszone tussen
toeslagmateriaal en cementsteen te ‘versterken’. De verbetering van de overgang wordt
veroorzaakt door:
(i) de verbeterde deeltjesstapeling van de cementachtige componenten in de over-
gangszone; (ii) de gereduceerde micro-ontmenging in de overgangszone; (iii) het vermo-
gen van puzzolanan om te reageren met calciumhydroxide tot (extra) cement-gel.

In het algemeen leidt het gebruik van puzzolanan tot de vorming van een dichtere
overgangszone met een kleinere hoeveelheid calciumhydroxide. Het calciumhydroxide
vertoont ook een geringere oriëntatie. Tevens wordt de dikte van de overgangszone
kleiner. Verder draagt verminderde beschikbaarheid van kalk in de overgangszone waar-
schijnlijk in belangrijke mate bij aan de vermindering van de expansie in geval van alkali-
silika reactie die veelal waargenomen wordt bij composiet cementen.

Toevoeging van puzzolanan als vliegas, silica fume en gecalcineerde kaoliniet maar ook
latent hydraulische stoffen als gemalen gegranuleerde hoogovenslak aan portland cement
leidt tot vermindering van de mobiliteit van agressieve stoffen in beton. Dit blijkt met
name uit het feit dat (i) de diffusiecoëfficiënten van Cl−, Na+ en K+ ionen in beton
significant kleiner worden; (ii) de afname van de snelheid waarmee water uit beton
verdampt en (iii) de vermindering van het waterabsorptievermogen.

Deze effecten zijn voornamelijk te danken aan een vernauwing van de poriën in de bulk
cementsteen matrix en vergroting van de tortuosititeit hierin. In mindere mate draagt
de verbetering van de overgangszone hieraan bij.

In het algemeen wordt de weerstand (duurzaamheid) van beton tegen sulfataantaasting
vergroot door de vermindering van transport van water, waterdamp en ionen. De
kwetsbaarheid van beton voor destructieve alkali-silica reacties (in het geval dat het
beton reactieve toeslagmateriaal bevat) neemt af en de bescherming van staal
wapening tegen chloride indringing wordt verbeterd.

De hechtsterkte van cementsteen aan toeslagmateriaalkorrels als functie van de uithar-
dingstijd variërt afhankelijk van het type toeslagmateriaal. Echter voor dezelfde leeftijd
vermindert de hechtsterkte bij een toenemende water-cement faktor, ongeacht het
gebruikte type toeslagmateriaal. Deze studie toont tevens aan dat, voor dezelfde leeftijd
en dezelfde water-cement faktor, cementsteen van portland cement klasse A sterker is
dan de overeenkomstige mortel. Dit effect is zichtbaar voor alle mengsels, ook al zijn de
α-kwarts zanddeeltjes aanmerkelijk sterker dan de cementsteen. Het verminderen van de
hechtsterkte van cementsteen aan toeslagmateriaal bij een toenemende water-cement
faktor kan worden toegeschreven aan de heterogeniteit van en microstructurele defecten
in de overgangszone, een grotere dichtheid aan microscheuren, een grotere hoeveelheid
geliointegreerde calciumhydroxide, zwak gebonden cement hydratatieproducten en de
daarmee geassocieerde hogere microporositeit. Dezelfde effecten zijn verantwoordelijk
voor de lagere druksterkte van de mortel in vergelijking met de overeenkomstige
cementsteen.

Toevoeging van silica fume en metakaoliniet verhoogt de druksterkte van mortels en de
hechtsterkte van cementsteen aan toeslagmateriaal significant. Echter, de toevoeging
van silica fume en metakaoliniet leidt niet tot een significante toename van de druksterk-
te bij portland cementsteen, aansluitend niet voor de in deze studie gebruikte water-binder
faktoren en hoeveelheden silica fume en metakaoliniet. Op basis van de verkregen
resultaten wordt geconcludeerd dat deze verbetering in druksterkte bij mortels het
gevolg is van een diktevermindering van de overgangszone en een dientengevolge betere
spanningsoverdracht tussen matrix en toeslagmateriaal.
Acknowledgements

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Finally, and most of all, I wish to thank my family for their patience, understanding and assistance during the entire study period.
List of related publications

All the chapters in this thesis, with the exceptions of Chapters 1, 2 and 10 are composed of articles which have been published or are yet to be published (In Press) or intended for publication.

Chapter 3
The original article is published as: "Effects of water-cement ratio, quantity and fineness of sand on the evolution of calcium hydroxide in set portland cement systems".

Chapter 4
This chapter is a summary of three articles as follows:
a. "Orientation of calcium hydroxide at the cement paste-aggregate interface in mortars in the presence of silica fume: A contribution".

b. "The chemistry of the pore solution of silica fume-blended portland cement pastes".

c. "Orientation of portlandite at the paste-aggregate interface and strength development of the portland cement paste-aggregate bond in mortars in the presence of microsilica".

Chapter 5
The original article is published as: "Evolution of calcium hydroxide and microstructural development of fly ash-portland cement paste systems".

Chapter 6
The original article is published as: "Effects of pozzolans on the aggregate-cement interface in relation to alkali-silica reaction".

Chapters 7 to 9 are intended for submission for publication in the Journal of Cement and Concrete Research.
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Chapter 1

Introduction

1.1 General

Concrete may be modelled to consist of cement paste, pore water and inserts. The inserts may be aggregate particles or fillers, fly ash particles or other pozzolanic materials, reinforcements, and fibres of steel, glass, or natural and synthetic organic materials. As such, different types of interfaces between the inserts and the cement paste may exist.

There is ample evidence that the properties of concrete such as the compressive strength, the tensile strength, the bond strength, modes of failure, the bending stiffness and the permeability are significantly influenced by the nature of interfaces existing between the cement matrix and the inserts. For this reason, the paste-insert interfacial zone is regarded as a weak link in concrete. Since the early eighties efforts aimed at improving the quality of this so-called weak interfacial regions around inserts in concrete, particularly, the cement paste-aggregate interfacial zone have intensified. However, due to lack of understanding about these interfaces, very little attempts have been made to improve them. At the moment, for instance, there is no simple method of predicting how much improvement can be made in the overall performance of concrete through improvements of the interfacial zone.

This thesis deals with a study about the cement paste-aggregate interfaces in concrete. It is aimed at examining the microstructural characteristics of these interfacial regions around aggregate particles and their effects on the compressive strength, the adhesive strength of pastes to coarse aggregate particles, the water absorption capacity, and the diffusivity of ions and gases into concretes prepared with and without mineral additions.

1.2 Outline of the thesis

Each chapter is composed of an abstract, a short introduction including the aims of the study, experimental methods employed, results and discussion, conclusions, and references. Owing to the fact that for each chapter, a brief background and literature review regarding that study is given, the literature review and discussion in Chapter 2 has been kept as brief as possible to avoid repetitions.

It is worthwhile to note that the work presented in this thesis is concerned only with interfacial zones between cement paste and normalweight or conventionally used aggregate particles. No lightweight aggregates such as LYTAG\textsuperscript{R}(1), for example, were considered. In addition, the terms "interfacial zone", "transition zone", "interfacial region", "transition region", "interfacial layer" and "transition layer", all refer to the same material, that is, the paste layer that is formed around aggregate particles in concrete.

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(1) LYTAG\textsuperscript{R} is an artificial lightweight produced by sintering of fly ash particles to form pellets.
It is also worthwhile to mention that in all the mixes containing mineral additions, the latter were used as *partial portland cement replacements* (by mass).

Chapter 1 forms the introduction to this thesis. It includes a general introduction, the objectives, and the outline of the thesis.

In Chapter 2 a literature review about interfacial zones around aggregate particles in cement-based composite materials is given.

Chapter 3 deals with the rate of precipitation, morphology and crystal orientation of calcium hydroxide in set portland cement paste systems. Special attention has been given to the nature of the cement paste-aggregate interface.

Chapter 4 examines the action of silica, a submicroscopic and highly reactive mineral addition on the paste-aggregate interfacial zone in concrete. In particular, the reduction in the amount and orientation of calcium hydroxide at the paste-aggregate interface, and the densification and thinning of the transition zone around aggregate particles in concretes are elucidated. The consequences of these beneficial effects on the strength and the durability of concretes containing such additions are demonstrated in Chapters 8 and 9.

Chapter 5 is focused on the role of fly ashes, used as partial cement replacement materials, on the evolution of lime in concrete, and on the structure of the paste-aggregate interfacial zone. The chapter describes how the interfacial zone can substantially be densified through (i) improved particle packing of the ash particles in the interstices between the cement grains; and (ii) the pozzolanic reaction between the ashes and Ca(OH)₂ to form more additional cementitious compounds.

Chapter 6 deals with the effect of some pozzolans\(^\text{(2)}\) and blast furnace slag (in the form of portland blast furnace slag cement) on the paste-aggregate interface in relationship to the alkali-silica reaction.

Chapter 7 outlines the role of the paste-aggregate interfacial zone on the transport capacity of fluids in concrete.

Chapter 8 is concerned with the influence of secondary cementitious materials on the paste-aggregate interface in relation to transport of fluids in concrete.

Chapter 9 examines the role of silica fume and calcined metakaolinite on the cement paste-aggregate interfacial zone in relationship to the strength of concrete.

Chapter 10 is a summary of the thesis, including some suggested recommendations for further study.

\(\text{\textit{A pozzolan} is a siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value but which will in finely divided form and in the presence of moisture chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (ASTM C-125).}\)
Chapter 2

2.1 Interfaces in concrete

In hardened concrete, a number of interfaces between cement paste and inserts may exist. These may be classified broadly into five groups as follows [1]:

(i) interfaces between the various phases that make up the cement paste, including interfaces between the cement paste and the unhydrated or partially hydrated cement;
(ii) interfaces between the cement paste and the unreacted or partially reacted pozzolanic materials;
(iii) interfaces between the cement paste and aggregate particles;
(iv) interfaces between the cement paste and steel reinforcements;
(v) interfaces between cement paste and fibres that may be present in special concretes.

In the sections that follow, a review of the microstructural features of interfacial zones around aggregate particles and their influences on the strength and the durability of portland cement composites are presented. As mentioned already in Chapter 1, the research work itself concerns only interfaces and bonding between cement pastes and normalweight aggregate particles. Not considered are interfaces and bonding in the particulate materials or phases within the cement pastes such as, (a) intraparticle bonding involving interatomic forces within individual hydration products, such as those within C-S-H\(^{1}\) or Ca(OH)\(_2\), and (b) interparticle bonds, involving atomic forces which bond the individual particles to each other and to grains of the anhydrous cement. Also interfacial morphologies between cement pastes and continuous and discontinuous reinforcements (iv and v above) will not be discussed.

2.2 Microstructure of the cement paste-aggregate interfacial zone

During mixing, compaction and placement of concrete, the aggregate particles interact with the surrounding cement paste. As a result, the microstructure of the cement paste at the immediate vicinity of aggregate particles differs in several respects from the microstructure of the cement matrix. In this section, a review of the microstructural characteristics of the cement paste-aggregate interfacial zone is given.

One of the first workers to study the microstructure of the paste-aggregate interfacial zone was Farran [2]. He examined the nature of the bond between different types of minerals and portland cement pastes at normal temperatures. A summary of his observations are as follows:

\(^{1}\) Abbreviations used by cement chemists: C-S-H = calcium silicate hydrate (amorphous or semi-crystalline of varying stoichiometries. See also Appendix at page 125).
(i) that the bond between calcite or dolomite and cement paste was stronger than that of other minerals;

(ii) that the bond strength with fine-grained calcite was better than that with coarse-grained calcite rock;

(iii) that "corrosion" of calcite surfaces in contact with the cement paste used occurred.

He found the paste-calcite bond strength to be higher than the rest of the minerals examined and concluded that this effect was due to the "corrosion" of the calcite surfaces. He explained that the "corrosion" was brought about by a slight dissolution of the calcite surfaces with subsequent 'epitaxial' formation of calcium hydroxide-calcite solid solution. This product, according to him, formed a "bridge" across the paste-calcite interface which increased the bond strength.

Buck and Dolch [3] performed a similar study but on a more elaborate scale using different minerals and aggregates. They reported similar observations to support the conclusions of Farran. They proposed that the reaction between the fine-grained, nondolomitic limestone and the portland cement paste was due to attack on the carbonate by alkali solutions in the cement paste. Some of the calcite, according to them, "transformed" into calcium hydroxide, which precipitated with a definite orientation at the rock-paste interface.

The results of the investigations carried out by Farran [2] and Buck and Dolch [3] indicate that at the interfacial zone between cement paste and calcareous aggregates, a kind of chemical reaction occurs in which calcium hydroxide is produced with a definite orientation to the aggregate surface.

Using a scanning electron microscope (SEM), Suzuki and Mizukama [4,5] studied the microstructure of the cement hydration products at the paste-aggregate interfacial zone. They observed that on each rock type, various phases of cement hydration products formed. But the crystallinity and the amount of hydrates formed varied from one type of aggregate to the other.

A more intriguing characteristics of the paste-aggregate interfacial zone was presented by Hadley [6], and later by Barnes et al. [7,8]. They used a SEM equipped with an energy dispersive X-ray analyzer (EDAX) to study the micromorphology of the interfacial zone. Glass and α-quartz granules were used as model "coarse aggregates". With the aid of the EDAX facility, they were able to estimate the chemical composition of the hydration products in the interfacial zone. They reported the formation of a continuous film of cement hydrates predominantly calcium hydroxide Ca(OH)$_2$, intermixed with C-S-H and ettringite as a deposition on the glass and quartz surfaces.

Initially, their method of study received some criticisms because the glass and α-quartz 'aggregates' used for the studies were considered to be unrepresentative of conventionally used aggregates. For that matter, their interpretations were regarded as non-applicable to typical concrete systems. However, since their report, evidence from a number of studies involving cement paste-aggregate interfaces in typical concrete systems have supported their interpretations [9-12].

The microstructure of the interfacial zone which was modelled by Barnes et al. [7,8] has been presented in detailed by Diamond [13] as follows:
(i) At the immediate vicinity of the aggregate surface is a "duplex film" of Ca(OH)$_2$ topped by or occasionally intermixed with C-S-H. Sometimes this duplex film occurs in close intimacy with the aggregate. At early ages of hydration, this duplex film is relatively porous. With increase in age, the film modifies into a dense layer, sometimes bonding with the surrounding cement paste. The side of the film in contact with the aggregate is a layer of crystalline Ca(OH)$_2$, $\approx 0.5$ $\mu$m thick. Following this layer is a thin deposit of C-S-H gel, in the form of short fibres, that extend into the cement paste. The total extent of the duplex film is $\approx 1.0$ $\mu$m.

(ii) Next to the "duplex film" is the "transition zone". This region is relatively larger, $\approx 50$ $\mu$m wide, including the "duplex film". Generally, this zone contains a large number of hollow-shell hydration grains [6-8], and enriched in larger Ca(OH)$_2$ crystals and ettringite, AF$_1$.

The occurrence of a large number of hollow-shell hydration grains suggests that cement hydration is accelerated at the interfacial zone. This is presumably because of an availability of excess water at the vicinity of the aggregate particles. Also, since the growth of large crystals of calcium hydroxide and ettringite is enhanced in a more open system, the occurrence of such large crystals at the interfacial zone is an indication of the existence of higher porosity.

Besides the model presented by Hadley [6] and Barnes et al. [7,8], the microstructure of the paste-aggregate interfacial region has also been characterized by Zimbelmann [14]. He performed a combination of tensile bond strength tests and SEM studies on debonded paste-rock composites at various ages. Following these studies, he presented a model of the microstructure of the interfacial zone as follows:

a. Directly at the surface of the aggregate is a dense layer $\approx 2-3$ $\mu$m thick and composed essentially of Ca(OH)$_2$ covering a network of ettringite crystals. This layer may be equivalent to the 'duplex film' found by Barnes [7,8]. According to Zimbelmann, this layer is formed during the early ages of hydration, that is, up to about 10 hours old. After about 12 hours the Ca(OH)$_2$ forms a continuous closed layer which he referred to as the 'contact layer'.

b. Directly adjacent to the contact layer is a zone $\approx 5-10$ $\mu$m thick - the 'intermediate layer'. This layer consisted for the most part of needle-shaped ettringite crystals, leaf- or flake-like Ca(OH)$_2$, sporadic needle-shaped calcium silicate hydrates (C-S-H) and "big" hexagonal Ca(OH)$_2$ crystals aligned steeply with respect to the aggregate surface.

c. The 'transition zone', $\approx 10$ $\mu$m thick which is characterized by dense paste which merged into the bulk cement paste.

Zimbelmann attributed the origin of the interfacial zone to the formation of thin films of water $\approx 10$ $\mu$m thick on cement grains and around large aggregate particles in fresh concrete. The formation of water films on the aggregate particles seems quite likely. However, the formation of such films on the cement grains appears doubtful since after mixing, placement and subsequent compaction of the concrete are likely to destroy such films. A similar explanation has been suggested by Conjeaud et al. [15], but no direct evidence of water film has been reported.
The microstructural features of the interfacial zone, which has been outlined by the foregoing investigators, have also been observed by several workers [16-21]. The general observation is that the micro-characteristics of the paste-aggregate interfacial region in cement-based composites is different from that of the bulk cement matrix. Compared to the matrix, there is a high proportion of larger and better-crystallized hydrates, predominantly calcium hydroxide and ettringite. The calcium hydroxide crystals have a preferential orientation in such a way that their basal cleavage planes are nearly perpendicular to the aggregate surface. The porosity of this region is higher than the bulk matrix. A schematic representation of the transition zone in concrete is shown in Figure 1.

![Diagram](image)

*Figure 1: Schematic representation of the transition zone in concrete. 1 = aggregate; 2 = Ca(OH)₂; 3 = C-S-H; 4 = Ettringite [25].*

2.3 Texture of cement hydration products at the interfacial zone

A recent advance in the understanding of the microstructure of the interfacial zone is concerned with the texture of the cement hydrates at the paste-aggregate interface. The texture refers to the mode of occurrence or pattern of orientation of the hydration products at the interfacial zone with respect to the aggregate surface.

A unique technique developed by Grandet and Ollivier [9,23], based on X-ray diffraction analysis, is the most commonly known and extensively used method for studying the texture of the hydrates at the interfacial zone. This method has been exploited in the present work; details of the procedure are given in Chapters 3-5 of this book.

Using this technique, Grandet and Ollivier presented data to indicate that calcium hydroxide crystals in the transition zone are preferentially oriented with their c-axes perpendicular to the aggregate surface. They found a parameter which shows the relationship between the diffraction intensities of the (001) plane and the (101) plane of Ca(OH)₂ crystals in the transition zone. This parameter, known as the orientation index, Iₜₜ, or degree of orientation, was highest (> 1.0) at the aggregate
interface, and approached a value of unity in the cement matrix. Figure 2 shows the orientation index, $I_{OH}$, versus distance from the aggregate surface for quartz and marble. The method has been used to study several factors which affect the orientation of calcium hydroxide crystals and other hydrates such as ettringite at the cement paste-aggregate interfacial zone [12].

![Graph showing orientation index versus distance from interface](image)

**Figure 2:** Index of orientation, $I_{OH}$, versus distance from polished aggregate surface for quartz and marble [Redrawn from Ref. 27].

More recently, Monteiro and Mehta [23] used this method to study the concentration of ettringite at the interfacial zone. They demonstrated that the concentration of ettringite is high at the aggregate interface and decreased to a constant value in the bulk paste as shown in Figure 3.

![Graph showing intensity versus distance from interface](image)

**Figure 3:** Variation in peak intensity of ettringite as a measure of its concentration in the interfacial zone [Redrawn from Ref. 27].
Yuan and Guo [24] studied the structure of the interfacial zone using a combination of the technique of Grandet and Ollivier [9,22] and bond strength measurements on cement paste-marble composites. After scanning electron observations of the debonded cement pastes-marble surfaces, they characterized the interfacial zone (from the aggregate surface into the bulk paste) as follows. First, a duplex film consisting of calcium hydroxide crystals, followed by a C-S-H film, and a porous network of ettringite and C-S-H. Their model of the interfacial zone is schematically represented in Figure 4. This description seems to be in agreement with the description given by Barnes [7,8] and Monteiro (in Mehta [25]). They attributed the formation of the "duplex film" at the aggregate surface to a heterogeneous nucleation and subsequent growth of Ca(OH)$_2$ and C-S-H from an oversaturated solution. Their analysis of surface and interfacial free energies indicated that Ca(OH)$_2$ was more likely to nucleate and grow on an aggregate surface than in the bulk paste. In other words, their results showed that favourable thermodynamic conditions exist at the aggregate surface more than in the bulk paste for crystallization and growth of Ca(OH)$_2$.

![Figure 4: Schematic representation of the cement paste-aggregate interfacial zone (Redrawn from Ref. 24).](image)

The work of Yuan and Guo [24] was supported by the previous work of Yuan and Odler [26] on C$_3$S-marble composites, in which the overall Ca/Si molar ratio was highest at the interface and decreased into the bulk matrix. This Ca/Si trend delineated an interfacial zone of ≈ 100 μm thick in which the ratio was higher than 3 as shown in Figure 5. These results were considered to indicate a possible migration of Ca$^{2+}$ and OH ions from the bulk paste towards the interface for crystallization.

### 2.4 Chemical nature of the cement paste-aggregate interfacial bond

A number of investigations have shown that chemical reactions sometimes do occur between C$_3$A (3CaO.Al$_2$O$_3$) which is present in cement and calcite from calcareous aggregates to form "carboaluminates" [27]. The assessments of the effects of these chemical reactions on strength though, have not been consistent. Cussino and Pintor [28] and Cussino et al. [29] reported that a kind of chemical
reaction occurs between calcite, $C_3A$ or $C_4AF$, and water to produce $3CaO.Al_2O_3.CO_2.11H_2O$. They referred to this compound as "carboaluminate". By examining polished marble samples covered with portland cement paste with an X-ray diffractometer, Grandet and Ollivier [22] also identified "carboaluminate" hydrates $3CaO.Al_2O_3.CO_2.11H_2O$ at the interfacial zone. Zimbelmann [30] concluded from bond strength studies that a kind of chemical reaction occurred between cement paste and limestone aggregates. This reaction, according to him, increased the bond strength. Monteiro and Mehta [31] used SEM to identify a calcium carbonate-calcium hydroxide compound, reported its XRD pattern, and suggested that the reaction was responsible for the increased strength of concrete containing limestone aggregate.

![Ca/Si ratio vs Distance from interface](image)

*Figure 5: Average CaO/ SiO$_2$ molar ratio of the hydrated C$_3$S paste as a function of the distance from the marble-paste interface (Redrawn from Reference 26).*

Carboaluminate hydrates have also been suggested to form between cement paste and calcareous aggregates by Yuan and Guo [24] and Yuan and Odler [26]. Using a SEM, Yuan and Guo [23] observed the surfaces of marble to be "corroded" after debonding cement paste-marble composites. According to them this "corrosion" was an indication of "dissolution" of the marble in the alkaline fluid to form Ca(OH)$_2$. The formation of the "carboaluminate" layer at the rock-cement paste interface was found to be beneficial for the marble-cement paste bond. They concluded, however, that excessive dissolution of the carbonate rock with subsequent precipitation of calcium hydroxide at the interface adversely affected the bond strength.

In the case of siliceous aggregates, chemical reaction has not yet been recognized at normal temperatures by most investigators. Zimbelmann [30] concluded from microscopic studies of the paste-quartz aggregate bond at a temperature of $\approx 20^\circ$C that no chemical reaction was involved. Massazza and Costa [27] reported that at relatively high temperatures of $\approx 60^\circ$C, hydrolysis of lime with siliceous aggregates usually takes place to form calcium silicate hydrates. Based on bond strength data, Scholer [32] suggested later that some siliceous aggregates could produce some form of "chemical bonding", although the nature of the chemical
bonding was not clearly described. No such chemical reaction involving siliceous aggregates at normal temperatures has been confirmed yet.

It appears from the foregoing section that a kind of chemical reaction involving some constituents of the cement paste and calcareous aggregates takes place at normal temperatures. The nature of the reaction and its effects on the mechanical behaviour and the durability of concrete are not well understood. Additional investigations are required to clarify this issue.

2.5 Porosity and grain arrangement at the interfacial zone

Considering the open microstructure of the interfacial zone, and the relatively coarser and better-crystallized hydrates, one will expect the porosity of the interface to be higher than that of the bulk cement paste without any doubt. However, opinions vary on this subject. Tognon and Cangiano [33] compared the porosity of the pastes in mortars to the porosity of neat cement pastes of the same water-cement ratios and ages, after statistically normalizing the data. Their study was done with the aid of a mercury intrusion porosimeter. They observed differences between the calculated and the measured porosimetric values and attributed the differences to the higher porosity of the interfacial zone. Kayyali [34] performed a similar study on pastes, mortars and concrete but concluded that the interfacial zone was lower in porosity.

More recently, Scrivener [17-20] has developed a method for quantitatively characterizing the paste-aggregate interfacial zone in cement composites. She used a combination of backscattered electron imaging and quantitative image analysis to study particulates at the interfacial zones in plain concretes and concretes containing mineral additives. The information obtained by this method has been shown to correlate well with quantitative information obtained by other methods such as X-ray diffractometry, mercury intrusion porosimetry, etc. [17-20]. Figure 6 is a summary of the results of some of her studies. The figure shows that, the amount of anhydrous cement grains is lowest in the vicinity of the aggregate, and increases into the bulk paste. Her results confirmed the observations made by Zimbelmann [14,30], and a previous investigation by Scrivener and Gartner [19] who found little or no anhydrous cement grains within a zone of \( \approx 15-25 \mu \text{m} \) around coarse aggregate particles. The figure also shows that the porosity, on the other hand, is highest at the interface, and decreases with increasing distance into the bulk paste. These porosity data also support an earlier study by Farran [2], who used light microscopy to examine thin sections of mortars and observed the presence in some cases of interfacial zones with increased porosity.

The higher porosity at the aggregate interface and the low amount of cement grains in the interfacial zone, have been attributed to the poor packing of cement grains, and to the ‘wall-effect’ and micro-bleeding under coarse aggregate particles as illustrated in Figure 7 [25].

2.6 Thickness of the cement paste-aggregate interfacial zone

The thickness of the cement paste-aggregate interfacial layers is usually taken to be the distance from the surface of the aggregate where the cement paste has a
distinctive microstructure. It is variable depending on the type of aggregate and cement used, the water-binder ratio of the mix, the age of the composite, the nature of bonding between the paste and aggregate particles, and the method used to estimate it.

![Graph](image)

Figure 6: Microstructural gradients (anhydrous material and porosity) in the interfacial region of concrete made with ordinary portland cement (Redrawn from Reference 20).

![Diagram](image)

Figure 7: Schematic representation of bleeding in freshly deposited concrete.
1 = Aggregate particles
2 = Cement paste
3 = Visible bleed water
4 = Internal bleed water
or micro-bleeding [25].

The usual thickness ranges between 50 and 100 µm. In some cement composites, however, it is found to be as thin as 1 µm [35], resembling the duplex film reported by Barnes et al. [7,8,13], or it could be more massive, extending several microns from the aggregate surface [35]. Farran et al. [16] studied double replicas
of abraded surfaces of mortars up to about 35 μm away from the aggregate surface. They found within this region, a distinct microstructure of the cement paste which was taken to represent the interfacial zone. Zimbelmann [30] reported the thickness from bond strength studies to be ≈ 25 μm, while Grandet and Ollivier [9], using a semi-quantitative X-ray technique, found this zone to be ≈ 40 μm thick. Using a SEM with secondary electron imaging to examine fracture surfaces and with backscattered electron imaging to examine polished specimens, Struble [21], and Scrivener and Pratt [18], in separate studies found the thickness to be ≈ 50 μm. In a similar study, Yuan and Odler [26] reported the thickness to be ≈ 100 μm. Their result was obtained from an estimation of the Ca/Si ratio from C₃S-marble composites using electron probe micro-analysis (EPMA).

In typical concrete systems, the thickness of the cement pastes which are ‘sandwiched’ between the aggregate particles ranges between 80 to 150 μm [1,13]. Of this, the thickness of the interfacial zone ranges between 25 to 100 μm [9,21,27]; the volume of which represents approximately 30 to 50% of the total volume of the cement matrix. It is clear that the interfacial region forms a significant proportion of the cement paste. This emphasizes the need for a better understanding of its character and the role it plays on the mechanical behaviour and the durability of concrete.

2.7 Microhardness of the paste-aggregate interfacial zone

The microhardness value Hᵥ is a useful parameter which indicates the compactness of the cement paste system. A lower value implies that the cement paste is either soft or contains a higher amount of micropores, which is an indication of higher porosity.

The first reported work about the microhardness of the interfacial layer was by Lyubimova and Pinus [36]. They measured microhardness across the cement paste-aggregate interface for different rocks and cements. Their results showed a variation of microhardness from the aggregate interface into the bulk paste. At a distance of ≈ "2-3" μm from the aggregate surface, a high microhardness value Hᵥ ≈ 20 was measured. This was followed by a softer region with Hᵥ ≈ 5, and then another zone ≈ 10-50 μm thick into the bulk paste - a region with a relatively constant microhardness value of about 10. The shape of the Hᵥ distribution of the interfacial zone showed a ‘valley’ or a ‘trough’ representing the softer interfacial layer.

Yuji [37] obtained similar microhardness distribution using ordinary sand particles and slag particles used as aggregates. From his plot, he obtained a ‘valley’ at a distance of about 20-30 μm from the aggregate surface. The results of his study for specimens containing the sand particles are shown in Figure 8.

The ‘trough’- or ‘valley’-shaped distribution of the Hᵥ data at the immediate vicinity of the aggregate is an indication of the occurrence of a higher microporosity, or a lesser cement paste at the interface. Mehta and Monteiro also [38] investigated the effect of age on the microhardness value of the interfacial film. They observed an increase in value of about 25% from 30-day old film to 1-year old film. This suggests that as hydration progressed, the interfacial zone became gradually filled with cement hydrates. Since the interfacial zone contains a lesser amount of
cement grains than the bulk cement paste [20], the increased amount of cement hydrates with age is likely to result from migration of ions such as $\text{Ca}^{2+}$ and $\text{OH}^-$ from the bulk paste matrix to the interface.

![Image of microhardness value - Hv](image)

*Figure 8: Curves of microhardness at the paste-sand interface in mortars prepared with ordinary portland cement; $a = 7$ days; $b = 28$ days (Redrawn from Reference 37).*

### 2.8 Strength of the cement paste-aggregate interfacial bond

Extensive studies on bonding in concrete by Hsu and Slate [39], Sha and Slate [40], Hsu et al. [41], Slate and Olsefki [42], and Alexander et al. [43] indicate that the interfacial bond between coarse aggregate and cement paste or mortar is the "weakest link" in concrete with respect to strength.

According to Mehta [25], the strength between the hydration products and the aggregate particles is the force of adhesion resulting from the van der Waals force of attraction. Since the adhesive strength at any point depends on the volume and size of voids present, it is not surprising that the paste-aggregate interfacial zone is the weakest link in concrete. He explains that where there is crystallization of new products in the voids of the interfacial zone by slow chemical reactions between the components of the cement paste, or between some of the constituents of the cement paste and the aggregate, the adhesive strength between the paste and the aggregate could increase. Such strength contributions occur for example, when siliceous constituents of the paste, such as fly ash, silica fume and slag react with calcium hydroxide to form calcium silicate hydrates (C-S-H); or the formation of "carboaluminate" hydrates in the case of a reaction between calcareous aggregates and $\text{C}_3\text{A}$ in the cement [22,27-29]. On the other hand, according to Marchese [44], the large calcium hydroxide crystals in the interfacial zone tend to possess less adhesion capacity. This is because of their lower specific surface and correspondingly weak van der Waals forces of attraction. Also, because of their oriented structure in the transition zone, the large calcium hydroxide plates serve as preferred cleavage sites allowing cracks to occur preferentially along their weakly bonded basal cleavage planes.
Hsu and Slate [39] reported that with increasing age, the paste-aggregate bond strength increased. They explained, however, that the weaker bond strength compared to the tensile strength of the paste was in part, due to the formation of "bond cracks" at the aggregate interface even before the application of any load. Their work also showed the existence of "bond cracks" at the aggregate interface, even when the concrete was kept in a continuously wet environment.

2.9 Effect of the paste-aggregate interfacial bond on the strength of concrete

There are varied opinions about the effect of the paste-aggregate bond on the strength of concrete. From bond strength measurements, Alexander et al. [43] found a linear correlation between concrete strength, and the paste and bond strengths. Their results showed that as the bond strength increased, the compressive strength of concrete also increased. On the other hand, Fagerlund [45], Hsu et al. [41], and Perry and Gillot [46], concluded that the cement paste-aggregate bond was not important to concrete strength. In fact, Perry and Gillot [46] found little effect of bond strength on compressive strength above the stress level at which bond cracks are initiated.

When concrete is subjected to load, cracks may initiate and propagate owing to the high tensile stress concentrations in the specimen (produced by interactions between the aggregates and voids within the concrete) [47]. In a detailed study about the internal behaviour of concrete subjected to stress, Hsu et al. [41] and Sha and Slate [40] observed micro-cracks in both the cement paste and at the paste-aggregate interfacial zone. The crack density at the paste-aggregate interface was found to be higher than that in the paste. Using microscopic and X-ray diffraction techniques, Hsu et al. [41] observed directly the cracking of plain concrete in compression. They reported that even before loading began, cracks were observable at the paste-aggregate interface; these "micro"-cracks or presumably "shrinkage" cracks are produced as result of the hydration of the cement. Their study showed that up to about 0.30 of the ultimate strength, $f_{c'}$, there was very little or no extension of these cracks. Beyond 0.30$f_{c'}$, the cracks began to grow under increasing load. After about 0.50$f_{c'}$ the "bond cracks" also began to extend through the matrix, forming bridges between the coarse aggregate particles. Finally, beyond 0.75$f_{c'}$, the "matrix or mortar cracks" began to connect each other, forming a more extensive network. This indicates further that the cement paste-aggregate interfacial zone is the weakest region of concrete. In general, three types of micro-cracks can be distinguished [40,48]. These include:

1. **Bond or adhesion cracks**: these are micro-cracks which exist at the interface between coarse aggregate and the mortar.

2. **Mortar or paste cracks**: which are micro-cracks existing within the mortar or the paste, and along the interface of sand grains.

3. **Aggregate cracks**: these are micro-cracks mostly in coarse, but sometimes also in fine aggregate particles.

Figure 9 is a schematic illustration of these microcracks. The study of Sha and Slate [40] about failure pattern in concrete also revealed that most of the bond failures occurred within the interfacial layer. Failures occurring directly at the
paste-aggregate interface were also common. Glücklich [49] found the number of microcracks in the interfacial region to increase with increasing application of load. Studies show that by increasing the paste-aggregate bond strength the compressive strength of concrete tends to increase [50-56]. Hsu et al. [41] and Perry and Gillot [46] noticed that, by increasing the bond strength, the stress level at which extensive microcracking began also increased. This effect is the reason for the increase in brittleness with increasing compressive strength.

In a similar study, Mindess and Diamond [57,58] reported that cracking in mortars and concretes tended to initiate at the interfacial region, and that the crack path generally ran within the interfacial zone, at a distance of a few microns from the surfaces of the aggregate particles themselves.

![Figure 9: Area containing five paste or mortar cracks marked (1, 2, 3, 4, and 5), 2 adhesion or bond cracks (marked I and II) and 1 aggregate crack (marked a-c); (Redrawn from Reference 48).](image)

Thus it appears, there is a general agreement that the interfacial zone is a ‘weak link’ in the structure of normal concrete with regard to strength. In very high strength cement paste systems, where the paste-aggregate bond is relatively strong, differences in opinion do exist as to the nature of the crack growth and propagation in mortars and concrete. While Bentur and Mindess [59] observed cracks to go around aggregate particles, Regourd [50], Sarkar and Aitcin [55], and Odler and Zurz [60] observed cracks to go through the interfacial layer at a few microns away from the paste-aggregate interface.

2.10 Effect of the paste-aggregate interfacial zone on the durability of concrete

There is little published information on direct studies relating the effect of the paste-aggregate interfacial zone on the durability of concrete. Most of the published work involve investigations in which porosity or permeability were examined. Mindess et al. [in Reference 53] and Wakely and Roy [61] and Malek and Roy [62] reported that the paste-aggregate interfacial zone does not seem to play any major role in determining the permeability of concrete, and hence may probably not
influence the durability of concrete. Valenta [63, 64] and Tognon and Cangiano [33], however, reported some contrary findings. They examined the effect of the interfacial zone on the permeability and the durability of concrete from freeze-thaw and pore structural studies respectively. They showed that the interfacial layer contributed significantly to the permeability and the durability of concrete. Xie and Tang [65] performed electrical conductivity measurements on mortar specimens containing ordinary portland cement paste and quartz aggregates with the intent of delineating the effect of the paste-aggregate interfacial zone on the conductivity of mortars. Their results demonstrated that the interface material was more electrically conductive than the paste matrix. Norton and Pletta [66] presented data to indicate that increasing the volume concentration of aggregate increased the permeability of concrete. Their results were supported by the work of Nyame [67], who studied the permeability of normal and lightweight mortars, and concluded that by increasing the aggregate volume, interfacial effects seemed to increase the permeability. Toy [68], Murata [69], and Bracs et al. [70] also demonstrated that a reduction of the maximum aggregate size reduced the permeability of portland cement-based composites. The foregoing review shows that the interfacial zone in one way or another may influence the permeability of concrete and for that matter, the durability of concrete. However, because all these studies do not directly relate the role of the interfacial zone on the durability of concrete, one cannot tell the how significant this role may be. Further research into this effect is required to provide solutions to this problem.

2.11 Effect of additives of the portland cement paste-aggregate interfacial zone

2.11.1 Mineral additives

Bentur et al. [51, 56] investigated the effect of addition of silica fume on the paste-aggregate interfacial zone. They found out that the silica fume addition improved significantly the structure of the transition zone by densifying it. Goldman and Bentur [56] observed that for the same water-binder ratio, the compressive strengths of silica fume concretes were significantly higher than those of silica fume, pastes as well as those of plain (silica fume-free) concretes of the same ages. They concluded that the main beneficial effect of addition of silica fume to concretes was the result of the improvement of the structure of the interfacial zone.

Regourd [50], Sarkar and Aitcin [55], Detwiler and Mehta [71], Cheng-yi and Feldman [72], Odler and Zurz [60] and Sarkar et al. [73] all found the paste-aggregate interfacial zone to be denser in silica fume concretes than in plane portland cement concretes. In general, they found the paste-aggregate bond to be improved by addition of silica fume. In contrast to these observations, Darwin et al. [74] found lower bond strengths for mixes containing silica fume. They attributed the lower bond strength to the absence of calcium hydroxide at the paste-aggregate interfacial zone in the presence of silica fume. They also ascribed the increase in strength of the silica fume concretes to an increase in strength of the cement paste matrix rather than the interfacial zone.

Detwiler et al. [75], using the technique of Grandet and Ollivier [9, 22], investigated the influence of blastfurnace slag cement on the structure of the transition zone. They concluded that in the presence of sufficient quantity of slag (up to ≈ 30% by
mass of cement), less crystals were formed at the paste-aggregate interface. They attributed this to the ability of the slag to form a dense paste at the interfacial zone, thus inhibiting the transport of Ca\(^{2+}\) ions to the aggregate surface for precipitation. In a recent study Mehta and Monteiro [38] showed the amount and the orientation index of Ca(OH)\(_2\) at the interfacial zone to be decreased by addition of silica fume and fly ash. They also found the thickness of the transition zone to be reduced. Saito and Kawamura [76] and Gjov et al. [77] have also found the thickness of the interfacial zone to be reduced by addition of pozzolans to concrete.

2.11.2 Chemical additives

Zimbelmann [30] showed that by coating the surface of polished aggregate particles with tensides, the structure of the interfacial zone and bonding of paste to aggregate particles could be improved. Xueqan et al. [78,79] performed similar tests using sand and limestone aggregate particles coated with water glass (sodium silicate). They found the bond strength of paste to the aggregates and the compressive strengths of mortars prepared with the pretreated aggregates to be higher than mixes containing untreated aggregates. Although the results of these studies are quite interesting, the practical potential of these techniques may be limited. This is because, on singular aggregate particles, the adhesion of the fresh paste to the treated rock surface is carefully done. So that when the cement paste is being cast against the rock, the chemical agent on the surface of the aggregate is practically not disturbed. In practice, the tumbling and shearing caused by the coarse aggregates particles in the wet mix may remove the tensides and or chemical coatings which may probably reduce their effective performance.

2.11.3 Polymer dispersions

Su and Bijen [80,81] showed that by using acrylic polymer dispersions in conjunction with portland cement, the structure of the paste-aggregate interfacial zone could be improved. The investigation showed the adhesive strength of pastes to aggregates could be improved by using polymer-modified cement pastes. They found the amount of pores spaces to be decreased, and the density of cracks at the interfacial zone to be reduced.

2.12 Concluding remarks

The purpose of this brief literature survey has been to highlight the microstructure of the paste-aggregate interfacial zone and the role it plays on the strength and the durability of concrete. The survey shows that in concrete, interfacial zones with distinct microstructural features exist between cement paste and aggregate particles. In general, these interfacial zones contain more calcium hydroxide than the bulk cement paste matrix. Moreover, the calcium hydroxide crystals are not randomly oriented. They exhibit a preferred orientation with regard to the surface of the aggregate.

The review also shows that most of the studies regarding the character of the transition zone have been approached from micro-level techniques, such optical microscopy. For example, micro-porosity, micro-cracks, and cement hydration products at the interfacial zone have been observed visually using a scanning electron microscope. The elemental and chemical composition of the hydration
products at the transition zone have been estimated by energy dispersive spectrometry (EDS/EDAX) and semi-quantitative electron probe micro-analysis (EPMA). While nearly all investigators agree on the existence of a relatively higher amount of calcium hydroxide at the interfacial zone, differences in opinion exist on the question of porosity. One group of investigators believe that the interface is comparatively higher in porosity than the bulk paste. Others are of contrary opinion. Also, whereas there is substantial evidence that chemical reactions exist between cement paste and carbonate rocks, opinions concerning the role of these reactions on the mechanical properties of concrete are varied. Additional information regarding this subject is required to resolve this issue.

With regard to the role of the interfacial zone on the mechanical properties and the durability of concrete, there are also two diversified schools of thought. This aspect of the interfacial zone needs further investigation.

The survey shows that from the few attempts made to improve the structure of the interfacial zone, mineral additives, such as silica fume, pulverised fuel ash and blast furnace slag, and chemical additives such as water glass and tensides, as well as polymer dispersions seem to show considerable improvements of the microstructure of the interfacial zone.

It is important to point out from this literature study that, whereas a great deal of effort has been made to characterize the microstructure of the interfacial zone, relatively little attempts have been made to improve this weak region of concrete. This is because in the first place, the volume of cement paste constituting the interfacial zone is usually assumed to form an insignificant part of the total volume of concrete and therefore not important as far as improvements in the property of concrete is concerned. And in the second place, most of the information obtained about the character of the interfacial zone from micro-level techniques have not been adequately translated to the bulk properties of concrete such, as the compressive strength and the permeability. This is perhaps the reason why at the moment there is no simple way of predicting how much improvement can be made in the overall performance of concrete through improvement of the interfacial zone.

In this thesis the above considerations are discussed in the light of the experimental results obtained.

References


Chapter 3

Effects of water-cement ratio on the evolution of calcium hydroxide in set portland cement pastes and mortars

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(Refereed)

Abstract

The water-cement ratio and the presence of aggregate particles are shown to influence the evolution of calcium hydroxide in set portland cement paste systems. Increasing the water-cement ratio from 0.30 to 0.50 caused an increase in Ca(OH)$_2$ content in both portland cement pastes and mortars at all ages of hydration. For the same water-cement ratios, however, the calcium hydroxide content of the mortars were found to be significantly higher than those of the pastes. The results have been interpreted on the basis of a "through-solution" mechanism of formation of Ca(OH)$_2$ in which, after the hydrolysis of the calcium silicates C$_3$S and C$_2$S, calcium hydroxide precipitates out of the pore solution as crystals. With respect to the mortars the sand particles are believed to act as a "sink" for the Ca(OH)$_2$ crystals which precipitate out of the pore solution. With increasing water content the Ca$^{2+}$ and OH$^{-}$ ions become easily transported through the aqueous phase to the inert sand surfaces where favourable thermodynamic conditions exist for crystallization and growth of the Ca(OH)$_2$ crystals.

Introduction

It is well known that when portland cement undergoes hydration under normal conditions, one of the major products formed is calcium hydroxide. In a fully hydrated portland cement paste it occupies approximately 20% of the solid material [1]. Calcium hydroxide, otherwise called portlandite or lime, exerts a significant influence on the physico-mechanical characteristics of hardened portland cement systems (pastes, mortars, concretes). In terms of chemical attack of cement paste, it is found to be the least resistant of the hydrated phases of portland cement. Lime, in the presence of moisture, is highly vulnerable to carbonation, sulphate attack, and leaching by acids. Moreover, from equilibrium solubility studies in the system C-S-H, it has been shown that Ca(OH)$_2$ is the least stable of the hydrated cement paste, its solubility depending on the pH-value of the surrounding solution [2].

On the other hand, with respect to corrosion of reinforcements in concrete, lime plays a major role by acting as a buffer for the alkalinity of the pore fluid which passivates the reinforcement. In general, understanding the mechanism of trans-
port and deposition of lime in hydrated portland cement systems serves as an essential tool in monitoring the performance of such systems.

This chapter presents results of a number of tests which were performed in order to study the evolution, mode of occurrence, rate of precipitation, morphology, and pattern of crystallization of $\text{Ca(OH)}_2$ in hydrated portland cement systems. In addition, the effects of sand on lime distribution in mortars and micro-characteristics of the transition zone between cement paste and inserts will be discussed.

**Materials and experimental methods**

**Materials**

The cement used in preparing mixes for these investigations was an ordinary portland cement (OPC), equivalent to the Dutch Cement Standard NEN 3550 Type A or ASTM Type I portland cement. The chemical composition and other properties of the cement have already been presented in a previous paper [3]. The quartz sand was clean and inert ($\alpha$-quartz); the maximum grain size was about 0.5 mm.

**Sample preparation and test procedures**

Two separate tests were performed in this study. These were, free lime content determinations by the method of chemical extraction using Franke technique [4] and semi-quantitative X-ray diffraction analysis (XRD). The above two tests were supported by scanning electron microscope studies on similar portland cement composites. In all cases the water-cement ratio (w/c) ranged from 0.30 to 0.50 for both pastes and mortars. To reduce surface bleeding and to improve uniform mixing during hardening, the sealed specimens were rotated on a rotating device at a relatively low speed for periods between 4 and 24 hours depending on the water-cement ratio of the mix.

(i) Calcium hydroxide, CH content determination

The $\text{Ca(OH)}_2$, content of cement pastes and mortars were determined by Franke method. This is a chemical extraction technique which measures the amount of calcium ions that are taken into solutions. The following standard procedure was employed.

The samples were cast into plastic tubes, sealed and stored in a fog room at a temperature of about 20°C. At the required age for analysis, a representative sample of the specimen was oven-dried at 105°C to a constant weight and the free water content determined. Later, the sample was ground to a high degree of fineness and 0.5 g of the dry sample was then added to 25 ml of a mixture of acetoacetic ester and isobutyl alcohol (30 ml acetoacetic ester + 200 ml isobutyl alcohol) and stirred. The mixture was boiled for 1 hour, filtered, and the residue washed with 20 ml of isobutanol once. After washing, 20 ml of methanol was mixed with the filtrate and titrated against $\text{HCl}$ (0.1 M), using bromophenol blue (1 ml) as an indicator. The end point occurred when the solution changed from blue to yellow.

In order to calculate for the calcium hydroxide content in the samples, the free and non-evaporable water contents of the composites were required. These parameters
were determined for each of the specimens using the standard procedures (BS 1881, Part 6) on representative samples. For each specimen, three analyses were made; the average value of the three data was considered as the representative value for the specimen.

(ii) **Semi-quantitative XRD analysis**

The texture (occurrence and orientation) of CH at the paste-insert interfacial zone was determined by a semi-quantitative X-ray diffraction technique based on the method developed by Grandet and Ollivier [5]. Four composite specimens consisting of two cement pastes and two mortars were prepared by casting each specimen separately against a polypropylene plastic plate with the aid of a cylindrical PVC tube. The PVC tubes were fixed to the plates with the aid of a silicone rubber. Obviously, the polypropylene plastic plate is not used in concrete, however, in the present study, it was used as a "model coarse aggregate" because experience from the trial tests showed that after separation of the composite specimens some of the paste adhered to the limestone rock specimens which were used during the trials. This made the estimation of the distance from the aggregate surface and the overall data inaccurate. The use of the plastic plate enabled easy separation of the cement paste from the plate without any remnants on the plate. Although paste-aggregate specimens cast in this way do not adequately simulate the real paste-aggregate composite in mortars and concretes, for reasons of comparisons, the test results could provide an indication of the characteristics of the interfacial zone. In mortars and concrete, the shearing and tumbling of the solid particles during mixing tends to improve the packing of the grains. Lack of such mixing effects in the case of pastes, such as in this study, may serve as a limiting factor. However, since the same substrate is used, the data obtained from the test could provide a good indication of the effects of sand on the microstructure of the interfacial zone.

The water-cement ratio of the composites was 0.30 and the sand-cement ratio of the mortar specimens was 0.40. After casting, the specimens were wrapped in a plastic foil and stored in a fog room at approximately 20°C. At the specified periods of curing (7 and 100 days), the specimens were removed from the fog room and stored in a desiccator. The drying process caused shrinkage of the specimens which easily separated at the plastic interface. The freshly-separated surfaces of the specimens at the paste side were then analyzed with a Philips X-ray PW1130 diffractometer using CuKa radiation generated at 40 kV, 20 mA. The goniometer in the diffractometer had 1° scatter slits, 0.1° resolving slits, and a scanning speed of 1° 20 per minute.

(iii) **Scanning electron microscope studies**

For the scanning electron microscope (SEM) studies, portions of specimens were cut and freeze-dried to prevent further hydration. Thenafter, freshly-fractured surfaces were coated with a thin film of nickel or gold, mounted onto stubs, and examined using a JEOL, JSM-840A SEM. The SEM was equipped with energy dispersive X-ray analyzer (EDXA).

In order to perform quantitative analyses (electron probe microanalyses, EPMA), the specimens needed to be polished to a high degree to remove almost all relief. This was achieved with the aid of a suitable polishing device consisting of a synthetic cloth impregnated with 1.0 μm diamond from an aerosol spray with
alcohol. Prior to polishing, the specimens were reinforced with epoxy resin by vacuum-impregnation. After polishing, a thin coating of carbon and nickel was evaporated onto the cleaned surface for subsequent examination and analysis in the SEM.

Results and discussion

Results

Effect of water-cement ratio on evolution of CH

The effects of water-cement ratio on the evolution of calcium hydroxide in portland cement pastes and mortars are shown graphically in Figures 1 and 2.

Figure 1: Effect of water-cement ratio on the evolution of calcium hydroxide in cement pastes as a function of age.

Figure 3 compares the Ca(OH)$_2$ content of the pastes to those of the mortars for the same water-cement ratios of 0.40 and 0.50. The Ca(OH)$_2$ values are presented as percent by mass of pastes or mortars. The data reveal that for the same water-cement ratio, the Ca(OH)$_2$ content of the mortars are relatively higher than those of the pastes. The higher lime values of the mortars over and above those of the pastes is likely to be due to the presence of the inert quartz sand particles in the mortars, which served as favourable sites for nucleation and growth of the CH crystals, which were precipitating out of the pore solution in contact with the mortar. This effect of sand in mortars has also been suggested by Cheng-yi and Feldman [6].

Growth and morphology of calcium hydroxide

Figures 4 and 5 are SEM micrographs of freshly-fractured surfaces of 1-day and 7-day old cement pastes showing the euhedral single plates of CH in pores or voids
within the cement paste. Figure 6 shows a micrograph of an euhedral to a subhedral CH crystal in a large pore within the paste. Figure 7 (an enlargement of Figure 6) shows that the CH crystal occur together with two or more distinct sizes.

![Graph showing Ca(OH)₂ content as a function of age for different w/c ratios.](image)

*Figure 2: Effect of water-cement ratio on the evolution of calcium hydroxide in cement mortars as a function of age.*

![Graph showing Ca(OH)₂ content as a function of age for different w/c ratios.](image)

*Figure 3: Relationship between the evolution of calcium hydroxide in portland cement pastes and mortars as a function of age.*

Micro-characteristics of the paste-aggregate interfacial zone

**a. SEM examinations**

Figures 8 to 11 show similar SEM micrographs of mortar specimens showing the microstructure of the paste-aggregate interfacial zone. There is a thin layer of paste (≈ 1-2 µm thick, marked D) in intimate contact with some of the aggregate.
particles. This layer is similar in structure to the "duplex film" reported by Diamond [1]. Relatively more crystalline hydrates such as calcium hydroxide and ettringite with less cement paste occur at the paste-aggregate (quartz) interface. It could be seen from Figures 4 to 7 that in the bulk paste, crystallization of CH is confined mainly to the voids within the paste.

![SEM micrograph](image)

*Figure 4: SEM micrograph of a freshly-fractured surface of a 1-day old portland cement paste showing a CH crystal within the paste (w/c = 0.40). PS = pore space; 2 = CH; 3 = C-S-H phase.*

In the mortars, however, in addition to crystallization of CH in the pores within the bulk paste, there is also crystallization of CH at the paste-quartz interface as revealed in the micrographs of Figures 10 and 11. The sand surfaces of the sand particles seem to be favourable sites for crystallization of CH. This effects will be discussed in detail under the section 'discussion'.

Figures 10 to 13 show the pattern of cracking and fracture in the mortars. Three types of cracks can be distinguished. These are:

(i) cracks which occur preferentially at and along the interface between the sand particles and the cement paste;

(ii) cracks which occur through the cement paste; and

(iii) cracks which run preferentially through the large plates of calcium hydroxide (Figures 10 and 11).

Most of the cracks from the micrographs seem to result from the shrinkage associated with the drying of the specimens prior to observation in the SEM. Investigations, however, reveal that fine, ill-defined shrinkage cracks also do exist at the paste-sand interfaces in the wet state of the specimen prior to drying, and also before application of any load [7-9]. The crack and fracture patterns that were observed in the mortars were not observed in the plain cement paste. In the plain cement pastes only fine, tortuous microcracks were observed. Similar observations were made by Bentur and Mindess [10] and Mindess and Diamond [9,11]. Figures 10 and 11 show that the cleavage planes of the calcium hydroxide crystals form part of the weak planes.
Figure 5: SEM micrograph of a freshly-fractured surface of 7-day old portland cement paste showing CH crystals in a large pore within the paste (w/c = 0.40). PS = pore space; 2 = CH; 3 = C-S-H phase.

Figure 6: SEM micrograph of a freshly-fractured surface of a 28-day old portland cement paste showing euhedral-subhedral CH crystals in a large pore within the paste (w/c = 0.40). PS = pore space; 2 = CH; 3 = C-S-H phase.

b. Spot analyses

The CaO and SiO₂ data (expressed as Ca/Si) were obtained on polished specimens by area and spot analyses of the cement paste in the transition zone and the bulk paste. The spot analyses data were obtained at intervals of 2 to 10 μm away from the sand surfaces towards the bulk paste with a spot diameter of 0.5 μm. The take-off angle was 40⁰, the accelerating voltage was 15 kV, and the counting time was 50 seconds. In all 200 spot analyses each were made for the 7 and 28-day old specimens. The analyses were somehow selective in the sense that distinctive-
ly visible crystals of calcium hydroxide and ettringite were avoided as much as possible during the analytical processes. The results (average data at various distances from aggregate interface) which are presented in Figure 14 show that for both the 7 and 28-day old specimens, the Ca/Si values are high at the aggregate interface and decreases gradually into the bulk paste. This means that at the interfacial zone the paste is richer in CaO than in the bulk paste. The values tend to increase with increase in age presumably due to further hydration of the cement. For the interfacial region, the average Ca/Si values were 2.97 and 3.08 for the 7 and 28-day old specimens respectively. In the bulk paste, the values obtained for the same ages were 1.83 and 1.86. The higher Ca/Si values of the paste in the transition zone suggests that the structure and composition of the paste in this region is different from the bulk paste. The results suggest that the paste in the interfacial zone may be intermixed with very fine crystals of CH or ettringite [12,13]. Calcium hydroxide is also known to occur as a semi-crystalline to amorphous particles within the C-S-H phase [14].

![Figure 7: Enlargement of Figure 6 showing various sizes of Ca(OH)$_2$.](image)

![Figure 8: SEM micrograph of a freshly-fractured surface of a 1-day old portland cement mortar showing the character of the paste-sand interface (w/c = 0.40). 1 = sand; 2 = CH; 3 = C-S-H phase; 4 = ettringite; ps = pore space; D = “Duplex film”.](image)
Figure 9: SEM micrograph of a freshly-fractured surface of a 7-day old portland cement mortar showing the occurrence of CH at the paste-sand interface (w/c = 0.40). 1 = sand; 2 = CH; 3 = C-S-H phase; 4 = ettringite; D = “Duplex film”.

Figure 10: SEM micrograph of a freshly-fractured surface of a 100-day old portland cement mortar showing the character of the paste-sand interfacial zone (w/c = 0.40). 1 = sand; 2 = CH; 3 = C-S-H phase; c = crack; f = fracture.

c. X-ray diffraction studies

The XRD analysis on pastes and mortars was carried out to characterize the interfacial zone. It was also done in order to determine and compare the pattern of crystallization of CH at the paste-insert interface and to examine the effects of sand on lime distribution in mortars.

At the interfacial region between cement paste and inserts the degree of orientation of CH crystals can be evaluated by comparing the X-ray diffraction intensities of
the \{001\} and \{101\} planes of the CH crystals. For randomly oriented calcium hydroxide crystals, the orientation index, $I_{CH}$, is defined as:

$$I_{CH} = \frac{I(001)/I(101)}{0.74} = 1.00$$

On the basis of this ratio, values of $I_{CH}$ higher than 1.00 indicate preferential orientation of the CH crystals parallel to the surface of the insert.

Figure 11: SEM micrograph of a freshly-fractured surface of a 100-day old portland cement mortar showing the occurrence of CH at the paste-sand interface (w/c = 0.40). 1 = sand; 2 = CH; 3 = C-S-H phase; c = crack; f = fracture.

Figure 12: SEM micrograph of a freshly-fractured surface of a 1-day old portland cement mortar showing the occurrence of CH at the paste-sand interface (w/c = 0.40). 1 = sand; 2 = CH; 3 = C-S-H phase; ps = pore space; c = crack; f = fracture.
Figure 13: SEM micrograph of a freshly-fractured surface of a 100-day old portland cement mortar showing the occurrence of CH at the paste-sand interface (w/c = 0.40). 1 = sand; 2 = CH; 3 = C-S-H phase; c = crack; f = fracture.

Figure 14: Distribution of the Ca/Si ratio of the paste at the interfacial zone of 7 and 28-day old opc mortars (w/c = 0.40).

In other words, preferential orientation of the CH crystals implies that the crystals are oriented in such a way that their c-axes are perpendicular to the insert surface. This technique of X-ray diffraction analysis and successive abrasion of the paste surface to estimate the thickness of the transition zone was used to determine and compare the pattern of crystallization of CH crystals at the interfacial zone for all the specimens. In Figures 15 and 16, the degree of orientation of CH at the paste-plastic interfacial zone for pastes and mortars have been plotted as a function of the distance from the plastic interface.
From the figures three distinct trends can be seen. In the first case, the orientation index of CH at the aggregate interface is high and approaches a value of 1.00 in the bulk paste. This feature is eminent in the neat cement paste as well as the mortar for both the 7 and 100-day old specimens. In the second case, the degree of orientation of CH at the interfacial zone is higher for the cement pastes than for the mortars for the two ages for which analyses were done. For both ages also the extent or width of the interfacial zone is shorter for the mortars than for the pastes. Precipitation of CH on the fine sand particles (which are distributed nearly homogeneously) within the mortar specimens is likely to be responsible for the
lower values of the $I_{\text{ch}}$ in the interfacial zone of the mortar composite. The precipitation of the CH on the sand particles in the mortars as shown in Figures 10 and 11, tend to reduce the amount of Ca$^{2+}$ and OH ions that are transported to the plastic (larger aggregate) surface for precipitation. As a consequence, the values of $I_{\text{ch}}$ for the mortars become lower than those for the pastes. Finally, from Figures 15 and 16, the degree of orientation values of CH appear to be higher for the older specimens than for the younger specimens. This implies that with time, the crystals of calcium hydroxide become more oriented with their c-axes perpendicular to the interface.

Discussion

At the onset of hydration of plain portland cement systems, the evolution of Ca(OH)$_2$ in the solid phase of the system is controlled by two factors: the availability of water and the solubility of Ca$^{2+}$. The water is necessary for hydrolysis of the calcium silicates, C$_3$S and C$_2$S to release Ca$^{2+}$ ions into the pore solution and also for transportation of these ions from the hydrolysed C$_3$S and C$_2$S grain surfaces into the bulk pore solution for crystallization, once supersaturation is attained. By increasing the water-cement ratio from 0.30 to 0.50, more cement grains become hydrolyzed to release Ca$^{2+}$ ions into the pore solution. The rate of cement hydration becomes increased, hence faster rate of evolution of CH. In addition, the higher water content also facilitates easier transport of the Ca$^{2+}$ to favourable nucleation sites (pore spaces) for precipitation and crystal growth. The second factor which affects the discharge of Ca$^{2+}$ from the pore solution is due to the effects of soluble alkalis from the outer zone of the cement grains. Most of these soluble alkalis occur as sulphate (Na$_2$SO$_4$-K$_2$SO$_4$-CaSO$_4$ phases) deposits in a form of fine crystallites (several $\mu$m in maximum dimension) on the surface of the C$_3$S and C$_2$S grains [15,16]. Their solubility helps control the solubility of Ca$^{2+}$ by means of the common ion effect which is governed by the solubility product of Ca(OH)$_2$ given as:

$$K_{\text{Ca(OH)}_2} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

As more of the soluble alkalis dissolve, Ca$^{2+}$ will precipitate out of the pore solution in the form of CH and AFT, or combine with other species to form the C-S-H phase. With increasing water content more cement grains surfaces become attacked by water molecules which dissolve more alkalis. The rate of discharge of Ca$^{2+}$ from solution consequently becomes increased owing to the increased concentration of the alkalis in the liquid phase. This results in faster rate of precipitation of CH into the solid phase. Also, with increasing water-cement ratio, the rate of cement hydration will increase which will cause more calcium hydroxide to be produced. Furthermore, the capillary porosity of portland cement pastes is known to increase with increasing water content. Since crystallization of CH is more favourable in pores and free spaces within the cement paste system, the quantity will tend to increase as the water-cement ratio increases. Crystals formed have enough space to grow bigger without much interference from other solid phases in the system. This explains the reason why the CH contents were found to increase with increase in water-cement ratio from 0.30 to 0.50.

In this study, the evolution of CH in the mortars has been observed to be enhanced by the availability of sand on which the CH crystals could nucleate and grow. Also,
in the mortars, the evolution of CH has been found to increase with increasing water-cement ratio. However, compared to the pastes for the same water content, the values for the mortars were found to be higher than those of the pastes. The absence of stable materials (fillers, such as the sand) in the cement pastes on which nucleation of CH could favourably occur is likely to account for the lower values of CH in the pastes compared to those of the mortars. In the cement pastes, precipitation of CH on unhydrated cement grains may occur during the early ages of hydration. But however, owing to chemical instability of the cement grains through dissolution by the pore water, further crystallization and growth of the CH may be disrupted. In the bulk pastes also, growth of the CH crystals is limited only to the capillary pores where free space exists. The transition zone in plain portland cement is, however, known to be more porous than the bulk paste [17]. Moreover, favourable thermodynamic nucleation conditions could exist at the sand interfaces. Within this zone, therefore, CH can crystallize better than the bulk paste. This feature, coupled with the stability of sand aggregates, in part, explain the reason why the evolution of lime is higher in mortars than cement pastes for the same water-cement ratios. The sand particles in the mortars possibly act as a 'sink' for the crystals of Ca(OH)\(_2\) precipitating out of the pore solution. The mechanism of formation of Ca(OH)\(_2\) can be viewed as a conventional physico-chemical process of:

\[
\text{Dissolution} \quad \rightarrow \quad \text{Transportation (of Ca}^{+2} \text{ and OH}^{-}) \quad \rightarrow \quad \text{Nucleation} \quad \rightarrow \quad \text{Crystal growth}
\]

The lower values of \(I_{CH}\) of the mortar specimens compared to those of the pastes is likely to be due to grain refinement of the CH crystals, caused by the sand particles in the mortars. Crystallization of CH on the sand particles in the mortar tends to reduce the amount of Ca\(^{2+}\) ions that are transported to the coarser aggregate (polypropylene plastic) surface for precipitation. In other words, instead of crystallization of large hexagonal plates of lime at the paste-sand interface, very small crystals of CH are produced at the sand-paste interfaces in the mortar and also at the mortar-plastic plate interface. This ultimately tends to reduce the quantity and degree of orientation of the CH crystals at the mortar-plastic interface than the paste-plastic interface as observed in this study.

**Conclusions**

An investigation into the effects of water-cement ratio, quantity, and fineness of sand on the evolution of lime in set portland cement systems has been carried out. On the basis of the results obtained from the study, the following conclusions can be drawn:

1. In hardened cement pastes and mortars, Ca(OH)\(_2\) is present in two or three locations as follows: (i) intermixed with the C-S-H phase or (ii) partially infilling of voids, or (iii) at the paste-aggregate interfacial zone.
2. In both cement pastes and mortars, the evolution of Ca(OH)\(_2\) was found to increase by increasing the water-cement ratio from 0.30 to 0.50.
3. For the same water-cement ratios, however, the calcium hydroxide content of the mortars at a particular age were found to be significantly higher than those for the pastes, which can be explained by the nucleation of calcium hydroxide on the sand surfaces.
4. At the interfacial zone, calcium hydroxide crystals are preferentially oriented with their c-axes perpendicular to the paste-aggregate interface. The degree of orientation becomes stronger with increase in age.

5. It is indicated that at increasing aggregate surface available in concrete, the size and degree of orientation of lime crystals at the aggregate interfaces decreases.

6. In the transition zone, the Ca/Si values were found to be significantly higher than in the bulk paste.

References

2. V.V. Savenkov and V.L. Cherniavskii, Proc. 6th Int. Congress on Chemistry of Cement (Moscow), Sec. II-9, 1974.
Chapter 4

Orientation of portlandite at the portland cement paste-aggregate interfacial zone in the presence of silica fume

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(Refereed)

Abstract

A combination of an SEM-EDAX facility and an X-ray diffractometer has been used to study the crystallization pattern of calcium hydroxide (CH) at the interface between portland cement paste and aggregates. The SEM investigation was carried out on fractured surfaces of portland cement mortars with and without silica fume using secondary electron imaging in the SEM. Evidence from the SEM observations and the results of the XRD studies showed that addition of silica fume as partial cement replacement densified the transition zone. In addition, the quantity and the degree of orientation of calcium hydroxide at the interface were substantially reduced, and the thickness of the interfacial zone was decreased from about 45 μm at 7 days to less than 10 μm at 100 days of curing. These improvements in the structure of the interfacial zone are of paramount importance to the strength of concrete.

Introduction

It is known that silica fume addition to portland cement densifies the paste because of its filler effect and its high reactivity with calcium hydroxide which is released by the hydration of the cement to produce extra C-S-H gel [1]. These effects lead to pore refinement of the cement paste which improves the strength and the durability of silica fume blended cement systems [2-4].

In recent years it has been found that the use of fine pozzolans densifies the interfacial zone between aggregates and cement paste [5-7]. The interface is thought to be a weak link in concrete with respect to permeability and also to limit concrete (tensile) strength. The present article summarizes the results of an investigation into the effects of partial cement replacement by silica fume on the structure of the interfacial zone.

Materials and experimentation

Materials

The materials used were: ordinary portland cement (opc), equivalent to the ASTM Type I portland cement and meeting the Dutch Cement Standard NEN 3550; silica fume (sf); two rock aggregates, a granite and a limestone; and an aqueous solution of sulphonated naphthalene formaldehyde superplasticizer (Conplast®). The silica
fume (sf) existed in a powdered form and was added to the mix in the dry form. The Bogue composition of the portland cement is given in Table 1 and the chemical composition and other physical properties of the silica fume are given in Table 2.

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<table>
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<th>Chemical composition and properties</th>
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Experimental procedure

a. Portlandite orientation at the interfacial zone

One of the techniques commonly used to evaluate the degree of preferred orientation of CH crystals at the interfacial zone and to characterize the extent of the transition region is the method developed by Grandet and Ollivier [8]. This is a two-step technique that involves casting of cement paste onto a piece of rock to form a composite specimen followed by X-ray diffraction analysis of the debonded paste surface to obtain some information about the interfacial zone. The most important parameter used is the orientation index of CH crystals within this transition region. This index is obtained by measuring the X-ray diffraction intensities of the (001) and the (101) planes of CH crystals after successive abrasion of the transition zone to estimate its thickness. The method is based on the fact that in the bulk paste matrix the CH crystals are randomly oriented. The ratio \( R \), between the \( I(001) \) and \( I(101) \) peak intensity of randomly oriented CH crystals is 0.74, and the orientation index, \( I_{CH} \), defined as:

\[
I_{CH} = \frac{I(001)}{I(101)} / 0.74
\]

Values of \( I_{CH} \) higher than 1.0 imply preferential orientation of the CH crystals with their c-axes perpendicular to the aggregate interface. In other words, within the interfacial zone the parallel plates (or stacked plates) of CH are oriented parallel to the aggregate surface.
In order to obtain the same surface texture of the rock prisms, and to enable accurate estimation of the thickness of the interfacial zone, all the rock prisms were polished to the same surface smoothness. The pastes were then cast onto the polished surface of the rock prisms to form paste-rock composites. The X-ray analysis was done in combination with successive abrasion of the paste surface to estimate the thickness of the transition zone.

Recently workers [9,10] have questioned the applicability of this method to simulate the situation in real concrete, suggesting that formulation of the composite specimens whereby a relatively thick mass of cement paste is cast onto a flat and polished piece of aggregate does not adequately simulate the mixing processes that occur in real mortars and concrete. In the paste-rock composites, lack of shearing and tumbling of the aggregates during formulation, which in the case of real concretes and mortars is known to improve the packing of the solids, serves as a limiting factor. In particular, in the presence of mineral additives such as silica fume the mixing processes in real concrete are believed to play a major role in the dispersion of the silica fume particles [10].

The authors share similar views with these workers about the limitations of the Grandet and Ollivier technique. They are, however, of the opinion that the mixing will only affect the size of the weak interfacial zone but for purposes of comparison, the technique provides a good indication of the effects of additions on interfacial microstructure.

In the present study the Grandet and Ollivier technique was used to examine the character of the transition zone between cement pastes and aggregate in the presence of silica fume. The orientation index and density determination of pastes (by helium pycnometry) were used to determine the extent of the interfacial zone for various paste-aggregate combinations.

b. Ca(OH)₂ content of pastes and mortars

The amount of Ca(OH)₂ liberated in pastes and mortars with water-binder ratio of 0.40 was determined by the method of Franke [11]. A detailed description is given in reference [12].

c. Rate of evolution of heat

The rate of hydration for periods up to three days was measured on pastes by the Research Division of ENCI in Maastricht. The pastes contained 0 and 20% (by mass) of silica fume. The water-binder ratio was 0.45.

d. SEM-EDAX studies

The SEM studies were carried out on fractured portions of the mortars. Prior to the SEM studies the specimens were freeze-dried to prevent further hydration. Then the newly-fractured surfaces were coated with a thin film of nickel or gold, mounted onto stubs and examined in the SEM. Two SEMs were used: a JEOL, JSM-840 SEM and an ISI-40. Both SEMs were equipped with energy dispersive analytical X-ray facilities (EDAX).


e. Microhardness measurements

The microhardness measurements were made using a microhardness tester, Leitz Miniload 2. The composite specimens were cast into a cylindrical polypropylene plastic tube with the rectangular rock prism in the middle. Prior to testing, the specimens were sawn into two halves. The middle sections were then well-polished (till No. 1000 grit) with silicon carbide and alcohol before measuring the hardness. Using the pyramidal indenter in the setup, indentations were made on 28-day old pastes with and without sf. From the impressions made, the Vickers microhardness values, $H_v$ of the pastes in the vicinity of the aggregate were calculated.

f. Curing of specimens

After formulation, all the mixes were stored in a fog room at approximately 20°C until required for testing. The specimens meant for the XRD studies were stored in sealed plastic jars under nitrogen to prevent carbonation.

Results and discussion

Effects of partial cement replacement by silica fume on $I_{CH}$

Figures 1 and 2 show the effects of silica fume addition on the maximum orientation index, $I_{CH,max}$, of CH crystals at the paste-aggregate interfacial region. The $I_{CH(max)}$ value represents the orientation index prior to grinding, that is, the very first $I_{CH}$ value immediately after separation of the paste from the aggregate. For all the specimens studied this first $I_{CH}$ value was the highest, hence the designation, $I_{CH(max)}$. For the sake of brevity, only the data for granite are presented in this text.

![Orientation index - ICHmax](image)

*Figure 1: Effects of partial replacement of portland cement by silica fume on $I_{CH}$ at the paste-aggregate interfacial zone (1 and 7 days of curing).*
For the 1 day old specimens, the $I_{\text{CH}(\text{max})}$ values increased with increasing silica fume dosage as illustrated in Figure 1. This effect is possibly due to the increase in water-cement ratio associated with increase in silica fume content at the onset of hydration. It may also be due to acceleration of cement hydration and the availability of more nucleation sites for crystallization of the cement hydration products. No superplasticizer was used for the mix with 5% sf dosage. Yet it has a relatively higher $I_{\text{CH}(\text{max})}$ value than the reference mix, possibly because the higher water-cement ratio of the sf mix caused increased cement hydration, thus faster CH evolution at the onset of hydration [13-15].

![Figure 2: Effects of partial replacement of portland cement by silica fume $I_{\text{CH}}$ at the paste-aggregate interfacial zone (28 and 100 days of curing).](image)

Although the water-to-binder ratio of the sf pastes is 0.30, the effective water-cement ratio is higher owing to the partial replacement of portland cement by the silica fume. A 5% (by mass) replacement of cement by silica fume gives, for example, a water-cement ratio of 0.32, 10% (by mass) gives 0.33 and 20% (by mass) yields 0.38. Increase in water-cement ratio and the presence of amorphous silica in portland cement pastes are known to increase the rate of cement hydration [13,14]. After 1 and 7 days of hydration, the $I_{\text{CH}(\text{max})}$ values of the blended mixes decreased while those of the reference mixes increased (Figure 2). By 100 days, the $I_{\text{CH}(\text{max})}$ values had decreased substantially; the extent of decrease being proportional to the sf dosage in the mix. The reduction in the $I_{\text{CH}(\text{max})}$ values of the sf blends is most likely to be due to the pozzolanic reaction between the CH and the sf; the reaction being more pronounced for higher sf dosages. This is not surprising since the likelihood of more sf particles occurring at the interfacial zone is greater with higher dosages of sf than with lower sf dosages. Also as hydration progressed, the diffusion of $\text{Ca}^{2+}$ ions from the bulk paste towards the aggregate surface in the silica fume mixes to form CH will be inhibited because of the formation of a denser paste system [3,5]. Thus the preferential orientation of the CH crystals will be decreased.
Effects of silica fume on the thickness of the interfacial zone

Figures 3 to 5 show the effects of addition of silica fume as partial cement replacement on the extent of the interfacial zone. With increasing age, the addition of silica fume reduced the thickness of the interfacial zone.

The relatively higher CH content at the interfacial zone for the 20% sf mix favours the pozzolanic reaction which results in the production of extra C-S-H gel to fill the available pores thereby densifying and homogenizing the paste in the near vicinity of the aggregate. This progressive pozzolanic reaction is obviously the reason for the ‘thinning’ of the interfacial zone in the blended mix in comparison with the reference mix. These results are consistent with the findings of Monteiro et al. [16,17] and the previous work of the authors [7,18].

![Graph showing orientation index - ICH for OPC and 80% OPC + 20% SF at 7 days and 28 days](image)

**Figure 3:** Effects of partial replacement of portland cement by silica fume on the thickness of the interfacial zone (age = 7 days).

![Graph showing orientation index - ICH for OPC and 80% OPC + 20% SF at 28 days](image)

**Figure 4:** Effects of partial portland cement replacement by silica fume on the thickness of the interfacial zone (age = 28 days).
Ca(OH)$_2$ content

The Ca(OH)$_2$ content of the cement pastes and mortars are shown in Figure 6. The reaction of silica fume with Ca(OH)$_2$ started early, and by 90 days of hydration most of the Ca(OH)$_2$ produced had reacted. It is interesting to note that the Ca(OH)$_2$ content of the mortars are higher than their corresponding pastes. Precipitation of Ca(OH)$_2$ at the surface of the sand particles is known to accelerate the evolution of Ca(OH)$_2$ in the mixes [4,12].

Rate of evolution of heat

The effect of silica fume addition on the rate of heat evolution of portland cement at a water-to-binder ratio of 0.45 is shown in Figure 7. The figure shows two peaks for the mixes. The first peak occurred at the same time for both mixes, that is, immediately after mixing. Unlike the reference mix, however, the second peak for the silica fume mix was accelerated. It occurred at about 8 hours after mixing, while that of the plain mix occurred at about 12 hours after mixing. The presence of the silica fume, however, did not prolong or reduce the duration of the dormant period. The acceleration of the second peak of hydration for the silica fume mix is an indication of increased rate of cement hydration of the silica fume mix.

This increased rate of hydration of the silica fume paste is believed to be at least, in part, attributable to the ability of silica fume to provide nucleating sites for the cement hydration products (such as Ca(OH)$_2$, C-S-H and ettringite, Aft). This is possible during the first few hours of hydration when silica fume still exists as chemically inert material [4,18,19]. With silica fume particles in the fresh paste, the C-S-H gel, ettringite, and Ca(OH)$_2$ have more nuclei on which crystallization can take place. Crystallization of the hydration products on the silica fume particles leaves more surfaces of the cement to be attacked by the free water in the fresh mix. This accelerates the cement hydration process which causes greater evolution of heat.
In a similar study, Kurdowski and Nocun-Wczelik [14] showed that the presence of reactive silica powder accelerated the reaction of C₃S with water. They found out that by increasing the reactive silica content, the development of heat became greater. They concluded that the C₃S hydration was controlled by the conditions governing the liquid phase and that the reaction rate was dependent on the ease of transportation of Ca²⁺ ions from the surface of the C₃S grains to the solution. In other words, C₃S hydration was controlled by the consumption of Ca²⁺ ions from the solution as a result of the Ca(OH)₂ and C-S-H precipitation.
From the foregoing discussion, it is most likely that the presence of silica fume will lower the Ca$^{2+}$ ion concentration in the solution firstly by precipitation as small crystals of Ca(OH)$_2$ on the surfaces of the sf particles, and then by reacting to form C-S-H. This process is likely to be the result of the increased rate of cement hydration of the silica fume blend as shown in Figure 7. Grutzek et al. [18] showed that Ca$^{2+}$ ions in solution were necessary for the dissolution of silica fume particles, which acted as sites for nucleation of calcium hydroxide crystals. Increased rate of cement hydration in the presence of silica fume has also been reported by Cheng-Yi and Feldman [4].

**Microstructure of the paste-aggregate interfacial zone**

Figures 8 to 11 are SEM micrographs of the paste-aggregate interface without silica fume (8 and 9) and with silica fume (10 and 11) respectively. At early ages (up to about 7 days) some crystals of CH were observable at the aggregate interface in all the mortar mixes. As hydration proceeds the CH at the aggregate interface in the sf blends disappeared, obviously due to the pozzolanic reaction between the microsilica and the CH.

In Figure 10, the portlandite crystals at the aggregate interface is partially dissolved in the presence of the silica fume with an apparent formation of C-S-H. By 28 days of aging, most of the CH crystals had nearly completely dissolved, leading to the formation of a dense paste system which is well-bonded to the aggregate particles as shown in Figure 11. The improved bonding of paste to aggregate in the sf mortars clearly explains the improved paste-aggregate adhesion strength of the sf blends as shown in the previous section. In contrast to that, the reference mortar exhibited a heterogeneous and porous interfacial zone. The paste was poorly bonded to the aggregate particle and calcium hydroxide crystals were also visible in considerable amounts at the interface. In Figure 11, there is virtually no CH at the paste-aggregate interface. Figure 12 shows the microstructural development of the interfacial zone for the plain mortar (a) and the silica fume blend (b).

![Figure 8: SEM micrograph of a fractured surface of the plain (reference) mortar showing the microstructure of the interfacial zone (7 days old). 1 = aggregate; 2 = CH; 3 = Paste.](image_url)
Figure 9: SEM micrograph of a fractured surface of the plain (reference) mortar showing the microstructure of the interfacial zone (28 days old). 1 = aggregate; 2 = CH; 3 = Paste.

Microhardness

The results with limestone rock composite are presented in Figure 12. The data show that the hardness of the interfacial zone was substantially increased by addition of silica fume if compared with ordinary portland cement paste of the same water-to-binder ratio. The ‘trough’ or ‘valley’ formed at the aggregate interface in the reference paste is substantially flattened by addition of 20% (by mass) of silica fume.

Figure 10: SEM micrograph of a fractured surface of the portland cement mortar containing silica fume showing the structure of the interfacial zone (7 d). 1 = aggregate; 2 = CH; 3 = paste.
Figure 11: SEM micrograph of a fractured surface of the portland cement mortar containing silica fume showing the structure of the interfacial zone (28 d). 1 = aggregate; 2 = CH; 3 = paste.

The addition of the silica fume as partial portland cement replacement tended to homogenize the microhardness distribution and, for that matter, the homogeneity of the paste. The improvement in the microstructure at the interfacial zone of the microsilica blends is attributed to the improved grain packing and reduced microbleeding at the aggregate particle interface soon after formulation of the mix. These physical effects laid the 'platform' for further pore structural improvements through the cementation of the solids together with the extra C-S-H gel produced from the pozzolanic reaction between the microsilica and the CH at the paste-aggregate interface.

Figure 12: Microstructural development of the paste-aggregate interfacial zone after about 1 day in plain portland cement mortar (a), and portland cement mortar containing silica fume (b). 1 = aggregate; 2 = CH; 3 = cement paste; 4 = partially hydrated cement grains; sf = silica fume particles; Aft = ettringite; D = duplex film.
Figure 13: Effects of partial portland cement replacement by silica fume on the microhardness of the transition zone between paste and limestone rock used (28 days old).

Conclusions

Replacement of part of cement by silica fume accelerated cement hydration. This acceleration was caused: (i) by the increased in water-cement ratio associated with the reduction in cement content by partial substitution of the cement by silica fume and (ii) by the nucleation effects of the additional surface provided by the silica fume particles. During the initial stages of hardening, silica fume acted as an effective filler with its submicroscopic particles acting as nuclei for crystallization of the portland cement hydrates. Later, silica fume was transformed through the pozzolanic reaction into calcium silicate hydrates which increased the density of the matrix.

The microstructure of the paste-aggregate interfacial zone was strongly affected by silica fume. The quantity of calcium hydroxide was reduced; the orientation of the calcium hydroxide crystals was decreased; the thickness of the transition zone was decreased; and the density of the interface was increased.

These improvements in the microstructure of the interfacial zone are believed to be responsible for the higher strengths of the silica fume mixes compared to the reference mixes.

References


Chapter 5

Evolution of calcium hydroxide and microstructural development of the paste-aggregate interfacial zone in fly ash-portland cement paste systems

Joseph A. Larbi* and Jan M. Bijen**

(Refereed)

Abstract

The evolution and distribution of calcium hydroxide, CH and the development of microstructure during the hydration of three low-calcium fly ash-portland cement blends with water-solids ratio of 0.40 have been investigated. During the first month of hydration, the CH content of the blends was found to be relatively higher than the plain mix, if a dilution effect due to replacement of cement by an inert material is taken into account. After 28 days of hydration the CH content in the blends began to decrease. SEM observations of specimens revealed the occurrence of large, well-crystallized CH plates in intimate contact with some of the fly ash particles at younger ages and even after six months of aging. The study also showed that the characteristics of the fly ashes, such as the glass content and the fineness of the ash particles seem to exert major influences on the rate of evolution of CH in the fly ash blends. Semi-quantitative X-ray diffraction analyses performed on specimens cast against polypropylene plastic plates used as "modelled coarse aggregates" showed reduction in the thickness of the interfacial zone for the fly ash-portland cement pastes from about 60 μm to less than 15 μm within one month of hydration. In the case of the plain portland cement pastes no significant changes were observed. The degree of orientation of CH crystals within the interfacial region also was significantly affected by the fly ashes, although by this age of hydration the CH data showed little or no evidence of pozzolanic reaction.

Introduction

Calcium hydroxide, CH, is one of the hydrated phases of portland cement paste. It is produced during hydrolysis of the calcium silicates C₃S and C₂S in portland cement when the cement is mixed with water. In fly ash-portland cement blends, as hydration proceeds, part of the calcium hydroxide is believed to react with the fly ash to produce additional C-S-H products. This is often referred to as the pozzolanic reaction or lime-binding of fly ashes. A measure of the rate of lime-binding by fly ashes is often used as an evaluation of the reactivity of fly ashes in mortars and concrete [1-5]. Fly ashes, however, have complex characteristics, differing in fineness, morphology, mineralogical composition, and glass content.

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These characteristics of fly ashes tend to affect the hydration processes, the hardening and the microstructure development of the blended cement paste.

Although the lime-binding test is very often used as a predictive test for the pozzolanicity of fly ashes in concrete and mortars, very little attention has been given to the effects of fineness, particle morphology, mineralogical composition and glass content of fly ashes on the evolution and distribution of lime in fly ash-portland cement blends. The aim of this study was to examine the effects of three low-calcium fly ashes with different particle fineness, mineralogical composition, and glass contents on the evolution and distribution of lime in portland cement pastes and mortars. In addition, the influence of these fly ashes on the extent of the interfacial zone as well as the orientation of calcium hydroxide crystals within this zone were studied.

**Experimental procedures**

**Materials**

The materials used for preparing the blends in this study included an ordinary portland cement (OPC) equivalent to ASTM Type I portland cement, three low-calcium fly ashes FA, EFA, and LM equivalent to ASTM Type F fly ashes, and alpha-quartz flour (q.f.). The fly ashes FA and LM are from a dry-bottom boiler, while EFA is from a wet-bottom boiler (reference 6). The chemical composition and other properties of the OPC and the fly ashes are given in Tables 1 and 2.

<table>
<thead>
<tr>
<th>Composition</th>
<th>% (by mass)</th>
<th>Bogue composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.9</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>62.0</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>S₂O₃ (as gypsum)</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>Alkalies eq. Na₂O</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Free water</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Insoluble residue</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3.1</td>
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</tr>
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</table>

The glass content of the ashes which were determined by a quantitative X-ray diffraction technique [6] are given in Table 3. EFA has the greatest glass content. There is, however, not much difference in their SiO₂ contents. The particle size distribution of the ashes were determined with the Malvern 2600 Particle Size Analyzer. The results are presented in Figure 1. The figure shows that EFA is relatively the finest of the three ashes, followed by FA and LM respectively. All the blends were prepared with 20% (by mass) substitution of cement with the ashes. The water-cement ratio of the plain mixes was 0.40 and the water-solids ratio (water/cement + fly ash or quartz flour) of the blends was 0.40.
Sample preparation and test procedures

In all, three separate tests were performed in this study. The tests included, free lime content determinations by method of chemical extraction using the Franke method [7] and semi-quantitative X-ray diffraction studies on composite specimens. The above two tests were supported by scanning electron microscope studies on portions of the specimens.

Table 2: Composition and properties of fly ashes used [Ref. 6]

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>FA</th>
<th>EFA</th>
<th>LM</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>54.6</td>
<td>50.0</td>
<td>51.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>27.0</td>
<td>25.6</td>
<td>33.0</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>7.6</td>
<td>6.5</td>
<td>4.8</td>
</tr>
<tr>
<td>CaO</td>
<td>2.9</td>
<td>4.3</td>
<td>2.0</td>
</tr>
<tr>
<td>MgO</td>
<td>2.3</td>
<td>2.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.6</td>
<td>2.2</td>
<td>0.4</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.4</td>
<td>3.8</td>
<td>1.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.4</td>
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</tr>
<tr>
<td>Water content</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>2.1</td>
<td>3.9</td>
<td>4.9</td>
</tr>
<tr>
<td>Specific gravity</td>
<td></td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td>% &gt; 45 μm</td>
<td>22.5</td>
<td>7.0</td>
<td>23.5</td>
</tr>
</tbody>
</table>

Table 3: Mineralogical composition of the fly ashes used

<table>
<thead>
<tr>
<th>Minerals (%)</th>
<th>FA</th>
<th>EFA</th>
<th>LM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>4.5</td>
<td>1.8</td>
<td>5.1</td>
</tr>
<tr>
<td>Mullite</td>
<td>11.4</td>
<td>2.1</td>
<td>22.8</td>
</tr>
<tr>
<td>Magnetite</td>
<td>0.6</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Total crystalline</td>
<td>16.5</td>
<td>4.6</td>
<td>28.4</td>
</tr>
<tr>
<td>Glass</td>
<td>83.5</td>
<td>95.3</td>
<td>71.6</td>
</tr>
</tbody>
</table>

Figure 1. Cumulative particle size distribution plot for the three fly ashes.
Calcium hydroxide, CH content determinations

The amount of calcium hydroxide in the blends at a particular age was determined by a chemical analytical method developed by Franke [7]. The details of this test method is given in reference [8] or Chapter 3.

Semi-quantitative XRD analysis

This investigation was carried out to find out the effects of the fly ashes on the texture (occurrence and orientation) of Ca(OH)$_2$ at the paste-aggregate interface. A semi-quantitative X-ray diffraction technique based on the method developed by Grandet and Ollivier [9] was used. Eight composite specimens consisting of four blended cement pastes (EFA and LM) and four plain pastes were prepared for the study. The details of the procedure and necessary precautions taken have already been described in reference [8] or Chapter 3.

Scanning electron microscopic studies

For the scanning electron microscope (SEM) studies, portions of specimens were cut and freeze-dried to prevent further hydration. Then after, freshly-fractured surfaces were coated with a thin film of nickel or gold, mounted onto stubs, and examined using two SEMs: a JEOL, JSM-840A SEM and an ISI-40 SEM. Both SEMs were equipped with energy dispersive X-ray analyzer (EDAX).

Results and discussion

Evolution of CH in the plain mixes

In the assessment of the extent of pozzolanic reaction between fly ashes and CH in portland cement blends, it is a common practice of many workers to use the ‘hypothetical’ curve of CH (the curve obtained by multiplying the CH of the plain mixes by a diluting factor) as a basis for comparing the CH-binding of the ashes [1,2]. As an evaluation of the reliability of this method of assessment, 20% (m/m) of the cement was replaced by α-quartz flour in one of the mixes and the calcium hydroxide content determined as a function of age. The results are presented in Figure 2.

The middle curve represents the CH data for the actual case where part of the cement was replaced by an inert filler. The dotted curve is the hypothetical case. It represents the calcium hydroxide content expected in the plain mix if 20% (m/m) of the cement were replaced by a corresponding amount of an inert filler. The data for this curve were obtained by multiplying the CH content of the plain mix (OPC) by a factor of 0.80.

The results show that the CH data in the actual case of replacement of cement by an inert filler far exceed those of the ‘hypothetical case’. As it is, this method of assessment of the reactivity of fly ashes in portland cement blends is relatively biased and may tend to underestimate the reactivity of some fly ashes. Part of the difference in CH development between the ‘experimental results’ and the ‘hypothetical data’ is likely to be due to the higher water-cement ratio in the former case. In the ‘actual case’, the higher water content will cause hydration to proceed faster and to a greater extent than in the ‘hypothetical case’ [10]. The CH data obtained
from the ‘actual case’ mixes is likely to be higher than the ‘hypothetical case’. A comparison of the CH data on the basis of the ‘actual case’ data seems to simulate better the situation in practice than the ‘hypothetical data’.

**Figure 2.** Evolution of CH in plain mixes as a function of age (w/c = 0.40).

**Effects of the fly ashes on evolution of CH**

The effects of the three fly ashes on the evolution of calcium hydroxide in portland cement mortars as a function of age are shown graphically in Figure 3. It appears from the figure that during the early ages of hydration (up to 28 days), mixes with coarser ashes seem to contain higher calcium hydroxide than the corresponding plain portland cement mix.

**Figure 3.** Effects of the fly ashes on evolution of CH in the blends (w/s = 0.40).
The highest values occur in the LM blends, the fly ash with the coarsest particle size distribution and lowest glass content. Although the pozzolanic reaction might have already started during the first week of hydration, the CH data of the blends do not show this effect as the values continue to increase up to about 28 days of hydration.

SEM studies on fractured surfaces of the mortars show CH in contact with some of the α-quartz grains in the plain mixes as well as on the fly ash particles as shown in Figures 4, 5 and 6. Further SEM observations revealed that some of such CH crystals still remained in intimate contact with the fly ash particles even after 180 days (six months) of aging as shown in Figures 7 and 8. These results are in agreement with observations made by Diamond et. al. [1].

![Figure 4. SEM photo showing CH on α-quartz particle (7 days old). 1 = aggregate; 2 = CH; 3 = paste.](image)

![Figure 5. SEM photo showing CH on FA ash particles (7 days old). 2 = CH; 3 = paste; P = fly ash particles.](image)
Figure 3 further shows that after 28 days of hydration, the CH contents of the fly ash blends tend to deviate from the plain mix. The CH values start to decrease and by 90 days of hydration, the values are significantly lower than the CH data for the corresponding mix with 20% (m/m) of inert sand flour. This effect is obviously due to the pozzolanic reaction between the fly ashes and the CH produced by the cement. If the ‘hypothetical’ curve were used as a basis for comparison, the pozzolanic reaction would have been underestimated. The layer of hydrates (presumably C-S-H) marked ‘D’ immediately outside the fly ash particle surface in Figure 6 (7 days old) is likely to be a product of the pozzolanic reaction (11). This suggests in this case, that the pozzolanic reaction had already started even before the CH contents of the blends started to decrease at about 28 days of aging. After about 6 months this layer becomes denser and relatively thicker as revealed in Figure 7.

![Figure 6. SEM photo showing CH on EFA ash particle (7 days old). 2 = CH; 3 = paste; P = fly ash particles; D = ‘duplex film’.

![Figure 7. SEM photo showing CH on FA ash particles (180 days old). 2 = CH; 3 = paste; P = fly ash particles.](image-url)
A comparison of the three fly ash blends shows that in both the pastes and mortars, the evolution of CH after 7 days appears to be in the order of LM > FA > EFA. By 90 days of hydration, the decrease in the CH content of the blends relative to the 28 days' seem to be in the order EFA > FA > LM which is the same order of their particle fineness and glass contents. It appears from the results that the evolution and consumption of CH in the fly ash-portland cement blends is influenced by the particle fineness and glass content of the ashes. The glass composition could also be significant in the evolution and consumption of CH in the blends, however, the relative importance of these two factors cannot be assessed on the basis of the present data. On the basis of the CH-consumption by the ashes as a measure of the pozzolanic reactivity in the portland cement systems, it appears the most reactive ash is EFA, followed by FA and LM respectively.

Figure 8. SEM photo showing CH on LM ash particles (180 days old). 2 = CH; 3 paste; P = fly ash particles.

XRD studies

At the interfacial zone between coarse aggregates and cement paste in plain portland cement concrete the paste is known to be more porous with better-crystallized hydration products than the bulk paste. Calcium hydroxide is found in large quantities as thin, hexagonal plates with higher degree of orientation in this zone than in the cement matrix (9,10,14). Moreover, this zone is considered as the 'weakest link' in concrete. The above-mentioned characteristics in plain concrete are, however, localised in areas of excess water, usually trapped under coarse aggregates or reinforcements owing to bleeding in the freshly placed concrete. The XRD analysis on the fly ash blends was carried out to examine and compare the effects of the fly ashes on the pattern of crystallization of CH at the paste-aggregate interface and the extent of the interfacial zone in the presence of fly ashes.

At the transition zone the degree of orientation of the CH crystals can be determined by comparing the X-ray diffraction intensity of the (001) plane to that of the
(101) plane of the CH crystals. For randomly oriented calcium hydroxide crystals, the orientation index, \( I_{CH} \), defined as:

\[
I_{CH} = \frac{I(001)/I(101)}{0.74} = 1.0
\]

This means that values of \( I_{CH} \) higher than 1.0 indicate preferential orientation of the CH crystals parallel to the surface of the aggregate. In other words, preferential orientation of the CH crystals implies that the crystals are oriented in such a way that their c-axes are perpendicular to the aggregate surface. This technique of X-ray diffraction analysis and successive abrasion of the paste surface (with a No. 600 emery paper) to estimate the thickness of the transition zone was used to determine and compare the pattern of crystallization of CH crystals at the interfacial zone for all the specimens. In addition, the effects of the fly ashes on the thickness of the transition zone were also examined.

Figures 9 and 10 show the effects of the fly ashes on the orientation index, \( I_{CH} \) of CH within the interfacial region. The plots show that at the aggregate interface calcium hydroxide crystals are preferentially oriented with their c-axes perpendicular to the aggregate surface, regardless of the presence of the fly ashes. This occurs for both the 7 and 28-day old composite specimens.

![Figure 9. Degree of orientation of CH at the paste-"coarse aggregate" interfacial zone (7 days old).](image)

In Figures 9 and 10, the \( I_{CH} \) values of the fly ashes in the immediate vicinity of the aggregate interface (10-50 \( \mu \)m) are relatively lower than those of the plain mixes. For the purposes of comparison, the \( I_{CH} \) data of a plain mix with 20% (m/m) of powdered \( \alpha \)-quartz have also been plotted on the graphs. The results show that at the immediate vicinity of the aggregate, the fly ashes tend to reduce the orientation of CH. This result is consistent with the results of Saito and Kawamura [14] where fly ashes were found to reduce the \( I_{CH} \) at the aggregate interface. It can be seen from Figure 9 that the quartz flour also tends to reduce the degree of
orientation of the CH crystals, although the reduction is relatively lower compared to that of the blended mixes. Another important effect of the fly ashes is that the thickness of the interfacial region is reduced from about 60 μm to about 15 μm.

![Orientation index - ICH](image)

*Figure 10. Degree of orientation of CH at the paste-"coarse aggregate" interfacial zone (28 days old).*

This effect is not observed for the quartz flour. These features suggest the following possible phenomena:

(a) that the fly ash particles tend to affect the orientation of CH in the paste-aggregate interface during hydration; their nearly homogeneous distribution in the pastes during mixing tend to reduce the amount of CH that is precipitated in the interfacial region of the aggregates by acting as favourable nucleating sites for the CH as observed in Figures 4 and 5;

(b) that compared to the α-quartz flour particles which are virtually inert, some of the fly ash particles, presumably the very fine ones occurring at the interfacial region go into solution and react with some of the CH precipitated in this region, thereby reducing the quantity and degree of orientation; this is particularly so since the mix with EFA (which is finer and has a higher glass content than LM) has the lowest $I_{CH}$ values within this region;

(c) that the occurrence of the fly ash and α-quartz particles at the interfacial region tend to interfere with the orientation and growth of the CH crystals, thereby reducing the degree of CH orientation; in the plain opc-paste where no such 'fillers' exist at the interfacial region, the CH crystals are free from such interference and can easily grow;

(d) that the relatively finer and spherical fly ash particles are likely to fill up the interstices of the cement grains forming the paste at the aggregate interface so that less open water-filled spaces will be left for the growth of CH crystals; (e) that the improved particle packing (multi-modal grain size distribution of paste) caused by the fly ashes tends to reduce entrapped or (micro)-bleeding water at the aggregate interface which negatively affects CH growth and orientation at the aggregate interface.
Figure 10 shows that the fly ashes significantly influence the degree of orientation CH at the interfacial zone by 28 days of hydration. There is a considerable reduction in the maximum values of I_{CH} for the fly ash blends. The reduction in the maximum value of I_{CH} for the LM mix is quite remarkable. By 28 days of aging, the maximum I_{CH} value of 6.4 for the LM mix at 7 days had reduced to about 2.5 and that of 3.8 for the EFA mix at 7 days to about 2.1. For the plain mixes, however, there is an increase in values.

Figure 10 also shows that by 28 days of hydration, the effects of EFA and LM on the interfacial zone are practically identical. The I_{CH} distribution of the two fly ash blends are virtually the same. They also tend to reduce the thickness of the interfacial zone by nearly the same amount. These effects are almost the same regardless of the fact that EFA is finer and has a higher glass content than LM. It is also interesting to note that although by 28 days of aging the CH values of the fly ash blends in Figure 3 had not decreased, at the interfacial zone the effects of the fly ashes on CH were quite pronounced. Also in Figure 3, there is quite a significant difference between the CH data for the EFA and the LM blends by 28 days of aging. At the transition zone, however, the data for these blends seem identical. These features suggest that in the presence of fly ashes the processes which take place at the interfacial zone which results in the microstructural changes and the ‘thinning’ of the interfacial zone may proceed at a relatively faster rate than in the bulk paste.

The results also suggest that at the interfacial zone the pozzolanic reaction between CH and the fly ashes is faster than in the bulk paste. It can be deduced from the results that at the interfacial zone the fly ash particles occurring there are presumably relatively very fine. For each kind of fly ash the relatively finer particles can dissolve faster than the coarser ones and by reacting with the CH at the interfacial zone tend to reduce the quantity of CH faster that in the bulk paste. This way the reactivity of fly ashes with different fineness and other characteristics seem to be the same at the interfacial zone. This is likely to be the reason for the identical I_{CH} data for EFA and LM at the interfacial zone at 28 days of aging.

Conclusions

The evolution and distribution of calcium hydroxide in three low-calcium fly ash-Portland cement blends with water-solids ratio of 0.40 and cured for times up to six months have been studied. On the basis of the results obtained the following conclusions could be drawn:

1. During the first one month of hydration of the portland cement studied, the data obtained from CH measurements showed little evidence of pozzolanic reaction. SEM studies, however, showed evidence of reaction products in the immediate vicinity of some of the ash particles even as early as 7 days. The ash particles also served as nuclei for precipitation of CH and C-S-H. Some of the CH crystals remained in intimate contact with the ash particles even after about six months of hydration. This is not a unique property of fly ashes since it is also observed for other non-reactive materials.
2. The fly ashes affected the interfacial zone of the cement paste-aggregate interface greatly. The thickness of the zone was substantially reduced and the degree of orientation of the CH crystals at the interfacial zone was decreased. These effects are regarded to be due to improved particle packing at the interface and the reduced micro-bleeding, as well as to the pozzolanic reaction between the ashes and the CH at the interface. The reduction in the thickness of the interfacial zone is considered to be a major contribution to the effects of fly ashes on properties of concrete such as strength and permeability.

3. The pozzolanic reaction of the interface appears to be eminent at an earlier age than in the bulk of the paste. This is likely to be due to accumulation of finer fly ash particles at the interface.

4. The finer and the more glassy the fly ash is, the greater the lime consumption appears to be.

References

Chapter 6

Influence of metakaolinite, blast furnace slag and Ludox® on the aggregate-cement interface in relation to alkali-silica reaction

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and

J.M.J.M. Bijen, INTRON and TU-Delft, The Netherlands

Summary

This paper reviews the influence of pozzolans and blast furnace slag on the hydration of portland cements at the interface with aggregate. It is shown that the addition of pozzolans and blast furnace slag as partial cement replacement has a strong influence on the microstructure of the interfacial zone. The amount of portlandite is reduced, the orientation of the crystals is decreased, and the density of the interface material is increased. The reduced amount of portlandite at the interface will decrease the availability of Ca²⁺ and OH ions from Ca(OH)₂, and the increase in density will reduce the penetration of ions into potentially reactive grains. The beneficial effects of the pozzolans appears to be particularly pronounced at the interface.

Introduction

In recent years, investigations have revealed the importance of the presence of calcium hydroxide and alkali-ions in the vicinity of alkali-reactive grains [1]. Water molecules, hydroxyl ions and alkali-ions penetrate reactive grains. When the alkalinity is high enough, the Si-O-Si bonds are raptured and an alkali-silica-gel is formed. In this reaction, the hydroxyl concentration diminishes and must be replenished by new to maintain the rapture process. Sufficient inflow of these ions is of importance. The presence of Ca(OH)₂-rich "halo" around aggregate grains and the porous character of this interfacial zone facilitate this.

The alkali-silica reaction alone does not lead irrevocably to disruptive expansion. The latter occurs only when the inflow of water and ions exceeds the outflow of silicate ions. When lime is present in the pore water in the vicinity of a reactive grain precipitation of calcium silicate hydrates will occur in the grain or directly on the grains and hampers the transport of silicate ions further away. Alkalinity of the cement paste, presence of lime in the vicinity of the reactive grains, and the ease of diffusion of these ions are the three main factors determining the negative effects of alkali-silica reaction.

Alkali-silica reaction: The situation in the Netherlands

In the Netherlands, alkali-silica reaction has not been observed yet unless in rare cases where special aggregates have been used. The main aggregates, river-gravel
and sand are not alkali-reactive. This is likely to be the main cause of the absence of this degradation. Another favourable condition however, is that, in about 75% of the concretes made, composite cements containing pozzolans or latent hydraulic additions are used. Either portland blast furnace slag cement (> 65% slag) or portland fly ash cement (with ≈ 25% of fly ash) is used.

Pozzolans or latent hydraulic additions are known to reduce the expansion caused by alkali-silica reaction. More than 25% replacement of cement by fly ash, the use of 10 to 20% of microsilica, and more than 50% ground granulated blast furnace slag, etc. are well known measures that can, and have been taken to reduce the expansion sufficiently. Generally, this is due to reduced alkalinity, reduced lime content and decreased permeability of the cement paste system. Less attention has been drawn to the effects of pozzolans on the interfacial zone between paste and aggregates where the alkali-silica reaction initiates.

At Delft University of Technology this interfacial region is investigated in depth. The effects of various additions on the transition zone is studied [2-5]. In this article, a summary of the results of an investigation using calcined metakaolinite, blast furnace slag cement and a synthetic colloidal silica, Ludox® is presented and discussed in relation to the disruptive alkali-silica reaction. The effects of pulverised fly ash and silica fume will be discussed in Chapter 8.

Materials

In this section, a brief descriptions of metakaolinite, blast furnace slag and Ludox® are given.

Metakaolinite: This is the product obtained from thermal activation or dehydroxylation of kaolin (Al₄Si₂O₁₀(OH)₈) at temperatures of ≈ 450 - 800°C. After dehydroxylation, metakaolinite will not rehydroxylate, but in the presence of water it will readily react with calcium hydroxide and alkalis to form cementitious products.

Blast furnace slag: This is a by-product of the iron and steel industry which is composed essentially of lime (CaO), silica, and alumina, with minor amounts of magnesia, alkali and iron oxides. In this study, the blast furnace slag existed as portland blast furnace slag cement with ≈ 70% (by mass) of slag.

Ludox®: This consists of synthetic colloidal silica dispersed in a solution of NaOH. The NaOH solution acts as a stabilizer for the amorphous silica particles by reacting with the silica surface to produce a negative charge. The charged silica particles repel each other which results in a stable product.

The chemical composition and other properties of the ordinary portland cement (OPC) as well as the ordinary portland blast furnace slag cement (PBFS) applied in this study are given in Table 1. The characteristics of the metakaolinite and the sythetic colloidal silica are given in Table 2.

The water-to-binder ratios of the composites were 0.30 and 0.40. In this text, binder means (cement + pozzolan or latent hydraulic addition). Details of the materials and experimental procedures are given in references 2 to 5. In this paper, only brief descriptions of the tests are given.
### Table 1: Chemical composition of materials

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>Portland cement</th>
<th>Blast furnace slag cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.9</td>
<td>29.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.6</td>
<td>7.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.9</td>
<td>1.7</td>
</tr>
<tr>
<td>MgO</td>
<td>1.5</td>
<td>6.9</td>
</tr>
<tr>
<td>CaO</td>
<td>62.0</td>
<td>49.0</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.1</td>
<td>2.9</td>
</tr>
<tr>
<td>Free water</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Insoluble residue</td>
<td>4.1</td>
<td>3.7</td>
</tr>
<tr>
<td><strong>Specific gravity</strong></td>
<td><strong>3.10</strong></td>
<td><strong>2.95</strong></td>
</tr>
<tr>
<td><strong>Specific surface</strong> (Blaine: m²/kg)</td>
<td><strong>300±20</strong></td>
<td><strong>400±50</strong></td>
</tr>
</tbody>
</table>

### Table 2: Composition and other properties of the pozzolans

<table>
<thead>
<tr>
<th>Composition and properties</th>
<th>% (by mass)</th>
<th>Metakaolinite (MK)</th>
<th>Ludox (LD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>55.5</td>
<td>40.0*</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>39.7</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Na₂O equivalent</td>
<td>1.9</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.52</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>Specific surface</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>of solids (m/g)</td>
<td>14.8</td>
<td>230.0</td>
<td></td>
</tr>
<tr>
<td>Mean grain size</td>
<td>1.4 μm</td>
<td>12.0 nm</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>Colour</td>
<td>milky white</td>
<td>opalescent</td>
<td></td>
</tr>
</tbody>
</table>

* % (by mass) of silica as SiO₂ in aqueous NaOH solution

### Test procedures

(i) **Semi-quantitative XRD analysis**

The method developed by Grandet and Ollivier, the so-called Tallouse method [6] was used to determine the occurrence and orientation of calcium hydroxide at the paste-aggregate interface. The reference pastes and the pastes containing the mineral additives were cast on polished surfaces of granite rock prisms with the aid of a PVC tube. Details of the sample preparation and testing procedures are given in references 2 to 5 (Chapters 3 to 5).

At the transition zone the degree of orientation of calcium hydroxide crystals can be determined by comparing the X-ray diffraction intensity of the {001} plane to
that of the \{101\} plane of lime crystals. For randomly oriented calcium hydroxide crystals, the orientation index, $I_{\text{CH}}$, is defined as:

$$I_{\text{CH}} = \frac{I(001)}{I(101)} = 1.00$$

Values of $I_{\text{CH}}$ higher than 1.00 indicate preferential orientation of the lime crystals parallel to the surface of the aggregate. In other words, preferential orientation of the CH crystals implies that the crystals are oriented in such a way that their c-axes are perpendicular to the aggregate surface.

By successive abrasion of the paste surface (with no. 600 emery paper) and X-ray diffraction analysis after every removal, the thickness of the zone with preferential lime orientation can be determined. This zone is likely to coincide with the interfacial zone.

(iii) SEM-EDAX studies

For the scanning electron microscope (SEM) studies, portions of the specimens were cut and freeze-dried to prevent further hydration. After that, freshly-fractured surfaces were coated with a thin film of nickel or gold, mounted onto stubs and examined with the secondary electron imaging in the SEM. Two SEMs were used: a JEOL, JSM-840 SEM and an ISI-40. Both SEMs were equipped with energy dispersive X-ray analyzer (EDAX).

Results and discussion

Calcium hydroxide at the interface

Effect of metakaolinite

The effect of addition of metakaolinite on the orientation index, $I_{\text{CH}}$, is shown in Figures 1 and 2 for 7- and 100-day old composite specimens. The water-binder ratio of the mixes was 0.40, and the aggregate used was granite [7]. It is clear from the two figures that for both ages, the addition of metakaolinite decreases the relative amount and the degree of orientation of the calcium hydroxide at the vicinity of the aggregate.

Effect of blast furnace slag

Figure 3 shows the effect of age on the maximum orientation index value $I_{\text{CH(\text{max})}}$ for OPC and PBFSC. The $I_{\text{CH(\text{max})}}$ value is the orientation index value immediately after debonding of the paste from the aggregate, that is prior to grinding. For all the specimens studied, this first $I_{\text{CH}}$ value was the highest, hence the designation $I_{\text{CH(\text{max})}}$ [5 and Chapter 4].

It is also interesting to note that the thickness of the interfacial zone has decreased from about 40 nm at 7 days of hydration to less than 10 nm at 100 days of hydration.
Figure 1: Effects of addition of metakaolinite on the degree of orientation of CH at the cement paste-granite interfacial zone (Age: 7 days).

Figure 2: Effects of addition of metakaolinite on the degree of orientation of CH at the cement paste-granite interfacial zone (Age: 100 days).

Up to about 28 days the amount of calcium hydroxide and the orientation index values at the interfacial zone are higher for PBFSC than for OPC. The graph, however, shows that after about 7 days, the orientation index values for PBFSC decrease. This suggests a reduction in the amount of calcium hydroxide at the interfacial zone possibly resulting from the hydration of the slag and the pozzolanic reaction between the slag and calcium hydroxide. It could also mean that as a consequence of the hydraulic action of the slag, after about 7 days of hydration the interfacial layer becomes densified, in which case the ease of transport of Ca$^{2+}$ and OH$^{-}$ ions to the interface for crystallization of calcium hydroxide becomes
reduced. Portland blast furnace slag cements and ordinary portland cement containing slags as partial cement replacements are known to form a more discontinuous paste pore structure and an impermeable paste system than plain ordinary portland cements [8,9].

Figure 3: Effect of age on the maximum degree of orientation of CH at the paste-granite interfacial zone for OPC and PBSFC pastes.

Figure 4: Degree of orientation of CH at the paste-granite interface in ordinary portland blast furnace slag cement paste system (Age: 1 day).

Figures 4 and 5 show the distribution of ICH at the interfacial zone for OPC and PBFSC at ages of 1 and 7 days respectively. Relative to the ordinary portland cement, the much finer ordinary portland blast furnace slag cement shows already a decrease in orientation of lime crystals by 7 days of hydration. The interfacial region for the portland blast furnace slag cement is also significantly thinner compared to that of the ordinary portland cement.
Figure 5: Degree of orientation of CH at the paste-granite interface in ordinary portland blast furnace slag cement paste system (Age: 7 days).

Effect of Ludox®

Figure 6 shows the effect of addition of the synthetic colloidal silica, Ludox®, on the orientation index at the interfacial zone. Obviously, the orientation is already reduced significantly during the first 7 days of hydration for the colloidal silica. This is possibly due to the higher specific surface and better dispersion of the amorphous silica in the mix. Ludox® occurs as a liquid and was added to the mix water and homogenized before mixing with the cement.

Figure 6: Effects of addition of colloidal silica, Ludox®, on the degree of orientation of CH at the paste-granite interfacial zone (Age: 7 days).
Microstructure of the paste-aggregate interface

SEM studies with microprobe analyses show that in mortars containing the blending agents, Ca(OH)$_2$, which initially crystallized at the interface disappears later on when reaction with the pozzolans has occurred. Figures 7 and 8, for example show the microstructure of the paste-aggregate interfacial zone for a 100-day old OPC mortar and PBFSC mortar respectively. In general, a denser interface is observed when these additions are used in combination with portland cement.

![Image of microstructure](image)

*Figure 7: SEM photo of a fractured surface of OPC (reference) mortar showing the microstructure of the interfacial zone (Age: 100 days). 1 = Aggregate; 2 = CH crystals; 3 = Paste.*

![Image of microstructure](image)

*Figure 8: SEM photo of a fractured surface of PBFSC mortar showing the microstructure of the interfacial zone (Age: 7 days). 1 = Aggregate; 3 = Paste.*
Conclusions

The addition of pozzolans such as metakaolinite to concrete or the use of composite cements containing Ludox® or ground granulated slag has a strong effect on the microstructure of the interfacial zone. The quantity of lime is reduced, the orientation of the lime crystals is decreased, the thickness of the interfacial zone is decreased, and the density of the interface is increased.

The significantly reduced amount of lime at the interface as well as the reduced permeability of the interfacial region will decrease the buffer of hydroxyl, OH⁻ ions. Also, the densification and the ‘thinning’ of the interfacial region will reduce the penetration rate of ions into the reactive grain.

The beneficial effects of additions are much more pronounced at the interfacial zone than in the bulk paste matrix. These effects are likely to be of paramount importance for reducing the alkali-silica reaction in concrete.

References


Chapter 7

The role of the cement paste-aggregate interfacial zone on water absorption and diffusion of ions and gases in concrete

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Synopsis

The role of the paste-aggregate interfacial zone in relationship to water absorption and diffusion of ions and gases in concrete has been investigated. Portland cement pastes and mortars, with water-cement ratios of 0.30, 0.40 and 0.50 were used for the study. Total porosity and pore size distribution studies show that the paste-aggregate interfacial zone is more porous than the cement matrix. However, a simple mathematical normalization of the data from water sorptivity of pastes and mortars, Cl⁻ and Na⁺ ion diffusion in specimens, and methanol adsorption all point to the fact that the paste-aggregate interfacial zone plays a minor role in the absorption of water and diffusion of ions and gases in concrete. In normalweight concretes, the cement matrix is the continuous phase and appears to be dominant with respect to water absorption and diffusion of ions and gases.

Introduction

According to Diamond [1], the paste in concrete is confined to narrow ribbons, approximately 80 to 150 μm, separating the sand and aggregate particles, and frequently interrupted by air voids. On a micro-scale, the cement paste can further be divided into two zones: the bulk paste matrix and the paste that is formed at the immediate vicinity of the aggregate particles, called the interfacial zone.

Unlike the bulk matrix, the microstructure of the interfacial zone is characterized by coarser crystals, less cement paste, more capillary pores, and preferred orientation of calcium hydroxide crystals [2-5].

Investigations also reveal that in addition to the large number of capillary voids and oriented calcium hydroxide crystals, very fine microcracks exist at the transition region, even before application of load on concrete [6,7]. On the average, the transition zone is ≈ 50 μm [8,9], that is, about one-third of the average thickness of the cement paste in concrete.
To date, the effect of the paste-aggregate interfacial zone on fluid transport into concrete is not completely understood. Some studies suggest that the interfacial zone does not play any major role in determining the transport capacity of fluids into concrete, and hence may probably not influence the durability of concrete [10-12]. Other studies, on the other hand, show contrary findings [9,13-15].

Considering the thickness and the character of the interfacial region in relation to the bulk cement paste, its potential as a preferential path for ingress of aggressive chemical fluids into concrete is high. The aim of this paper is to report the modifications observed in the transport of fluids into portland cement mortars formulated with non-porous sand particles. The paper directs attention to the role of the interfacial zone in the transport processes, and relates the modifications observed to the permeability and the durability of concrete.

Materials and experimentation

Experimental strategy

As mentioned in the introduction, the intent of this study was to show the role of the interfacial zone between cement paste and aggregate particles on the transport of fluids in concrete. As such, the strategy adopted in the experimentation was to measure some properties of neat cement pastes such as total porosity, pore size distribution, absorptivity, diffusivity, etc., and compare them to corresponding 'cement pastes' in mortars otherwise denoted as 'mortar pastes'. For this reason, all the mixes - pastes and mortars, were prepared with the same water-cement ratios, and cured under the same conditions. The only variable between the set of pastes and the corresponding set of mortars was the inert and non-porous sand particles in the mortars. In this way it was possible to compare the properties of equal volumes of plain cement pastes with corresponding volumes of 'mortar pastes'. This procedure enabled the effects of the interfacial zone on the transport of fluids in the mortars to be delineated. Throughout this investigation, mortars were used in place of concrete for the following reasons:

(i) to maximize the amount of cement pastes in the mixes for comparative purposes;
(ii) to avoid possible complications by introducing another variable involving coarse porous aggregate particles which have significant absorptivities; and
(iii) to avoid the need of thick specimens necessary with respect to the size effects of the coarse aggregates.

However, to check the representativeness of the results, three water-cement ratios, two cement types, two sand-cement ratios, and various curing ages of the mixes were studied. In this investigation, only ordinary portland cement paste without any admixtures were used. In a subsequent paper [16], the effects of mineral admixtures such as pulverised fly ash, silica fume and metakaolinite on the transport of fluids in concrete will be presented.

Materials

As a basis for the investigation, an ordinary portland cement (OPC) equivalent to ASTM Type I, and a rapid hardening portland cement (RHPC) equivalent to ASTM
Type III cement, were used for the study. The two cements differed mainly in their fineness and their C₃S content as shown in Table 1. The Bogue compositions of the cements are also given in Table 1. The sand was a non-porous α-quartz. The gradation and the proportions of each size used in formulating the mortars are given in Table 2.

Table 1: Bogue composition of portland cement

<table>
<thead>
<tr>
<th>Mineral</th>
<th>% (by mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASTM Type I</td>
</tr>
<tr>
<td>C₃S</td>
<td>50.2</td>
</tr>
<tr>
<td>C₂S</td>
<td>19.6</td>
</tr>
<tr>
<td>C₃A</td>
<td>9.8</td>
</tr>
<tr>
<td>C₄AF</td>
<td>8.9</td>
</tr>
<tr>
<td>Fineness (Blaine, m²/kg)</td>
<td>300±20</td>
</tr>
</tbody>
</table>

Table 2: Gradation and proportion of sand in mortars

<table>
<thead>
<tr>
<th>Size (mm)</th>
<th>Proportion % (by mass of sand)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80 - 1.25</td>
<td>20</td>
</tr>
<tr>
<td>0.40 - 0.80</td>
<td>30</td>
</tr>
<tr>
<td>0.25 - 0.50</td>
<td>30</td>
</tr>
<tr>
<td>0.13 - 0.25</td>
<td>20</td>
</tr>
</tbody>
</table>

Specimen preparation

All the mixes were prepared with a laboratory type, table-top Hobart Model A-200 mixer. The materials were proportioned by mass and mixed according to standard methods of mixing as detailed in ASTM C-109. The water-cement ratios were 0.30, 0.40 and 0.50; and the sand-cement ratios (by mass) were 0, 1.0 and 2.0. Following mixing, each specimen was cast separately into 100x100x100 mm steel moulds, carefully compacted by vibration, and then transferred into a fog room at approximately 20°C. After 1 day the specimens were demoulded and cured in lime-saturated solutions at 20°C until they were required for testing. At required ages of testing, the blocks of pastes or mortars were removed from storage and cored into cylinders or sawn into slices for testing. In a preliminary water absorption study (on 35 mm diameter and 100 mm thick slices, cut from 35 mm diameter and 100 mm long cores of pastes and mortars), the top and bottom 20 mm portions of the specimens (in the direction of casting) were found to have relatively variable water absorptivities, presumably due to particulate settlement before hardening. The middle 60 mm portion was found to have nearly constant water absorptivity. For this reason, in all the tests (on specimens with water-cement ratios of 0.40 and 0.50), the top 20 mm and the bottom 20 mm portions of the blocks (in the direction of casting) were sawn off and were not used for further studies. Surface bleeding was observed and measured for the ordinary portland cement pastes and
mortars with water-cement ratios of 0.50. However, an estimation of the effective water-cement ratio after hardening showed that the measured bleeding had not changed the original water-cement ratio significantly. The effective water-cement ratios of both the pastes and the mortars were comparable, therefore no corrections were made for the water absorption data obtained.

Experimental procedures

a. Pore size distribution studies

Information on the pore size distribution of pastes and mortars was obtained with the aid of a mercury intrusion porosimeter. The size of the specimens used for this test was ≈ 2.5 g. All the specimens were oven-dried at 105°C to a constant weight before testing. A Carlo Erba Porosimeter-2000, with a maximum pressure of 200 MPa was used for the study. A contact angle of 141.3° was assumed throughout the testing. In addition to mercury intrusion porosimetry, the density of all the specimens were also determined by helium pycnometry.

b. Methanol adsorption

The methanol adsorption tests were done using cylindrical discs, 20 mm in diameter and 5 mm thick. For each specimen, three discs were used. The data obtained represent the average data of the three discs. All the specimens were (water)saturated surface-dried and soaked in methanol for 24 hours before being used for the adsorption tests. Following removal from the methanol solution, the weight of the discs were recorded and quickly transferred into a desiccator (partly-filled with fresh silica gel at 20°C) for drying under vacuum. This period of drying to a constant weight lasted between 5 to 10 days depending on the type and the age of the specimen. Drying in this manner, is believed to preserve the structural integrity of the specimens [17] and is therefore suitable for pretreatment of specimens for methanol adsorption and capillary water suction studies. At the start of the adsorption test, the dried weight of the specimens were recorded. The specimens were then placed in a desiccator together with a small quantity of methanol. The desiccator was then evacuated for approximately 1 minute. The weight gain up to a total period of 72 hours was recorded.

c. Rates of diffusion of Cl⁻ and Na⁺ into specimens

The rates of diffusion of Cl⁻ and Na⁺ ions into plain portland cement pastes and corresponding mortars were monitored using two compartment diffusion cells similar to the cells used by Kondo et al. [18]. The specimens consisted of 100x100x5 mm rectangular plates removed from the central portions of 100x100x100 mm blocks of pastes and mortars with the aid of a diamond saw. The water-cement ratio of the mixes was 0.40 and the sand-cement ratio of the mortars was 1.0. For each prism, at least six to eight plates were removed. The end 20-mm pieces of the blocks were discarded and not used in any of the subsequent studies. After sawing, the plates were stored in Ca(OH)₂ saturated solutions until they were required for testing. Prior to the diffusion test, the surfaces of each of the plates were carefully polished with a 600-grade emery
paper, rinsed with de-ionized water, surface-dried with a tissue before being fitted into the diffusion cells. The edges of the plates in contact with the container were sealed with a vaseline gel. After fitting and sealing the test specimens in place, the cells were filled at one side (compartment B, or solution B), with saturated Ca(OH)$_2$ solution at room temperature of 20±2°C and at the other side (the parent solution, compartment A, or solution A) with 0.5 M NaCl in saturated Ca(OH)$_2$ solution. The volume of each compartment was $\approx 1500$ cm$^3$. The experimental setup for which Cl$^-$ and Na$^+$ diffusion was studied is shown in Figure 1.

![Figure 1: Experimental setup for one of the diffusion cells.](image)

1 = saturated Ca(OH)$_2$ solution + 0.5 N NaCl  
2 = specimen (paste or mortar)  
3 = sat. Ca(OH)$_2$ solution  
4 = container (polypropylene plastic)  
5 = opening for collection of samples

After various diffusion times, the concentrations of Cl$^-$ and Na$^+$ ions were determined by removing 20 cm$^3$ portions of the solutions from each cell for analyses. The Cl$^-$ concentration was determined by titration, and that of Na$^+$ by inductively coupled plasma spectrometry (ICP). The titration method involved addition of an appropriate excess volume of silver nitrate, AgNO$_3$ solution and titrating against potassium thiocyanate, KCNS solution. Ammonium ferric sulphate was used as an indicator.

Sampling of the solutions was done after 3, 5, 7, 14, 21, 28 and 35 days. The combined volume of samples taken from each compartment was $\approx 9\%$ of the total volume of solutions in each compartment. But because at every period of sampling, equal volume of solution was removed from each cell, the errors possibly involved with this method of sampling was assumed to be negligible.

After the experimental setup was completed, there was an initial delay time during which diffusion of Cl$^-$ and Na$^+$ across the 5 mm-thick specimens was established.
At the onset of diffusion, the ion flux, $J$ (mole cm$^2$ s$^{-1}$) entering solution B is given by:

$$ J = D_i \cdot \frac{(C_s - C_b)}{l} $$

(1)

where, $D_i$ = diffusion coefficient of Cl$^-$ or Na$^+$

$l$ = thickness of the specimen

$C_s$ = concentration of ion within the specimen at the surface adjacent to solution A

$C_b$ = concentration of ion within the specimen at the surface adjacent to solution B

However, during the test $C_s$ and $C_b$ could not be measured, so the ionic concentrations of solutions A and B, that is, $C_A$ and $C_B$, were measured.

From kinetics of ionic diffusion, the ion flux entering solution B is also given by:

$$ J = \frac{V \cdot dC_B}{A \cdot dt} $$

(2)

where, $V$ = volume of solution B

$A$ = surface area of specimen transmitting the ions

Combining Equations (1) and (2) and integrating between the time of initial ion diffusion into solution B, that is, time, $t_0$, and a subsequent time, $t$, and assuming that $C_A$ remained constant over the diffusion period, gives

$$ \log_e \left\{ 1 + \frac{C_B}{(C_A - C_B)} \right\} = \frac{D_i \cdot A}{Vl} \cdot (t - t_0) $$

(3)

Hence, for $C_A >> C_B$, then

$$ C_B = \frac{D_i \cdot A}{Vl} \cdot C_A \cdot (t - t_0) $$

(4)

Thus, the (effective) diffusion coefficient $D_i$ could be calculated from slope of the rectilinear plot of $C_B$ against $t$ [18-22].

d. Water absorption

The water absorption for each mix was measured by a method used by Powers and Brownyard [23] on cored specimens prepared from the same batch of mortar used for the mercury intrusion studies. Before testing, all the specimens were dried in the same way as the specimens used for the methanol adsorption studies in the
foregoing section. The dimensions of the specimens were: diameter, 35 mm and thickness, 10 mm. The water absorption experiment itself involved exposing the top surface of the dried cores to water and measuring the gain in weight of the specimens with time.

From kinetics of water absorption [24-26], the amount of water that is absorbed per unit surface area $Q$, (at a constant temperature) after time $t$, is given by:

$$ Q = A + S_{eb} \cdot t^{(1/2)} $$  \hspace{1cm} (5)

where,

- $Q$ = amount of water absorbed per unit surface area
- $t$ = the time taken to absorb $Q$ amount of water, and
- $S_{eb}$ = coefficient of absorptivity which depends on the initial moisture content of the specimen
- $A$ = a constant which arises from the filling of the open surface porosity on the inflow surface and along the sides of the specimen

Thus, using the slopes of the rectilinear plots of $Q$ versus $t^{1/2}$, the water absorptivity, $S_{eb}$, of each specimen was obtained.

**Results and discussion**

**Pore size distribution of pastes and mortars**

Figure 2 shows the results of the pore size distribution studies for 100-day old samples prepared at a water-cement ratio of 0.40, and sand-cement ratios of 0, 1.0 and 2.0. The data in Figure 2 were calculated as percent total volume of mortars. Figure 2 shows that as the volume fraction of the sand increases from 0 to 2.0, the capillary porosity ($r > 0.1 \mu m$) also increases by a factor of 15. When, however, all the pores, down to $\approx 0.003 \mu m$ are considered, then the paste has the maximum total porosity. The total porosity decreases with increasing volume of sand in the mortar.

Porosity and pore size distribution data presented on the basis of the total volume of the mortar are limited in meaning especially, when interfacial effects are to be considered. This is because, as the sand volume increases, the proportion of the paste in the sample (which contains the pores) decreases. Since the sand particles are non-porous, the amount of voids or pores also decreases by virtue of the decreasing volume of paste. In order to make meaningful comparisons, the porosity and pore size distribution data were calculated as percent by volume of the paste portion of each mortar. This was done in two steps, as follows:

First, the volumes of the components of the mortars, that is, cement, sand, and water, were calculated using their densities. Then the volume of sand was subtracted from the total volume of the original mix to obtain the paste volume. The paste portions were then used to ‘normalize’ all the data. The results are presented in Figure 3. The curve labelled $OPC\#MP$ represent the ‘normalized’ data. It can be seen that as the volume of the sand in the mortars increases the total
porosity of the paste in the mortars, down to \( \approx 0.003 \, \mu m \) now increases. The plots also show a marked increase in capillary porosity - a factor of 70 as the volume concentration of sand increases from 0 to 2. Similar effects have been observed by Feldman [27].

![Porosity - % (v/v of mortar)](image)

*Figure 2: Pore size distribution of mortars plotted as volume percent of mortar (w/c = 0.40; age = 100 days).*

![Porosity - % (v/v of paste portion)](image)

*Figure 3: Pore size distribution of mortars plotted as volume percent of paste portion in mortar (w/c = 0.40; age = 100 days).*

**Methanol adsorption**

Figures 4 and 5 show the total methanol adsorbed by 10-day old specimens with water-cement ratios (w/c) of 0.30 and 0.40, and sand-cement ratios (a/c) of 0 and 1.0. The adsorption period was 1 hour for the data in Figure 4, and 72 hours for
the data in Figure 5. The OPCMPs denote the data obtained by ‘normalizing’ the data on the basis of the paste portion (by volume) of the mortars. The results show that in the presence of sand particles, methanol adsorption of cement pastes is about 20-125% faster than without sand particles. The water-cement ratio of the cement pastes and the adsorption period do not seem to affect this trend. The higher adsorption capacities of the pastes in the mortars suggest that the pore structure of the paste in mortars is different from the pore structure of plain cement pastes with the same water-cement ratio.

*Figure 4: Methanol adsorbed by pastes and mortars for a period of time* $t = 1$ hour ($w/c = 0.40; a/c = 1.0$; age = 10 days at start of test).

*Figure 5: Methanol adsorbed by pastes and mortars for a period of time* $t = 72$ hours ($w/c = 0.40; a/c = 1.0$; age = 10 days at start of test).
Chloride and sodium diffusion

The rates of diffusion of Cl and Na\(^+\) ions in 10-day old specimens with water-cement ratio = 0.40 and sand-cement ratios of 0 and 1.0 are presented in Figures 6 and 7 respectively.

![Graph of Diffused Cl- ions](image)

*Figure 6: Rate of diffusion of Cl ions in pastes and mortars (w/c = 0.40; a/c = 1.0; age: 10 days at start of test).*

![Graph of Diffused Na+ ions](image)

*Figure 7: Rate of diffusion of Na\(^+\) ions in pastes and mortars (w/c = 0.40; a/c = 1.0; age: 10 days at start of test).*

The plots were obtained using Equation 4. The results show that diffusion of Cl and Na\(^+\) ions is more rapid in the plain cement paste, OPCP, than the corresponding mortar, OPCM. If, however, the data are considered on the basis of the paste volume in the mortar, OPCMP, then the diffusion process is faster in this paste than the same volume of paste without sand, OPCP.
The data in Figures 6 and 7 indicate that in the presence of the sand particles, ionic transport through hardened cement paste increases. Using the slopes of the plots in Figure 6 for Cl\(^-\) and Figure 7 for Na\(^+\), in combination with Equation 4, the diffusion coefficients, \(D_i\), for OPCP, OPCM, and OPCMP were calculated. The results are presented in Table 3. From the table it follows that the rate of diffusion of Cl\(^-\) and Na\(^+\) ions through a 10-day old 'mortar paste', OPCMP, is nearly 1.5 times (that is, \(\approx 50\%\)) faster than the corresponding paste without sand, OPC. The modification in the rates of diffusion in the mortars is likely to be due to the formation of a more permeable interfacial material around the aggregate particles.

<table>
<thead>
<tr>
<th>Ionic species</th>
<th>(Di (\text{cm}^2/\text{s}) \cdot 10^{-8})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OPCP</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>1.3</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>1.6</td>
</tr>
</tbody>
</table>

**Water absorption**

a. Effect of water-cement ratio

In Figure 8 the results of water absorption for 10-day old mortars with sand-cement ratios of 0 and 1.0, and water-cement ratio of 0.40 are presented. Figure 9 shows the data for specimens with w/c = 0.50. The results from the two graphs show that regardless of the water-cement ratio, water absorption is faster in the 'mortar pastes', OPCMPs, than water absorption in corresponding plain cement pastes, OPCPs.

![Figure 8: Rate of water absorption of pastes and mortars with w/c = 0.40 and a/c = 1.0. (Age = 10 days at start of test).](image-url)
b. Effect of cement type

The kinetics of water absorption in specimens prepared with rapid hardening portland cement, RHPC ASTM Type III is illustrated in Figure 10.

The figure shows that the modification observed in the rate of water absorption of the ‘mortar paste’ in Figures 8 or 9 is not limited to ASTM Type I portland cement only, but also to ASTM Type III cement. The observed effect with the Type III cement is, however, less remarkable compared to that of the Type I cement. The grains of the Type III cement are finer than those of the Type I cement. So grain
density of the Type III cement at the sand interfaces is likely to be higher than that of the Type I cement. This will cause the interfacial permeability to be less. Also, the Type III cement has a higher C₃S content than the Type I cement (Table 1), so the initial rate of cement hydration will be faster, resulting in the production of a denser paste at age = 10 days than the corresponding paste prepared with Type I cement.

c. Effect of sand volume concentration

Figure 11a shows the rate of water absorption of 10-day old mortars with water-cement ratio = 0.40, and sand-cement ratios of 0, 1.0, and 2.0. As the volume concentration of the sand increases the samples exhibit lower rate of water absorption. As explained already, this is because as the volume of the sand in the mortar increases, an increasing proportion of the sample becomes sand, which is non-porous. This effect decreases the proportion of the cement paste (which contain the pores) in the mortar. The effect also tends to ‘mask’ the true porosity of the paste in the mortar sample (Figure 3), and results in underestimation of the true water absorption capacity of the ‘mortar paste’.

![Graph showing water absorbed vs time for different ratios of sand to cement](image)

*Figure 11 (a): Rate of water absorption by mortars (plotted with respect to the volume of mortars; w/c = 0.40; age = 10 days at start of test).*

Using the ‘normalized’ data in Figure 11b, the modification in the water absorption, caused by the increasing volume concentration of the sand becomes evident. The same effects were observed for porosity and pore size distribution of the mortars in Figure 3. Using Equation 5, and the slopes of the curves in Figures 7 to 11, the water absorptivities of the specimens were determined. The results are presented in Table 4.

The $S_{w}$ values for the ‘mortar pastes’ are comparatively higher ($≈ 1.3$ to $2.0$ times) than the values for corresponding plain cement pastes. This means that, for the same water-cement ratio and age, transport of water through cement pastes in mortars is likely to proceed at a faster rate than transport of water in plain cement pastes, prepared without aggregates.
Figure 11 (b): Rate of water absorption by mortars (plotted with respect to the volume of the paste portion of the mortars; w/c = 0.40; age = 10 days at start of test).

Table 4: Water absorptivities of specimens (age = 10 days)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$S_{Ob}(Kg.m^{-2}.s^{-2}) \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a/c</td>
</tr>
<tr>
<td>OPCP</td>
<td>0.0</td>
</tr>
<tr>
<td>OPCM</td>
<td>1.0</td>
</tr>
<tr>
<td>OPCMP</td>
<td>1.0</td>
</tr>
<tr>
<td>OPCM</td>
<td>2.0</td>
</tr>
<tr>
<td>OPCMP</td>
<td>2.0</td>
</tr>
<tr>
<td>RPWP</td>
<td>0.0</td>
</tr>
<tr>
<td>RPWCP</td>
<td>1.0</td>
</tr>
<tr>
<td>RPWCMP</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Discussion

The modification of fluid transport in the mortars as a function of sand-cement ratio appears to arise from cement paste-sand interfacial effects; it may be explained as follows. As the sand volume in the mortar increases, the number of particles of the sand, and for that matter, the number of interfacial zones formed per unit volume of mortar also increases. Thus, when all the volumes of the interfacial regions formed around the sand particles are summed up, the total amount obtained per unit volume of mortar sample, that is:

\[
\frac{\text{Volume (interface)}}{\text{Volume (mortar)}}
\]

becomes increased. This means that, as the volume of aggregate in the mortar increases, there will be a gradual predominance of the microstructural characteris-
tics of the interfacial zone over those of the bulk paste. Thus, if the interfacial zone around the sand particles in the mortars is found to have a more permeable character, then it follows that, with increasing sand content, the mortar paste will be more permeable.

From the results of the pore size distribution studies it was observed that the increase in sand-cement ratio from 0 to 2 was accompanied by an increase in capillary porosity by a factor of 70. This effect (that is, the higher capillary porosity), is likely to be one of the characteristics of the interfacial zone. Scrivener et al. [28] using backscattered electron imaging combined with quantitative image analysis found relatively higher proportion of larger pores ($r > 0.1 \mu m$) at the transition zone than in the bulk paste. Uchikawa et al. [29] and Feldman [27] attributed the formation of such coarse pores ($r > 0.1 \mu m$) in mortars and concrete to interfacial effects. Similar conclusions were drawn by Nyame [30].

The results of this study show that the interfacial zone is more porous than the bulk paste. However, considering the $\text{OPCM}/\text{OPCP}$ factors obtained from the simple mathematical normalization of the diffusion and water absorption data (1.5 to 2.0 for the diffusion tests and 1.3 to 2.0 for the water absorption test) in comparison with the much larger increase in capillary porosity, then the role of the interface on fluid transport in concrete can be considered to be relatively minor. The results of the study suggest that fluid transport processes in concrete are controlled mainly by the cement matrix.

Conclusions

The role of the paste-aggregate interfacial zone on the transport of fluids in mortars have been investigated. The conclusions from the results are as follows:

1. The porosity and pore size distribution of the cement paste that was formed in the mortars were found to be different from those of the plain cement pastes; the total and capillary porosities of the paste that was formed in the mortars were found to be higher than the corresponding cement pastes prepared without sand. The modification of the pore structure of the cement pastes in the mortars was more pronounced with increasing volume of sand.

2. Fluid transport through the "mortar pastes" was found to be comparatively faster than fluid transport through plain cement pastes of the same age and water-cement ratio. However, relative to the increase in capillary porosity, the effect of the paste-aggregate interface appears to be small. The results suggest that the paste matrix is the continuous phase in concrete and is mainly responsible for the fluid transport processes in the concretes.

References


29. Uchikawa, H., Uchida, S. and Hanehara, S., "Relationship between structure and penetrability of Na ion in hardened blended cement paste, mortar and concrete". 8\textsuperscript{th} Intl. Conf. on Alkali-Aggregate Reaction, Kyoto, pp. 121-128, 1989.

Chapter 8

Influence of pozzolans on the portland cement paste-aggregate interface in relation to diffusion of ions and water absorption in concrete

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and

J.M. J. M. Bijen
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Materials and Environmental Research
Sittard, The Netherlands

Synopsis

The influence of three secondary mineral additions on the paste-aggregate interfacial zone in relation to water absorption and ionic diffusion ions in concrete has been investigated. The data were obtained from the kinetics of moisture movement into and from mortars, rates of diffusion of Cl⁻, Na⁺ and K⁺ ions in mortars; scanning electron microscopy examinations of specimens; and pore structural studies from mercury intrusion porosimetry. The mineral additions improved the resistance of the mortars to water absorption and Cl⁻, Na⁺ and K⁺ diffusivity. From the present results and the results of a previous study on pastes and mortars without additions, it is concluded that the improvement is mainly due to a densification of the bulk paste matrix and not to a decrease in the thickness of the interfacial zone between cement paste and aggregate.

Introduction

General

Secondary cementitious materials, such as fly ash, metakaolinite and silica fume, and latent hydraulic additions like blastfurnace slag are known to improve the durability of portland cement concrete in a number of ways. The most obvious one is the reduction of permeability, which in turn, increases the resistance of the concrete to chemical deterioration and improves the protection of reinforcement by the concrete cover against chloride penetration. In most cases the reduction in permeability is attributed to (i) the improvement of the paste pore structure resulting from the refinement of the capillary pores through formation of secondary C-S-H and other reaction products from the pozzolanic reaction, and (ii) the reduction of the calcium hydroxide content of the bulk cement paste. The effect of the pozzolanic materials and blastfurnace slag on the paste-aggregate interfacial zone - a 'weak link' in concrete is rarely discussed. In three of our previous reports [1-3], the use of slag as well as pozzolans in combination with portland cement
was shown to improve substantially, the structure of the interfacial zone. In this paper, the influence of some mineral additives on the transport of fluids in mortars are presented in the light of the beneficial effects of these pozzolans on the paste-aggregate interfacial zone.

**Research significance**

*a. Reinforcement corrosion*

The deterioration processes of concrete, whether affecting the concrete itself or causing reinforcement corrosion, are determined largely by the ability of the concrete to resist penetration of aggressive agents from the environment. In steel reinforced concrete structures, the high alkalinity of the surrounding cement matrix usually passivates the steel from potential damage by corrosion [4,5]. Under certain conditions, however, this passivation may be destroyed and render the steel to corrosion. Such is the case when concrete becomes contaminated with chloride through ingress from deicing salts, or when concrete is located in or near seawater [4]. In such situations, the ease of diffusion of chlorides from the surrounding environment into the concrete becomes a major factor, among other things in determining the potential corrosion of the reinforcement. As part of this study, the inhibiting effect of secondary cementitious materials on the penetrability of chlorides into concrete is examined.

*b. Alkali-silica reaction*

Alkali-silica reaction occurs in concrete when Na\(^+\), K\(^+\), and OH ions from the pore solution of the cement paste, or from the environment react with certain forms of silica in the aggregates to form alkali-silica gel [6,7]. In the presence of lime the reaction is known to be capable of causing expansion [6-9]. It is capable of causing considerable damage to concrete structures, which eventually may fail. If the alcalis come from the cement paste pore solution, the reaction process is represented in Equation 1.

\[
\text{SiO}_2 + 2\text{NaOH / KOH} + \text{H}_2\text{O} = \text{Na}_2\text{SiO}_3 \cdot 2\text{H}_2\text{O} \quad (1)
\]

If the reaction results from penetration of alkali salts from the environment such as from alkali chlorides used as deicing agents, then the reaction process occurs in two stages as represented in Equations 2 and 3.

Step I: \[
\text{Ca(OH)}_2 + 2\text{NaCl} = 2\text{NaOH} + \text{CaCl}_2 \quad (2)
\]

Step II: \[
\text{SiO}_2 + 2\text{NaOH} + \text{H}_2\text{O} = \text{Na}_2\text{SiO}_3 \cdot 2\text{H}_2\text{O} \quad (3)
\]

Thus, by whichever process these alcalis enter concrete, if they become accessible to the reactive siliceous aggregates, an alkali-silica gel is likely to form.
In real life structures, concretes are very often exposed to alkalis from an outside source such as deicing salts; or from the sea; or even from groundwater. If concrete containing reactive aggregates is in contact with alkalis from an external source, the damaging effects of these alkalis will depend on (i) their ability to penetrate into the concrete, and (ii) their concentration levels in the concrete.

The harmful effects of alkalis in concrete, with regard to the alkali-silica reaction have been studied by several workers [6,7,10-12]. Unfortunately, most of the alkalis considered in such works, involved intrinsic alkalis, produced within the pore fluid of the concrete. Few studies [11,14], have given consideration to the effect of alkalis supplied from an external source on the alkali-silica reaction. In this paper, some data from external supply of alkalis by means of diffusion are presented. The information is used to evaluate the effectiveness of some pozzolans in inhibiting the penetrability of alkalis into concrete.

Materials and experimental details

Materials

The cement used for the test, ASTM Type I portland cement, contained 0.75% Na₂O equivalent. The mineral additions were: a wet-bottom boiler ASTM Class F fly ash (EFA), a Norwegian source silica fume (SF), and a thermally-activated kaoline (MK). The main characteristics of the cement and the three pozzolans are given in references 1 to 3 and Table 1.

<table>
<thead>
<tr>
<th>Chemical composition and other properties</th>
<th>% (by mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metakaolinite MK</td>
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<td>SiO₂</td>
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</tr>
<tr>
<td>Al₂O₃</td>
<td>39.7</td>
</tr>
<tr>
<td>Na₂O Equivalent</td>
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</tr>
<tr>
<td>Specific gravity</td>
<td>2.52</td>
</tr>
<tr>
<td>Specific surface (BET, m²/g)</td>
<td>14.8</td>
</tr>
<tr>
<td>Mean grain size (μm)</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The proportions of the mineral additions used to replace the cement was 0 and 20% by mass of the cement. The fine aggregate was a non-reactive (α-quartz) commercially available sand [15]. A sulphonated naphthalene formaldehyde (SNF) superplasticizer was used in the SF and MK mixes to improve workability and dispersion of the silica fume and metakaolinite particles. The dosage used was 1% by mass of binder.
Experimental procedures

a. Sample preparation

A table-top laboratory mixer, Hobart Model A-200 was used in formulating all the mixes. The details of the mixing procedure, the specimen preparation for storage, and the curing regimes are given in references 1, 3 and 15. The water-binder ratio (w/s) of the mixes was 0.40, and the sand-binder ratio (a/s) was 1.0.

b. Chloride and alkali diffusion tests

The experimental details for which the kinetics of diffusion of Cl⁻, Na⁺ and K⁺ ions was measured have already been described in reference [1]. The specimens consisted of 100x100x5 mm rectangular plates removed from the central portions of 100x100x100 mm blocks of mortars by means of a diamond saw. The mortar blocks had been previously cured in Ca(OH)₂ saturated solutions for 100 days. After the experimental setup was completed all subsequent measurements were done at a constant temperature of 20°C. The Cl⁻ concentration was determined by titration, and the Na⁺ and K⁺ concentrations by ICP-spectrometry.

c. Water absorption

The method used to measure the capillary water absorption have been described in [1]. The specimens measured 50 mm in diameter and 10 mm thick. Prior to the test, the specimens were dried by methanol exchange technique described already in reference 1.

d. Pore size distribution analyses

Qualitative information about the pore structure of the mortars was obtained by monitoring the rate of loss of moisture from 100x100x5 mm mortar discs in an oven at 40°C. The initial condition of the specimens was saturated surface-dried (SSD). For each mix, and at a required age, three slices were tested. The results reported in this paper represent the average data of the three test samples. Equation 3 was used to evaluate the rate of loss of moisture from the specimens.

\[ Q' = \frac{(M_{\text{sat}} - M_{40^\circ C})}{(M_{\text{sat}} - M_{105^\circ C})} \times 100\% \]  

(3)

where, \( Q' \) = relative moisture loss within a time period, \( t \)
\( M_{\text{sat}} \) = mass of saturated surface-dry specimen
\( M_{40^\circ C} \) = mass, oven dried at 40°C
\( M_{105^\circ C} \) = mass, oven dried at 105°C

For quantitative information of the pore structure of the mortars, a mercury intrusion porosimeter was used. The size of the specimens was ~ 2.5 g. All the specimens were oven-dried at 105°C to a constant weight before testing.
A Carlo Erba Porosimeter-2000, with a maximum pressure of 200 MPa was used for the study. A contact angle of 141.3° was adopted throughout the testing.

e. Cement paste-aggregate interfacial zone

The character of the cement paste-aggregate interfacial zone was studied by two methods: semi-quantitative XRD technique [16] and scanning electron microscopy. The details of the techniques are given in reference 15.

Results and discussion

Results

Pore structure

Figure 1 shows the rates of drying curves for the 100-day old mortars, dried in an oven at 40°C. As can be seen the blended mortars dry at a slower rate than the plain mortars. This effect is most pronounced in the silica fume mortar, SFM, and least remarkable in the fly ash mortar, EFAM. The effect is probably due to the occurrence of finer, more tortuous and less accessible pores in the blended mortars.

![Water loss - % (m/m of mortar)](image)

*Figure 1: Rate of loss of water from mortars with and without pozzolans (w/s = 0.40; a/c = 1.0; age = 100 days).*

The mercury intrusion porosity curves for OPCM, MKM and EFAM after 100 days of curing are presented in Figure 2. The results show that the reference mortar has the highest total mercury intrusion porosity at 100 days of hardening.

The data also show that MKM is denser than EFAM. Of the three mortars, the reference mortar (containing no pozzolanic addition) OPCM, has the highest capillary pore volume, followed by EFAM and MKM. Scrivener et al. [17] using backscattered electron imaging combined with quantitative image analysis found
relatively higher proportion of larger pores ($r > 0.5 \, \mu m$) at the transition zone than in the bulk paste. Uchikawa et al. [12] and Feldman [18] attributed the occurrence of coarser pores ($r > 0.5 \, \mu m$) in mortars and concrete to the porous character of the paste-aggregate interfacial zone. The lower capillary pore volume of EFAM and MKM suggests that the paste-sand interfacial zones of these mortars have been densified. It also suggests that the pores in the paste matrix are smaller. The densification may have resulted partly from (i) the improved particle packing of the cementitious materials in the blended mortars, especially at the paste-sand interfaces [2,19], and partly from (ii) the deposition of secondary hydrates arising from the pozzolanic reaction between the blending components [2,3].

![Figure 2: Pore size distribution of mortars plotted as volume percent of mortar (w/s = 0.40; a/s = 1.0; age = 100 days).](image)

**Calcium hydroxide at the paste-aggregate interface**

The effects of partial portland cement replacement by MK, SF or EFA on the paste-aggregate interface have been reported already [2,3 (Chapters 4-6). Using the information from Chapters 4 to 6, the orientation index, $I_{CH}$, and the thickness of the interfacial zones, $δ (\mu m)$, for various composites at specified ages were calculated. The results are presented in Tables 2 and 3.

**Table 2: Maximum orientation index of Ca(OH)$_2$ crystals $I_{CH_{max}}$ and thickness of the interfacial zone, $δ$, for paste-granite composites at various ages of curing (w/s = 0.40).**

<table>
<thead>
<tr>
<th>Composite specimen</th>
<th>7 days</th>
<th>100 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I_{CH_{max}}$</td>
<td>$δ (\mu m)$</td>
</tr>
<tr>
<td>OPC</td>
<td>2.9</td>
<td>49.4</td>
</tr>
<tr>
<td>80% OPC + 20% MK</td>
<td>2.0</td>
<td>39.7</td>
</tr>
</tbody>
</table>
From the data in Tables 2 and 3, the minimum and maximum $\delta$ values of the reference mixes are $\approx 52.0$ $\mu$m and $32.7$ $\mu$m respectively. Considering the thickness of the ribbons of cement paste in normal concrete to be $\approx 80-150$ $\mu$m, with an average of about $100$ $\mu$m [Reference 1 in [15]], then using these data, a simple mathematical analysis shows that the interfacial zone occupies about 30 to 50% of the total volume of cement paste in normal concrete.

Table 3: Maximum orientation index of Ca(OH)$_2$ crystals $l_{\text{CHmax}}$ and thickness of the interfacial zone, $\delta$, for paste-granite composites at various ages of curing ($w/s = 0.40$).

<table>
<thead>
<tr>
<th>Composite specimen</th>
<th>7 days</th>
<th>28 days</th>
<th>100 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$l_{\text{CHmax}}$</td>
<td>$\delta$ ($\mu$m)</td>
<td>$l_{\text{CHmax}}$</td>
</tr>
<tr>
<td>OPC</td>
<td>3.3 (5.0)</td>
<td>53.8 (54.5)</td>
<td>3.6 (5.9)</td>
</tr>
<tr>
<td>80% OPC + 20% EFA</td>
<td>3.8 (39.0)</td>
<td>50.9 (54.5)</td>
<td>2.2 (2.2)</td>
</tr>
<tr>
<td>80% OPC + 20% SF</td>
<td>2.5</td>
<td>50.9</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Data in brackets were obtained using polypropylene plastic plate as a "model coarse aggregate". (n.d. = not determined).

With regard to the effects of the mineral additives on the cement paste-aggregate interfacial zone, the following deductions can be made:

(a) With increasing age, the values of the orientation index, $l_{\text{CH}}$, increased for the reference mix, and decreased for the blended composites. The latter suggests a decreasing content of Ca(OH)$_2$ at the interface, which possibly results from the pozzolanic reaction of the blending materials.

(b) At 7 days, the $l_{\text{CH}}$ values of the blended mixes were lower than those of the plain mixes; but the thickness of the paste-aggregate interfacial zones of the blended cement composites were approximately the same as those of the reference mixes. This suggests that at 7 days of hydration there was some pozzolanic reactivity of the blending materials, but not enough to cause appreciable densification and reduction of the thickness of the transition zone.

(c) As the curing period increased, the thickness of the interfacial zones of the reference mixes remained nearly the same, although the $l_{\text{CH}}$ values increased. For the blended mixes, the interfacial zones became thinner, and the $l_{\text{CH}}$ values decreased further. This suggests that in the blended cement composites, as curing progressed, there was gradual densification of the interfacial layer probably by conversion of Ca(OH)$_2$ at the interface (by the pozzolanic reaction) into secondary C-S-H and other hydrates - a kind of an 'elimination-by-substitution' reaction.
transformation of the porous interfacial region into a more compact layer. The decrease in the thickness of the transition zone of the blended mortars means that the volume of the more permeable region which may be used as a preferential path for diffusion of ions and transport of water is also reduced.

**Diffusion of Cl\(^-\), Na\(^+\) and K\(^+\) ions**

The kinetics of diffusion of Cl\(^-\) in the mortar specimens are illustrated in Figure 3. It is evident from Figure 3 that the blended mixes offer a higher resistance to the diffusion of Cl ions in the mortars. Using the slopes of the plots in Figure 3 for Cl and similar data from graphs plotted for Na\(^+\) and K\(^+\), the coefficients of diffusion, D, of the ions were determined. The results and other relationships are presented in Table 4.

![Figure 3: Rate of diffusion of Cl\(^-\)ions in mortars with and without pozzolans (w/s = 0.40; a/s = 1.0; age: 100 days at start of test).](image)

**Table 4 (a): Coefficient of diffusion of ionic species in portland cement mortars with and without pozzolans**

<table>
<thead>
<tr>
<th>Ionic Species</th>
<th>(D_i) (cm(^2)/s).10(^{-9})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OPCM</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>5.97</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>1.88</td>
</tr>
<tr>
<td>K(^+)</td>
<td>2.59</td>
</tr>
</tbody>
</table>

It can be seen that:

(i) The use of ordinary portland cement in combination with the pozzolans increased the resistance of the mortars to diffusion of Cl\(^-\), Na\(^+\) and K\(^+\) ions. For example, the diffusion of Cl ions in the 100-day old plain mortar...
at 20°C is nearly sixty times as fast as the rate of diffusion of Cl ions in the MK or the SF mortars.

Table 4 (b): Ratio of $D_i$ of OPCM to $D_i$ of the pozzolans

<table>
<thead>
<tr>
<th>Ionic species</th>
<th>$D_i$ OPCM</th>
<th>$D_i$ OPCM</th>
<th>$D_i$ OPCM</th>
<th>$D_i$ OPCM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_i$ MKM</td>
<td>$D_i$ MKM</td>
<td>$D_i$ MKM</td>
<td>$D_i$ MKM</td>
</tr>
<tr>
<td>Cl</td>
<td>1</td>
<td>59.7</td>
<td>54.3</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>1</td>
<td>62.7</td>
<td>62.7</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1</td>
<td>37.0</td>
<td>43.2</td>
<td></td>
</tr>
</tbody>
</table>

(ii) The metakaolinite (MK) and the silica fume (SF) were more effective than the Class F fly ash (EFA) in limiting the diffusion of ions in the mortars. The diffusion rate in the case of EFA decreases with time indicating the slow pozzolanic reaction which is typical of most Class F fly ashes [20].

The results of this study are in agreement with the work of Page et al. [21], Collepardi et al. [22], Dhir et al. [23], Sturrup and Hooton [24], Uchikawa et al. [12], and Sarkar and Aitcin [25].

Water absorption

The rates of water absorption of the mortars are shown in Figure 4. From the slopes of the plots, the water absorptivities, $S_{ab}$, of the mortars were calculated.

![Water absorbed, Q (kg/m²)](image)

*Figure 4: Rate of water absorption of mortars with and without pozzolans (w/s = 0.40; a/s = 1.0; age = 100 days).*
The results are presented in Table 5. Of the three pozzolans, MK was the most effective pozzolan in minimizing water absorption although the two other pozzolans also improved the resistance of the mortars to inflow of water.

Discussion

In a previous investigation [15, Chapter 7], it was found that the interfacial zone in portland cement mortars greatly increased capillary porosity relative to pure portland cement pastes, but had a relatively small effect on the transport of fluids. It was suggested that the cement matrix, as a continuous phase, controlled the transport processes in concrete. Although the interfacial zone was found to be significantly more porous than the bulk cement paste, it was found to play only a relatively small role in the transport processes in concrete. This is presumably because the large pores at the interfacial zones are not interconnected with each other but rather the relatively small pores of the matrix.

Since in the blended cement mortars, there is a substantial decrease in the rate of transport of water and the diffusion of Cl⁻, Na⁺ and K⁺, ions this marked decrease in the transport capacity must be due to the improvement in the microstructure of the cement matrix.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Sab ((\text{Kg} \cdot \text{m}^{-2} \cdot \text{s}^{-2}) \times 10^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPCM</td>
<td>1.02</td>
</tr>
<tr>
<td>80% OPC + 20% MK</td>
<td>0.45</td>
</tr>
<tr>
<td>80% OPC + 20% SF</td>
<td>0.62</td>
</tr>
<tr>
<td>80% OPC + 20% EFA</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Also, from the results of a previous study [15, Chapter 7], it was shown that only a factor of 1.3 to 2.0 was obtained for the diffusion of ions in the mortar specimens investigated. The 'continuous phase', which was found to control the transport processes was the bulk cement matrix. In this study, however, the data in Table 5 (b) show that in the presence of silica fume and metakaolinite, a factor of \(\approx 35-60\) is obtained when the diffusion process in the plain mix is compared to the SF and MK mixes. These high ratios are obtained regardless of the fact that the thickness of the paste-aggregate interfacial zone in these systems is not "zero" as shown in Tables 2 and 3.

Therefore the increased resistance of the fluids against penetration of aggressive ions of the blended cement mortars must be due in part to the improvement of the microstructure of the paste-aggregate interfacial layer, but more importantly, to the marked improvement or the densification of the matrix of the blended mixes. This
observation is in agreement with the results of Malek and Roy [26], who concluded after a similar study that the diffusion process of chloride in concrete is mainly controlled by the composition of the cementitious matrix.

Conclusions

The influence of pozzolans on the paste-aggregate interfacial zone in relationship to transport of water and diffusion of Cl\textsuperscript{-}, Na\textsuperscript{+} and K\textsuperscript{+} ions in mortars has been studied. On the basis of the results presented in this paper, the following conclusions can be drawn:

- Addition of the pozzolans, MK, SF and EFA to portland cement as partial cement replacement affected the transport of processes in the mortars: (a) the rates of diffusion of Cl\textsuperscript{-}, Na\textsuperscript{+} and K\textsuperscript{+} ions in the mortars were inhibited greatly; (b) the rate of loss of water from the mortars; and (c) the rate of water absorption of the mortars were remarkably reduced by use of the pozzolans.

- The substantial effects must be mainly due to improvement in the permeability of the bulk paste matrix because the effects are much larger than in the case where the interfacial zone is removed.

References

1. Bijen, J. and Larbi, J., "Increase in durability by improvements in aggregate-cement paste interface". Submitted for presentation at the ACI Intl. Conf. on Durability of Concrete, Montreal, Canada, August, 1991.


Chapter 9

The role of silica fume and metakaolinite on the portland cement paste-aggregate interfacial zone in relationship to the strength of mortars

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and

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Abstract

In this paper, the effects of partial portland cement replacement by silica fume and metakaolinite on the interfacial zone in relationship to the compressive strength of mortars and the adhesive strength of pastes to aggregates are presented. Portland cement pastes and mortars containing 0 and 20% (by mass) of silica fume or metakaolinite with water-to-binder ratios of 0.30, 0.40 and 0.50 were used for the study. The results show that addition of silica fume and metakaolinite increases the strength of concrete primarily by densifying cement matrix and the interfacial zone. The latter effect tends to 'reinforce' the cement paste-aggregate bond and makes the aggregate a more effective contributor to the compressive strength development.

Introduction

Silica fume and metakaolinite have been shown to improve the microstructure of cement paste in concrete by densifying the cement matrix and the porous paste-aggregate interfacial zone [1-3]. These beneficial effects have been shown to result in a pronounced increase in the resistance of concrete to penetration of aggressive compounds [3]. In this study, the role of these mineral additions on the paste-aggregate interfacial zone in relationship to (i) the compressive strength development of portland cement mortars, and (ii) the adhesive strength of pastes to aggregates are examined.

Materials and experimental methods

Materials

ASTM Type I portland cement (OPC), silica fume (SF) and metakaolinite (MK), were used in this study. Silica fume is a by-product of the silicon and ferrosilicon industry, and metakaolinite is the product obtained from thermal activation of
kaolin. The compositions and other properties of these materials are given in references 2 and 3. Commercially available sand meeting ASTM C 109 with a maximum grain size of 5.0 mm and a fineness modulus of 3.29 was used for preparing the mortars. For the bond strength tests, granite and limestone rock prisms were used. The binder for the pastes and mortars contained 0 or 20% (by mass) of silica fume or metakaolinite as partial cement replacement. The mixes were formulated with a laboratory type Hobart Model A-200 mixer. Water-to-binder (w/s) ratios of 0.30, 0.40 and 0.50 were used. Owing to the extremely fine particle size of the silica fume and the metakaolinite, a high-range water reducing admixture (superplasticizer) at a dosage of 1.0% (by mass of the binder) was used to disperse the binder and to improve the plasticity of the blends.

Experimentation

Compressive strength

The compressive strength of the pastes and corresponding mortars were determined on 40x40x40 mm cubes under saturated-surface dry conditions. The mixes were formulated by mixing first the sand and the cement at a low speed. This was followed by addition of part of the water (while mixing at a moderate speed) and the superplasticizer to form a slurry. The metakaolinite or silica fume was then added and mixed at a relatively higher speed for 1 minute. The final stage lasted for a period of 2 minutes (after a pause of 1 minute) during which the rest of the water was added. The total mixing time lasted for 10 minutes. The corresponding pastes were prepared in the same manner except that the mixing time for the blends was extended to 15 minutes to break any agglomerates formed. All the specimens were stored in plastic-covered moulds in a fog room at 20°C for 1 day, and then demoulded and cured in lime-saturated solutions until required for testing. The curing period ranged from 1 day to 3 months. For each mix, and at a specified age, three specimens were tested; because the variability in the data was low (see Appendix), the average value of the three data was considered as the representative value.

Adhesive strength of pastes to aggregates

A special steel-made vertical alignment device which was mounted onto a 5 kN capacity tension machine, INSTRON 1122, was used together with the tension machine to measure the adhesive strength of pastes to aggregates. The vertical alignment device enabled the specimen to be aligned vertically in the direction of loading without any deflections.

The rock prisms to be used for the adhesive strength tests were first cut into cylinders, 34 mm diameter and 15 mm high. After cutting, the surface to be contacted with paste was polished with a rotating wheel using four successively finer emery papers (240, 320, 600, and 800 grits). The rock prisms were then dried in a laboratory atmosphere for 48 hours before they were used. The cement paste-aggregate composite specimens were formulated by fixing a polypropylene plastic tube onto the polished aggregate surface with a plastic adhesive tape and then filling the tube with fresh cement paste. The water-to-binder ratios used were 0.30 and 0.40.
All the composite specimens were stored in lime-saturated solutions in a fog room at approximately 20°C until required for testing. At a specified age, three specimens representing a particular rock-paste composite were tested. The average value of the three data was used as the representative value (see Appendix). The curing period for these test specimens ranged from 1 day to 6 months.

Results and discussion

a. Plain mixes

Compressive strength development

Figures 1 and 2 show the compressive strength development of plain OPC pastes and mortars as a function of age. Although the sand particles themselves are stronger than the cement pastes, the results in Figures 1 and 2 show that the plain pastes are comparatively stronger than the corresponding mortars (see Appendix for statistical comparison of the data).

![Compressive strength - (MPa)](figure1.png)

*Figure 1: Compressive strength development of plain OPC cement pastes and mortars as a function of age (w/c = 0.4; specimens cured in a fog room at 20°C in lime-saturated solutions).*

Adhesive strength of pastes to aggregates

Figure 3 shows the effect of water-cement ratio on the adhesive strength of pastes to granite and limestone. The adhesive strength of pastes to aggregates tends to decrease with increase in water-cement ratio. Since the adhesive strength depends among others on the porosity of the interface and the amount of cement gel which is in intimate contact with the aggregate [4], the decrease in adhesive strength with increase in water-cement ratio is likely to be due to a higher porosity and a lower amount of cement gel at the interface. The paste-aggregate interfacial zone is known to be more porous than the bulk paste [5,6].
Figure 2: Compressive strength development of plain OPC cement pastes and mortars as a function of age (w/c = 0.50; specimens cured in a fog room at 20°C in lime-saturated solutions).

Figure 3: Effect of water-cement ratio on the adhesive strength of cement pastes to granite and limestone (w/c = 0.30 and 0.40; specimens cured in a fog room at 20°C).

b. Mixes containing silica fume and metakaolinite

Compressive strength development

The influence of silica fume and metakaolinite on the compressive strength development of cement pastes and mortars is illustrated in Figures 4 to 7. There is
essentially no difference in the strength development between the SF or the MK pastes on the one hand and the plain cement pastes on the other hand as shown in Figures 4 and 5.

On the contrary, it is evident from Figures 6 and 7 that the silica fume and metakaolinite mortars display higher compressive strengths than the corresponding plain mortars. This higher strength development is already observed as early as one day after the formulation of the mortars. The silica fume and the metakaolinite appear to accelerate the strength developments of the mortars. The results also show that there is virtually no difference between the compressive strength of the SF mixes and the MK mixes. For that matter subsequent discussion of the compressive strength data will be confined to the silica fume.

A comparison of the compressive strength development of mortars and pastes containing 0 and 20% silica fume at w/s = 0.40 is presented in Figures 1, 2, 8 and 9. Figures 1 and 2 represent the plain mixes and Figures 8 and 9, the silica fume blends. With no silica fume, the paste is relatively stronger than the mortar. In contrast to that, the mixes containing silica fume show a reverse trend. The mortars are comparatively stronger than the pastes.

![Graph showing Compressive strength vs Age - Days](image)

*Figure 4: Effects of addition of SF and MK on the compressive strength development of portland cement pastes (w/s = 0.40; specimens cured in a fog room at 20°C in lime-saturated solutions).*

**Adhesive strength of pastes to aggregates**

In Figures 11 and 12, the adhesive strength data of pastes to aggregates with and without SF or MK are graphically presented. The SF or MK dosage was 20% (by mass) as partial portland cement replacement. The tensile strength values for the granite and the limestone rocks were 3.8 N/mm² and 5.2 N/mm² respectively. It is clear from Figures 11 and 12 that compared to the reference paste, addition of silica fume or metakaolinite improves the adhesive strength of pastes to aggregates. This occurs for both the granite and the limestone rocks used. It is interesting also to note that the improved adhesive strengths with the SF or MK pastes were...
noticeable as early as 1 day of curing. This increased adhesive strength at 1 day for the SF and MK blends is probably due to the improved solids packing of the cement grains (≈ 10-30 μm diameter) and the SF or MK particles (≈ 0.1 μm and 1.4 μm average diameter respectively) and the reduced micro-bleeding at the paste-aggregate interface [2,6]. The increase in the rate of cement hydration is also likely to contribute to the early adhesive strength development [1]. Subsequent increase in adhesive strength is probably due to the production of C-S-H gel through the pozzolanic reaction between the SF or MK and the CH produced from the cement hydration.

![Compressive strength vs. Age](image1)

**Figure 5:** Effects of addition of SF and MK on the compressive strength development of portland cement pastes (w/s = 0.50; specimens cured in a fog room at 20°C in lime-saturated solutions).

![Compressive strength vs. Age](image2)

**Figure 6:** Effects of addition of SF and MK on the compressive strength development of portland cement mortars (w/s = 0.40; specimens cured in a fog room at 20°C in lime-saturated solutions).
Figure 7: Effects of addition of SF and MK on the compressive strength development of portland cement mortars (w/s = 0.50; specimens cured in a fog room at 20°C in lime-saturated solutions).

Figure 8: A comparison of the compressive strength development between silica fume pastes and mortars (w/s = 0.40; specimens cured in a fog room at 20°C in lime-saturated solutions).

Microstructural features

In previous investigations, the microstructure of the interfacial zone between aggregate and paste have been described [2, Chapters 3, 4 and 6]. The main differences in interfacial microstructure of plain portland cement mixes and blended cement mortars are summarized in Table 1.
Figure 9: A comparison of the compressive strength development between silica fume pastes and mortars (w/s = 0.50; specimens cured in a fog room at 20°C in lime-saturated solutions).

Figure 10: Effects of addition of silica fume on the adhesion strength of pastes to aggregates (w/s = 0.30; specimens cured in a fog room at 20°C).

Discussion

Two effects may be attributed to the observed improvement in the strength of mortars when silica fume and metakaolinite were used in conjunction with portland. These are:

1. Improvement of the interfacial zone: this is brought about by the better particle packing and the pozzolanic reaction which result in the formation of a denser and a stronger mortar.
2. Improvement of the bulk paste matrix: also brought about by better particle packing and the pozzolanic reaction which also result in the formation of a denser and a stronger mortar.

From the results of the present study, the improvement of the strength of the mortars in the presence of SF and MK cannot be due to effect '2' above, that is, the improvement of the bulk paste matrix because no differences between the compressive strength of the plain OPC pastes and the OPC-SF or OPC-MK pastes were observed although differences were observed in permeability, pore size distribution and capillary porosity [Chapter 8]. Therefore the effect on compressive strength must be due to improvement of the interfacial zone.

\[\text{Adhesive strength} - \text{(MPa)}\]

\[\text{Age - Days}\]

\[\text{Broken in paste}\]

\[\text{OPC} + 0\% \text{ MK: GRAN.}\]

\[\text{50\% OPC + 20\% MK: GRAN.}\]

\[\text{OPC} + 0\% \text{ MK: LIME.}\]

\[\text{80\% OPC + 20\% MK: LIME.}\]

\[\text{Figure 11: Effects of addition of metakaolinite on the adhesion strength of pastes to aggregates (w/s = 0.40; specimens cured in a fog room at 20°C).}\]

From the above discussion, the lower compressive strength development of the portland cement mortars compared to their corresponding cement pastes (Figures 1 and 2) is likely to be due to interfacial effects which result in a less effective transfer of stress from the cement matrix to the aggregate particles. This observed effect is in agreement with the work of Powers [13] (presented in Figure 12) which shows that for the same gel-space ratio*, the presence of sand particles tends to lower the compressive strength of cement pastes. Powers attributed this effect to inhomogeneities with respect to the elastic properties of mortar and to a modification of the mode of failure of cement pastes in the presence of sand particles.

When silica fume or metakaolinite is added to mortars as partial cement replacement, the interfacial zone becomes denser and thinner [2,3]. This interfacial improvement leads to a better transfer of stress from the matrix to the sand particles.

* The gel/space ratio is the ratio of the solid products of hydration to the space available for these hydration products. In other words, the gel/space ratio is a representation of the capillary porosity of the cement paste.
Since the sand particles are comparatively stronger (higher modulus of elasticity) than the matrix, this effect results in a higher compressive strength development of the SF or MK mortars compared to their corresponding pastes and to the plain OPC-mixes. The transfer of stress from matrix to aggregate (with a higher modulus of elasticity) is illustrated schematically in Figure 13.

Table 1: Main differences in microstructure between plain portland cement mortar and blended cement mortars

<table>
<thead>
<tr>
<th>Property</th>
<th>Plain mortar</th>
<th>Blended cement mortar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Texture of paste</td>
<td>Less compact</td>
<td>More compact</td>
</tr>
<tr>
<td>Ca(OH) content</td>
<td>High per (unit volume)</td>
<td>Little or none</td>
</tr>
<tr>
<td></td>
<td>Crystals more oriented</td>
<td>May be oriented at young ages</td>
</tr>
<tr>
<td></td>
<td>Crystal orientation increases with age of</td>
<td>Orientation decrease with age due to the</td>
</tr>
<tr>
<td></td>
<td>concrete</td>
<td>pozzolanic reaction</td>
</tr>
<tr>
<td>Duplex film</td>
<td>Occurs on some aggregate</td>
<td>Sometimes occurs in fly ash concretes</td>
</tr>
<tr>
<td>Cracks and fractures</td>
<td>High density</td>
<td>Low density</td>
</tr>
<tr>
<td>(per unit volume)</td>
<td>Often occur along aggregate interface</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sometimes occur along Ca(OH) cleavage planes</td>
<td></td>
</tr>
<tr>
<td>Paste-aggregate bond</td>
<td>Weak</td>
<td>Strong</td>
</tr>
</tbody>
</table>

Other investigators have suggested other causes for the for the difference in effects of mineral additions on the strength of pastes and mortars. In [6,8], it is suggested that in cement pastes, the ultrafine cementitious additions such as silica fume or metakaolinite (> 5% by mass of cement as solids) are not effectively dispersed even in the presence of superplasticizers and after prolonged period of mixing. For this reason, although cement hydration may be accelerated, because some of the particles exist as "clumps", complete dissolution of these clumps for subsequent pozzolanic reaction is not achieved. Only partial dissolution of the particles is achieved. In the mortars, however, the tumbling and shearing of the aggregate particles with the silica fume or metakaolinite particles during the mixing process tend to break any "clumps" formed. In brief, the performance of these additions in pastes is according to these investigators limited due to inhomogeneous mixing.
Figure 12: Strength versus gel-space ratio of neat cement pastes and mortars (Redrawn from Powers [13]).

\[ E_a > E_m \]

Figure 13: Schematic representation showing the transfer of stress from matrix to aggregate under compressive load.

Conclusions

1. Addition of silica fume and metakaolinite increased significantly, the compressive strength of mortars and the adhesive strength of pastes to aggregates.

2. Silica fume and metakaolinite, however, did not show significant strengthening effects in cement pastes, at least, for the water-binder ratios considered in this study.

3. The strengthening of the silica fume and the metakaolinite mortars are believed to be due primarily to the thinner and more compact interfacial zone which improved the transfer of stress from the matrix to the aggregate particles.
References


Comparison of means

A two-tailed Student's t-test was performed to determine whether significant differences existed between the means of the compressive and tensile strengths that were compared. In the Student's t-test, the test statistic which is used to establish whether there is a significant difference between the means is given by (**):

\[
t_0 = \frac{[\mu_1 - \mu_2] - \delta}{s_p(1/n_1 + 1/n_2)^{1/2}}
\]  

(1)

where,
- \(\mu_1\) = mean of variable 1
- \(\mu_2\) = mean of variable 2
- \(\delta\) = difference between means
- \(s_p\) = square root of the pool variance
- \(n_1, n_2\) = number of sample size for variables 1 and 2

Equation 1 was used to test the following hypothesis:

- \(H_0:\ \mu_1 = \mu_2\) no significant difference between the means
- \(H_1:\ \mu_1 = \mu_2\) significant difference between the means
- D.F. = \(n_1 + n_2 - 2\) (D.F. = degrees of freedom)

A confidence level (\(\alpha\)) and the degrees of freedom were used to obtain values from standard tables. Based on the values from the tables and the calculated value of \(t_0\), the hypothesis was accepted or rejected. In order to use the Student's t-test it was necessary to establish whether the variances of the two variables were the same or differ. The F-test was used for such a test. The test statistic for the F-test is given as:

\[
F = \frac{s_1^2}{s_2^2}
\]  

(2)

where, \(s_1^2 > s_2^2\).

A confidence level (\(\alpha\)) and degrees of freedom, \(v_1\) and \(v_2\) were used to obtain a value from the standard F-Tables. The value obtained from the tables was used to establish whether the variances are the same or not.

This method was used to test the means of all data that were compared. An example is given below for the plain mixes with water-cement ratios of 0.40 and 0.50.

<table>
<thead>
<tr>
<th>W/c</th>
<th>Age</th>
<th>(\alpha)</th>
<th>sd</th>
<th>n</th>
<th>F value</th>
<th>t value</th>
<th>Prob. (Conf. level)</th>
<th>Population comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>p</td>
<td>m</td>
<td>p</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>28</td>
<td>47.2</td>
<td>40.8</td>
<td>4.8</td>
<td>4.2</td>
<td>6</td>
<td>1.3</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>72.2</td>
<td>58.5</td>
<td>2.7</td>
<td>1.7</td>
<td>6</td>
<td>2.4</td>
<td>11.7</td>
</tr>
<tr>
<td>0.5</td>
<td>28</td>
<td>44.9</td>
<td>36.4</td>
<td>1.4</td>
<td>0.3</td>
<td>6</td>
<td>22.7</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>56.3</td>
<td>51.0</td>
<td>1.8</td>
<td>3.7</td>
<td>6</td>
<td>4.2</td>
<td>2.8</td>
</tr>
</tbody>
</table>
In A1,

\[
\sigma_c = \text{mean compressive strength}; \\
sd = \text{standard deviation}; \\
n = \text{number of samples} \\
p = \text{cement paste} \\
m = \text{mortar}
\]

For all the means compared (compressive strength and the adhesive strength), significant differences were found to exist between them.

Chapter 10

Conclusions and recommendations for further research

Conclusions

The character of the interfacial zones around aggregate particles in concrete, and their significance on the properties of concrete have been investigated. In this chapter, conclusions of the results of the research, and recommendations for further studies are presented.

The character of the portland cement paste-aggregate interfacial zone

The microstructural features of the transition zone between portland cement paste and aggregate particles in concrete are considerably different from those of the bulk matrix. The zone is less compact than the bulk matrix, with a higher proportion of calcium hydroxide. The calcium hydroxide crystals have a preferential orientation in such a way that their c-axes are nearly perpendicular to the surface of the aggregate. This texture of calcium hydroxide, however, does not occur at the vicinity of all aggregate particles; near some aggregate particles, there is virtually no calcium hydroxide.

A higher density of fractures and microcracks occurs at the interfacial zone than in the bulk matrix. Most of the fractures tend to run directly along the paste-aggregate interface and along the cleavage (weak) planes of the calcium hydroxide crystals. The cement hydration products at the vicinity of the aggregate particles are loosely bonded to one another and to the aggregate particles. Compared to the aggregate particles and the bulk cement paste, the hardness value of the interfacial layer is the lowest. It is also the most porous component of concrete. Thus, in normal concrete, the interfacial layer between the bulk cement paste and the aggregate particles can be considered as a 'weak link'. On the average, the interfacial zone is ≈ 50 μm thick and occupies about 30 to 50 % of the total volume of cement paste in concrete.

Microstructural development of the interfacial zone

The formation of the 'weak interfacial' region in ordinary portland cement concrete is the result of two effects: (i) micro-bleeding, which causes 'pockets' of water to be entrapped around the aggregate particles, and (ii) inefficient packing of the cement grains (≈ 10-30 μm average diameter) at the aggregate interface, otherwise known as the "wall effect", which causes less cement particles to come close to the surface of the aggregate. These two factors are the result of the nature of the fresh mix. Consequently after placement of concrete and at the onset of hardening, the region close to the aggregate surface is virtually devoid of cement grains but rather filled with water. This causes local micro-solution-filled pores (local regions of higher water-cement ratios) to occur in the vicinity of the aggregate particles. As hydration progresses, the voids in the transition zone are
not effectively filled with cementitious reaction products due to the nature of cement reaction process (the reaction products are deposited at the surface of the cement particles). This leads to the formation of a more open and porous paste than the bulk matrix. Also, owing to the higher water-cement ratio at the interface and the large number of pore spaces, transportation of Ca\(^{2+}\) ions from the bulk cement paste to the interfacial zone is easily facilitated. At the paste-aggregate interface, crystallization conditions are more favourable than in the bulk cement paste. Thus, in the vicinity of the aggregate particles, crystalline hydration products, consisting essentially of calcium hydroxide and ettringite are easily formed.

**The role of the interfacial zone on the water absorption and diffusion of ions and gases in concrete**

Although the interfacial zone in portland cement concrete is more porous than the bulk paste, this study shows that it plays a minor role in the absorption of water and the diffusion of ions and gases in concrete. Considering the range of water-cement ratios used in this study, it is evident that water absorption and diffusion of ions and gases in concrete are very much controlled by the bulk paste matrix which is the only continuous phase in concrete. The water absorption and the diffusion of ions and gases are influenced only to a minor extent by the porous interfacial zone.

**Influence of mineral additions on the portland cement paste-aggregate interfacial zone**

Good quality pozzolans such as fly ash, silica fume, and metakaolinite, and latent hydraulic binders such blast furnace slag can be used in conjunction with portland cement to improve the structure of the interfacial zone. Alternatively, composite cements, such as blast furnace slag cement (\(\approx 70\%\) by mass of slag) and fly ash cement (\(\approx 20\%\) by mass of fly ash) as is done already in The Netherlands may be used to ‘reinforce’ the weak structure of the paste-aggregate interfacial zone. The improvement of the interface results from (i) the improved particle packing of the cementitious components at the interface; (ii) the reduced surface bleeding and micro-bleeding at the interfacial region; and (iii) the ability of the pozzolans to react with calcium hydroxide at the interface to produce additional cement gel.

In general, the action of the pozzolans and blast furnace slag leads to the formation of a denser interface, with reduced quantity and decreased orientation of calcium hydroxide. There is also a decrease in the thickness of the interfacial zone. The decreased availability of calcium hydroxide at the interface is likely to be a major contribution to the reduced alkali-silica expansion observed with blended cements or cement with additions.

**Effect of addition of pozzolans on the transport of water and diffusion of ions in concrete**

Addition of pozzolans such as pulverised fly ash, silica fume, and thermally activated kaolin to portland cement as partial cement replacement inhibits the transport of aggressive agents in concrete. In particular:
(a) the rates of diffusion of Cl⁻, Na⁺ and K⁺ ions in concretes are minimized significantly;
(b) the rate of loss of water from concretes, and the water absorption rate of concretes are also remarkably reduced by use of the pozzolans.

These effects have been shown to be mainly due to improvement in the pore size distribution of the bulk matrix and only to a minor extent to the improvement of the interfacial zone. In general, the reduced rate of transport of water, vapour and ions increases the resistance (durability) of concrete against sulphate attack. It decreases the vulnerability of concrete towards the destructive alkali-aggregate reaction (in the case of concrete containing reactive aggregates), and it improves the protection of steel reinforcement against chloride penetration.

**Effect of the interfacial zone on the strength of mortars**

The adhesive strength of cement paste to aggregates varies depending on the character of the interfacial zone and the type of aggregate used. For a more open or porous interfacial zone as in the case of mixes with high water-cement ratios, the adhesive strength of cement pastes to aggregate is low and vice versa. It also increases as the hardening period increases, because as cement hydrations progresses the porosity of the interfacial zone and the bulk paste matrix decrease. This increases the adhesive strength of the paste to aggregate particles.

The study also shows that for the same age, and with the same water-cement ratio, ordinary portland cement pastes have higher compressive strengths than their corresponding mortars. This effect is observable for all the mixes regardless of the fact that the sand particles are considerably stronger than the cement pastes.

The decrease in adhesive strength of cement pastes to aggregates with increasing water-cement ratio is ascribed to interfacial effects, namely, the heterogeneity and microstructural defects of the interfacial layer (higher density of microcracks, higher amounts of oriented calcium hydroxide, loosely-bonded cement hydration products, and the associated higher micro-porosity). The same effects are regarded likely to contribute to the lower compressive strength values of the mortars compared to the cement pastes.

**Effect of addition of pozzolans on the paste-aggregate interfacial zone in relationship to the strength of mortars**

Addition of silica fume and metakaolinite increases significantly, the compressive strength of mortars, and the adhesive strength of cement pastes to aggregates. Silica fume and metakaolinite addition, however, do not show the same strengthening effects in portland cement pastes, at least for the water-binder ratios used, and the dosages of silica fume and metakaolinite considered in this study. On the basis of the results obtained, it is believed that these improvements are likely to be due to the decrease in thickness of the interfacial zone and the better stress transfer between matrix and aggregate particles.
Recommendations for further research

Structural development of the interfacial zone

It is recommended that further research be carried out to explore the mechanism of adhesion of hydrates to the aggregate particles and in particular, the mechanism of "duplex" forming and the preferential orientation of the calcium hydroxide at the interfacial zone. A study based on the thermodynamics of crystal growth and adhesion to aggregate particles from measurements of surface energies of aggregates and hydrates may be helpful. Consideration should also be given to the direction of casting.

One of the objectives of the study was to investigate the origin, causes, and factors leading to the formation of the weak interfacial regions in concrete. The results of the research has provided insight into the nature of the interfacial zone and its effects on concrete. These findings apply to normalweight concrete, that is, concrete prepared with normalweight aggregates. Currently, there is a great deal of interest in producing high-performance concrete systems containing lightweight aggregates or other more porous aggregates such as aggregates made from demolished concrete. It is recommended that the present investigation be extended to cover concretes containing these aggregates. A study using backscattered electron imaging combined with quantitative image analysis may be useful in characterizing the microstructure of the interface.

Also, in this thesis, the role of the cement paste-aggregate interfacial zone on the absorption of water and the diffusion of ions and gases in concrete was studied on specimens not subjected to loading. It is generally known that when concrete is subjected to load, cracks initiate and propagate owing to the high tensile stress concentrations in the specimen (produced by interactions between the aggregate particles and voids). The amount of cracks produced tends to increase as the load increases. Thus, under conditions of loading, it is likely that some of the cracks that initiate at the aggregate interfaces may merge into one another. This is likely to affect the absorption of water and the diffusion of ions and gases in concrete. It is recommended that further studies be pursued to examine the role of the interfacial zone on the permeability of concrete in general.

Methods of improving the paste-aggregate interfacial zone

It is recommended that further studies be pursued to explore the use of other additions, such as polymer dispersions, ion-exchange resins, water glass, etc. to improve the structure of the interfacial zone and bonding of pastes to aggregate particles. A study involving the use of water-soluble polymers and polymer dispersions in combination with mineral additions and portland cement is also recommended. In addition, it is suggested that further investigations on the effect of MICRO- interfacial zone improvement on the MACRO- improvement of the properties of concrete be carried out.
Appendix

List of symbols and abbreviations

a
a/c
a/s
AFt
ASTM
B.E.T. value

Blaine fineness

\( c \)
\( C_a \)
\( C_b \)

CH
C\(_3\)A
C\(_4\)AF

C\(_2\)S
C\(_3\)S

C-S-H gel

C/S
Class F fly ash

\( \delta \)
\( D_1 \)
EDAX
EPMA

E\(_a\)
E\(_m\)
f.a.
f\(_u\)

H\(_v\)
I\(_{CH}\)

ICP (ICAP)

L.O.I.
m/m

Aggregate
Aggregate-cement ratio
Aggregate-binder (solids) ratio
Ettringite: \( \text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_2.25\text{H}_2\text{O} \)
American Society for Testing Materials
Specific surface measured with the apparatus of Brunauer, Emmett and Teller (The nitrogen adsorption technique)
Specific surface measured with the Blaine apparatus (via the air flow through standard compacted powder) cement
Concentration of solution A (m moles/liter)
Concentration of solution B (m moles/liter)
Calcium hydroxide, \( \text{Ca(OH)}_2 \)
Tricalcium aluminate: \( 3\text{CaO}\cdot\text{Al}_2\text{O}_3 \)
Tetracalcium aluminoferrite: \( 4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3 \)
Dicalcium silicate: \( 2\text{CaO}\cdot\text{SiO}_2 \)
Tricalcium silicate: \( 3\text{CaO}\cdot\text{SiO}_2 \)
Calcium-silica-hydrate (amorphous or semi-crystalline of varying stoichiometries)
CaO/\( \text{SiO}_2 \) molar ratio
Fly ash with a low calcium content (originating from combustion of bituminous coal)
Thickness of the interfacial zone
Diffusion coefficient
Energy dispersive X-ray analyzer
Electron probe micro-analysis
Static modulus of elasticity of aggregate
Static modulus of elasticity of matrix
Fly ash
Ultimate compressive strength
Microhardness value
Orientation index of calcium hydroxide crystals
Inductive coupled (argon) plasma spectrometry
Loss on ignition
Mass by mass
MK
M_{sat}

Mullite
opc
OPCM
OPCP
pbfrc
pfa
Portlandite
psd
Q
R.H.
RHPC
e
RHPCM
RHPCMP

RHPCP
s
S_{ab}
s.d.
s.f.; sf
SEM

\sigma_c
\tau
V; v
w
w/c; w-c
w/s; w-s
XRD

Metakaolinite
Mass of saturated surface-dried specimen
Al_2Si_2O_5
Ordinary portland cement
Ordinary portland cement mortar
Ordinary portland cement 'mortar paste'
Ordinary portland cement paste
Portland blast furnace slag cement
Pulverised fuel ash
Calcium hydroxide, Ca(OH)_2
Particle size distribution
Quantity of water absorbed
Relative humidity (%)
Rapid hardening portland cement
Rapid hardening portland cement mortar
Rapid hardening portland cement
'mortar paste'
Rapid hardening portland cement paste
Sand; solids; binder; seconds
Water absorptivity
Standard deviation
Silica fume
Scanning electron microscopy
(microscope)
Compressive strength
Time
Volume
Water
Water-cement ratio
Water-binder (solids) ratio
X-ray diffractometry (diffractometer)
Curriculum vitae

Joseph Aduamoah Larbi was born on September 23, 1954 at Boso in Ghana. He took his primary school education at his hometown, and his high school education at Asamankese Secondary School and Pope John's College, Koforidua. In 1982, he obtained his B.Sc. (Eng.) Honours Degree in Geological Engineering from the University of Science and Technology, Kumasi, Ghana. From 1982 to 1984, Mr. Larbi worked on a full-time basis as a research and teaching assistant at the Faculty of Engineering, University of Science and Technology, and on a part-time basis as a research assistant at the Geotechnical and Construction Materials Division of the Building and Road Research Institute, Kumasi, Ghana. From September 1984 to August 1985, he followed a Postgraduate Diploma course in Materials Evaluation and Exploration Geochemistry at ITC-TU Delft, from which he earned a diploma with honours. In September 1985, he proceeded to Canada to pursue further studies. In September 1987, he was awarded the degree of Master of Applied Science (M.A.Sc., Geological Engineering) from the Faculty of Engineering, University of Windsor, Ontario. His area of specialization was Durability of Construction Materials, and for his masters thesis, Mr. Larbi developed a new method for screening potentially reactive aggregates in concrete as well as treatment techniques for reducing alkali-aggregate reactivity in concrete. During the period of his study at University of Windsor, he worked as a research and teaching assistant in engineering geology and durability of construction materials. Since October 1987, he has been employed at the Department of Mechanics and Structures of the Faculty of Civil Engineering, Technical University of Delft as a research assistant.