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FRACTURE BEHAVIOR OF HARDENED CEMENT PASTE INCORPORATING MINERAL ADDITIONS

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ABSTRACT

Various powder materials have been added on the hydration of cement to improve its mechanical and chemical properties. Industrial waste or by-product powder is consumed in large quantities as aggregates or hydraulic reactants. In the present study, hardened cement pastes (HCP) were prepared with ordinary portland cement containing fine powder consisting of isotropic graphite or glass waste to investigate their microstructure and mechanical properties. Fracture behavior was investigated by compact tension, by which the fracture energy and fracture toughness of a specimen were obtained. The amount of calcium hydroxide and Ca/Si molar ratio of C-S-H were constant in spite of being mixed with graphite. Graphite powder did not take part in the hydration of cement. An improvement in fracture toughness and a remarkable plastic behavior were observed because of the dispersion of graphite particles. On the other hand, glass waste powder reacting with alkaline solution in the pores resulted in decreasing the Ca/Si molar ratio of C-S-H. Similar behavior was observed in a mixture of cement and fine blast furnace slag. Bending and compressive strength increased, but fracture toughness decreased. The lower elastic fracture energy in HCP containing reactive fine powder facilitated crack propagation and enlarged the fracture surface.

INTRODUCTION

Utilization of mixtures of various powders is necessary in the cement industry for enhancement of multiple functional properties. In particular, it is hoped to use waste materials or by-products in the development of improved chemical or mechanical properties in cement paste or concrete. Blast furnace slag is already used in order to lower heat evolution and develop long-term strength. Recently, limestone has also been used. These inorganic materials are prepared as a ground fine powder. Therefore, mechanical properties of hardened cement paste (HCP) containing these materials must be discussed in relation to their hydraulic properties and interaction at the surface of the powder. Fracture behavior was also important in evaluating the durability of HCP when employed with other industrial materials.

In the present study, the HCP was prepared with ordinary portland cement containing fine isotropic graphite or glass waste. The microstructure and mechanical properties of HCP were investigated after curing in moist air for 3 months at room temperature. The mechanical properties and fracture behavior were discussed and compared with those in the HCP containing blast-furnace slag(1). Isotropic graphite powder is the by-product in the finishing process of graphite body. Since graphite does not react with cement paste, only the dispersion effect of particles in cement paste is discussed. Glass waste is obtained by crushing and grinding used bottle glass. Hydration of the pore solution in cement paste and reaction with cement paste are taken into consideration, as is the case with the HCP containing blast-furnace slag.

EXPERIMENTAL

Mixing ratio and curing condition of HCP

The HCP was prepared with ordinary portland cement and graphite (Blaine approx. 3000 cm^2/g) or glass powder (Blaine approx. 4000 cm^2/g), replacing cement with additions up to 40 wt%. In the case of blast-furnace slag (Blaine approx. 8500cm^2/g), gypsum of 5 wt% was added(1). All pastes were added to water containing a water reducer of 1wt% to keep a consistent flow value in the water/solid ratio range of 0.28-0.32. Rectangular specimens 2x2x10 cm^3 were cast and cured for 3 months in moist air.

Hydrates and microstructure

Identification and quantitative analysis of hydrates were performed by XRD and DTA-TG analysis. The Ca/Si molar ratio of C-S-H was estimated by EDX after separation of hydrates with heavy liquid(2). The C-S-H was obtained easily as the float. The microstructure of the HCP was observed using SEM together with EDX, which clarified the hydrates near the propagated crack on the fracture surface.

Mechanical properties

The compressive strength was calculated from the contact area (2x2 cm^2) and applied load. Ten specimens for each mixing ratio were used for the test with cross head speeds of 50 kg/sec. After finishing the fracture test, cone-shaped scraps were confirmed at the upper and lower parts of the specimens to judge the occurrence of shear fracture. Bending strength was also estimated in the ten specimens by a three-point loading. The lower span width was 8 cm and cross head speed was 0.1 mm/min. The Weibull's modulus of the specimen for any mixing ratio was above 10, which showed a slight deviation in strength.

Fracture behavior of HCP using Compact Tension specimens

A uniaxial tensile test was performed using a Compact Tension specimen, as shown in **Fig. 1**. The crack mouth displacement (CMD) was measured by a strain gage on a Ω -type bronze plate. The load-displacement (P-u) curve was measured by repetition of load and unload with a crosshead speed of 0.1 mm/min. The total fracture energy was calculated from the total area of P-u curve divided by double the fracture surface area. Elastic fracture energy and plastic energy dispersion were obtained by shifting the irreversible residual displacement to the origin(3). Fracture toughness K_{IC} was estimated using fracture load, specimen size, and shape coefficient as a function of nondimensional crack length.

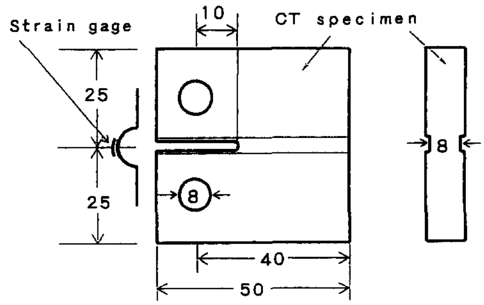

Fig. 1 Compact tension specimen

RESULTS

Mechanical properties of HCP containing mixtures

The bending strength and compressive strength of the HCP containing mixtures were shown in **Fig. 2** and **3**, respectively. Upon mixing with graphite powder, neither strength developed independently of the mixed content. When mixing with glass powder, homogeneous HCP was not cast in the replacement of 40 wt% due to the difference in specific gravity. However, high bending strength and compressive strength were observed. In particular, bending strength at the replacement of 10 wt% doubled to the level of that of glass-free HCP. When mixed with slag powder, which has a hydraulic property similar to glass powder, the bending and compressive strengths increased but the rate of increase differed from that of the HCP containing glass powder(1).

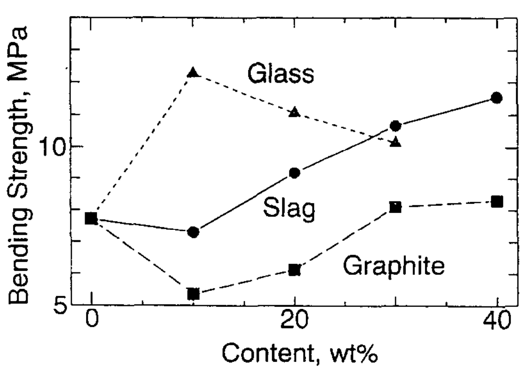

Fig. 2 Bending strength of HCP

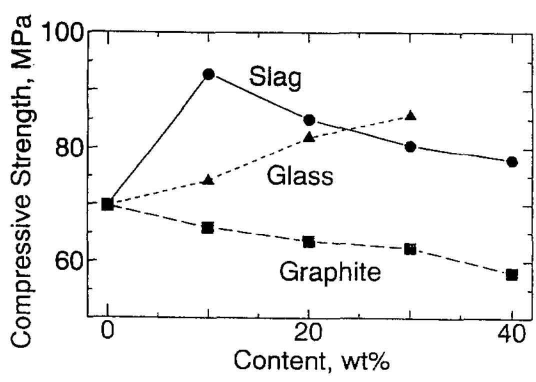

Fig. 3 Compressive strength of HCP

Uniaxial tensile test using CT specimens

Load-displacement (P-u) curves of the HCP containing mixtures of 20 wt% were shown in **Fig. 4**. Nonlinear elastic behavior and stable fracture behavior were observed before or after the maximum load point for any specimen. Under unloading/reloading cycles, the unloading line was straight but did not return to the origin. The irreversible residual displacement was confirmed for nonlinear materials. The total fracture energy γ_{WOF}, elastic fracture energy γ_e and plastic energy dissipation γ_P were calculated from the P-u curves and shown schematically in **Fig. 5** with mixed content. The γ_{WOF} was the sum of γ_e and γ_P (shadowed in the figure), which varied from 20 to 50 J/m^2. These values were lower than that of mortar after hydration for 7 days, 83.8 J/m^2(4). The γ_P of HCP containing graphite was almost constant, but γ_e decreased and then increased with mixed content. The γ_e of HCP containing glass dropped independently of the mixed content to cause a decrease in γ_{WOF}.

Fracture toughness estimated by CT specimen was shown in **Fig. 6**. A slight increase was observed when mixed with graphite, but a decrease when mixed with glass or slag. These changes in fracture toughness corresponded to those of γ_e or γ_{WOF}. The HCP having a high fracture toughness also showed a high γ_e or γ_{WOF}.

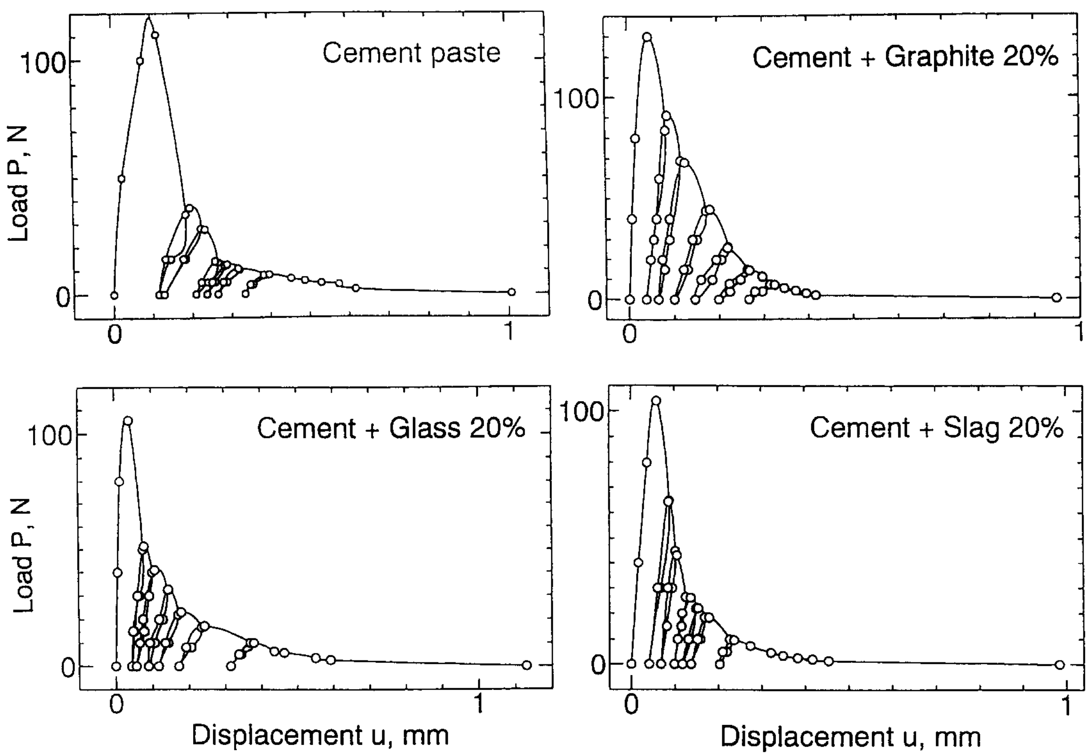

Fig. 4 P-u curves of HCP

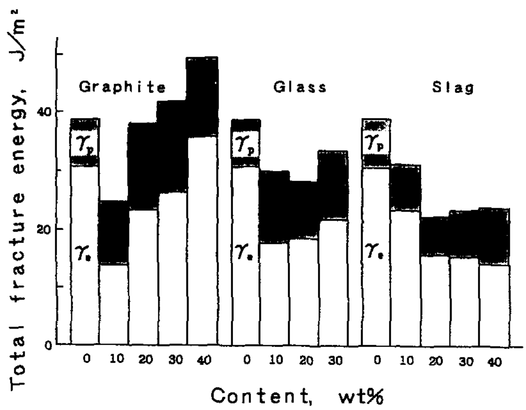

Fig. 5 Fracture energy of HCP

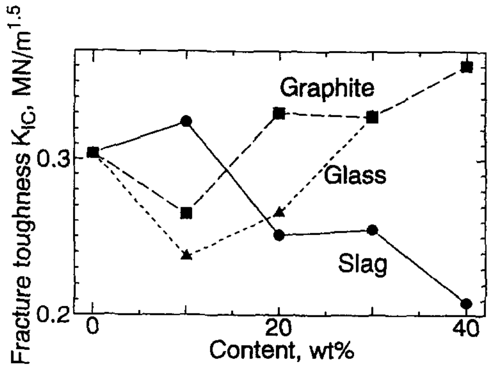

Fig. 6 Fracture toughness of HCP

DISCUSSIONS

Mechanical properties and microstructure

In concrete or mortar subjected to load, the fracture origin or course of a propagated crack is considered to be hydrates, interface of hydrates and aggregate or unhydrated particles(5). For specimens in this experiment, most cracks were propagated through C-S-H or calcium hydroxide in hydrates of cement paste, and a few cracks did develop around unreacted mixed particles. No cracks in the graphite or glass particles were observed. Therefore, fracture behavior depended on the hydrates of HCP. The amount of compound estimated by DTA-TG and Ca/Si molar ratio of C-S-H were shown in **Table 1** and **Fig. 7**, respectively.

In the HCP containing graphite, the amount of calcium hydroxide was in proportion to the initial amount of ordinary portland cement. Graphite had no effect on the hydration of cement particles. The Ca/Si molar ratio in C-S-H was constant even when mixed with graphite. A normal C-S-H similar to that in graphite-free HCP was expected. The decrease in strength was mainly due to the weak cementitious property between graphite particles and hydrates. The dispersion effect of the unreacted particles was not exhibited on the instantaneous fracture.

Table 1 Amount of compound

Mixture	Content (wt%)	H_2O	$Ca(OH)_2$ (wt%)	$CaCO_3$
Glass	0	28.8	20.8	6.4
	10	31.5	19.9	7.8
	20	29.8	17.2	8.3
	30	30.6	15.7	8.2
Graphite	10	18.7	12.1	—
	20	15.3	8.6	—
	30	14.5	6.8	—
	40	13.5	6.7	—

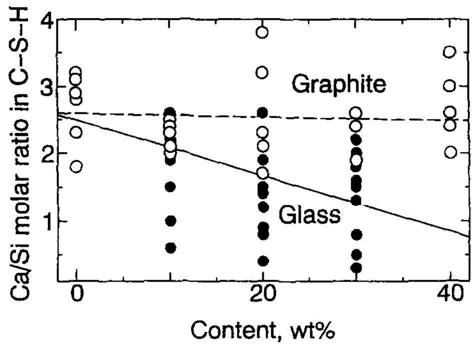

Fig. 7 Ca/Si molar ratio of C-S-H

In the HCP with or without glass, calcium hydroxide, calcium carbonate and unreacted alite were observed. Larger amounts of calcium hydroxide formed than might be expected from the initial amount of portland cement. The excess formation of calcium hydroxide consumed the dissolved calcium ions from the glass powder. The increase in calcium carbonate was explained by an increase in pH in the pore solution due to the alkaline ions dissolved from glass. The decrease in Ca/Si molar ratio despite an increase in the amount of C-S-H in the mixture was caused by the sodium and silicate ions dissolved from glass. A similar C-S-H was observed in HCP mixed with alkaline solution(2).

The increase in these hydrates together with the ion dissolution from glass particles contributed to an improvement in strength. However, the increases in bending and compressive strength were not proportional to each other. The replacement of over 10 wt% for bending strength and over 30 wt% for compressive strength became ineffective. The desirable content was different , which might be dependent on the fracture mode. The specimen was subjected in mode I to a bending test and in mode II to a compressive test. The latter mode consisted mainly of shear stress. The number of unreacted glass particles at the fracture surface contributed to an increase in the frictional coefficient. This increase in compressive strength was not detected in the fine slag particles.

Fracture energy and fracture toughness

Resistance to the propagation of a crack consists in stress relaxation at the front of the crack and a crack-shielding effect behind the crack tip(6,7). In this experiment, microcracks, which were mainly capillary pores in the cement paste, were observed in front of the main crack. The unhydrated cement or addition particles brought a refraction in the crack or grain bridging. Elastic fracture energy γ_e, which corresponded to the formation energy of the fracture surface, was higher in the addition free HCP. Stress relaxation at the crack tip was the main deterninate of the fracture behavior of this normal HCP.

In the HCP containing graphite, except in the 10 wt% replacement mixture, γ_e did not decrease upon mixing with graphite. The hydration mechanism and Ca/Si molar ratio in C-S-H were similar to those for addition-free HCP. The increase in γ_e of the mixed content was considered to depend solely on the crack refraction around the graphite particles. In the HCP containing glass powder, which reacted with cement in the same manner as blast furnace slag, a low γ_e was observed independent of mixed content. The lower Ca/Si molar ratio in C-S-H resulted in changes ion the morphology and microstructure of C-S-H which, in turn, decreased the number of microcracks at the crack tip.

The friction among projected particles and grain bridging at the fracture surface are also important in discussing the fracture behavior of the HCP having long crack(8,9). In particular, large unreacted particles remaining in the HCP promote resistance to crack propagation and exhibit plastic behavior after the maximum load point in the P-u curve. In the HCP containing unreacted graphite particles, a high plastic energy dissipation γ_P was observed independent of mixed content. Graphite particles must bridge the space between the fracture surfaces, but with cement paste having weak cementitious properties. The increase in fracture toughness also contributed to the particle dispersion effect. Hillemeier et al. also observed the increase of fracture toughness of HCP mixing with quartz sand(10). On the other hand, glass particles react with cement paste and become small after hydration for 3 months. The only increase in γ_P corresponded rather to the friction in the rough fracture surface of the HCP containing glass particles(9).

CONCLUSIONS

The mechanical properties and fracture behavior of hardened cement paste (HCP), containing a fine powder of isotropic graphite and glass waste were discussed in reference to the hydrates and microstructure. The following conclusions were obtained:

(1) In the HCP containing graphite, fracture toughness was enhanced by the dispersion of unreacted particles, accompanied by high fracture energy. No increases in bending and compressive strength were observed. Graphite did not participate in hydration of the cement, but maintained a similar Ca/Si molar ratio to that in mixture free HCP with small amounts of calcium hydroxide.

(2) In the HCP containing glass, increases in bending and compressive strength were observed. Fracture toughness decreased due to the lowering of fractural energy. The formation of C-S-H having a lower Ca/Si molar ratio and a different morphology directly effected the mechanical properties of HCP.

REFERENCES

1. T.Nishikawa, K.Koibuchi, S.Ito and M.Takatsu, 9th Int. Cong. on Chem. of Cement, Vol.IV, 665-70(1992).
2. T.Nishikawa and K.Suzuki, Cem.Concr.Res., **24**, 176-82(1994).
3. M.Sakai, Y.Goto and M.Inagaki, J.Ceram.Soc.Japan, **94**, 153-58(1986).
4. V.C.Li, C-M Chan and C.K.Y.Leung, Cem.Concr.Res., **17**, 441-52(1987).
5. I.Jawed, G.Childs, A.Ritter and S.Winzer, Cem.Concr.Res., **17**, 433-40(1987).
6. H.M.Jennings, Mater.Sci.Tech., **4**, 277-84(1988).
7. B.Cotterell and Y-W Mai, J.Mater.Sci., **22**, 2734-38(1987).
8. L.J.Struble, P.E.Stutzman and R.Fuller Jr.,J.Am.Ceram.Soc., **72**, 2295-99(1989).
9. D.A.Lange, H.M.Jennings and S.P.Shah, J.Am.Ceram.Soc., **76**, 589-97(1993).
10. B.Hillemeier and H.K.Hilsdorf, Cem.Convcr.Res., **7**, 523-36(1977).