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DURABILITY AND POZZOLANIC REACTION OF FLY ASH CONCRETE EXPOSED TO VARIOUS OUTSIDE ENVIRONMENTS

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In this study, outside exposure tests of fly ash concrete were started in 2009 at various places in Japan in order to assess the effect of the differences of the exposure environment on the variation of long term durability of fly ash concrete and the degree of pozzolanic reaction of fly ash. This paper shows the results of durability monitoring over seven years from the start of exposure testing and the degree of pozzolanic reaction after seven years. The durability of fly ash concrete is improved due to pore structure complicated by the pozzolanic reaction. The degree of pozzolanic reaction of fly ash in concrete exposed under any conditions ends up being the same when enough time has elapsed, such as seven years, regardless of differences in exposure conditions.

Keywords: Compressive strength, Volume resistivity, EPMA, Pore size distribution, Tortuosity, Chloride ion permeation resistance.

1 INTRODUCTION

Fly ash (FA) is a byproduct of coal-fired power generation. When mixed with concrete, fly ash contributes to improved long-term strength, reduced water content per unit volume, prevention of temperature cracking, improved durability, and so on. The mechanism that improves the durability of FA concrete is considered to be the densification of the hardened cement structure that proceeds with the pozzolanic reaction introduced by the FA (Japan Fly Ash Association 2015). Generally, concrete durability is assessed by accelerated testing of various kinds. However, the relationship between the degradation observed under accelerated test conditions and the degradation observed in concrete structures in their real service environments is not always clear. Real concrete structures are exposed to many variations in climatic conditions, temperature conditions and other conditions, making it difficult to evaluate their durability in a uniform manner. To evaluate the durability of FA concrete in real environments, we have been conducting outdoor exposure testing of FA concrete at three locations in Japan since 2009. We used wall-shaped large specimens for exposure testing in order to better simulate conditions experienced by real structures. Each year, we have been extracting concrete core samples from these test specimens in our year-to-year concrete durability monitoring activities. This paper covers FA concrete monitoring results over seven years from the start of exposure, providing data on the aging degradation of durability-related physical properties such as strength and volume resistivity in different environments. Aiming to find out how pozzolanic activity may vary according to environment, we selected three test locations differing greatly in terms of environmental conditions, and analyzed data from concrete core samples in three test locations for seven years from the start of exposure, paying attention to hydrate and pore size distribution in concrete structure.

2 OVERVIEW OF EXPOSURE TESTING

2.1 Tested Concrete Types and Composition

Table 1 lists the materials composing the tested concrete specimens. Table 2 shows the composition in terms of mixing ratios. The FA used is FA of Type II as defined in Japan Industrial Standard. The exposure testing addressed FA concrete of two types that differ in the FA substitution ratio: 20 % substitution (FA20) and 30 % substitution (FA30). For comparison, testing was performed also on normal concrete made of Portland cement (OPC). As to concrete composition, we chose the widely used mixing ratios of W/P = 55 %, s/a = 43 %, slump = 12 cm, and air mixture = 4.5 %.

2.2 Exposure Specimens and Exposure Sites

As shown in Figure 1 each exposure test specimen is given a wall-like geometry: 770 mm (W) x 540 mm (H) x 300 mm (D). For the evaluation of year-after-year degradation, a single concrete core sample (74 mm in diameter) was extracted from each specimen every year. The specimen was kept in the formwork for seven days after casting. After the formwork was removed, each specimen was left alone indoors for four weeks to age the material and then placed outside in test location to start outdoor exposure testing. The specimens were exposed to environments at three locations that differ greatly in terms of environmental conditions as shown in Table 3. All specimens are undergoing exposure testing since 2009.

2.3 Durability Monitoring through Concrete Core Sampling

We have been extracting a single concrete core sample from each exposure test specimens every year. The following tests and measurements performed on concrete core samples every year.

(1) Compressive strength

The specifications of the samples used in compressive strength testing were as follows: cylindrical samples of 100 mm in diameter and 200 mm in height for test performed at the material age of 28 days; cylindrical samples of 74 mm in diameter and 100 mm in height cut out from concrete core samples for tests performed annually from one to seven years from the start of exposure.

(2) Volume resistivity

Volume resistivity of concrete is highly related with the chloride ion permeation resistance. From this viewpoint, we used the volume resistivity as an indicator of durability in this study. The volume resistivity of each core sample was measured according to JSCE K 562-2008 (2008).

(3) Pore size distribution

The structural density of the concrete is identified as a factor contributing to durability. In order to evaluate this structural density, we performed pore size distribution measurement using mercury press-in method. Each sample for pore size distribution measurement was prepared by using a cutter blade to cut an approximately 5 mm square block out of the mortar portion of the concrete core sample at a depth of 150 to 160 mm from the surface, and each extracted sample was used after freeze drying.

Table 1. Materials used.

Specification
Ordinary Portland Cement Density: 3.16 g/cm^3, Blaine specific surface area: 3,310cm^2/g
JIS type Ⅱ, Density: 2.25 g/cm^3, Blaine specific surface area: 3,800 cm^2/g
Sea sand, Density: 2.57 g/cm^3, Water absorption: 1.30%
Crushed stone (G_{max}=20mm), Density: 2.85 g/cm^3, Water absorption: 1.58%
AE water reducing agent AE agent

Table 2. Mix proportion of Concrete.

Type of Concrete	W/P [%]	s/a [%]	F/(C+F) [%]	Unit content [kg/m^3] W	C	F	S	G
OPC			0	159	289	0	779	1,144
FA20	55	43	20	151	220	55	785	1,154
FA30			30	146	186	80	790	1,161

Table 3. Exposure site.

Site (Symbol)	Exposure environment
Hokkaido (Site H)	Subarctic zone, Inland area
Kanagawa pref. (Site K)	Temperate zone, Inland area 2km far from seashore
Okinawa pref. (Site O)	Subtropical zone, Marine environment

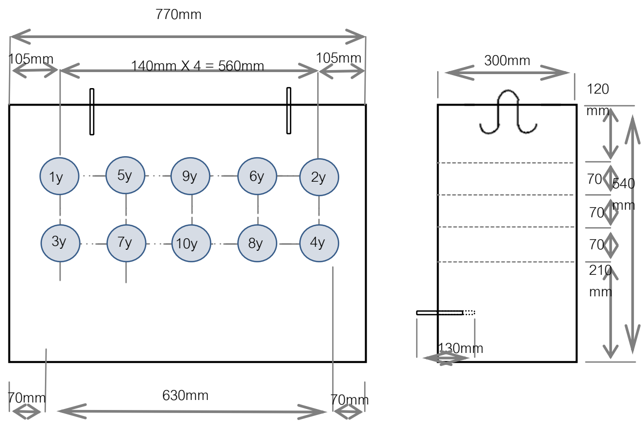

Figure 1. Outline of Exposed specimen.

2.4 Evaluation of Pozzolanic Activity

As targets, we chose specimens exposed to greatly different environments at three different locations: Site H in a cold zone, Site K in a temperate zone, and Site O in a sub-tropical zone. We evaluated pozzolanic activity in FA concrete specimens exposed for seven years. We evaluated pozzolanic activity using the following approach:

Presence or absence of $Ca(OH)_2$: We determined the presence or absence of $Ca(OH)_2$, which is required for sustaining pozzolanic activity, by means of TG analysis and XRD analysis. The sample for analysis was taken from the mortar portion of the core samples and preconditioned like a sample for pore size distribution measurement. This time, however, the material was analyzed after being crushed using a disk mill.

3 TEST RESULTS AND DISCUSSIONS

3.1 Year-to-Year Changes in Compressive Strength

Figure 2 shows year-to-year changes in the compressive strength (at three locations that greatly differ in environmental conditions). At every exposure test site, the difference in compressive strength between OPC concrete and FA concrete, which was evident before the start of exposure, almost disappeared by the third year of exposure. The results of measurements up to seven years from the start of exposure demonstrate some variation in strength over time because measurements were taken every year on a single core sample only. Nevertheless, at every site and irrespective of the FA substitution ratio, the strength was found to be similar between OPC concrete and FA concrete even after seven years had elapsed from the start of exposure.

3.2 Year-to-Year Changes in Volume Resistivity

Figure 3 shows year-to-year changes in the volume resistivity ρ. The curve in the chart shows regression by $\rho(t) = abt/(1+bt)$, where a and b are constants while t represents the exposure time. The greatness of volume resistivity value was in the order of FA30 > FA20 > OPC. The volume resistivity measured on OPC was low and remained almost constant. We found that the volume resistivity of FA concrete continued to increase in the first three to four years, then the rate of increase slowed down until the value almost stabilized at a certain level.

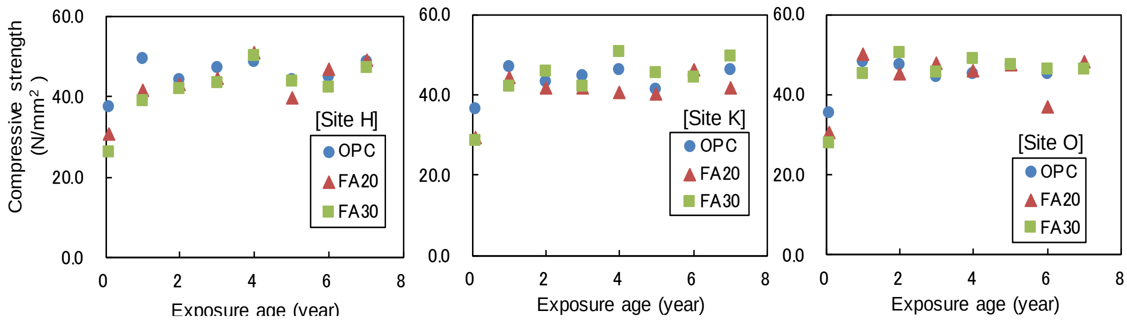

Figure 2. Changes in compressive strength with exposure age.

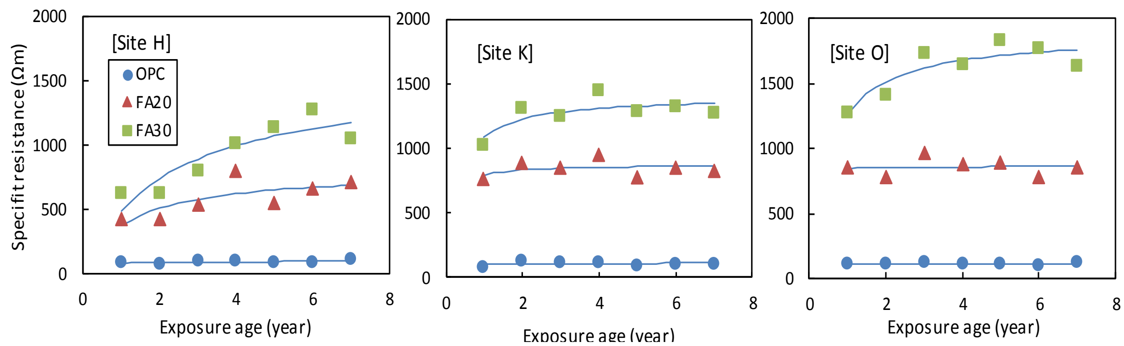

Figure 3. Changes in volume resistivity with exposure age.

3.3 Relationship between Pore Structure and Volume Resistivity

Figure 4 shows the relationship between the total pore specific surface area, derived from the pore size distribution measurement, and the volume resistivity. As shown in the chart, the increase in the total pore specific surface area was found to be in a linear relationship with the increase in the volume resistivity. The larger the volume resistivity of FA concrete, the larger is the total pore specific surface area. The greatness of volume resistivity suggests complexity of the pore structure, which may be referred to as "tortuosity". From the relationship between diffusion coefficient D, volume resistivity ρ, and tortuosity[1], we determined the ratio of FA to OPC in terms of tortuosity in pore structure (See Table 4. Note that the volume resistivity was derived from a regression curve). Based on this, it is surmised that the substitution of OPC by FA reduces the

[1] $\tau = D \propto \rho^{-1}, D \propto \tau^{-1}$

diffusion coefficient of the FA concrete by a factor of about 1/8 to 1/7 in the case of FA20, or by a factor of about 1/15 to 1/11 in the case of FA30.

Table 4. Tortuosity ratio of FA to OPC.

Symbol	Exposure site					
	H	A	K	F #1	F #2	O
FA20	7.22	7.97	7.69	8.34	7.09	7.55
FA30	12.30	11.24	12.00	15.07	13.81	15.46

Table 5. Value of Ca/Si at the peak of frequency distribution curve.

Symbol	Exposure site			Average
	H	K	O	
OPC	1.95	2.00	1.90	1.95
FA20	1.70	1.70	1.75	1.72
FA30	1.65	1.60	1.65	1.63

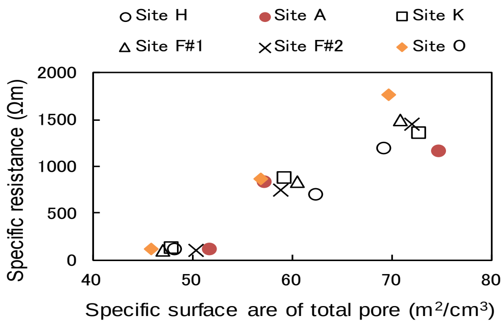

Figure 4. The relationship between the Specific surface area of total pore and volume resistivity.

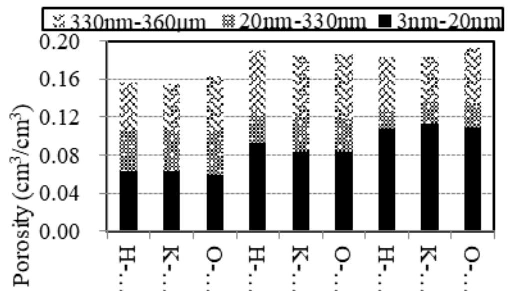

Figure 5. Pore size distribution.

3.4 Changes in the Pore Size Distribution with the Progress of Pozzolanic Reaction

Figure 5 shows pore size distribution determined by mercury press-in method. Pore diameters were divided into the following three ranges: 3 to 20 nm, 20 to 330 nm, and 330 nm to 360 µm. We can see from the chart that, as the FA substitution ratio increases, the total volume of pores with a diameter in the range between 3 to 20 nm increases while the total volume of pores with a diameter in the range between 20 to 330 µm decreases. The pores increased with a diameter in the range between 3 to 20 nm and the decrease of pores with a diameter in the range between 20 to 330 µm resulting from substitution by FA. It is assumed to be caused by changes in pores that take place with the progress of the pozzolanic reaction introduced by the FA. As to variation across sites, we found little variation in the volumes of pores of the above mentioned ranges that are affected by the pozzolanic reaction.

As a conclusion from the above, the study of the pore size distribution did not demonstrate any significant variation across sites in the progress of pozzolanic activity introduced by FA or in changes to pores resulting from it. This observation is consistent with the absence of variation across sites in the results of compressive strength tests performed on specimens after seven years from the start of exposure (Figure 2). In this study, we tested concrete after seven years from the start of exposure, and the test results suggest that, after the passage of this much of time, there would be little variation in the progress of pozzolanic activity across different sites distributed over the subarctic, temperate, and subtropical zones of Japan.

3.5 Presence or Absence of $Ca(OH)_2$

Figure 6 shows DTG analysis results of the mortar portion to seven years from the start of exposure. The chart shows for OPC a reduction of the weight of $Ca(OH)_2$ in the 400 to 500 °C temperature range. For FA concrete, however, the chart does not show any significant reduction of the weight of $Ca(OH)_2$. Figure 7 shows XRD analysis results. For OPC, the XRD analysis results indicate a clear peak of $Ca(OH)_2$ around 18.1° and also around 34.1°. For FA concrete, however, irrespective of exposure sites, the XRD analysis did not indicate any significant presence of $Ca(OH)_2$. As a conclusion from the above results, in all FA concrete specimens, almost all $Ca(OH)_2$ in the hardened substance had been consumed by the pozzolanic reaction, preventing any further continuation of pozzolanic activity. That is to say, even though the FA concrete specimens were exposed to different environmental conditions, the progress of the pozzolanic reaction in them over a long period of time had consumed almost all $Ca(OH)_2$ in them before seven years had elapsed, preventing any further continuation of pozzolanic activity.

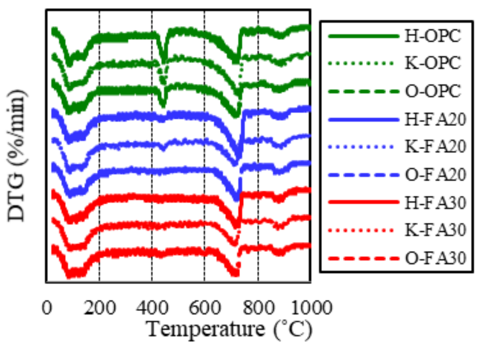

Figure 6. Results of DTG analysis.

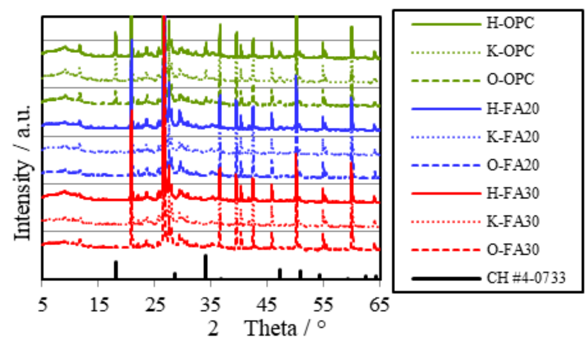

Figure 7. Results of XRD analysis.

4 SUMMARY

The following lists the findings in this study:

(1) The strength of FA concrete becomes approximately similar to that of OPC concrete by the third year from the start of exposure. The FA concrete compressive strength was found to vary across exposure sites up to two years had elapsed from the start of exposure, but no such variation was found in tests performed after three or more years from the start of exposure.

(2) The volume resistivity of FA concrete continued to increase for the first three to four years, then the rate of increase slowed down until the value was mostly stabilized at a certain level.

(3) It is surmised that the substitution of OPC by FA reduces the diffusion coefficient of FA concrete by a factor of about 1/7 to 1/8 in the case of FA20, and by a factor of about 1/11 to 1/15 in the case of FA30. We believe that this happened as pore structures became more complex as a result of the pozzolanic reaction introduced by the FA.

(4) We believe that the absence of variation across exposure sites is due to the fact that, at every exposure site, the calcium hydroxide in specimens was almost totally consumed by the time seven years had elapsed, preventing pozzolanic activity introduced by FA from continuing further.

References

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