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SULFATE RESISTANCE OF HIGH FLY ASH CONTENT CONCRETE

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ABSTRACT

Changes in length, compressive strength, dynamic modulus of elasticity and pulse velocity of high fly ash content concrete with replacement levels of up to 50 % when completely immersed in the 10 % Na_2SO_4 solution were periodically measured for 2 years. It was found from the measurements of mechanical properties that the 50 % replacement by fly ash was very effective in the improvement of the sulfate resistance of concrete. During 2 years of exposure to the 10 % Na_2SO_4 solution, high fly ash content concrete with the binder content of 400 kg/m^3 and with replacement level of 50 % was steadily gaining the compressive strength, and no detectable deterioration was observed. Chemical analysis data also showed that the excellence of high fly ash content concrete in the sulfate resistance was attributed primarily to the prevention of ingress of sulfate ions into concrete, resulting in little formation of gypsum and/or ettringite in concrete.

Introduction

The concrete gradually deteriorates with time and finally loses the strength when it is exposed to the sulfate-bearing water from the surroundings. It has been suggested that the sulfate resistance of concrete can be effectively improved by a partial replacement of portland cement by fly ash, although it is dependent on the physical and chemical properties of both portland cement and fly ash used (1,2). It is believed that the sulfate-related deterioration of concrete is mainly due to the expansion brought about by the formation of gypsum and/or ettringite, which arises from the reaction of sulfate ions with calcium hydroxide and calcium aluminate hydrate in concrete (3,4). Therefore, it can be expected that high fly ash content concrete will show a good resistance to the sulfate attack when it is properly designed and well cured, since its pore structure is fine and discontinuous, and the amount of calcium hydroxide produced in fly ash concrete is very small. However, the sulfate-related deterioration of concrete is a complicated phenomenon of physical and chemical process, and the mechanism of improvement of sulfate resistance by the addition of relatively large amounts of fly ashes is not still fully understood (5).

This paper presents the data on the 2-year exposure test of high fly ash content concrete with replacement levels of 30 % and 50 % in the 10 % Na_2SO_4 solution. The effects of replacement level by two types of fly ash on the sulfate resistance of concrete were investigated based on the measurements of compressive strength, length change and dynamic modulus of elasticity. Furthermore, the mechanism of deterioration of concrete due to the sulfate attack was discussed with the special interest to the microstructural features of deteriorated concrete.

Experimental

Materials and Mix Proportion

An ordinary portland cement with the specific gravity of 3.13 and the Blaine fineness of 3250 cm^2/g was used. Chemical compositions of ordinary portland cement and fly ashes used are presented in Table 1. Two types of ASTM Type F fly ashes were discharged from Takasago power station in Kanagawa prefecture in Japan ; FA-A is a high-quality and small-sized fly ash and FA-B is a low-quality and relatively large-sized one. Their physical properties are presented in Table 2. Fine and coarse aggregates from Hayatsuki river in Toyama prefecture were natural river sand (specific gravity : 2.69, water absorption capacity : 1.3 %) and crushed stone (specific gravity : 2.69, water absorption capacity : 0.8 %, maximum size : 25 mm), respectively. All concrete mixtures were made so as to have a slump of 50 ± 10 mm and to contain an air content of 5 ± 1 % by using the resin-type air-entraining admixture ; the unit content of binders (cement plus fly ash) was kept at 300 kg/m^3 and 400 kg/m^3, and replacement levels by fly ash were selected at 30 % and 50 %. Mix proportions of OPC and fly ash concretes are given in Table 3.

Experimental procedures

Cylindrical specimens, 75 mm in diameter and 150 mm in height, were prepared for the compressive strength test, and prismatic specimens, 100 mm by 100 mm by 400 mm, for the measurements of length change and dynamic modulus of elasticity (JIS A 1127). The sulfate resistance test was performed with a concentration of 10 % Na_2SO_4, in which the solution was periodically exchanged by the new one. Prior to the exposure to the 10 % Na_2SO_4 solution, the specimens were cured in water at 20 °C for 14 days and then stored at 20 °C for 14 days under a sealed condition. At the age of 28 days, the specimens were immersed completely in the the 10 % Na_2SO_4 solution.

TABLE 1 Chemical compositions of portland cement and fly ashes used (%).

	Ig.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
Portland cement	1.6	23.4	5.1	1.9	63.4	1.3	0.5	0.3	2.1
Fly ash A	1.9	54.7	22.8	7.4	8.9	1.8	0.7	0.6	---
Fly ash B	3.2	48.5	25.4	8.6	8.3	2.1	0.8	0.7	---

TABLE 2 Physical properties of fly ashes used.

Fly ash A (FA-A)	Moisture content : 0.2 %, Loss on ignition : 1.9 %, Specific gravity : 2.28, Blaine specific surface area : 3390 cm^2/g, Residual on 88 μm sieve : 0.3 %
Fly ash B (FA-B)	Moisture content : 0.2 %, Loss on ignition : 3.2 %, Specific gravity : 2.21, Blaine specific surface area : 3140 cm^2/g, Residual on 88 μm sieve : 11.4 %

TABLE 3 Mix proportions and properties of OPC and fly ash concretes.

	W/C	S/A %	Water kg/m^3	Cement kg/m^3	Fly ash kg/m^3	Sand kg/m^3	Gravel kg/m^3	Slump mm	Air %
OPC 300	0.51	38	153	300		694	1170		
FA-A 30%	0.47	38	141	210	90	697	1170		
FA-A 50%	0.46	38	137	150	150	694	1165		
FA-B 30%	0.49	38	146	210	90	689	1162		
FA-B 50%	0.48	38	145	150	150	686	1151	50±10	5±1
OPC 400	0.41	38	162	400		655	1103		
FA-A 30%	0.39	38	155	280	120	647	1089		
FA-A 50%	0.37	38	148	200	200	645	1084		
FA-B 30%	0.39	38	155	280	120	647	1087		
FA-B 50%	0.38	38	152	200	200	639	1073		

OPC: Ordinary portland cement, FA-A: Fly ash A, FA-B: Fly ash B

TABLE 4 Total pore volume and amount of $Ca(OH)_2$ of the 28-day old OPC and fly ash concretes.

	Total pore volume (cc/g)	Pore volume greater than 0.1 µm *(cc/g)	Amount of $Ca(OH)_2$ ** (%)
OPC 300	0.043	0.011	5.8
FA-A 30%	0.051	0.006	3.3
FA-A 50%	0.054	0.009	2.5
FA-B 30%	0.072	0.032	4.1
FA-B 50%	0.074	0.028	2.5
OPC 400	0.038	0.008	6.6
FA-A 30%	0.051	0.010	4.5
FA-A 50%	0.049	0.005	2.5
FA-B 30%	0.054	0.006	4.1
FA-B 50%	0.056	0.003	1.6

(cylindrical specimens,75 mm in diameter and 150 mm in height)
* Measured by MIP, which is expressed by cc per g of mortar
** Determined by weight losses in DSC-TG curves between 420 and 490 °C, which is given by mass of mortar

Physical and chemical properties of the 28-day old OPC and fly ash concretes are presented in Table 4. Physical properties measured are compressive strength (JIS A 1132), length change (JIS A 1129) and dynamic modulus of elasticity (JIS A 1127). Chemical properties measured are depth of carbonation by spraying a 1 % phenolphthalein ethanol solution, identification of reaction products by DSC-TG and X-ray diffraction analysis, and quantitative analysis of SO_3 content in concrete (JIS R 5201). Furthermore, microstructural features of the deteriorated concrete were elucidated by mercury intrusion porosimetry and scanning electron microscope.

Results and Discussion

External Appearance and Compressive Strength

The external appearance of OPC concrete with the cement content of 300 kg/m^3 after 2 years of exposure to the 10 % Na_2SO_4 solution is shown in Fig.1. In OPC concrete with the cement content of 300 kg/m^3, small longitudinal cracks occurred parallel to the edge of the specimen around 6 months of exposure time, and they developed to a severe pattern-cracking on the surface of cylindrical specimens, resulting in the complete decomposition of concrete by 2 years of exposure time, as shown in Fig. 1. This suggests that a relatively large expansion has occurred in OPC concrete with the cement content of 300 kg/m^3 during the exposure to the Na_2SO_4 solution. The degree of cracking on the surface in OPC concrete with the cement content of 300 and 400 kg/m^3 was more severe for cylindrical specimens than for prismatic specimens. This tendency is in good agreement with the results of the reference (6). On the other hand, most of fly ash concretes maintained an excellent visual condition during 2 years of exposure, except for the mixture with the binder content of 300 kg/m^3 and with the replacement level of 30 % in which small visible cracks occurred on the surface after 6 months of exposure time.

Figs. 2 and 3 show changes in the compressive strength of the concrete with the binder content of 300 and 400 kg/m^3 with the exposure time, respectively. During the exposure to the 10 % Na_2SO_4 solution, the compressive strength of OPC concrete with the cement content of 300 kg/m^3 gradually decreased after 3 months of exposure, which was about 80 % relative to the 28-day old compressive strength at 1 year of exposure time, whilst the reduction in compressive strength in OPC concrete with the cement content of 400 kg/m^3 was not so significant even at 2 years of exposure time. On the other hand, for fly ash concretes, the concrete containing FA-A showed a higher strength development than that containing FA-B during the exposure to the 10 % Na_2SO_4 solution ; the difference in compressive strength between both fly ash concretes became more marked in the mixture with the binder content of 300 kg/m^3 than that with the binder content of 400 kg/m^3. All fly ash concretes had the compressive strength greater than the 28-day old compressive strength independently of the binder content and the replacement level by fly ash when they were exposed to the 10 % Na_2SO_4 solution for 2 years. Especially, high fly ash content concrete with the binder content of 400 kg/m^3 and with the replacement level of 50 % showed an excellent resistance to the sulfate attack, their compressive strength being successively gaining with the exposure time.

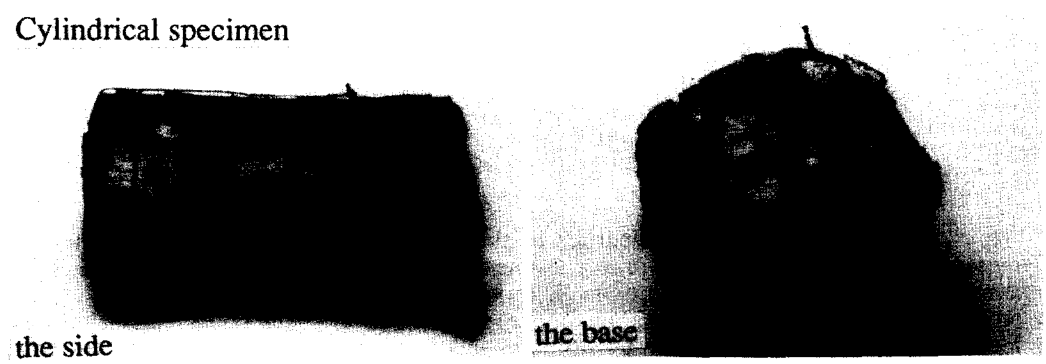

FIG. 1 External appearance of OPC concretes with the cement content of 300 kg/m^3 after 2 years of exposure to the 10 % Na_2SO_4 solution

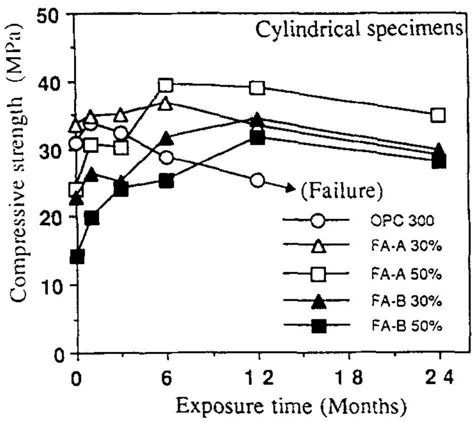

FIG. 2 Changes in compressive strength of the concrete with the binder content of 300 kg/m^3

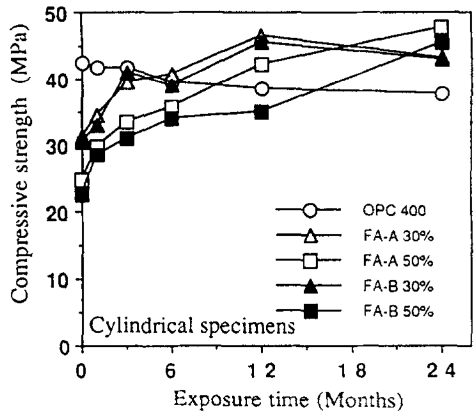

FIG. 3 Changes in compressive strength of the concrete with the binder content of 400 kg/m^3

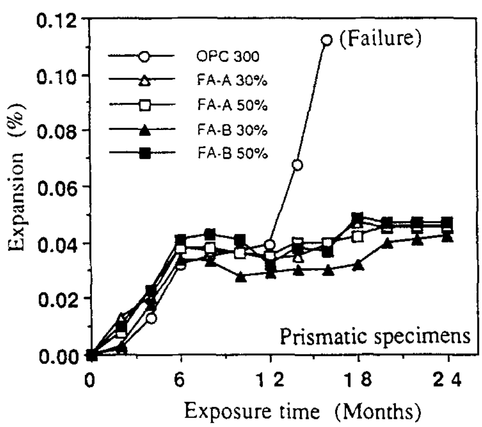

FIG. 4 Changes in length of the concrete with the binder content of 300 kg/m^3

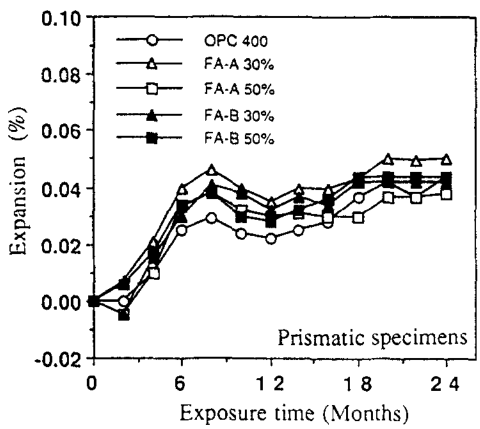

FIG. 5 Changes in length of the concrete with the binder content of 400 kg/m^3

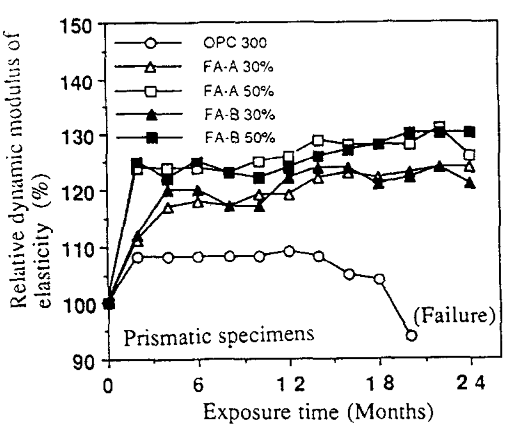

FIG. 6 Changes in dynamic modulus of elasticity of the concrete with the binder content of 300 kg/m^3

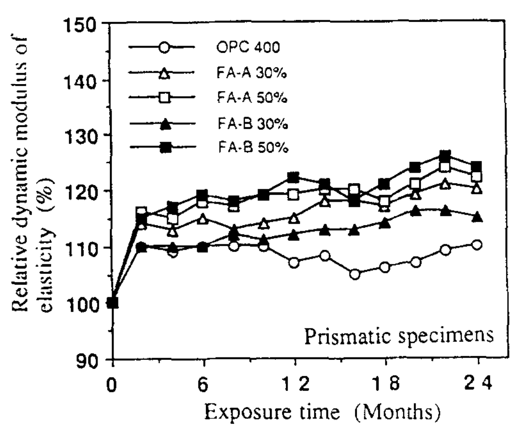

FIG. 7 Changes in dynamic modulus of elasticity of the concrete with the binder content of 400 kg/m^3

Length Change and Dynamic Modulus of Elasticity

Figs. 4 and 5 show changes in the length of the concrete with the binder content of 300 and 400 kg/m^3 with the exposure time, respectively. In OPC concrete with the binder content of 300 kg/m^3, a relatively large expansion was observed after 10 months of exposure time when the cracks on the surface had developed, resulting in the expansion of 0.12 % at 16 months of exposure, whilst that with the cement content of 400 kg/m^3 exhibited no expansion. On the other hand, all fly ash concretes slightly expanded during early stages of exposure time, but after 6 months no significant expansion was found independently of both the binder content and the replacement level by fly ash, which was in the range of 0.03 to 0.04 % after 2 years of exposure. The difference in expansion behavior as well as in the compressive strength between both fly ash concretes containing FA-A and FA-B was also small.

Figs. 6 and 7 show changes in the dynamic modulus of elasticity of the concrete with the binder content of 300 and 400 kg/m^3 with the exposure time, respectively. From the results, it is apparent that the change in the dynamic modulus of elasticity of OPC concrete with the exposure time is not so significant as expected from the measurements of length change, because the failure of prismatic concrete specimens due to the sulfate attack is limited at the corners of specimens, and the development of cracks to the central portions is not great even at 2 years of exposure time. In high fly ash content concretes, there appears to be a tendency of increase of the dynamic modulus of elasticity with an increase of both the binder content and the replacement level by fly ash.

Sulfur Trioxide Content in Concrete and Characteristics of Reaction Products

The sulfur trioxide content (SO_3) measured at surface layers within 20 mm from the surface in cylindrical specimens are presented in Table 5. In the case of OPC concrete with the cement content of 300 kg/m^3, the sulfur trioxide content near surfaces rapidly increased after 6 months of exposure time, and at 2 years of exposure time a relatively large amount of sulfur trioxide was measured not only near surfaces but also in central portions of cylinders, because the sulfate solution deeply penetrated into the concrete through small cracks after surface cracks had occurred.

TABLE 5 Sulfur trioxide content and neutralization depth of OPC and Fly ash concretes.

	Sulfur trioxide content* (%)				Neutralization
	0	6 months	1 year	2 years	depth ** (mm)
OPC 300	0.6	3.7	14.3	11.4	---
FA-A 30%	0.5	3.7	4.7	2.8	1.0
FA-A 50%	0.2	1.5	2.0	1.8	2.0
FA-B 30%	0.5	3.8	4.8	3.2	2.5
FA-B 50%	0.5	---	---	---	3.0
OPC 400	0.9	2.3	3.9	5.7	0.5
FA-A 30%	0.7	0.7	2.7	2.4	2.5
FA-A 50%	0.7	2.6	2.9	2.0	5.5
FA-B 30%	0.7	1.7	1.5	1.7	1.5
FA-B 50%	0.6	1.1	1.2	1.6	3.5

(cylindrical specimens,75 mm in diameter and 150 mm in height)
* Measured by a wet chemical analysis, which is expressed by percentage of dry mortar sample
* * Measured by spraying a 1 % phenolphthalein ethanol solution on broken surfaces of cylindrical specimens after 2 years of exposure to the 10 % Na_2SO_4 solution

OPC concrete with the cement content of 400 kg/m^3 also showed a tendency of the increase in sulfur trioxide content near surfaces with the exposure time, although its value was approximately half that of OPC concrete with the cement content of 300 kg/m^3 at 2 years of exposure time. On the other hand, it was found that all fly ash concretes showed a lower sulfur trioxide content near surfaces when compared with OPC concretes, and that for fly ash concretes, the greater both the binder content and the replacement level by fly ash, the smaller the sulfur trioxide content penetrating into concrete. It can therefore be concluded that a high replacement of portland cement by fly ash is very effective in preventing the sulfate solution from intruding into concrete.

Figs. 8 and 9 show DSC curves for OPC and fly ash concretes at various exposure time. DSC curves for OPC concrete with the cement content of 300 kg/m^3 indicate that the major reaction products are ettringite and gypsum, and that in deteriorated one with the cement content of 300 kg/m^3, both endothermic peaks for ettringite at 110 °C and gypsum at 140 °C significantly increase with the exposure time, which corresponds to the rapid decrease in an endothermic peak of calcium hydroxide at 460 °C. On the other hand, DSC curves for fly ash concrete also show that an endothermic peak for calcium hydroxide at 460 °C gradually decreases in the process of pozzolanic reaction of fly ashes, and that both endothermic peaks for ettringite and gypsum in fly ash concretes are relatively smaller than those in OPC concretes, especially for high fly ash content concrete with the binder content of 400 kg/m^3 and with the replacement level of 50 %. From the results of X-ray diffraction analysis, other reaction products such as monosulphate hydrate, thaumasite and calcite were also identified in the deteriorated OPC concrete with the cement content of 300 kg/m^3 (7). It can be observed from the results of DSC and X-ray diffraction analysis that the chemical attack on high fly ash content concrete in the 10 % Na_2SO_4 solution seems to be limited only to the proximity of the surface of concrete, whilst OPC concrete is corroded deeply and seriously.

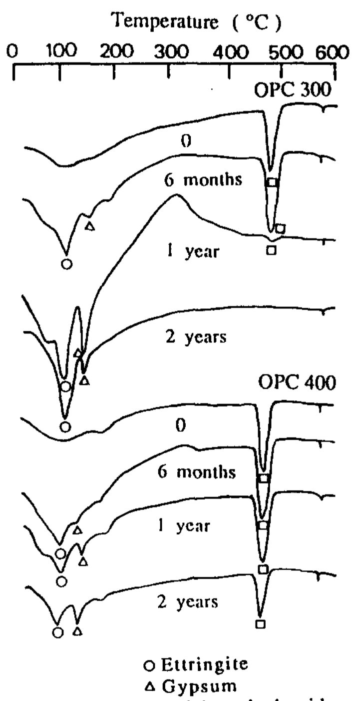

FIG. 8 DSC curves for OPC concretes with the cement content of 300 and 400 kg/m^3

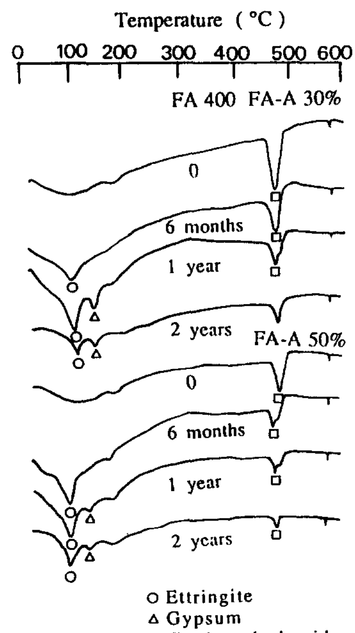

FIG. 9 DSC curves for fly ash concretes with the binder content of 400 kg/m^3 and with the replacement level of 50 % by FA-A

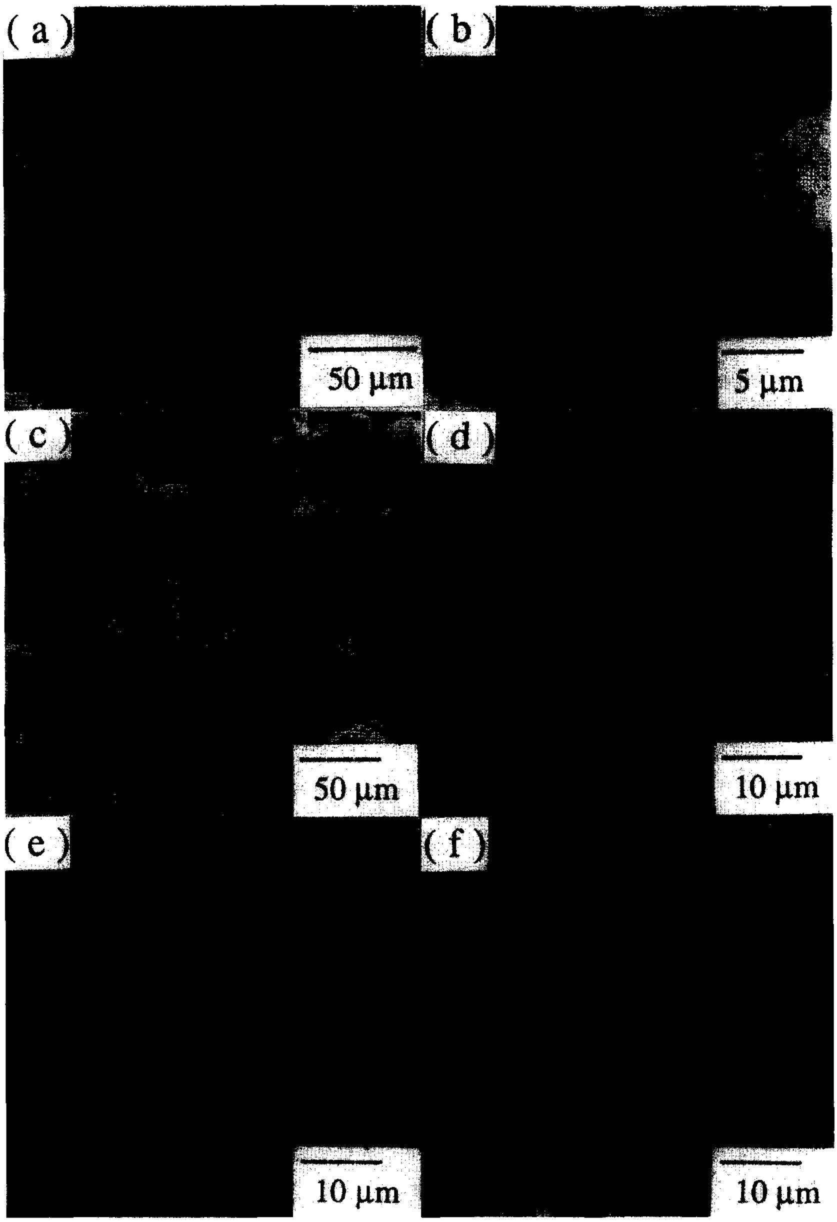

FIG. 10 Scanning electron microphotographs for OPC and fly ash concretes when exposed to the 10 % Na_2SO_4 solution
(a : OPC 300, 6 months, b : OPC 300, 6 months,
c : OPC 300, 1 year, d : OPC 300, 2 years,
e : FA 400, FA-A 50%, 1 year, f : FA 400, FA-A 50%, 2 years)

Microstructure and Pore Size Distribution

Fig. 10 shows SEM observations for OPC and fly ash concretes when exposed to the 10 % Na_2SO_4 solution. In OPC concrete with the cement content of 300 kg/m^3, it is observed that

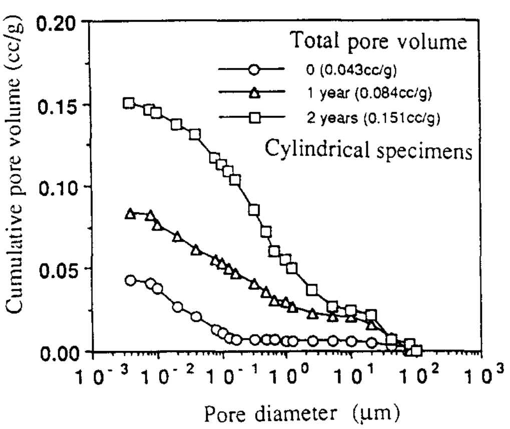

FIG. 11 Cumulative pore size distribution curves for OPC concretes with the cement content of 300 kg/m^3

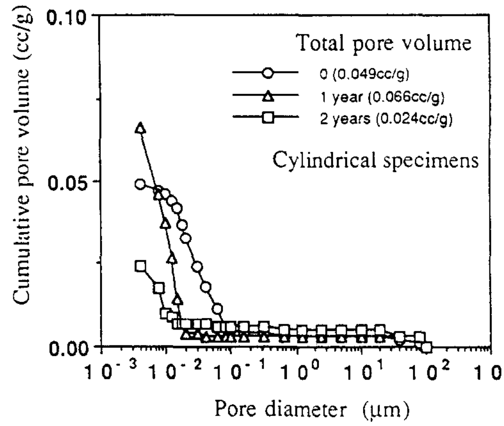

FIG. 12 Cumulative pore size distribution curves for fly ash concretes with the binder content of 400 kg/m^3 and with the replacement level of 50 % by FA-A

there exist plenty of cracks in the cement paste around fine aggregates, and that in the cracks or voids of deteriorated concrete, small rod-like crystals of ettringite are precipitated, as shown in Fig. 10 (a, b). Furthermore, in OPC concrete, gypsum which has produced along the cracks grows up to the large bundle of lath-like crystals in the range from 100 to 200 μm at 1 year of exposure time, as shown in Fig. 10 (c,d). It appears that the formation of large amounts of gypsum may contribute to the softening and scaling of surface layers of concrete, and subsequently to accelerate the deterioration of concrete due to the sulfate attack. On the other hand, in high fly ash content concretes, only a small amount of ettringite is observed mainly in air-voids near surfaces, which appears to be harmless in the deterioration of concrete (8). It is also apparent from SEM observations that the pozzolanic reaction of fly ashes can be progressing well even in the 10 % Na_2SO_4 solution, resulting in a dense texture of cement paste around fly ash particles, as shown in Fig. 10 (e,f). These results suggest that the formation of gypsum as well as ettringite may play an important role in the process of deterioration of concrete due to the sulfate attack (4).

Figs. 11 and 12 show pore size distribution curves for OPC and fly ash concretes at various exposure time. It is generally appreciated that the chemical durability of concrete is greatly affected by the penetrability of aggressive solution into concrete. With respect to the threshold value of pore diameter affecting the permeability of concrete, Mehta has pointed out that a good correlation is found between the water permeability of cement paste and the volume of pores with the diameter greater than 0.1 μm (9). In the comparison of pore size distribution between OPC and fly ash concretes having the same binder content shown in Table 4, it can be clear that the volume of pores with the diameter greater than 0.1 μm is decreased by the replacement by fly ash, although the total pore volume of fly ash concrete increases with an increase of the replacement level by fly ash. This suggests that the penetrability of sulfate solution into fly ash concrete is less even at early ages, which corresponds to the small amount of sulfur trioxide content measured near surfaces of concrete in fly ash concretes. In pore size distribution curves of OPC concrete with the cement content of 300 kg/m^3 shown in Fig. 11, there was a remarkable increase of volume of pores with the diameter greater than 0.1 μm during 2 years of exposure. This may be due primarily to the relaxation in the texture of cement paste and/or interfacial zone around aggregates due to the formation of expansive reaction products. However, in pore size distribution curves of high fly ash content concretes shown in Fig. 12, the peak of pore size distribution shifted toward the finer diameter along with the decrease in total pore volume. A drastic decrease of large and continuous pores especially in high fly ash content concrete may result in an excellent resistance of concrete to the sulfate attack. This result indicates that the effects of fly ashes on the improvement of sulfate resistance of concrete can be explained by the microstructural change associated with the pozzolanic reaction of fly ashes as well as the small content of calcium hydroxide (10).

Conclusions

The laboratory test data showed that the replacement of portland cement by relatively large amounts of fly ash effectively improved the resistance of concrete to the sulfate attack. Especially, high fly ash content concrete with the binder content of 400 kg/m^3 and with the replacement level of 50 % showed an excellent sulfate resistance during 2 years of exposure to the 10 % Na_2SO_4 solution. From the results, it can be concluded that high fly ash content concrete is not only economical but also beneficial for the improvement of chemical resistance.

The main results obtained in this study are summarized as follows ;

(1) High fly ash content concrete with the binder content of 400 kg/m^3 and with the replacement level of 50 % was still gaining the compressive strength and dynamic modulus of elasticity in the 10 % Na_2SO_4 solution, and no detectable trace of deterioration caused by the sulfate attack was found within a period of 2 years. The influence of type of fly ash on the sulfate resistance of high fly ash content concrete was also insignificant.

(2) The deterioration of OPC concrete in the 10 % Na_2SO_4 solution was related intimately to the relaxation of cement paste texture associated with the formation of both gypsum and/or ettringite. The formation of expansive reaction products in high fly ash content concrete was less and limited only near surfaces when both the binder content and the replacement level by fly ash was high.

(3) An excellent sulfate resistance of high fly ash content concrete was dependent both on the decrease in calcium hydroxide content in concrete and on the dense and discontinuous pore structure which resulted from the successive progress of pozzolanic reaction of fly ashes during the curing and exposure time.

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