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Effects of Polyvinyl Alcohol on Aggregate-Paste Bond Strength and the Interfacial Transition Zone

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Small amounts of polyvinyl alcohol (PVA) were added to cement paste in an attempt to increase the aggregate-paste bond strength. Specimens consisted of ordinary Portland cement mixed with PVA/water solutions and cast against ground surfaces of limestone and granite. The aggregate-paste bond strength after curing was tested in a wet state by three-point bending. The morphology of the interfacial transition zone was observed with scanning electron microscopy, and the composition was analyzed with infrared spectroscopy. The addition of 1.4 wt% PVA based on the mass of cement increased the strength for both limestone-paste and granite-paste bonds. The strength increase was about five-fold for limestone and nearly two-fold for granite. The failure mode also changed, from pure adhesive failure without PVA to cohesive failure of the aggregate with limestone and to a mixed cohesive failure of the paste and adhesive failure with granite. The gain in bond strength with the addition of PVA seems to arise from suppression of the porous interfacial transition zone and an inhibition of calcium hydroxide nucleation on the aggregate surface. ADVANCED CEMENT BASED MATERIALS 1998, 8, 66–76. *© 1998 Elsevier Science Ltd.*

KEY WORDS: Bond strength, Hardened cement paste, Interfacial transition zone

The bond between coarse aggregate and cement paste is known to be the weakest region in ordinary concrete. This bond fails first upon loading, initiating fracture of the concrete [1–3]. The weakness of the bond is attributed to the presence between the aggregate and cement paste of an interfacial transition zone, which is a porous calcium hydroxide-rich layer. The thickness of the interfacial transition zone is approximately 50 μm [4–9].

One means of strengthening the aggregate-paste bond is to add fine particles, such as silica fume [7,8] and polymer dispersions [10–13]. These particles are able to fit between the cement grains and densify the porosity of the zone. These materials need to be used at the level of 10–20% based on cement to be effective, and at that rate, they can add considerably to the cost. In addition, there can be handling problems, as with the silica fume [7]. However, the admixing of a small amount of water-soluble polyvinyl alcohol (PVA) was recently reported to have doubled the pullout strength and friction of steel fibers in cement paste [14]. The microstructure of the interfacial transition zone around steel fiber was found to have been considerably altered by PVA [15].

In the present study, small amounts of PVA in aqueous solution were added to cement paste to ascertain its effect on the bond strength between the paste and aggregate. The effects of PVA on the microstructure and the chemical composition of the interfacial transition zone between aggregate and cement paste were also studied.

Experimental Methods

Materials

The cement used was a commercial ASTM type I ordinary Portland cement. The PVA used was Airvol 805 (Air Products and Chemicals Inc., Allentown, Pennsylvania, USA), which was 87–89% hydrolyzed polyvinyl acetate in granular form. Its molar mass was relatively low: 31,000–50,000 weight average, 15,000–27,000 number average. Airvol 805 is a low foaming grade.

The limestone used was obtained from Stoneco, Inc., from the Ottawa Lake quarry (Ottawa Lake, Michigan, USA). The granite used was from Italy. It was medium grained and light gray in color.

Specimen Preparation

PVA powder was dispersed in cold water at a concentration of 16%, and this mixture was heated to 90°C with stirring to completely dissolve the PVA. The PVA

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solution was cooled to room temperature and diluted with water to the desired concentrations (1%, 2%, 3%, or 4%).

The limestone specimens were made in groups of four; the granite specimens were made individually. The limestone was cut into 25 mm × 102 mm × 13 mm (1 inch × 4 inch × 0.5 inch) blocks, which were immersed in water for 2 days to become completely soaked. The surfaces of the wet limestone blocks were ground with no. 400 silicon carbide paper, to minimize the effect of mechanical interlocking on the cement-aggregate bond, and then dried in air for 5 hours before casting the cement paste on them. The granite was cut into 25 mm × 13 mm × 13 mm (1 inch × 0.5 inch × 0.5 inch) blocks. The surfaces of the granite blocks were also ground with no. 400 silicon carbide paper and dried in air for 30 minutes before casting the paste on them.

The limestone blocks were placed into 25 mm × 102 mm × 89 mm (1 inch × 4 inch × 3.5 inch) plastic molds, and the granite blocks were placed into 25 mm × 13 mm × 76 mm (1 inch × 0.5 inch × 3 inch) plastic molds. For both the granite and limestone blocks, the bond surfaces were placed vertically in the mold to minimize the effect on the bond of cement paste bleeding or settling.

The cement powder was mixed with water or PVA solutions (1%, 2%, 3%, or 4% PVA) with a water cement ratio (w/c) of 0.35 to yield PVA contents of 0%, 0.35%, 0.70%, 1.05%, or 1.40% with respect to cement mass. The paste was cast around the aggregate blocks in the molds while vibrating the molds during casting. The cast specimens were carefully demolded after 24 hours and stored in lime-saturated water until tested.

Bond Strength Measurement

Following the cement-hardening procedure, the limestone-paste units were cut into 25 mm × 13 mm × 89 mm (1 inch × 0.5 inch × 3.5 inch) specimens and the side surfaces were ground with a no. 180 diamond grinding disk to expose clean aggregate-paste bond lines. The granite-paste units, which had been cast as individual specimens, were ground in the same way before testing. All specimens were tested in a wet state to avoid cracking caused by drying shrinkage. The bond strength was measured by a three-point flexural test with a span length of 51 mm (2 inch) using an Instron Series IX Automated Materials Testing System (Instron Corporation, Canton, Massachusetts, USA). The loading of the specimen is indicated in Figure 1. The number of specimens for each bond strength test was 8–12, and the average strength and standard deviation were calculated.

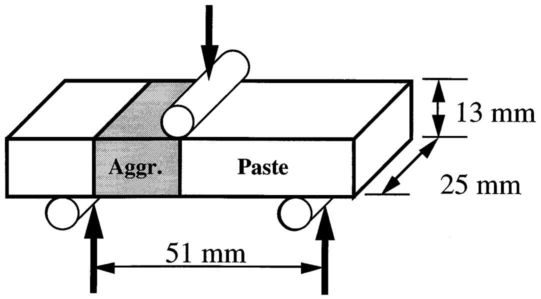

FIGURE 1. Diagram of three-point bending test used to measure the aggregate-paste bond strength. Specimen dimensions were 13 mm (0.5 inch) thick, 25 mm (1 inch) wide, and 89 mm (3.5 inch) long, and the separation between the support rods was 51 mm (2 inch).

Analysis of Interfacial Transition Zone

MORPHOLOGY. After undergoing the hardening reactions for 28 days, aggregate-paste bond specimens, with and without PVA, were sectioned across the bonding plane with a diamond saw to expose the aggregate-cement transition zones. For backscattered scanning electron microscopy, after drying in air, sectioned pieces were immersed in a low viscosity epoxy resin to allow the specimens to become impregnated with the resin. The resin was then hardened at room temperature for 1 day, and the specimen surfaces were polished with 12-μm alumina paper and 1 μm alumina powder. The nonpolar liquid, kerosene, was used as a coolant for the final polishing step and for washing the specimens in an ultrasonic cleaner between polishing steps. The polished specimens were dried under vacuum for 2 days and coated with carbon. The specimens were examined with a scanning electron microscope (Hitachi S-800, Hitachi, Japan) equipped with a backscattered electron detector.

In addition to sectioning with a diamond saw, the cured aggregate-paste bond specimens were also fractured on a plane perpendicular to the aggregate-paste bond surface. The fractured specimens were dried under vacuum for 2 days and coated with Au-Pd for observation by secondary electron emission with the scanning electron microscope. The drying invariably caused the granite, but not the limestone, to become debonded from the cement paste, both with and without PVA.

CHEMICAL ANALYSIS. For chemical analysis of the interfacial region, hardened limestone-paste bond specimens were cleaved at the interface by inserting a razor blade along the edge, and a layer of the cement paste within 10 μm of the aggregate interface was carefully removed by scraping with a razor blade. The interface was locatable because the aggregate had been sectioned and ground flat before the cement paste was cast against it.

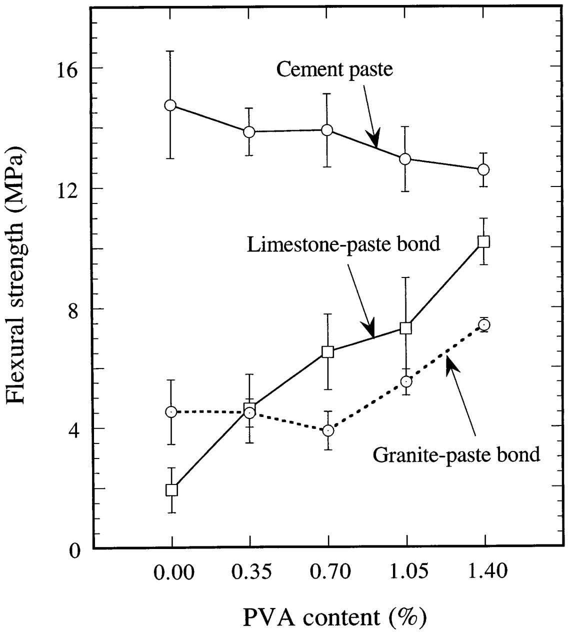

FIGURE 2. Flexural strengths of cement paste, limestone-paste bond, and granite-paste bond measured in three-point bending vs. PVA content. Tests were done with the specimens in a wet state after 28 days curing in lime-saturated water.

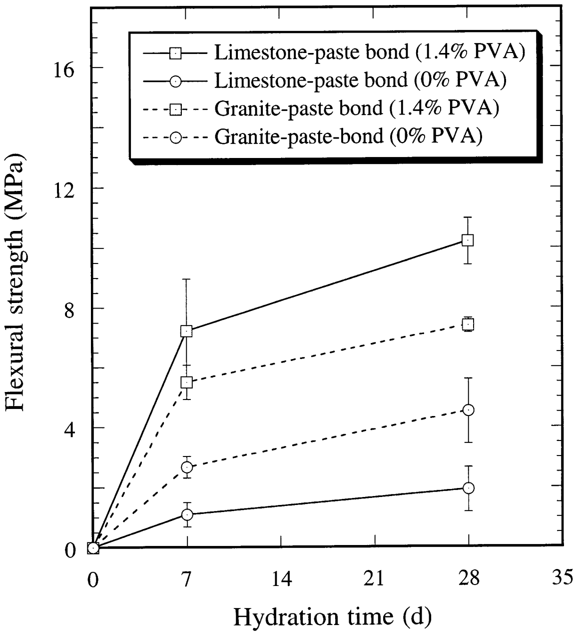

FIGURE 3. Flexural strengths of limestone-paste bond and granite-paste bond measured in three-point bending vs. hydration time. Tests were done with the specimens in a wet state after curing in lime-saturated water.

For both interfacial and bulk specimens, 2.2 mg of cement were mixed with 450 mg of KBr, and these were ground together in an agate mortar. All of the ground powder was placed in a sample holder for analysis. Fourier transform infrared (FTIR) spectroscopy (Mattson Galaxy Series FTIR 3020, Mattson Instruments, Madison, Wisconsin, USA) was performed in a diffuse reflectance mode.

Results

Effects of PVA Addition on Bond Strength

The effect of PVA content on the bond strength is indicated in Figure 2. Shown are the flexural strengths of the aggregate-paste specimens measured by three-point bending vs. PVA content. The flexural strength is the tensile stress acting on the bond between the cement and aggregate at the lower surface of the specimen when failure occurred. The aggregate-paste bond strength generally increased with increase in PVA content in the paste. With 1.4% PVA, the aggregate-paste bond strength was significantly increased for both limestone (from 1.9 to 10.1 MPa) and granite (from 3.9 to 7.5 MPa) above that without PVA. The three-point flexural bond strength values shown in Figure 2 for the specimens without PVA are comparable to those previously reported [1]. Equally significant for the granite-paste specimens was the reduction with PVA of the large specimen to specimen variation in bond strength that occurred without PVA. The error bars in Figure 2 show the standard deviations from 8–12 specimens.

Although the bond strength increased with PVA content, the cohesive strength of the paste decreased with PVA, as also shown in Figure 2. The paste strength decreased less rapidly than the bond strength increased, and the paste strength was still higher than the bond strength at 1.4% PVA.

The changes of the aggregate-paste bond strength with hydration time are shown in Figure 3. The better bonding with PVA developed at an early stage of hydration (at least by 7 days) and the differences in bond strength, with and without PVA, were more or less maintained with further hydration time (to 28 days).

The specimen failure mode was found to change with the addition of PVA. The mode changed from pure interfacial failure without PVA to cohesive failure of the aggregate with the limestone-paste specimens (Figure 4a) and to a mixed-mode interfacial-cohesive failure of the paste with the granite-paste specimens (Figure 4b). Since the limestone blocks failed first in many of the specimens with 1.05% PVA and in all specimens with 1.4% PVA, the bond strength values shown in Figure 2 for these specimens probably under-represent the actual bond strengths. Also, the variation in strength was caused largely by the heterogeneity of the limestone.

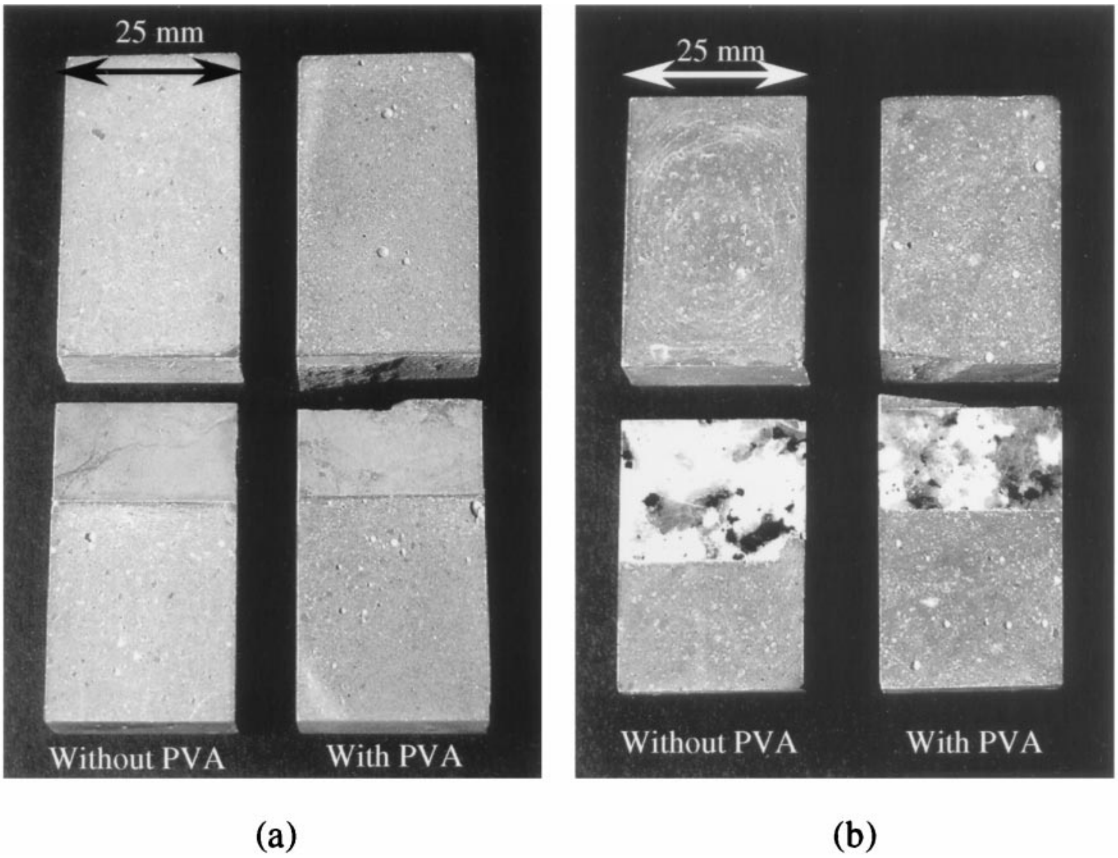

FIGURE 4. Failure behavior of aggregate-paste bond strength test specimens after 28 days hydration without PVA and with 1.4% PVA. (a) Limestone-paste. (b) Granite-paste.

Effects of PVA Addition on the Interfacial Transition Zone

TRANSITION ZONE MORPHOLOGY. The aggregate-cement transition zone was observed with the specimens hydrated for 28 days. The planes examined were obtained by sectioning perpendicular to the bond plane. The transition zones with limestone, without and with PVA in the cement paste, are shown in Figure 5 as scanning electron micrographs obtained in backscatter mode. The limestone aggregate is at the bottom and the cement is above. (The specimen without PVA had debonded.) Particularly noteworthy are the different thicknesses of the transition zones. Without PVA (Figure 5a), the porous transition zone is 30–50 μm thick, and an extensive survey found the thickness to range up to 100 μm. With PVA (Figure 5b), the transition zone was often 5–10 μm thick, and a similar extensive survey found the thickness to range 0–30 μm, with an average around 10 μm.

The transition zones in the hardened paste adjacent to flat granite surfaces are shown in Figure 6, again for pastes both without and with PVA. Shown in Figure 6 are scanning electron micrographs of paste fracture surfaces obtained by fracturing the paste perpendicular to the aggregate-paste interface. The interfaces with the flat granite surface are at the right. (The granite had debonded from both cement pastes during drying and is not shown.) Without PVA (Figure 6a), one can easily observe a porous layer extending away from the interface by 30–50 μm. The layer is mostly composed of calcium hydroxide platelets and looked white when observed with an optical microscope; cement grains were seldom seen in it. The right-hand edge of this specimen is not flat because some of the cement paste in contact with the granite surface broke away from the rest of the paste and stayed with the granite. This suggests that the failure occurred at least partly in the porous interfacial transition zone. For the paste with PVA (Figure 6b), however, almost no porosity can be seen, although small regions of calcium hydroxide platelets are occasionally observed at the interface. Also, many cement grains can be found near the interface, and the material density within 50 μm of the granite-paste interface appeared almost the same as that in the paste bulk. The edge of this specimen is straight, which indicates a clean cleavage at the inter-

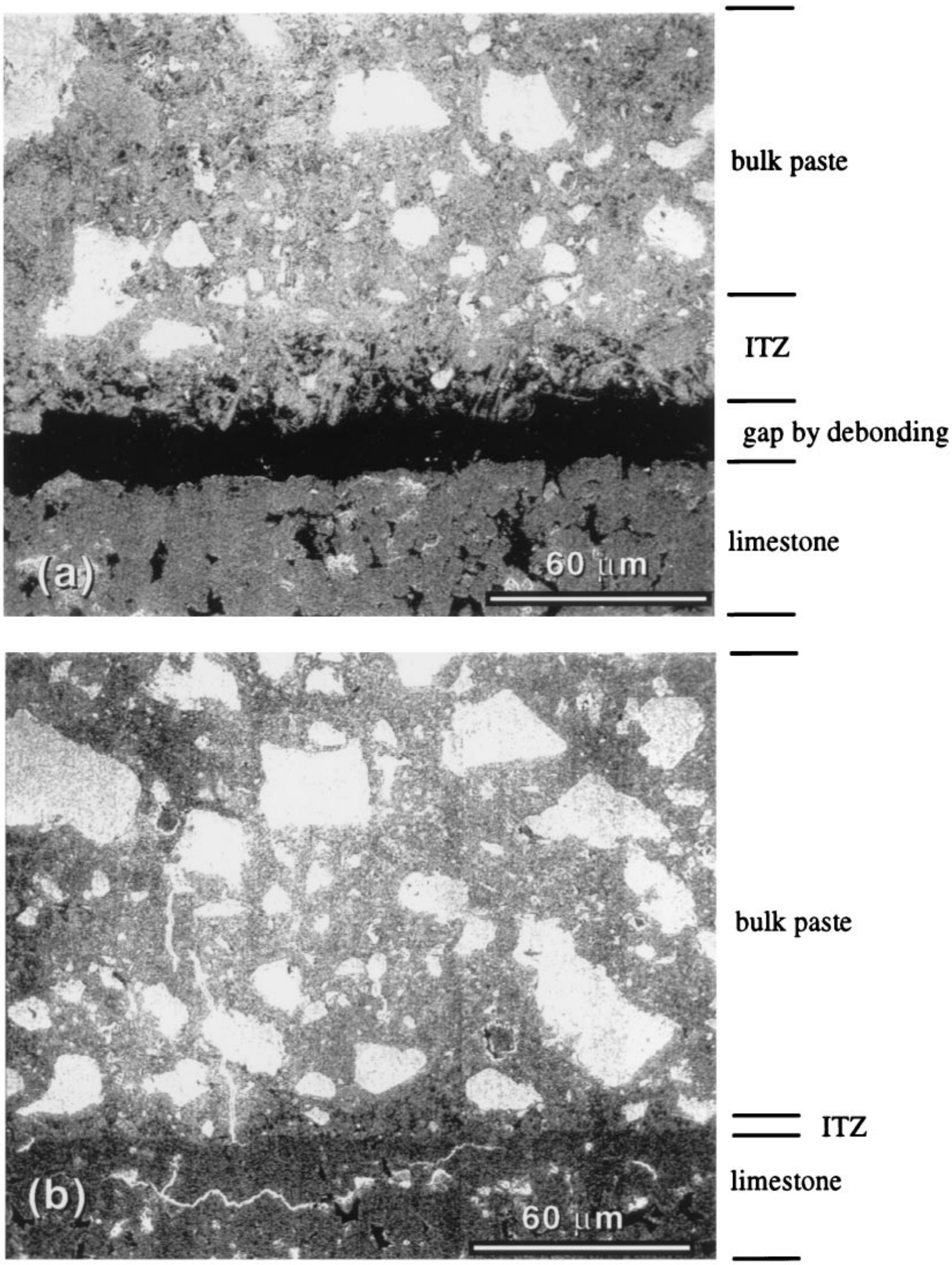

FIGURE 5. Scanning electron micrographs obtained in backscatter mode of cut and polished specimens showing the interfacial transition zone (ITZ) between the aggregate (limestone) and the cement paste. (a) Cement paste without PVA. (b) Cement paste with 1.4% PVA.

face between the flat granite surface and the cement paste.

COMPOSITIONAL CHANGES IN THE TRANSITION ZONE. The hardened cement paste both from the bulk and from within a 10-µm thickness of the aggregate surface were analyzed by diffuse reflectance FTIR, and the spectra are shown in Figure 7. The sharp peaks at 3643 cm^{-1} arose from calcium hydroxide ($Ca(OH)_2$), the absorption at 1400–1550 cm^{-1} arose from calcium carbonate ($CaCO_3$), as did the sharp peak at 880 cm^{-1}, and the peak around 950–1000 cm^{-1} arose from silicate ions (SiO_2). The absorption spectra from the bulk, without and with

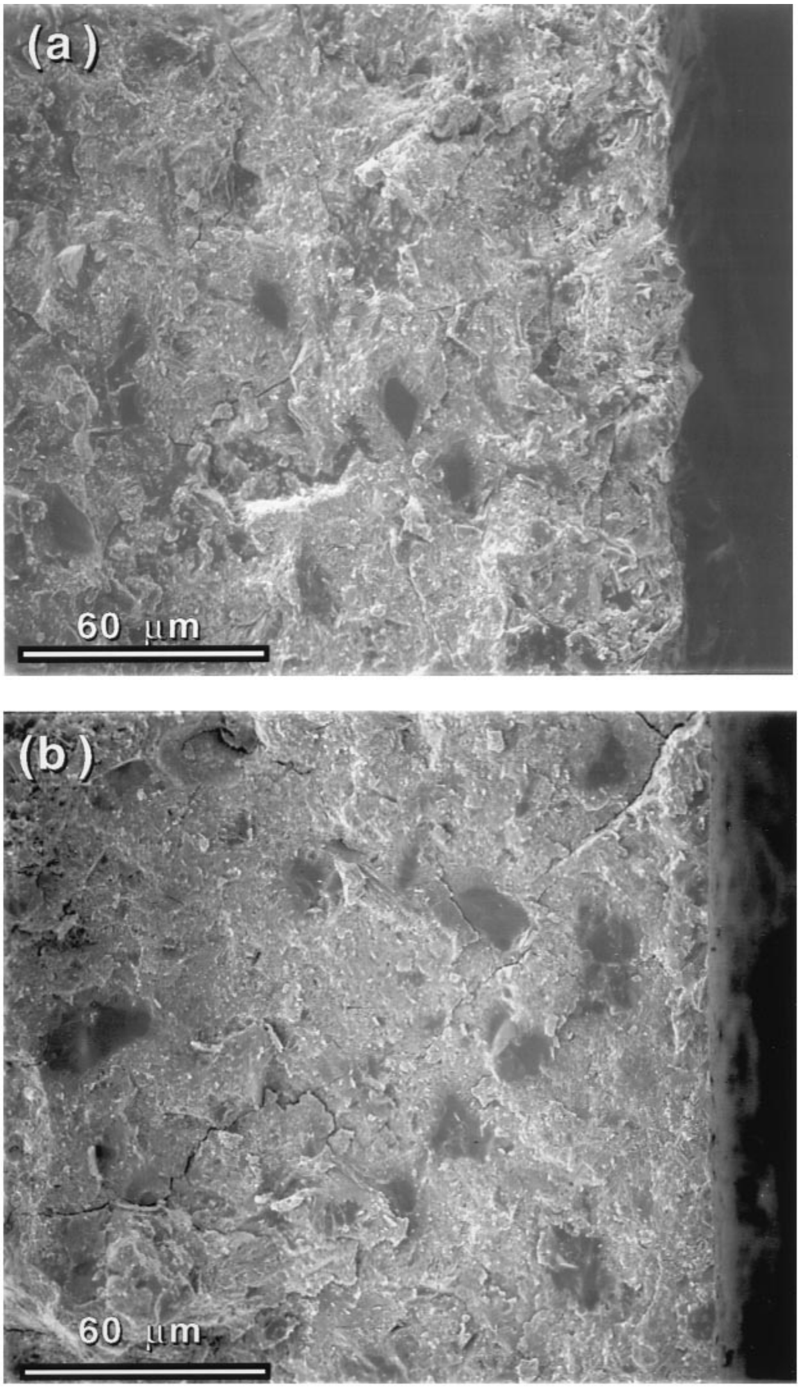

FIGURE 6. Scanning electron micrographs of the fracture surface of cement paste near the granite surface. (a) Cement paste without PVA. (b) Cement paste with 1.4% PVA. Granite blocks had debonded from the hardened cement pastes by drying shrinkage before the specimens were fractured.

PVA (Figures 7a and 7c), are seen to be essentially the same, with strong calcium hydroxide and silicate peaks and a modest amount of calcium carbonate.

The spectra from the interfacial regions, without and with PVA (Figures 7b and 7d), are very different. The absorption spectrum from the interfacial paste without PVA (Figure 7b) is considerably enhanced in calcium hydroxide, especially, and calcium carbonate, but it is largely depleted of silicate. In contrast, the absorption spectrum from the interfacial paste with PVA (Figure 7d) has a concentration of silicate more nearly like that of the bulk, much more calcium carbonate, and only one-third to one-half as much calcium hydroxide as the bulk. Also, the absorption peak for the silicate from the interface with PVA appeared at higher wavenumber than that from bulk, as seen in Figure 8. With hydration of the di- and tricalcium silicates, the silicate absorption moves upward in wavenumber. This indicates that the silicate at the interface was more hydrated than that in the bulk, perhaps fully hydrated.

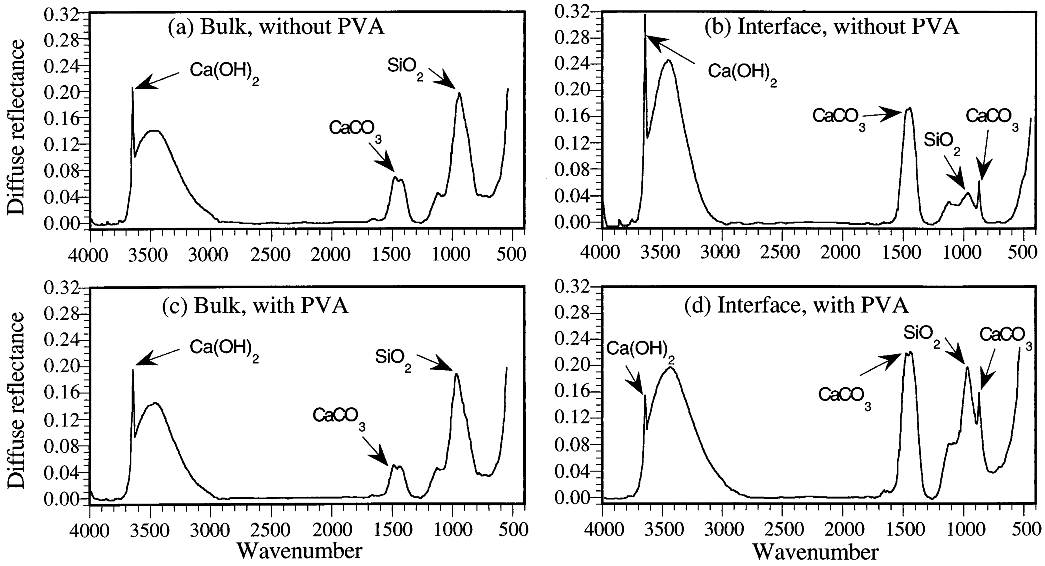

FIGURE 7. Diffuse reflectance FTIR spectra of hydrated cement specimens obtained after 28 days hydration from (a) the bulk paste without PVA, (b) the paste within 10 μm of limestone aggregate interface without PVA, (c) the bulk paste with 1.4% PVA, and (d) the paste within 10 μm of the limestone aggregate interface with 1.4% PVA.

Discussion

The addition of PVA to cement paste has induced a number of changes. The aggregate-paste bond strength was significantly increased, approaching the strengths of the paste and limestone aggregate themselves. Thus, the failure mode was changed from adhesive to cohesive failure of the paste or aggregate. The morphology and composition of the interfacial transition zone were also changed by the presence of PVA: the zone thickness was decreased, few large crystals of calcium hydroxide were found deposited on the aggregate surface, and the ratio of calcium hydroxide to silicate ion within 10 μm of the aggregate surface was much lower than that without PVA, and lower even than that of the bulk, with or without PVA.

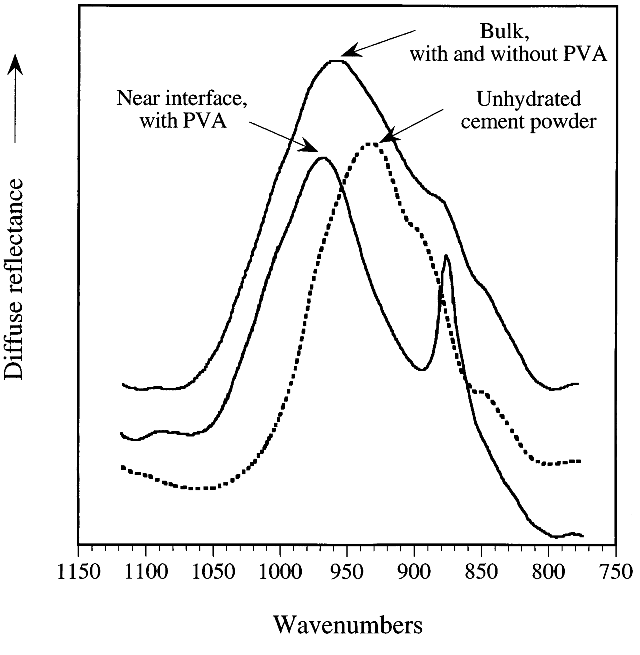

FIGURE 8. Silicate peaks of the diffuse reflectance FTIR spectra of hydrated cement specimens obtained from the bulk or from within 10 μm of the aggregate interface.

It is noteworthy that all of the bond strength improvements with PVA in this study were observed in the wet state. Improved bond strengths with large amounts of PVA seen in other studies [10,11,13] were all for the dry state, and the bond strength and other mechanical properties deteriorated rapidly when the specimens were wetted because the swollen polymer lost cohesion [13]. Therefore, the improvements of the aggregate-paste bond strength found in this study with the addition of a small amount of PVA seems to have been achieved by inducing changes in the cement paste and interface, not by the polymer acting as an adhesive or a load-carrying component. Although PVA may enhance the bond strength even more in the dry state, reliable mechanical tests were not possible under these conditions because of the severe shrinkage of the paste during drying that caused cracking at the aggregate-paste interface, as well as in the bulk paste.

The decrease of cement paste strength with PVA (Figure 2) was probably caused by increased air void content [16]. The air void content of the paste with 0.35–1.40% PVA increased by 1–4% compared to the paste without PVA.

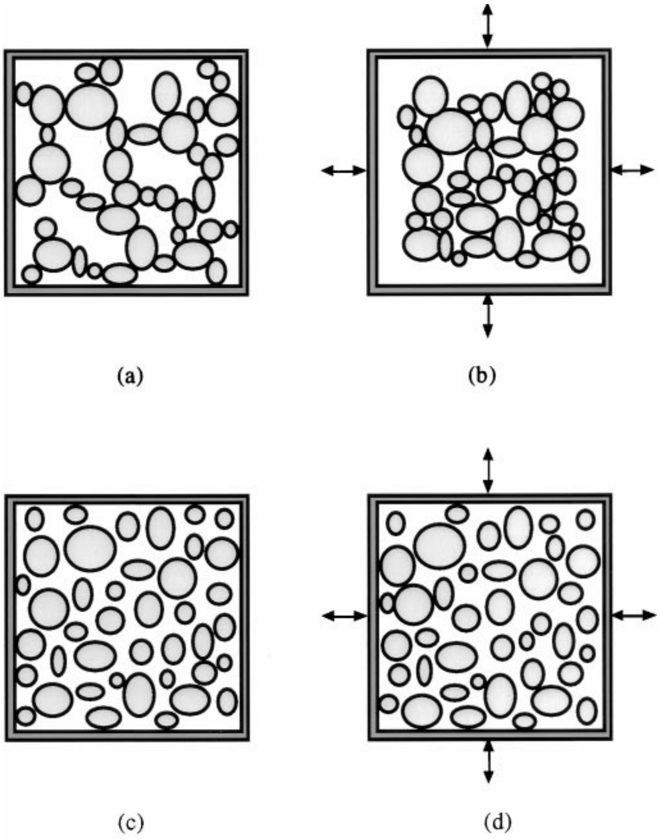

FIGURE 9. Diagrams showing (a) the wall effect by the flocculated cement particles in paste without PVA, (b) the formation of water-rich layer around the wall by the relative movements of wall and flocculating cement paste without PVA, (c) the well-dispersed cement particles in paste with PVA, and (d) the well-dispersed cement particles even after movements of wall and paste with PVA.

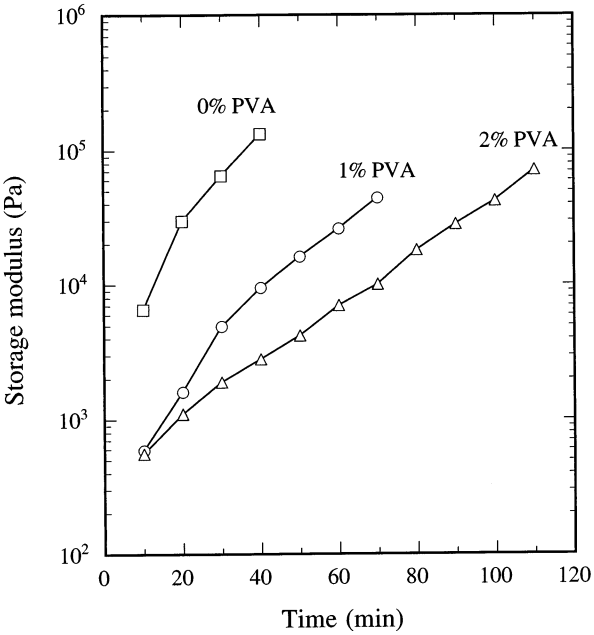

FIGURE 10. Change of storage modulus of cement pastes (w/c = 0.45; Bohlin rheometer, cup 15.4 mm, bob 14.0 mm; oscillatory mode; amplitude, 0.3%; frequency, 0.7 Hz; 25°C).

Changes in the Structure of the Interfacial Transition Zone

Two mechanisms suggested for the formation of the interfacial transition zone around aggregate are a wall effect and bleeding [17]. The wall effect arises from the flocculation of cement particles to form loosely organized structures [18,19]. This is illustrated in Figure 9a. Bleeding arises from the settling of cement particles either individually or as flocculated units, and vibration of concrete during casting may accelerate the bleeding around and especially under the aggregate [20,21]. The resulting structure of the cement particles is indicated in Figure 9b, where the bleeding is shown here around the periphery. Both the wall effect and bleeding occur in concrete, and each may explain the formation of the interfacial transition zone under different circumstances.

To examine the effect of PVA on the flocculation of cement particles, rheological measurements were done with fresh cement pastes (w/c = 0.45). The rheological behavior was measured using a Bohlin rheometer equipped with cup and bob (diameters of 15.4 and 14.0 mm, respectively). The storage moduli were obtained using an oscillatory mode with a small amplitude of 0.3%, so as to remain in the linear viscoelastic range, at a frequency of 0.7 Hz and at 25°C. The test was repeated every 10 minutes until the storage moduli reached 10^5 Pa. For each specimen, the measurements were completed within 3 hours of mixing, before the end of the dormant stage. The storage modulus represents the stiffness of the flocculated structure. As seen in Figure 10, with 1% PVA in the paste, the storage modulus was only about one-tenth of that of the reference without PVA at any given time after mixing, and the time to reach 10^5 Pa was more than twice that of the reference. With 2% PVA, the storage modulus decreased even more, except at the beginning, and the time to reach 10^5 was about three times that of the reference. Thus, the formation of flocculated structures by the cement particles is greatly reduced by the presence of PVA.

To examine the effect of PVA on bleeding, the upper surfaces of fresh cement pastes were observed with an optical microscope. When cement was mixed with plain water without PVA, a fairly thick layer of clear water formed on top of the paste. But as the PVA content increased, this bleeding was reduced, and with 1.4% PVA, almost no bleeding occurred. Figure 11 shows micrographs of the top surfaces of fresh pastes without and with PVA about 30 s after spreading 3-mm thick layers onto glass slides. The paste without PVA has a

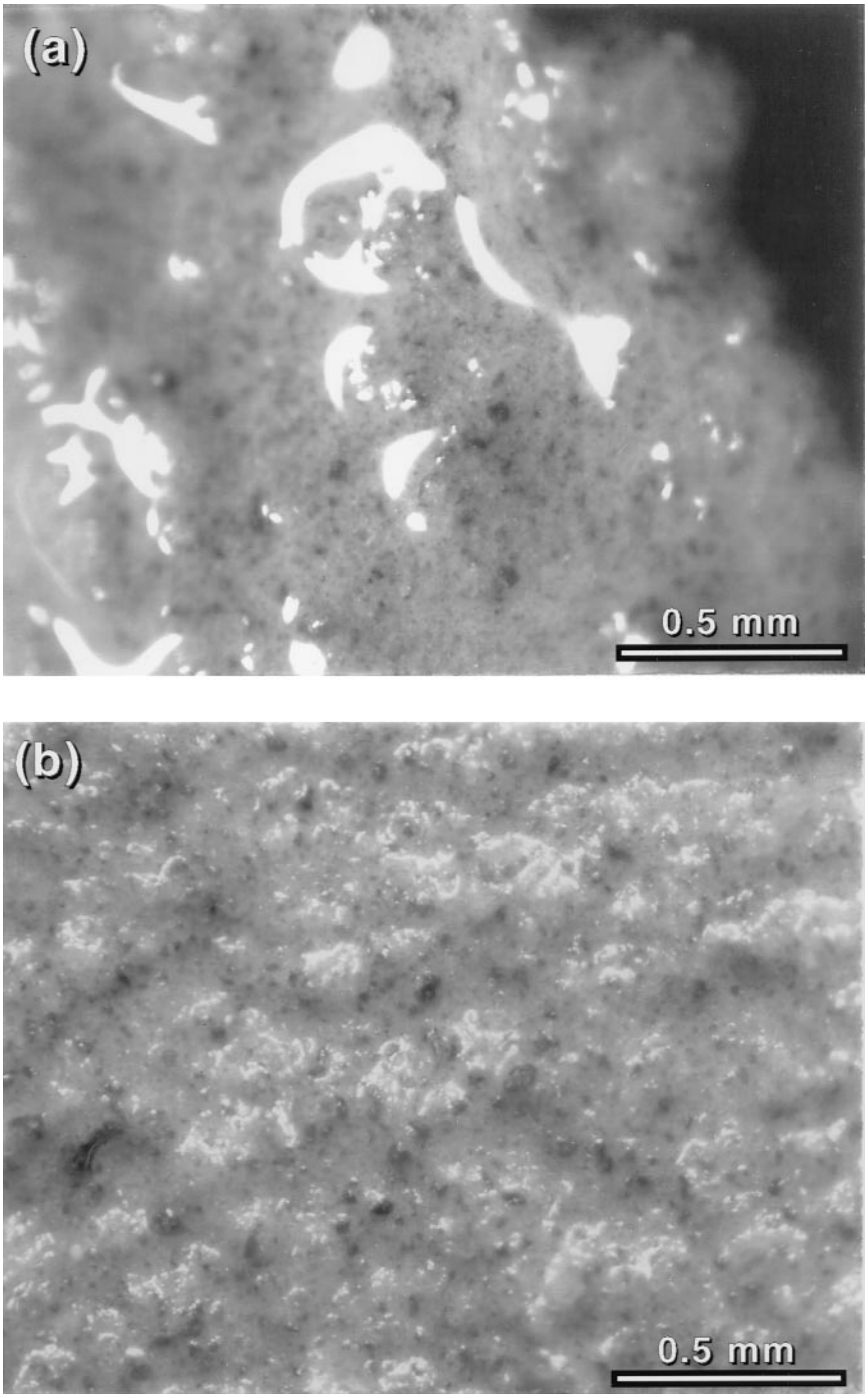

FIGURE 11. Optical micrographs of the top surfaces of fresh pastes showing bleeding of water. (a) Cement paste without PVA. (b) Cement paste with 1.4% PVA.

fairly thick water layer covering the cement paste, as indicated by the light reflections. That with 1.4% PVA has not developed such a layer, so that the rough surface of cement particles is seen.

Another aspect of bleeding is water drainage. The amount of water that drained from fresh cement paste (w/c = 0.35) sitting in a Buchner funnel, on a circle of filter paper, was measured. The paste was allowed to drain during the first 2 hours after mixing. The amount of liquid collected is shown vs. PVA content in Figure 12. As seen, the liquid collected without PVA in the paste was 4.8 wt%, based on the original weight of water, but this decreased by about two-thirds, to 1.7 wt%, when the paste contained 1.4% PVA (mass of PVA based on the mass of cement).

The decreased rigidity (storage modulus) of fresh paste with PVA seems to be caused by the PVA tending to disperse (or deflocculate) the cement particles, pos-

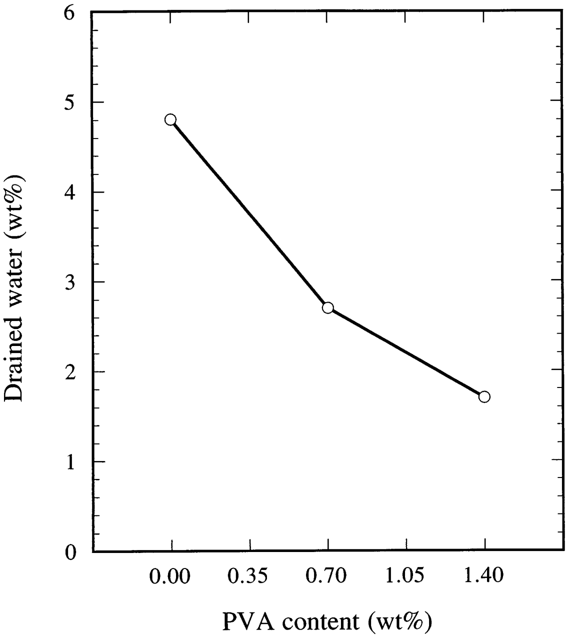

FIGURE 12. Mass fractions of drained water (based on total amount of water) from fresh pastes vs. PVA content (w/c = 0.35; draining time, 2 hours).

sibly through the steric repulsion of polymer molecules adsorbed on the surfaces of adjacent particle [22,23]. This dispersing effect presumably facilitates the packing of the cement particles near the surfaces of the aggregate and prevents the formation of a porous layer (Figure 9c), as well as reducing bleeding. The slightly higher viscosity of PVA solutions than water may also contribute to an increased efficiency of deflocculation during mixing and vibration and to reduced bleeding by slowing the packing of the particles (Figure 9d).

Changes in the Composition of the Interfacial Transition Zone

Previous work [24] has suggested that the presence of PVA during the hydration of cement may increase the amount of calcium silicate hydrate (C-S-H) while it decreases the amount of calcium hydroxide. The effect was suggested to arise from the effect of PVA on nucleation. An increase in the absolute amount of C-S-H was not able to be confirmed in the present experiments, though an increase in the relative amount of C-S-H in the transition zone seems to have occurred. The infrared spectra (Figure 7) indicated a near doubling of the silicate to calcium hydroxide ratio in the transition zone.

The usual formation of a calcium hydroxide layer (duplex film) on the aggregate surface at an early stage of hydration prevents contact of the aggregate with the C-S-H formed later. This may result in the poor bonding of cement paste with the aggregate even with a dense interfacial zone because of an apparent mediocre to poor adhesion between the aggregate surface and calcium hydroxide crystals or between calcium hydroxide crystal layers [5,6]. When PVA is used, however, the PVA molecules are able to adsorb on the aggregate surface, and this may prevent the growth of calcium hydroxide crystals on the surface possibly by inactivating crystal nucleation sites [24].

Possibly also contributing to the increase in adhesion between paste and limestone with PVA was the etching of the limestone surface and a greater involvement of calcium carbonate in the bond. The development of adhesion by the etching of limestone by cement after 56 days of curing was reported by Mehta and Monteiro [25]. This seems to be accelerated by PVA, as indicated by the increased $CaCO_3$ absorption in the infrared spectrum from the interfacial region vs. the bulk with PVA (Figure 7d vs Figure 7c). Enhanced adhesion has occurred with 28 days of hydration, and perhaps even with 7 days of hydration.

Conclusions

The bond strength between cement paste and aggregate (granite and limestone) was significantly increased by the addition of small amounts of PVA, causing cohesive failures of the cement paste and limestone aggregate. In addition, the variation in bond strength was reduced, relative to the strength itself for limestone aggregate and absolutely for granite aggregate. The gain in strength and reduction in strength variation seem to have arisen from: (1) a significant reduction in the thickness of the interfacial transition zone; and (2) a significant reduction or even elimination of the calcium hydroxide crystals that normally coat the aggregate surface and their possible replacement by calcium silicate hydrate (C-S-H) crystals. The changes in the interfacial transition zone seem to have arisen from the tendency for PVA to retard flocculation of the cement grains and to increase the efficiency of deflocculation by shear and vibration because of the increased viscosity. The reduction in calcium hydroxide crystallization on the aggregate surface possibly arose from the inhibition of nucleation of calcium hydroxide crystals by adsorbed PVA.

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