FLY ASH CHARACTERIZATION RELATED TO MITIGATION OF EXPANSION DUE TO ASR

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Abstract

This paper deals with the characters of fly ash related to its suppressing effect on ASR expansion of mortar. The suppressing effect of fly ash on ASR expansion depends on its "specific surface area" and "amorphous silica content". Especially, the specific surface area is the most important factor to mitigate ASR. At a low hydroxide ion concentration of pore solution, difference in the types of fly ash on the ASR expansion becomes rather small. In this study, a new index composed of specific surface area, amorphous silica content and alkali content of cement and fly ash is proposed. From the experimental results presented in this paper, this index proves to be well correlated with the suppressing effect of fly ash.

KEYWORDS: fly ash, glass phase, particle size distribution, hydroxide ion concentration

1 INTRODUCTION

It is well known that incorporation of fly ash into concrete is effective for mitigation of expansion due to alkali-silica reaction (ASR). Because calcium content of fly ash in Japan is relatively low, many cases of ASR damage can be suppressed by fly ash replacement ratio of 15-25%. However, the effectiveness of fly ash on the prevention of ASR expansion depends on the types of fly ash. Especially, phase compositions of fly ashes are varied and complex because combustion process and chemical compositions of coal are different for each power plant. Normally, the mineralogical composition of fly ash in Japan is quartz, mullite, hematite, magnetite, and glass phase. Pozzolanic reaction of fly ash depends on its glass content and chemical composition in the glass. Proper characterization of fly ash is necessary to make clear the suppressing mechanism of fly ash on ASR expansion.

The aim of this study is to clarify the dominant character of fly ash for mitigation of ASR expansion. In this paper, characterization of fly ash is discussed based on an accelerated test of mortar specimen incorporating fly ash and ASR reactive aggregate.

2 MATERIALS AND METHODS

2.1 Test specimens

Small mortar bar specimens (40×40×160mm) were prepared to evaluate the suppressing effect of fly ash on ASR expansion. Although these dimensions have serious concerns of alkali leaching, these specimens are considered to be applicable for clarifying the dominant character of fly ash for mitigation of ASR expansion.

Ordinary Portland cement was used, which has alkali content of 0.62% by mass Na_2O equivalent. Seven types of fly ashes produced in Japan were used. The chemical compositions of fly ashes are presented in Table 1. Physical properties of fly ashes are listed in Table 2. Andesite was used as aggregate that had been crushed and graded according to JIS A 1146 (Accelerated mortar bars test). Reactive phases of andesite were "cristobalite" and "volcanic glass". The ASR reactivity of the andesite was judged to be "not innocuous" according to JIS A 1145 (Chemical test); the dissolved silica "Sc" and reduction in alkalinity "Rc" were 192mmol/l and 67mmol/l, respectively.

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Plain mortar specimens (without fly ash) were prepared with the water-to-cement ratio of 0.45 and the sand-to-cement ratio of 2.26. The extra amount of NaOH solution was added to adjust the total alkali content up to 7 and 14kg/m^3. In the case of fly ash mortar, fly ash was mixed at 10, 20, and 30 % by volume of cement. In addition, the water content and the reactive aggregate content per unit mortal were kept constant. Diamond [1] pointed out that addition of NaOH solution enhances sulfate ion concentration resulting in lowering hydroxyl ion concentration at the early age. In this study, pore solution was extracted from plain mortar at 91 days and then hydroxyl ion concentration and sulfate ion concentration were analyzed. Hydroxyl ion concentrations of three mortar specimens which had the total alkali content of 3.5, 7 and 14kg/m^3, were 0.39, 0.69 and 1.53 mol/l respectively. Sulfate ion concentration of mortar specimens which had the total alkali content of 3.5, 7 and 14 kg/m^3, were 0.01, 0.02 and 0.08mol/l respectively. Hydroxyl ion concentration of pore solution is linearly correlated to the total alkali content in mortar in a long term and sulfate ion concentration is relatively low. This study mainly focused on the viewpoint of hydroxide ion concentration of pore solution although the effect of addition of NaOH solution on composition of pore solution and ASR expansion still remains controversial.

2.2 Accelerated mortar bars test

Mortar specimens were cured in the molds for 24 hours after casting. After they were removed from the molds, their initial length was measured. Then they were placed in a fog chamber for 6 months, in which the temperature was 40deg C and relative humidity (R.H.) was 100%. The length change was measured at 20deg C.

After accelerated mortar bars test, mortar specimens with an total alkali content of 14kg/m^3 were crushed and dissolved with hydrochloric acid for extraction of reacted andesite. Andesite was pulverized and analyzed by X-ray diffraction, XRD. Zincite was used for internal standard material of XRD analysis. Peak intensities of cristobalite (I_{cr}), plagioclase (I_{pl}), zincite (I_{zn}) were measured and the reaction ratio of cristobalite, $(I_{cr} - I_{pl})/I_{zn}$, was indirectly calculated. In this study, I_{pl}/I_{zn} was constant.

2.3 Phase composition of fly ash

The mineralogical composition of fly ash used in this study was quartz, mullite, hematite, magnetite, and glass phase. The amounts of quartz, mullite, hematite and magnetite were analyzed by XRD. Zincite was used for an internal standard material of XRD analysis. SO_3 was assumed to exist in the state of $CaSO_4$. The glass content of fly ash was calculated from the determined amount of crystal, which consists of quartz, mullite, hematite, magnetite, $CaSO_4$, and the loss of ignition. Silica content in glass phase was calculated for evaluation of fly ash reactivity.

2.4 Particle size distribution of fly ash

The specific surface area is also an important factor for evaluation of the fly ash reactivity. The Kozeny-Carman equation has been used for calculating Blaine specific surface area. This equation, however, cannot adequately estimate particle under 1μm in diameter. In this study, particle size distribution was analyzed with laser diffraction and scattering method analyzer. Samples were dispersed using ultra sonic wave in water for measurement. In this study, specific surface area, A_{FA}, from particle size distribution measured by using laser diffraction and scattering method analyzer, was calculated as follows.

$$A_{FAi} = \frac{\pi \cdot a_i^2}{\frac{\pi \cdot a_i^3}{6}} = \frac{6}{a_i} \quad (1)$$

$$A_{FA} = \sum \frac{x_i}{100} \cdot A_{FAi} = 6 \sum \frac{x_i}{100 \cdot a_i} \quad (2)$$

where

A_{FAi}: specific surface area of particles of fly ash of which the diameter lies between the sieve sizes of l_i and l_{i+1} (cm^2/cm^3)

A_{FA}: specific surface area of fly ash measured by laser diffraction and scatter analyzer (cm^2/cm^3)

x_i: percentage of particles of fly ash of which the diameter lies between the sieve sizes of l_i and l_{i+1} (%)

a_i: arithmetical average diameter of l_i and l_{i+1} $=(l_i+l_{i+1})/2$ (cm)

2.5 Characteristics of fly ash used in this study

Table 3 presents the phase compositions and A_{FA} of fly ash used in this study. It is noted that the fly ashes contain a high glass phase. Chemical compositions of glass are mainly silica and alumina. The calcium content of FA(E) is about 10% in glass phase. Thus, the basicity of glass phase in FA(E) is lower than those in case of the other fly ashes.

3 TEST RESULTS

3.1 Effects of fly ash on mitigation of ASR expansion

Figure 3 shows the expansion behavior of mortar incorporating FA(B) in case of 14kg/m^3 of total alkali content in mortar. The increase of replacement ratio of fly ash led to high mitigation of ASR expansion. Expansion ratio of fly ash mortar to that of plain mortar became constant from 28 days to 182 days. Therefore, the expansion ratio after 28 days will be used as an index in this study to evaluate suppressing effect of ASR expansion. Figure 4 shows the relationship between the replacement ratio of fly ash and the expansion ratio. The expansion ratio decreased with an increase in the replacement ratio of fly ash. The ability of fly ash in reducing ASR expansion also depended on the types of fly ashes. Generally, fly ash containing high calcium cannot suppress ASR expansion because C-S-H gel with low Ca/Si cannot be generated. The expansion ratio of FA(E), however, decreased with increasing fly ash replacement ratio although calcium content was relatively high. Sakai et al. [4] pointed out that pozzolanic reaction stops though a large amount of glass phase remained. The A_{FA} value of FA(E) is the largest in this study. Therefore, the suppressing effect of FA(E) was high even though its calcium content is the highest.

Figure 5 shows the relationship between the replacement ratio of fly ash and the expansion ratio in case of 7kg/m^3 of total alkali content in mortar. In case of 7kg/m^3 of total alkali content in mortar, differences in types of fly ash were small. In case of high hydroxide ion concentration, larger amount of fly ash were necessary to mitigate the dissolution of reactive phase in aggregate because sorption capacity of C-S-H gel with a certain Ca/Si is constant regardless of the hydroxide ion concentration. This indicates that the appropriate fly ash replacement ratio would depend on the hydroxide ion concentration of pore solution. That is why the expansion ratio of FA(E) is also small though calcium content of FA(E) is the highest.

3.2 Reaction ratio of cristobalite

Figure 6 shows the relationship between the replacement ratio of FA(B) and the $(I_{cr}-I_{pl})/I_{zn}$. The small $(I_{cr}-I_{pl})/I_{zn}$ value indicates a high reaction ratio of cristobalite. Reaction ratio of cristobalite decreases with an increase in the replacement ratio of fly ash. The reaction ratio of cristobalite is very sensitive to pH. Decrease in the reaction ratio of cristobalite implies lowering pH of pore solution because of incorporating fly ash in mortar.

4 DISCUSSIONS

4.1 Characteristics of pozzolanic reaction (literature review)

In the accelerated test, fly ash is stimulated by hydroxyl ion on the surface layer of fly ash particle and pozzolanic reaction phase is formed. The Ca/Si of pozzolanic reaction phase is lower than that of plain cement paste [2]. It was found that the sorptivity of C-S-H gel is correlated with its Ca/Si [3]. The lower the Ca/Si ratio of C-S-H is, the larger the alkali is sorbed on C-S-H gel. The Ca/Si of cement paste incorporating fly ash is relatively low because Si-rich glass phase is dissolved from fly ash particle surface.

In addition, reaction of fly ash is terminated even though a large amount of glass remained [4]. Glass phase cannot dissolve in the pore solution with low pH. Volcanic glass in andesite which composition is similar to that of glass phase in fly ash cannot dissolve at pH=13.6 [5].

These phenomena in cement-fly ash system indicate that specific surface area and chemical composition of glass phase are important characters to the mitigation of ASR expansion. It is expected that hydroxide ion concentration of pore solution affects the effectiveness of fly ash on ASR expansion.

4.2 Effect of fly ash characters

The effect of fly ash on ASR expansion is different depending on the replacement ratio, type of fly ash and alkali content of cement. In this chapter, the data were analyzed using fly ash characters.

Figure 7 shows the relationship between the total surface area of fly ash in mortar and the expansion ratio. The total surface area of fly ash in mortar is calculated as the products of A_{FA} and

V_{FA} (V_{FA}: the fly ash volume per unit). There is a good correlation between the total surface area of fly ash and the expansion ratio. This result shows good agreement with Sakai et al [4].

Pozzolanic reaction, however, is dependent on quantity and chemical composition of glass phase of fly ash. Especially, amorphous silica content ($aSiO_2$) is an important factor for creating C-S-H gel with low Ca/Si because acidic silanol site is most attractive for alkali sorption. The relationship between $aSiO_2 \times A_{FA}$, amorphous silica content in specific surface area and expansion ratio is shown in Figure 8. The expansion ratio strongly depends on amorphous silica content in A_{FA}.

Based on these data, a new index, α, is proposed for evaluation of suppressing effect of fly ash. The index, α is calculated as the product of amorphous silica content, specific surface area and fly ash volume per unit ($aSiO_2 \times A_{FA} \times V_{FA}$). This index implies the amorphous silica content in total surface area in mortar. Figure 9 shows the relationship between the proposed index "α" and the expansion ratio. There is a good correlation between α and the expansion ratio. The expansion ratio became almost constant when α becomes large, because of increasing sorption site resulted from large fly ash replacement. Previous work of this study revealed that the efficacy of phase composition of fly ash on ASR mitigation becomes larger in case of fly ash with low specific surface area [6]. The specific surface area is the most dominant character for mitigation of expansion due to ASR.

4.3 Effect of hydroxide ion concentration

It is clear that the effectiveness of fly ash in mitigating ASR depends on hydroxyl ion concentration of pore solution. As mentioned earlier, hydroxyl ion concentration of pore solution is linearly correlated to the alkali content of the cement. Figure 10 shows the relationship between $\alpha/[OH^-]$ and the expansion ratio. The expansion ratio decreases with an increase in $\alpha/[OH^-]$.

Amorphous silica content, total surface area and hydroxyl ion concentration of pore solution are dominating factors for mitigation of ASR expansion. This result indicates the importance to incorporate enough amount of fly ash with high specific surface area, so that the hydroxyl ion concentration of pore solution can be relatively low.

Because of the condition of raw materials for cement production, in other words, the change in alumina source from clay to coal ash after middle 80's, the maximum alkali level of Japanese Portland cement is limited to 0.65% by mass. As shown in Figure 10, the ASR expansion ratio became smaller with increasing of $\alpha/[OH^-]$. It is shown from the regression curve in this figure that the influence of variation of fly ash quality do not much affect the suppressing effect when α becomes large. Therefore, if the total surface area of fly ash mixed was sufficiently large and alkali content of cement is low, the influence of the quality of fly ash could become small. However, another source of external alkalis from environment such as deicing salt or sea water has been pointed out [7, 8]. In addition, alkali release from some kind of minerals such as glass and feldspar in aggregates is very controversial internationally. These phenomena increase the pH of pore solution. Thus, larger amounts of fly ash are needed for preventing ASR expansion. Previous work reported that 30vol% of fly ash is needed to suppress ASR in external alkalis environment or internal alkalis environment with alkali release aggregate.

5 CONCLUSIONS

This paper presented dominating factors that suppress ASR-related expansion. The results of this study are summarized as follows:

(1) The expansion ratio of fly ash mortar is affected by the specific surface area and silica content in glass phase of fly ash.

(2) The reaction ratio of cristobalite decreases with an increase in fly ash volume. Use of fly ash can suppress the ASR expansion because it can lower pH of pore solution.

(3) A new index composed of specific surface area, amorphous silica content and hydroxyl ion concentration of pore solution has been proposed. From the experimental results, this index proves to be well correlated with the suppressing effect of fly ash.

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Table 1 Chemical compositions of fly ash

	Chemical composition (%)									
	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	P_2O_5
FA(A)	1.83	65.13	23.94	4.56	2.23	0.89	0.31	0.69	0.00	0.42
FA(B)	1.53	65.16	29.43	2.20	0.57	0.30	0.16	0.25	0.00	0.40
FA(C)	1.44	63.57	26.87	4.79	1.47	0.56	0.23	0.68	0.10	0.28
FA(D)	1.48	62.49	23.33	4.00	4.90	1.31	0.47	0.75	0.49	0.77
FA(E)	1.14	55.17	21.34	5.69	11.71	1.75	0.81	1.04	0.81	0.55
FA(F)	2.09	60.32	25.06	4.53	4.53	1.21	0.43	0.76	0.33	0.74
FA(G)	1.19	57.82	30.10	4.99	3.46	0.83	0.36	0.79	0.03	0.42

Table 2 Physical properties of fly ash

	density (g/cm^3)	Blaine (cm^2/g)	BET (m^2/g)	Acctivity index	
				28days	91days
FA(A)	2.32	4070	2.23	90	101
FA(B)	2.26	4510	1.73	90	100
FA(C)	2.28	3440	1.48	90	95
FA(D)	2.30	3910	1.77	96	101
FA(E)	2.41	4100	1.75	97	101
FA(F)	2.24	3860	3.54	86	94
FA(G)	2.27	2100	0.84	80	91

Table 3 Phase composition and A_{FA} analyzed in this study

	Glass content (%)	Amorphous silica content (%)	Amorphous alumina content (%)	A_{FA} (cm^2/cm^3)
FA(A)	69.1	47.9	12.5	21627
FA(B)	53.9	38.3	11.8	24757
FA(C)	66.4	47.7	11.1	17249
FA(D)	79.9	51.2	16.4	22019
FA(E)	84.3	46.8	15.9	24781
FA(F)	66.6	43.1	11.3	17476
FA(G)	56.9	39.9	6.6	14715

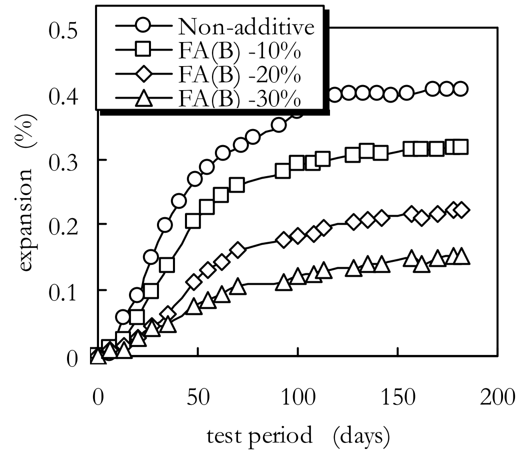

Figure 3 Expansion behavior of mortar incorporating FA(B) (total alkali content=14 kg/m^3)

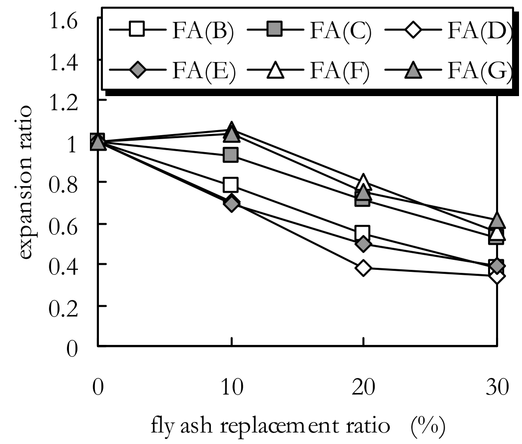

Figure 4 Fly ash replacement ratio vs. expansion ratio (total alkali content=14 kg/m^3)

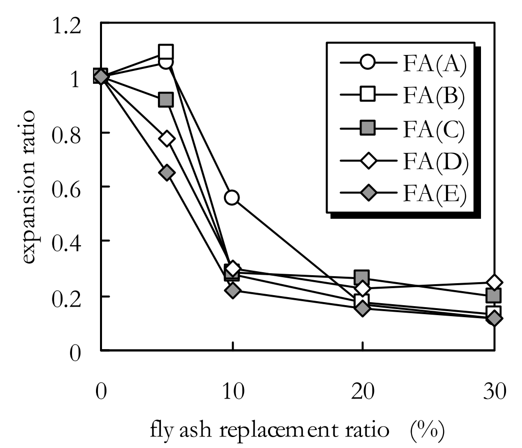

Figure 5 Fly ash replacement ratio vs. expansion ratio (total alkali content=7 kg/m^3)

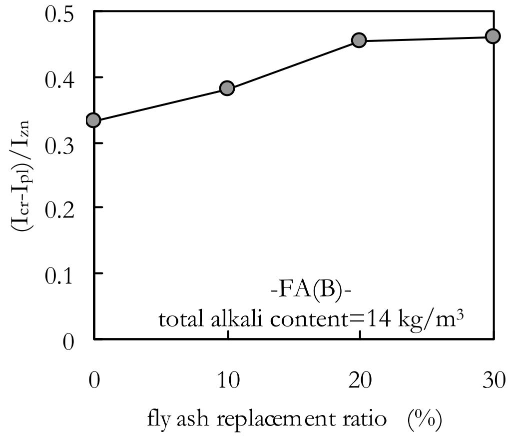

Figure 6 Fly ash replacement ratio vs. $(I_{cr} - I_{pl})/I_{zn}$ of andesite after test (FA(B), total alkali content=14 kg/m^3)

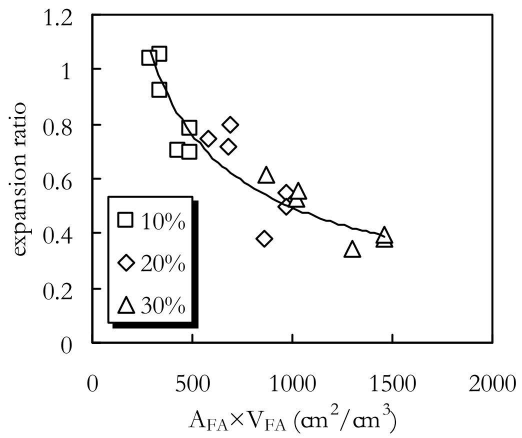

Figure 7 $A_{FA} \times V_{FA}$ vs. expansion ratio (total alkali content=14 kg/m^3)

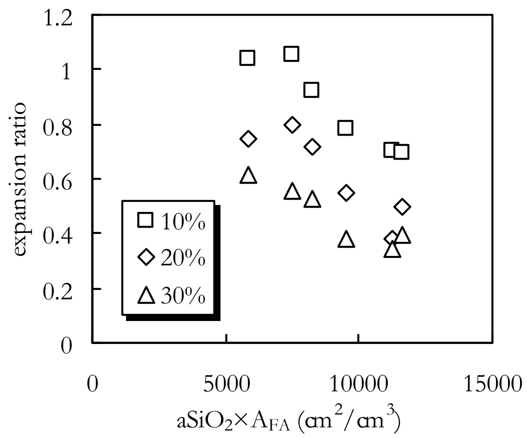

Figure 8 $aSiO_2 \times A_{FA}$ vs. expansion ratio (total alkali content=14 kg/m^3)

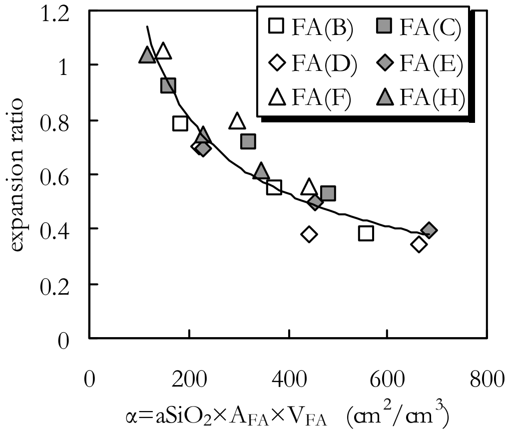

Figure 9 α vs. expansion ratio (total alkali content=14 kg/m³)

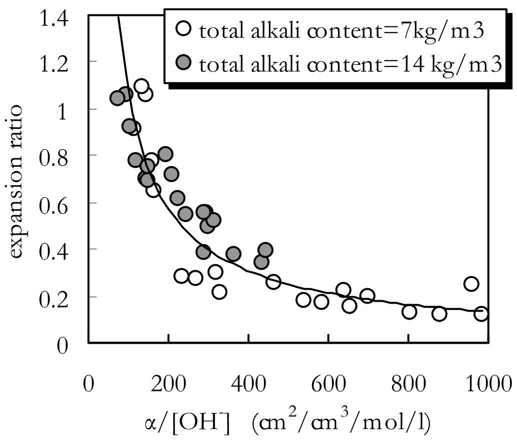

Figure 10. α/[OH⁻] vs expansion ratio