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Increase of bond strength at interfacial transition zone by the use of fly ash

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Abstract

The effects of the addition of silica powder, silica fume, fly ash, and hemihydrated gypsum to the interface of new-to-old paste on the enhancement of bond strength were investigated experimentally. Seven-day bond strengths for the specimens with pozzolanic materials added to the interfacial zone, except for silica powder addition, were slightly smaller than that for control without any additives, whereas the strength of all specimens with added pozzolanic materials were higher than that of the control at 28 days. It was suggested that increased effect of the bond strength at interfacial zone depended on the SiO₂ and CaO contents in the additives; higher SiO₂ and/or lower CaO contents were preferred. On the other hand, when a high CaO content fly ash was coated to the interface with some amount of hemihydrated gypsum, the bond strength enhanced significantly at 7 days, as well as at 28 days. This result suggests that the structure of the interfacial zone can be modified sufficiently by controlling the chemical components of the additives; even the use of fly ashes consisted of relatively high CaO and low SiO₂. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Interfacial transition zone; Bond strength; Fly ash; Pozzolan; Sulfate

1. Introduction

It is well known that the transition zone forms at the paste side between paste and aggregate or steel bar [1], and several microstructural models have been proposed [2-5]. Many researchers have focused on the transition zone between normal aggregate and paste and have reported that the transition zone possesses more porous structure than the bulk paste and the thickness is observed in a range about 20 to 100 µm, which depends on the characteristics of the surface in contact with fresh paste, water/cement ratio, chemical compositions, and so on. The formation of relatively large hexagonal calcium hydrate crystals and their orientation at the interface were considered to be very important to the characteristics of the zone [5–8]. Similar structures (but denser and/or thinner than those by normal aggregates) were also reported qualitatively at the interfaces of paste—some porous materials such as hardened concrete and some kinds of lightweight aggregate—even though those materials where a fresh paste was contacted can easily absorb free water [9,10].

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Modification of the microstructure in the transition zone has been one of great concern since durability, permeability, and strength of concrete are significantly influenced. Replacement of cement constituents with several pozzolanic materials, addition of some organic polymer, and reduction of thickness of water film by adding detergents have been investigated as modification methods [11–13]. In particular, many researchers reported the use of silica fume to be effective in densifying the transition zone structure because of a microfiller effect due to relatively fine particles and prevention from growing calcium hydrate crystals [14-16]. On the other hand, a large amount of fly ash has been generated at energy plants that use coal as by-product and is also available as an alternative to pozzolanic additives. However, the effect may be significantly dependent on the chemical and physical characteristics derived from coal types and combustion methods [17–19].

In this study, some fly ashes were coated on a base material with a fresh paste cast on it and the effects on the enhancement of the bond strength at the interface to the paste were investigated experimentally. The results were compared with work using some other pozzolanic materials (silica powder and silica fume). A more effective method employing the use of fly ash with another external additive for the bond enhancement was also investigated.

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2. Methods

2.1. Materials

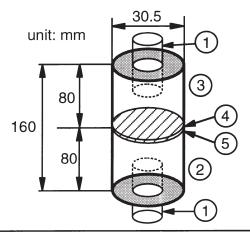
An ordinary Portland cement was used in this study. The materials added to the interfacial zone were three different fly ashes (FA1 to 3), silica fume (SF), silica powder (SP), and hemihydrated gypsum (HHG). The fly ashes were obtained from two kinds of combustors, a pulverized coal combustor and an atmospheric fluidized bed combustor. Different coals were used in each combustor. HHG was reagent grade (Wako Pure Chemical Ind. Ltd., Osaka, Japan). Silica powder for cosmetic productions was manufactured by a membrane emulsification method. The SF was a conventional by-product. The particle size distribution of these materials were determined by a centrifugal particle size distribution analyzer (SA-CP4L, Shimadzu Co., Kyoto, Japan). The Brunauer-Emmett-Teller (BET) surface area based on nitrogen adsorption was measured by using ASAP-2000 (Micromeritics Co., Norcross, GA, USA).

2.2. Testing procedures

A base material with or without coating of some additives had a fresh paste cast on the surface. A hardened cement paste was used as the base material. It was fabricated as follows: fresh cement paste (0.38 of water-cement mass ratio) was filled into a plastic pipe mould (30 mm in diameter and 80 mm in height) and a bolt was inserted at an axial center of the mould to join the testing machine. The specimen was cured in room temperature for 1 day and then in water at 20°C for 28 days. Subsequent curing was done in laboratory room air for more than a week.

The additives to coat the base material surface were prepared constantly with 0.38 of water-solid (cement and added material) mass ratio and 0.43 mass ratio of added material to Portland cement (with some exceptions).

To determine the bond strength, a direct tensile strength test was conducted. The schematic diagram of the specimen made up for the tensile test is shown in Fig. 1. The specimen was prepared as follows: the hardened cement paste surface in contact with the additives was polished with waterproof abrasive paper (#1200) to eliminate the effect of different surface roughness. A plastic pipe mould (30 mm in diameter and 80 mm in height) was set up on the mould of the base material with polished surface and sealed between the moulds with a silicon grease. The prepared paste containing the additives, mentioned above, was coated on the polished contact surface of the base material with a thickness of about a few hundred micrometers, and then a fresh cement paste with 0.38 of water-cement mass ratio was used to fill in the plastic mould immediately. A bolt was inserted into the end of specimen along the central axis to join it to a special mounting device of the testing machine. Subsequently, one set of the specimens (Fig. 1) was cured for 1 day at 20°C in laboratory air and cured in water at 20°C up to predetermined ages (7 or 28 days). Specimens without any ad-



bolt (16 or 8mm dia., used for connection to tension machine), 2. old hardened cement paste, 3. new hardened cement paste,
 coating layer of additives 5. interface

Fig. 1. Schematic diagram of the specimen.

ditives between the base material and the fresh paste were also fabricated for control experiments. Three to five specimens were tested for each prepared condition to observe the reproducibility.

The analysis of whether the structure of new-to-old paste interface in this study was similar to the transition zone formed at normal aggregate-paste interface was not carried out by conventional methods such as scanning electron miscroscopy and X-ray diffraction. However, the author surmised that the transition zone was more or less formed from the following reasons: (1) some researchers using hardened concrete and lightweight aggregates as a base materials, which were capable of absorbing water easily, reported the orientation of Poltlandite and high Ca concentration in the vicinity of the interface to paste [9,10]; and (2) the new-to-old paste interface was very weak based on the experimental facts that specimens with new-to-old paste interface always fractured just at the interface in tensile test of this investigation.

3. Results and discussion

3.1. Characteristics of materials used

The chemical compositions of the materials used as additives are listed in Table 1. The BET surface area and the mean particle diameter are listed in Table 2. The particle size distribution is also shown in Fig. 2. Silica powder had the largest BET surface area and its particle size distribution was less than 3 to 5 μm . The SF had a relatively wide particle size distribution, from less than 0.3 to 30 μm . A part of the particles might be agglomerated with each other. The fly ashes used were almost similar in relation to the surface area and the particle size distribution, while the chemical components were significantly different.

Table 1 Chemical components of ordinary Portland cement and materials used

	SiO_2	Al_2O_3	Fe_2O_3	Na ₂ O	CaO	MgO	K ₂ O	SO ₃
OPC	21.3	5.1	2.8	0.37	64.6	1.5	0.43	2.0
SP	99.9	-	-	_	_	_	_	-
SF	92.2	0.61	0.75	0.5	0.24	1.28	1.0	0
FA1	35.9	19.2	1.1	0.85	25.5	1.0	0.49	7.9
FA2	46.0	19.8	2.34	0.31	22.0	0.72	_	4.0
FA3	38.4	34.7	4.25	1.71	10.0	1.66	_	4.54
HHG	_	_	_	-	38.6	_	55.2	-

3.2. Failure modes of specimens tested

In the tensile tests, failures occurred in three different regions: (A) at the interface between the base material and the coating zone (or paste in the case of control specimens); (B) within the coating zone partly through the interface to the base material; or (C) in the old hardened paste. The fracture mode C always occurred at the cross section across the tip of the bolt inserted to join the tension machine. Therefore, the real bond strength for the specimen with failure C was higher than observed values. A wide variety of test configurations were used to determine the aggregate-cement bond strength [20]. Unfortunately, a favorable standard method has not been developed yet. It was possible to compare the effect of the additives on the bond strength, although the simple tensile test in this study did not always measure the real bond strength at or around the interface.

Most of the specimens were made up under the same experimental condition and were fractured at the same fracture mode; their tensile strengths were measured within an error range of no more than 10%, with some exceptions due to failures in the fabrication step and/or setting to the tension machine.

3.3. Effect of the addition of pozzolanic materials on the bond strength

The tensile strength for the specimens with various kinds of pozzolanic materials added to the interface is shown in Fig. 3. The results of the control specimen without any additives to the interface are also shown. At 7 days of curing time, with exception of the case of SP addition, the tensile strength of the specimens with added pozzolanic materials

Table 2
BET surface area and mean particle diameter of materials used

	Ordinary Portland cement	SP	SF	FA1	FA2	FA3	HHG
BET surface area (m²/g) D ₅₀ (μm)	0.866ª 18.4	303.8	19.46 3.9	3.79 9.1	10.58 10.6	_	3.39

^aBlaine specific surface area was 3290 cm²/g.

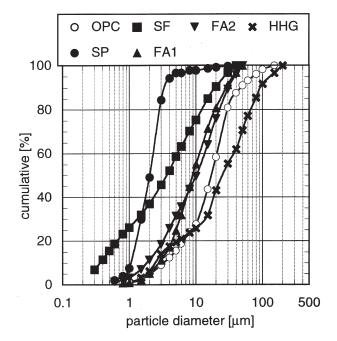


Fig. 2. Particle size distributions of the materials employed.

was less than that of the control, whereas the strength of the all specimens exceeded that of the control at 28 days. The fracture at 7 days was mode A or B, and then changed mode C at 28 days, with the exceptions of FA2 and FA3. Many researchers have reported that the appearance of the strength was slowed in the early curing period by adding pozzolanic materials such as SF and fly ash, because the overall poz-

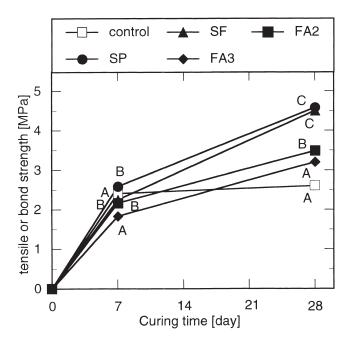


Fig. 3. Effect of addition of pozzolanic materials to the interface.

zolanic reaction was slow. However, the strength was enhanced, exceeding the reaction by a large amount within a few weeks. Some pozzolanic materials are known to behave as nucleation sites for crystallization of hydrated products and lead to formation of small crystals of calcium hydroxide and reduction of preferred orientation. In addition, the pozzolanic reaction with calcium hydroxide might reduce the content of calcium hydroxide in the transition zone and increase the density of this layer [1,14]. The present results seem to follow the previous findings. The higher strength of SP than that of the control at 7 days was caused by the mi-

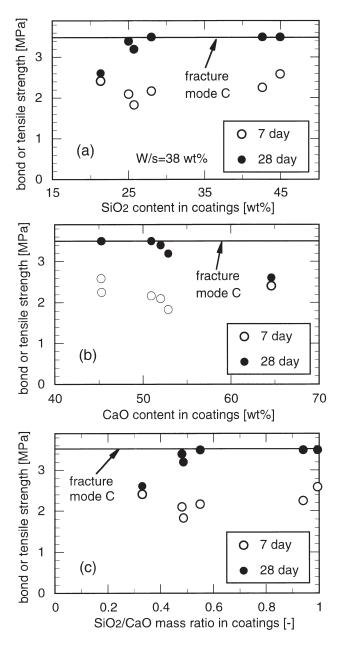


Fig. 4. Effect of SiO_2 and CaO contents in the coatings on bond strength: (a) SiO_2 content in coating vs. strength, (b) CaO content in coatings vs. strengths, and (c) effect of SiO_2/CaO mass ratio on strength.

crofiller effect and relatively high reaction rate, which depended on the large surface area, because the silica powder used in this study had the smallest particle size (see Fig. 2 and Table 2).

Figs. 4a, b, and c show the effect of SiO₂ and CaO contents in the coatings on the strength both at 7 and 28 days of curing time. The obvious dependence on SiO₂ and CaO contents was not observed for the tensile strength at 7 days of curing time. However, the bond strength at 28 days was enhanced with an increase in SiO₂ content and with an decrease in CaO content. The failure reached to mode C when the SiO₂/CaO mass ratio in the coatings was over about 0.55. This result indicates that chemical composition such as SiO₂ and CaO in the vicinity of the interface is one of the major factors for the increase in bond strength.

3.4. Effect of water content on bond strength

Fig. 5 shows the effect of water content in the coating on bond strength, with the result of SP presented as a typical example. The enhancement effect on the strength was lowered with an increase in the water content. In the case of 0.62 water/solid mass ratio, the failure of the specimen occurred at the region from the base material-coating interface through the coating zone (failure mode B), while mode C was observed in the case of 0.38 water/solid mass ratio. This result suggests that higher water content around the interfacial zone prevented its porous structure from densifying and that the reactivity of silica with calcium hydroxide might be lowered. Carles-Gibergues et al. [9] reported that excess water existing within the transition zone resulted in more free space available for large oriented Portlandite crystals. Thus, low water content of the coating was preferred for enhancement of the bond at the interface.

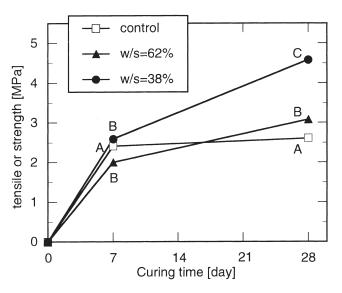


Fig. 5. Influence of water content in the coating on bond strength in the case of SP addition.

3.5. More effective improvement approach by using low-grade pozzolana addition

In Fig. 4, it was indicated that the addition of silica powder or SF was more effective than that of fly ashes in improving the interfacial zone structure. Other research has also reported this [15]. One of the reasons seemed to be the dependence of SiO₂ and CaO contents (see Fig. 4). However, fly ash might become effective for strength increase by addition of other materials, which participate with some reactions to increase strength. This may contribute to the extent of use of fly ash. Addition of some amount of sulfate with fly ash was investigated for this purpose.

Fig. 6 shows the effect of HHG addition with fly ash (FA2) to the interface on the strength at 7 and 28 days of the curing time (named FA4 in this figure). FA4 was prepared by mixing both fly ash (FA2) and HHG (0.11 of HHG/FA2 mass ratio and 0.43 of mass ratio of FA2 plus HHG to cement) as a coating. As can be seen in this figure, a significant improvement was observed for FA4. The failure already occurred in the base material (failure mode C) at 7 days of curing, while the specimens without the addition of the HHG, FA2 and control, fractured at the interface or within the coating zone (failure mode A or B). Moreover, the strength also increased at 28 days, compared with that of FA2 as well as the control. The obtained result of FA4 was comparable to that with the addition of SP or SF. This was caused by some chemical interaction with the paste, HHG, and components of fly ash. It was reported that sulfate ion influenced hydration of C₃A depending on the rate of crystallization of ettringite [9]. That research on the interface

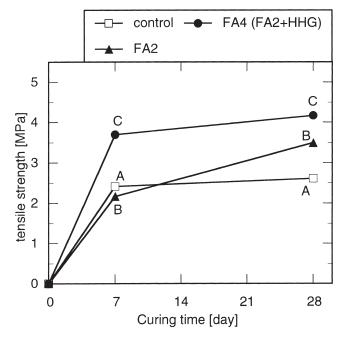


Fig. 6. Change of failure mode and strength by the use of an additive containing both fly ash and HHG.

between paste and hardened concrete suggested that when ettringite filled the porosity within the transition zone, there was less space available for the crystallization of large oriented calcium hydroxide crystals. Furthermore, HHG tended to dissolve faster than gypsum to form ettringite [9]. Some researchers also indicated that splitting and compressive strengths were increased by utilizing mixtures of fly ash and gypsum or sulfate due to promotion of the formation of cementitous materials [21-23]. Therefore, according to their findings, the result in this study seemed to arise from this highly reactive HHG with C₃A, although the analysis of the change of chemical constituent at the interface was not carried out in the present stage. Fly ash that had low SiO₂ and high CaO contents itself was able to be used as a most effective admixture by the simultaneous addition of some materials such as HHG by some fraction.

This is a preliminary study on the effect of the chemical composition change of the additives using fly ashes on the improvement of interfacial zone based on the bond strength point of view. The detail structural change around the interface by this method, the strength at long curing time, and the effect of some other components in fly ash need to be investigated in the next step. In addition, the application to a normal aggregate-paste interface should also be investigated.

4. Conclusions

In this investigation, the following results were obtained.

- The degree of the increase of the bond strength was influenced by water content and SiO₂/CaO mass ratio of the coatings on the interface. Higher SiO₂ and lower CaO contents of the additives were preferred in this experimental range. The bond strength increased with an increase in the curing time.
- 2. The bond strength was enhanced significantly at 7 days, as well as at 28 days, when a high CaO content fly ash was added to the interfacial zone with some amount of HHG. This result indicated that the structure of interfacial zone was able to be modified sufficiently by controlling the chemical components of the additives; even the use of fly ashes consisted of relatively high CaO and low SiO₂.

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