

## SUPPRESSION EFFECT OF FLY ASH ON ASR EXPANSION OF MORTAR/CONCRETE AT THE PESSIMUM PROPORTION

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### Abstract

This study reports the suppression effect of fly ash (FA) in mortar/concrete containing highly reactive aggregate at the pessimum proportion. The results of mortar tests showed that the suppression effect of FA was decreased when using highly reactive aggregate at the pessimum proportion compared to 100 vol% reactive aggregate. In addition, there was a possible shift to a smaller pessimum proportion of reactive aggregate by mixing in FA. From the concrete test, it can be concluded that an FA replacement ratio (ratio of cement replaced by FA) of 25 wt% or more is required to suppress ASR expansion when highly reactive aggregate is contained in concrete at the pessimum proportion.

**Keywords:** Pessimum proportion effect, fly ash, suppression effect

### 1 INTRODUCTION

Extensive research on the suppression of alkali-silica reaction (ASR) in mortar/concrete has confirmed the effectiveness of adding an appropriate amount of supplementary cementitious materials (SCMs) such as fly ash (FA) [1]. The use of FA blended cement and slag blended cement is recommended in Japan. Given the relatively low calcium content of FA in Japan, ASR damage can be significantly suppressed by a FA replacement ratio of 15 wt%. However, it has been found that although the current preventive measures are generally effective, there are limitations to the suppressibility of ASR-induced deterioration caused by certain types of reactive aggregate [2].

Katayama reported an interesting case of ASR-damaged concrete with 18 wt% of low-Ca FA [3]. Dark-colored “bronzite andesite” crushed stone occupying about 30 vol% of the coarse aggregate had produced expansion cracks. The reason why the FA was not effective in suppressing ASR, as explained by Katayama, is that the FA glass was less reactive than the hydrated rhyolitic glass and associated cristobalite in the aggregate. Another possible reason is the “pessimum proportion effect”, one of the features of ASR reported earlier by Stanton [4]. The pessimum proportion effect refers to the amount of reactive aggregate that induces the maximum expansion of mortar/concrete, which decreases when the content of reactive aggregate is increased or decreased from that amount. The mechanism of the pessimum proportion effect can be explained as the relationship between the consumption of alkali hydroxide in the pore solution and the reaction ratio of silica minerals [5]. Ichikawa proposed a simulation model for evaluating the pessimum proportion effect and pessimum size effect [6]. Highly reactive silica minerals such as opal, cristobalite and

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tridymite can react with alkali even in the case of low content so that their pessimum proportion is in the range of 5–20 wt% [7]. When such highly reactive aggregate is contained at the pessimum proportion in concrete, it can be assumed that a larger amount of FA should be added to the mix.

The present study reports the difference in suppression effect of FA depending on the reactive aggregate content in mortar/concrete. Based on the results of mortar tests, the mechanism behind the decreased effectiveness of FA on ASR suppression is discussed. From the results of concrete prism tests, the replacement level of FA for suppressing highly reactive aggregate at the pessimum proportion is investigated.

## 2 EXPERIMENTS

### 2.1 Materials

Five types of aggregate (labeled Ot1, Ot2, Ot3, Ks and Nt) collected from the same rubble field were used as reactive aggregate. Ot1, Ot2 and Ot3 were two pyroxene andesites and contained cristobalite and tridymite as reactive silica minerals, whereas Ks and Nt were land sand and two pyroxene andesite respectively and contained opal-CT, which shows high reactivity. Ks was coarse sand with particle size ranging from 1.2 to 5.0 mm. Opal-CT bearing tuff particles were included as a part of sand. Nt was coarse aggregate and made from andesite lava affected by later hydrothermal activity creating opal veins. Figure 1 shows the test results using the chemical method specified in ASTM C 289. Accordingly, the samples were judged as “potentially deleterious” or “deleterious”. Pure limestone having calcite content around 95 wt% was used as an inert aggregate.

Ordinary Portland cement (OPC) was used as the base material. Four types of FA labeled as R1, R1-4, T and H were prepared. Table 1, Table 2 and Table 3 show the bulk chemical composition, mineral composition and chemical composition of the FA glass phase, respectively. The chemical composition of the cement is also shown in Table 1.

### 2.2 Mixture proportions

#### *Mortar (Case 1)*

In Case 1, the effect of reactive aggregate proportion on the suppression effect of FA was investigated. Expansion behavior was examined in mortar with different amounts of reactive aggregate (Ot1, Ot2 and Ot3). Reactive aggregate was added to mortar bars (40×40×160 mm) in proportions of 10, 20, 30, 40, 60, 80 and 100 wt% of total sand content. The ratio of reactive aggregate content to sand by weight is represented as “R/S”. The ratio of water to cement and sand to cement was set at 0.50 and 2.125, respectively. The alkali content of mortar was adjusted such that  $\text{Na}_2\text{O}_{\text{eq}}$  of cement was 1.20 wt% by adding NaOH solution to the mixing water.

To check the suppression effect at the pessimum proportion, FA (R1) was mixed in at 20% by volume of cement in the case of R/S at 30 wt% and 100 wt%. The total alkali content per unit mortar was the same in the mixture proportions of mortar.

#### *Mortar (Case 2)*

In Case 2, the effect of replacement level of FA on the suppression effect at pessimum proportion was examined. Ks was added to mortar bars (40×40×160 mm) in proportions of 5, 20, 30 and 50 vol% of total sand content. The ratio of reactive aggregate content to sand by volume is represented as “r/s”. Case 2 experiments were carried out independently with Case 1 and different unit was used FA (H) was replaced with cement at 10, 20 and 30% by volume at each r/s. The ratio of water to cement and sand to cement was set at 0.50 and 2.25, respectively. The alkali content of mortar was adjusted such that  $\text{Na}_2\text{O}_{\text{eq}}$  of cement was 1.20 wt% by adding NaOH solution to the mixing water.

### *Concrete (Case 3)*

In the concrete prism test, the replacement level of FA for suppressing highly reactive aggregate at the pessimum proportion was investigated from the viewpoint of practical mix design. Nt was added to concrete in proportions of 10, 20, 30, 40, 60, 80 and 100 vol% of total coarse aggregate content. At a reactive coarse aggregate replacement level of 40 vol%, FA was replaced with cement at 15 and 25 wt%. The total alkali content ( $\text{Na}_2\text{O}_{\text{eq}}$ ) in concrete was set to 4.0 kg/m<sup>3</sup> by adding sodium hydroxide. The dimensions of the concrete specimen were 100×100×400 mm.

### **2.3 Expansion test**

At 24 h after casting, specimens were demolded and the initial length was measured immediately. Thereafter, specimens were stored in the humidity chamber at 40°C and 100 % RH. Change in length of mortar/concrete was measured using a contact gauge.

## **3 RESULTS AND DISCUSSION**

### *Case 1*

Figure 2 shows the expansion behavior of mortar at different reactive aggregate ratios (R/S). The expansion rate differed according to aggregate type and R/S. In the case of mortar with R/S of 20–40 wt% Ot1, expansion was rapid and large. Furthermore, the expansion rate of mortar with 10, 60 and 80 wt% R/S was moderate whereas that with 100 wt% R/S was the slowest. Mortar with Ot2 showed more rapid expansion than that of Ot1 and Ot3 at any R/S. Mortar with Ot3 showed relatively slower expansion compared with Ot1 and Ot2. Expansion behavior of Ot3-mixed mortar with respect to R/S showed the same tendency as that of Ot1: 10 wt% and 100 wt% Ot3 showed slower, smaller expansion than at other R/S. The relationship between the expansion level at the age of 182 days and R/S is shown in Figure 3. The pessimum proportion of all aggregates was almost 30 wt% and this trend agrees with that reported in previous papers [7].

Figure 4 show the expansion behavior of mortar with R/S of 30 wt% and 100 wt%. Replacement of FA with cement delayed the initiation of expansion at each R/S. The suppression effect of FA, however, was quite different at each R/S. The FA-mixed mortar with 30 wt% R/S showed significantly large expansion while that with 100 wt% R/S was non-expanding except for Ot2.

Here, the expansion ratio is introduced as the normalized index of the suppression effect of FA on ASR expansion. The expansion ratio is defined as the ratio of expansion level of FA-mixed mortar to that of non-mixed mortar; the lower the expansion ratio, the larger the suppression effect of FA. Figure 5 shows a comparison of expansion ratios with different R/S at 182 days of the accelerated period. In the case of R/S of 30 wt%, which is the pessimum proportion, the expansion ratio was larger than that in the case of R/S of 100 wt%. This tendency was the same in all the aggregates and strongly suggests that the suppression effect of FA decreased when using highly reactive aggregate at the pessimum proportion.

### *Case 2*

Figure 6 shows the relationship between r/s and expansion at 182 days of the accelerated period. The mortar with r/s of 30 vol% showed the largest expansion. The expansion of mortar containing 5 vol% of reactive aggregate was almost the same as that containing 50 vol%. Therefore, the pessimum proportion of Ks was determined as 30 vol%.

Figure 7 summarizes the expansion ratio of FA-mixed mortar at each r/s. In all r/s cases, the larger the replacement ratio of FA became, the smaller the expansion ratio became, although replacement at 10 vol% did not suppress ASR expansion. In the case of 20 vol% FA replacement ratio, the expansion ratio

of mortar with 50 vol% r/s was significantly smaller than that with 5 vol% r/s. This result agreed with Case 1. Therefore, the larger the r/s becomes beyond a pessimum value, adequate suppression effect of FA can be obtained. It is interesting that the expansion ratio of mortar with 20 vol% r/s was the largest when the FA replacement ratio was 30 vol% of cement, while the non-FA-mixed mortar showed a 30 vol% pessimum proportion. This result indicates the possibility that the use of FA causes a shift to a smaller pessimum proportion of the reactive aggregate.

*Discussion on the mechanism of decreased suppression effect of FA at the pessimum proportion*

One of the mechanisms behind FA suppression of ASR expansion can be attributed to the reduction in alkalinity of the pore solution. The addition of an appropriate amount of FA leads to the formation of C-S-H gel with lower Ca/Si ratio, resulting in lower concentrations of alkali and hydroxide ion in the pore solution [8]. On the other hand, highly reactive silica minerals such as opal-CT, chalcedony, cristobalite and tridymite can react with alkali even at a low alkalinity of the pore solution [5].

Figure 8 illustrates the mechanism behind the decreased suppression effect of FA at the pessimum proportion. In non-FA-mixed mortar, the pessimum proportion is dominated by the alkalinity of the pore solution and the reaction ratio of the silica minerals. The alkalinity of the pore solution decreases with the increase in reactive silica minerals due to consumption by reaction. Aggregates showing the pessimum proportion effect present higher Sc and Rc in ASTM C 289, so that such aggregates can reduce the alkalinity of the pore solution. Certain minerals such as clay in altered aggregate can also bind the alkali due to cation exchange. Therefore, when the proportion of reactive aggregate is larger than the pessimum proportion, the amount of alkali is not enough to react with the silica minerals. On the other hand, when the reactive aggregate is smaller than the pessimum proportion, the amount of reacted silica is not enough to generate expansive pressure. The pessimum proportion effect in non-FA-mixed mortar/concrete is explained by the illustration in Figure 8 (a).

When FA is mixed into mortar/concrete, the alkalinity of the pore solution decreases to a certain degree to attain equilibrium between the hydrated products and the solution, as shown in Figure 8 (b). The degree of decrease depends on the phase composition of cement hydrates with FA [9]. The reduced alkalinity of the pore solution decreases the reaction ratio of the silica minerals. Highly reactive silica minerals, however, can react with alkali even at a relatively low alkalinity. Thus, there is a shift to a smaller pessimum proportion of reactive aggregate from the original pessimum proportion in non-mixed mortar. In the case of a larger proportion of reactive aggregate, the reaction causes a significant decrease in alkali and terminates at a lower reaction ratio. In this case, the decreasing alkalinity due to mixing in FA results in a high suppression effect. On the other hand, a smaller amount of reactive aggregate shows a higher reaction ratio when the reactive aggregate is used at the pessimum proportion. At the pessimum proportion, the decrease in alkalinity due to consumption by reaction and being bound in some minerals is reduced so that the reaction ratio of highly reactive silica minerals increases. Therefore, a larger amount of FA should be replaced with cement when highly reactive aggregate is contained in mortar/concrete at the pessimum proportion.

Additionally, it is known that the cement with lower alkali content causes a shift to a smaller pessimum proportion of the reactive aggregate [6]. This phenomenon can be explained by above-mentioned illustration. When total alkali content in concrete is increased by adding some alkali as this experiment, there has a risk that the actual pessimum proportion is smaller than experimental data. Therefore, it can be said that a larger amount of FA should be replaced with cement in the actual condition.

### Case 3

A concrete test was performed to determine the amount of FA required to suppress ASR expansion of concrete at the pessimum proportion. Figure 9 shows the expansion behavior of concrete using different proportions of reactive coarse aggregate (Nt). Expansion started at an early stage of the accelerated period due to the high reactivity of opal-CT in Nt aggregate. Concrete containing 100 vol% Nt showed less than 0.05% expansion. The smaller the proportion of Nt became, the larger the expansion of concrete became. The results of the concrete test showed that the pessimum proportion ranged from 10 vol% to 40 vol%.

Figure 10 shows the expansion behavior of FA-mixed concrete at a 40 vol% proportion of reactive coarse aggregate. The results obtained at the 6-month point of the accelerated test showed that an FA replacement ratio of 15 wt% did not suppress ASR expansion at all even though the expansion of FA-mixed concrete was less than that of the non-mixed one. At a 15 wt% FA replacement ratio, T, which has lower glass content, was less effective than the other FAs. This is thought to be because the formation of C-S-H gel due to pozzolanic reaction was less than in the other FAs [9, 10]. An FA replacement ratio of 25 wt% suppressed ASR expansion to less than 0.04 %, which is the value classified as “potentially deleterious” according to CSA A23.2-27A-00. However, it was revealed that although the expansion of concrete at the pessimum proportion is delayed, the final expansion is large [11]. Therefore, long-term monitoring is necessary and this test is ongoing. From the results, it can be concluded that an FA replacement ratio of 25 wt% or more is required to suppress ASR expansion when highly reactive aggregate is contained in the concrete at the pessimum proportion.

The fact that the suppression effect of FA is decreased when highly reactive aggregate is contained at the pessimum proportion can be applied to other SCMs. Therefore, it is also necessary to investigate other SCMs for the amount required to suppress ASR expansion at the pessimum proportion.

## 4 CONCLUSIONS

This study reported the suppression effect of FA when using highly reactive aggregate at the pessimum proportion. Based on the mortar tests, the mechanism behind the decreased suppression effect of FA at the pessimum proportion was discussed. In addition, the replacement level of FA required to suppress ASR expansion was investigated by conducting a concrete test. The following conclusions can be drawn based on the test results in this study:

- (1) The suppression effect of FA was decreased when using highly reactive aggregate at the pessimum proportion. The mechanism can be explained from the standpoint of reduced alkalinity of the pore solution due to mixing in FA, consumption by reaction and aggregate reaction ratio.
- (2) It was proposed that the use of FA results in a shift to a smaller pessimum proportion of the reactive aggregate.
- (3) According to the concrete test results, an FA replacement ratio of 25 wt% or more even in the case of siliceous FA is required to suppress effectively ASR expansion of highly reactive aggregate at the pessimum proportion in concrete.

## 5. ACKNOWLEDGEMENT

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TABLE 1: Chemical composition and physical properties of materials.

Chemical composition (wt%)	OPC	FA			
		R1	T	R1-4	H
LOI	0.6	1.5	1.58	2.25	1.93
SiO <sub>2</sub>	21.79	60.17	61.16	59.05	56.16
Al <sub>2</sub> O <sub>3</sub>	4.98	22.24	29.69	23.72	26.03
Fe <sub>2</sub> O <sub>3</sub>	2.91	4.29	2.7	4.33	4.82
CaO	65.23	5.8	0.75	5.12	5.17
MgO	1.21	1.66	0.59	1.36	1.2
Na <sub>2</sub> O	0.31	0.48	0.18	0.44	0.55
K <sub>2</sub> O	0.47	0.97	0.34	0.87	1.15
SO <sub>3</sub>	1.72	0.79	0.12	0.63	0.91
P <sub>2</sub> O <sub>5</sub>	-	0.81	0.42	0.72	0.43
Total	99.22	98.71	97.53	98.49	98.35
Density (g/cm <sup>3</sup> )	3.16	2.3	2.26	2.24	2.29
Blaine (cm <sup>2</sup> /g)	3280	3910	4510	3860	2820

TABLE 2: Mineral composition of fly ash by XRD/Rietveld analysis.

	R1	T	R1-4	H
Quartz	7.6	18.6	10.2	7.3
Mullite	15.6	37.9	21.2	23.0
Magnetite	0.3	0.3	0.6	0.5
Hematite	0.3	0.9	0.4	0.5
Lime	0.1	0.0	0.3	0.2
Portlandite	0.1	0.0	0.3	0.2
Calcite	0.2	0.0	0.0	0.5
Periclase	0.2	0.0	0.3	0.1
Rutile	0.0	0.5	0.1	0.1
LOI+Moisture	1.4	1.6	2.2	1.8
Glass	70.0	38.8	60.7	65.8

TABLE 3: Chemical composition of glass in fly ash.

	R1	T	R1-4	H
SiO <sub>2</sub>	48.14	31.86	42.86	42.34
Al <sub>2</sub> O <sub>3</sub>	11.06	2.51	8.47	9.53
Fe <sub>2</sub> O <sub>3</sub>	3.65	1.5	3.31	3.75
CaO	3.77	0.15	3.12	4.62
MgO	1.42	0.59	1.08	1.10
Na <sub>2</sub> O	0.48	0.18	0.44	0.55
K <sub>2</sub> O	0.97	0.34	0.87	1.15
P <sub>2</sub> O <sub>5</sub>	0.81	0.42	0.72	0.43
Total	70.3	37.55	60.87	63.48

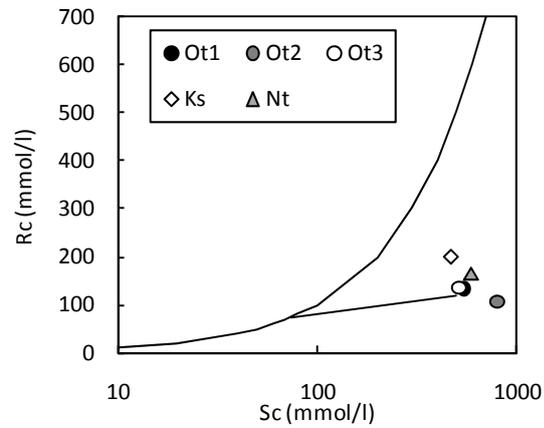


FIGURE 1: Chemical test results.

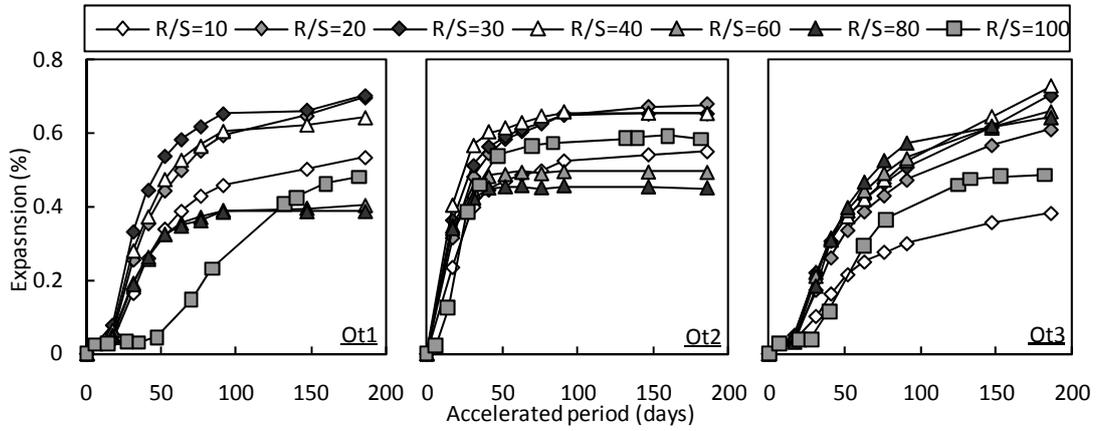


FIGURE 2: Expansion behavior of mortar at different R/S.

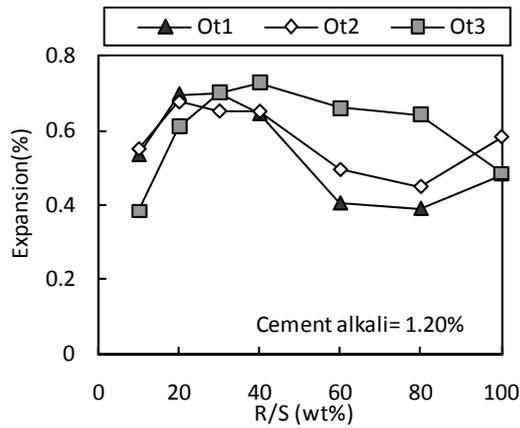


FIGURE 3: Relationship between R/S and expansion.

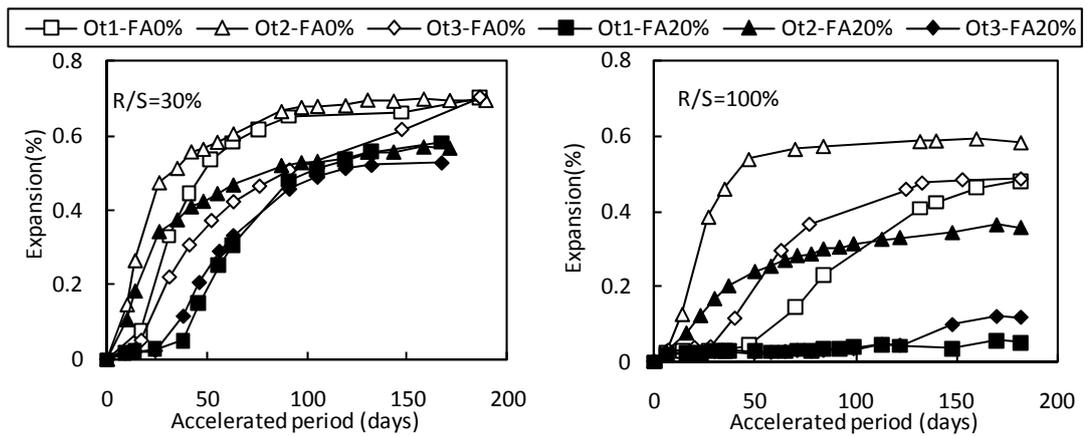


FIGURE 4: Expansion behavior of FA-mixed mortar at different R/S.

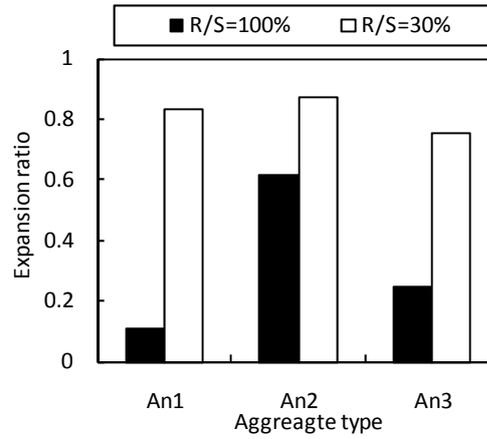


FIGURE 5: Expansion ratio of FA-mixed mortar to non-mixed mortar.

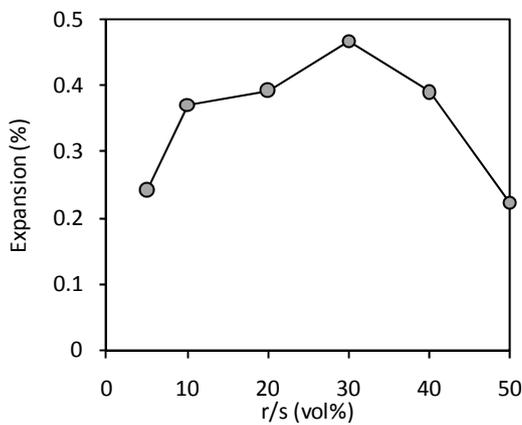


FIGURE 6: Relationship between r/s and expansion.

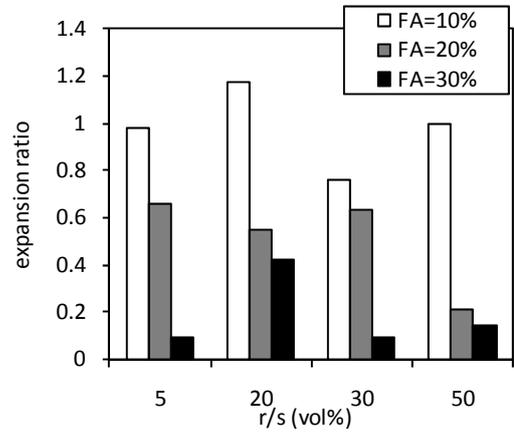


FIGURE 7: Expansion ratio of FA-mixed mortar at different r/s.

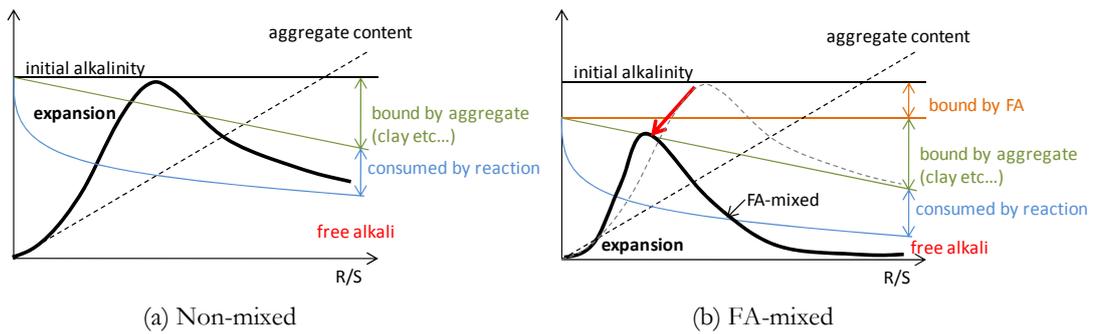


FIGURE 8: Illustration of the mechanism of decreased suppression effect of FA at the pessimum proportion.

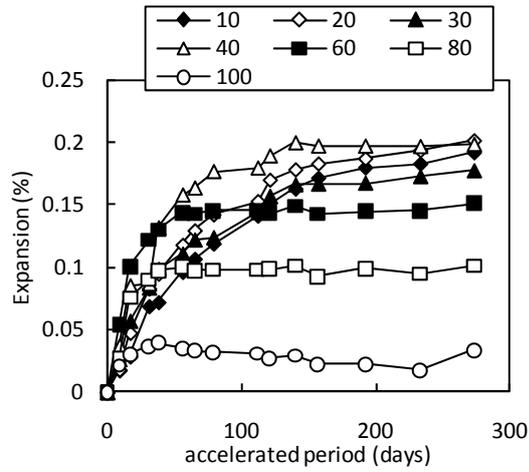


FIGURE 9: Expansion behavior of concrete at different Nt proportions.

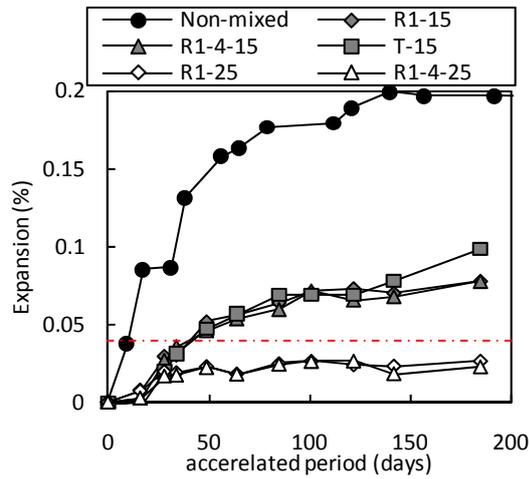


FIGURE 10: Expansion behavior of FA-mixed concrete at 40 vol% Nt.