Cement and Concrete Research 79 (2016) 243–256

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Microstructural characterization of ITZ in blended cement concretes and its relation to transport properties

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ARTICLE INFO

Article history:
Received 16 February 2015
Accepted 23 September 2015
Available online 23 October 2015

Keywords:
ITZ (B)
Blended cement (D)
Aggregate (D)
Characterization (B)
Transport properties (C)

ABSTRACT

The improvements in the overall performances of concrete with blended materials were often ascribed to the modification of its hardened paste in general. In this paper, the effects of limestone filler (LF) and slag (GGBS) on chloride migration and water absorption of concretes with systematically varied aggregate properties were evaluated from the view point of ITZ by using BSE image, EDS, and MIP analysis. It was found that the incorporation of moderate amount of LF and GGBS would compact the microstructure of both ITZ and bulk cement matrix. The reduction in the pore volume (>100 nm) contributes to the largest decrease in total porosity. Additionally, incorporating GGBS avoids the build-up of $Ca(OH)_2$ within ITZ and provides a more uniform microstructure. The mechanism for the improvement in limiting water and ions penetration was found to be mainly related to the densification of bulk cement matrix rather than the modification of ITZ.

1. Introduction

The interfacial transition zone (ITZ) is the region surrounding each aggregate particle, where the microstructure is modified by the presence of aggregate. The origin of ITZ lies in the so-called "wall effect," by the packing of the anhydrous cement grains against the relatively flat aggregate surface [1]. As a result of the anhydrous distribution, there is an increase in the amount of porosity in ITZ [2–4]. The microstructural features can be described by the sequence of its development from the time concrete is placed as follows [5–7]: (i) in freshly compacted concrete, water films form around the large aggregate particles. This would account for a higher water to cement ratio closer to the aggregate than away from it; (ii) in the same way as in the bulk cement matrix, calcium, sulfate, hydroxyl, and aluminate ions are produced by the dissolution of calcium sulfate and calcium aluminate compounds and are then combined to form ettringite and calcium hydroxide (CH). Owing to the higher water to cement ratio, these products in the vicinity consist of relatively larger crystals. Therefore, they form a more porous framework than in the bulk cement matrix; (iii) with the progress of hydration, poor crystalline C-S-H, and a second generation of smaller crystals of ettringite and CH start filling the empty space that exists between the framework created by the large ettringite and CH crystals. Higher porosity and orientation deposition of crystals, and fewer cement particles than in the bulk cement matrix characterize ITZ as the weakest link in the cement-based composites [1,5,8], and should be taken as an important consideration for the investigation of overall performances.

Extensive studies have highlighted the distinguishing microstructure of ITZ and its role on transport properties. It has been stated that the bigger the difference between the strengths of the ITZ and the surrounding matrix, the higher the tendency of micro-cracking in the ITZ [9,10]. In special cement composites where very excellent properties are needed, methods of modifying the ITZ play a very crucial role [10]. From a transport point of view, Breton et al. [11] pointed out that the effective diffusion coefficient of chloride ion is 6–12 times greater in the ITZ than in the bulk cement matrix. Therefore, it is necessary to impose some efforts to improve the quality of this weak region.

Based on the microstructural features, modification of ITZ can be achieved by using a finer cementitious material, pozzolanic materials, superplasticizer, and advanced mixing procedure [12–17]. These processes can be chiefly classified into two main types: (i) coating aggregate surfaces with some chemical reagents or polymers before mixing [18,19]. However, the pre-treatment process before concrete production will lead to a higher cost, and the practical potential may be limited; (ii) using mineral admixtures such as silica fume, fly ash, metakaolin for partial replacement of cement. Such materials participate in the particle packing, latent-hydraulic reaction and pozzolanic reactions which continue to densify the ITZ. Moreover, the fine particles can also act as growth nuclei for multiple generations of CH crystals which therefore have smaller size.

As indicated in literature, silica fume is a highly effective admixture for improvement of concrete properties, which can be due to the enhancement of ITZ [18,20–23]. Very fine silica fume particles are able

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http://dx.doi.org/10.1016/j.cemconres.2015.09.018
0008-8846/

to act as micro-filler and nucleation sites for crystallization of hydration products, leading to the formation of small crystals of CH and a reduced tendency for preferred orientation [21,22]. In addition, pozzolanic reaction between silica fume and CH increases ITZ density [23]. Rossignolo [21] has shown that the usage of 10% of silica fume caused a reduction of 36% in the ITZ thickness, in relation to the reference concrete. It was also observed that addition of silica fume increased interfacial bond strength and interfacial fracture energy by about 100% [24]. In addition to silica fume, the other blended materials used for improving the microstructure of ITZ normally involve metakaolin [25,26], fly ash [14,15,27], and rice husk ash [28].

Ground granulated blast-furnace slag (GGBS), which mainly contains calcium silicoaluminate with high reactivity [29], is a glassy by-product of blast furnace iron making. Generally, incorporating GGBS into blended binders can increase total porosity but refine the pore size [29–33]. The pore refinement by GGBS is attributed to the filling effect at macro-scale and to the latent-hydraulic property and pozzolanic reaction at micro-scale [29,32]. The beneficial effect of GGBS on pore refinement can improve the performance of materials, such as freezing action, carbonation, sulfate attack, gas penetration, chloride migration, and reinforcement bar corrosion [34–37]. Previous researches on the concrete containing GGBS have been conducted mainly with focus on the overall properties or on the properties of the pure cement paste. However, very limited information has been given with respect to the improvement of the weak ITZ region through using GGBS.

Incorporating GGBS in binary blends to improve the performance of concrete may have associated limitations with its use, such as early age strength and extended curing periods [37–39]. The use of appropriately proportioned ternary blends allows the effects of one powder to compensate for the inherent shortcomings of another. Among them, limestone filler (LF) is one of the potential materials which can offset the negative effects of GGBS especially on early age [38,40,41]. In general, LF improves the hydration rate of cement compounds and consequently increases the strength at early ages [42,43]. The main effects of LF are of physical nature which can cause a better packing of cement granular skeleton and a larger dispersion of cement grains. LF can also act as the crystallization nucleus for the precipitation of CH [40,44]. LF does not have pozzolanic properties, but it can react with the alumina phases to form calcium monocarboaluminate hydrate with no significant changes on the strength [44–46].

From the above description, it can be inferred that LF possesses the potential to alter the microstructure of ITZ by changing the initial particle packing and facilitating the formation of smaller CH crystals with less crystallization tendency in preferential orientations. However, no quantitative information has been given in this respect. Moreover, the development of ternary blends, associating Portland cement, LF, and GGBS, could be an alternative to modify the properties of ITZ by combining their beneficial effects, respectively. Previous investigations have shown the advantages of such ternary blends for the overall properties of concretes and pastes [38,40,41]. More investigation needs to be done to further understand the effect of GGBS and LF on the ITZ microstructure and its relation to the transport properties. Additionally, it is not clear whether improvement in properties of concrete containing blended binders are due principally to the enhanced ITZ or due to the densification of bulk cement matrix itself.

In order to address these questions, the ITZ microstructure in blended cement concretes were characterized by using a quantitative BSE image analysis and mercury intrusion porosimetry (MIP). The effects of GGBS and LF on chloride migration and water absorption of pastes and concretes with systematically varied aggregate volume content and grain size were also investigated. Additionally, the changes in overall performances due to the presence of GGBS and LF were linked to the variations in the corresponding ITZ microstructure.

2. Experimental

2.1. Materials

The cement used in this study was CEM I 52.5 N, and the blended materials involved slag (GGBS) and limestone filler (LF). The oxide composition and physical characteristics of these materials are given in Table 1. As the fineness is an important parameter for particle packing of binders, the particle size distribution curves of the materials were measured by the laser diffraction method (Mastersizer 2000) and are given in Fig. 1. In order to determine the effect of aggregate on ITZ microstructure and overall performance, sand (0/2 mm), gravel (1/5.6 mm and 1/8 mm) were employed and mixed as three size fraction. The sieve analysis of aggregates is given in Fig. 2, and the maximum size of 8 mm was employed to minimize the bleeding effect.

2.2. Mix design and sample preparation

Eight series of specimens were prepared in relation to the type and replacement levels of the blended materials. The percentage of different blended materials in each series is given in Table 2. For each series, samples with systematically varied aggregate volume content and grain size, hence, varied proportions of ITZs, were prepared (in Table 3). The mixtures are named "S**L**-Y" where "**" gives the substitution levels (C refers to the reference samples, "S" refers to slag, "L" refers to limestone filler), "Y" gives aggregate volume content and size features, "P" refers to neat paste. For instance, S60L10-4 corresponds to the binder containing 30% of OPC, 60% GGBS and 10% LF, and the volume fraction of aggregate 0/2 mm and 1/8 mm is 0.2 and 0.35, respectively. Finally, this study comprises:

i) A control series of Portland cement-based samples and seven blended compositions prepared with binary and ternary binders.
ii) For each series, five samples were prepared by varying the aggregate volume content and aggregate size systematically.

All mixtures were prepared with a water to binder (w/b) ratio of 0.45. The 24 h water absorption value which bring the aggregate to saturated and surface-dry condition was 0.9%, 1.1%, and 1.1% for aggregate 0/2 mm, 1/5.6 and 1/8 mm, respectively. Since the aggregate was predried before mixing, the amount of water needed to saturate it was calculated and added to the mixtures. For each mix, a number of $150 \times 150 \times 150$ mm^3 cubes were cast and placed with vibration. The intensity and duration of the vibration was adjusted according to the workability of each mix. Full compaction was considered to have been achieved when no significant amount of air bubbles escaped the top surface. All the samples were demolded after 24 h and then stored in the chamber with a constant temperature of 20 ± 2 °C and a relatively

Table 1
Chemical compositions and physical characteristics of cement, slag and limestone filler.

Composition	OPC	GGBS	LF
	Weight (% by mass)		
CaO	63.12	40.10	–
SiO_2	18.73	35.40	0.80
Al_2O_3	4.94	11.25	0.17
MgO	1.02	7.82	0.50
Fe_2O_3	3.99	0.89	–
SO_3	3.07	0.61	–
Na_2O	0.73	0.33	–
K_2O	0.47	0.62	–
$CaCO_3$	-	-	98.00
Loss on ignition (LOI, %)	2.12	0.31	43.90
Blaine fineness (m^2/kg)	353	410	753
Specific density (kg/m^3)	3092	2890	2676
Median particle size (μm)	15.7	12.5	9.4