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INHIBITING ALKALI–AGGREGATE REACTION WITH CHEMICAL ADMIXTURES

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1. INTRODUCTION

The alkali-aggregate reaction problem in reinforced concrete structures has had worldwide attention for the past 50 years. However, effective measures for inhibiting the alkali-aggregate reactions have not been found till now, and it is most important in the present concrete technology to find out such measures for improving the durability of the concrete structures. The present paper deals with some trials to inhibit the alkali-aggregate reaction with chemical admixtures and a cement modifier.

Mortars containing a reactive aggregate are prepared with various contents of chemical admixtures such as sodium silicofluoride, silane and lithium compounds and a cement modifier. Mortar specimens are molded, and cured by autoclaving. Then the expansion of the specimens is measured through autoclaving. From the test results, the effectiveness of the additions of the chemical admixtures and cement modifier in reducing expansion resulting from the alkali-aggregate reaction is discussed.

2. MATERIALS

2.1 Cement and Aggregates

Ordinary portland cement with an alkali content of 0.63% as Na_2O equivalent, Toyoura standard sand as a nonreactive aggregate and opaline amorphous silica as an alkali-reactive aggregate (size; 0.15-0.30 mm) were used in all the mixes.

2.2 Chemical Admixtures and Cement Modifier

Sodium silicofluoride (Na_2SiF_6), alkyl alkoxy silane (AAS), lithium carbonate (Li_2CO_3), lithium fluoride (LiF) and lithium hydroxide ($LiOH\ H_2O$) were used as chemical admixtures, and a styrene-butadiene rubber (SBR) latex was employed as a cement modifier for polymer-modified mortars.

3. TESTING PROCEDURES

3.1 Preparation of Specimens

The mix proportions of mortars containing a reactive aggregate were designed as shown in Tables 1 and 2. The total alkali content of the mortars is adjusted to be 2.0% as Na_2O equivalent, using sodium hydroxide. A mixture of 90 wt% nonreactive aggregate and 10 wt% reactive aggregate was used as an aggregate for the mortars. In accordance with JIS A 1171 (Method of Test Sample of Polymer-Modified Mortar in the Laboratory), the mortars were mixed using the mix proportions given in Tables 1 and 2. Mortar specimens 40x40x160mm were molded, and then subjected to a 24-hour-20°C-100% R.H.-moist cure.

Table 1 Mix Proportions of Mortars Containing Reactive Aggregate with Chemical Admixtures.

Type of Chemical Admixture	Chemical Admixture Content (wt% of Cement)	Cement: Aggregate (by Weight)	Water-Cement Ratio (%)	Flow
—	0	1 : 2.25	71.2	165
Na_2SiF_6	0.5		75.4	174
	0.7		75.4	174
	1.0		75.4	174
AAS	0.5		62.7	172
	0.7		63.7	172
	1.0		63.7	172
Li_2CO_3	0.5		76.2	166
	0.7		77.5	166
	1.0		77.5	168
LiF	0.5		75.4	168
	0.7		77.0	168
	1.0		77.5	168
$LiOH \cdot H_2O$	0.5		73.7	173
	0.7		73.7	175
	1.0		75.4	175

Table 2 Mix Proportions of Polymer-Modified Mortars Containing Reactive Aggregate with AAS.

Polymer-Cement Ratio (%)	Cement: Aggregate (by Weight)	AAS Content (wt% of Cement)	Water-Cement Ratio (%)	Flow
0	1 : 2.25	0	71.2	165
		0.5	62.7	172
		1.0	63.7	172
5		0	61.4	166
		0.5	64.1	172
		1.0	66.3	175
10		0	55.8	166
		0.5	59.2	165
		1.0	64.8	167
20		0	53.9	165
		0.5	56.4	165
		1.0	59.0	172

3.2 Measurement of Expansion

The measurement of the expansion of mortar specimens was conducted according to a rapid test method proposed by Nishibayashi et al[1]. Immediately after moist cure, the initial length of the mortar specimens was measured by a length comparator. Then the mortar specimens were cured by autoclaving at 128°C under a pressure of 2.5 kgf/cm^2 for 4 hours. After autoclaving, the mortar specimens were stored at 20°C and 100% R.H. for 24 hours for cooling, and their expansion was measured by the same comparator.

3.3 Strength Test

The autoclaved mortar specimens used for measuring their expansion were tested for compressive strength according to JIS A 1172 (Method of Test for Strength of Polymer-Modified Mortar). The relative compressive strength of the mortar specimens was calculated as follows:

$$\text{Relative compressive strength } (\%) = (\sigma i \, / \, \sigma o)\times 100 \qquad (1)$$

where σi and σo are the compressive strengths of the mortar specimens with and without chemical admixtures or a cement modifier respectively.

3.4 Observation of Microstructures by Scanning Electron Microscopy

The samples taken from the autoclaved mortar specimens were treated by D-dry method, and then observed by scanning electron microscopy.

4. TEST RESULTS AND DISCUSSION

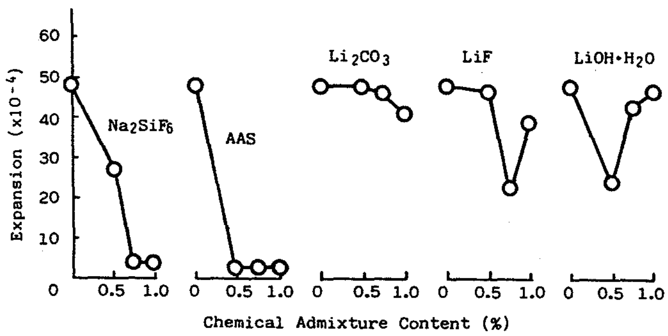

Fig.1 Effects of Chemical Admixtures on Expansion of Mortars Containing Reactive Aggregate.

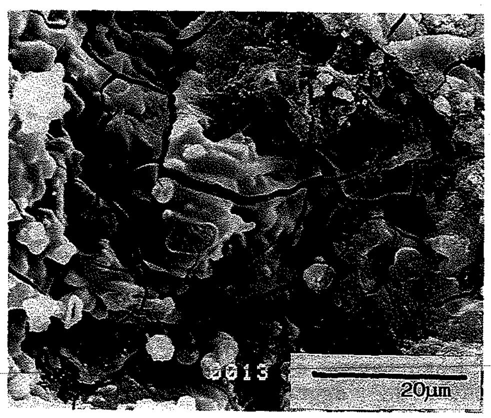

Photo 1 Microstructure of Gel Produced by Alkali-Aggregate Reaction in Mortar.

Figure 1 shows the effects of chemical admixtures on the expansion of mortars containing a reactive aggregate. The mortar containing the reactive aggregate without the chemical admixtures provides a large expansion of 48×10^{-4}. Such an expansion is caused by the water absorption of the gel produced by an alkali - aggregate reaction in the mortar as shown in Photo 1. Many cracks are observed in this photo , and suggest gel formation with a large amount of water in the mortar. With an increase in the admixture content, the expansion of the mortars containing the reactive aggregate with the chemical admixtures decreases, decreases to become nearly constant or reaches the minimum, depending on the type and content of the chemical admixtures. The expansion of the reactive aggregate-containing mortar with Na_2SiF_6 contents of 0.7% or more is reduced to 4×10^{-4}, which is about 1/12 of that of the mortar without Na_2SiF_6. The reasons for this extreme expansion reduction are found to be mentioned below. Like the insolubilization of ordinary water glass by adding Na_2SiF_6 as a common hardener[2], the gel produced by the alkali-aggregate reaction in the mortar appears to convert to an insoluble compound with strong siloxane linkages by adding Na_2SiF_6 because the gel is considered to be a kind of water glass. Therefore, many cracks as seen in Photo 1 are not found out in Photo 2. The microstructure of the gel in Photo 1 is very different from that of the insoluble compound. The expansion of the reactive aggregate-containing mortar with AAS contents of 0.5% or more is decreased to 2.5×10^{-4}, which is about 1/20 of that of the mortar without AAS. In general, AAS is used as a barrier penetrant for mortar and concrete to improve their watertightness. It is considered in the case of AAS addition to the mortar that AAS penetrates to the reactive aggregate, forms the water-repellent surface layers[3] and inhibits to a great extent the alkali-aggregate reaction in the presence of water. Moreover, AAS may act as an air-entraining agent, and entrain microspheric air in the mortar. Such an action of AAS also reduces the expansion of the mortar containing the reactive aggregate[4]. It is pointed out that the water-soluble silicates produced by the alkali-aggregate reaction are converted to insoluble silicates by lithium compounds[5],[6]. The expansion of the mortar containing the reactive aggregate is slightly decreased with increasing Li_2CO_3 content. The expansion of the reactive aggregate-containing mortar with an LiF content of 0.5% or an $LiOH \cdot H_2O$ content of 0.7% is reduced to about 25×10^{-4}, which is about a half of that of the mortar without LiF or $LiOH \cdot H_2O$. From the above-mentioned results, the lithium compounds are inferior to other chemical admixtures such as Na_2SiF_6 and AAS in inhibiting expansion due to the alkali-aggregate reaction. The chemical admixtures which appear to be the most effective in reducing the expansion are Na_2SiF_6 and AAS. The recommendable Na_2SiF_6 and AAS contents are 0.7 to 1.0% and 0.5 to 1.0% respectively.

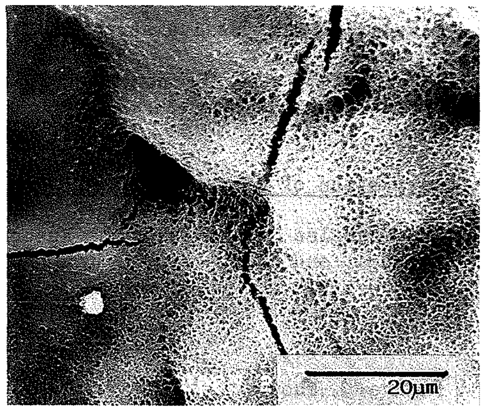

Photo 2 Microstructure of Gel Produced in Mortar with Na_2SiF_6.

Figure 2 represents the effect of polymer and AAS modifications on the expansion of mortars containing a reactive aggregate. The expansion of the polymer-modified mortars containing the reactive aggregate with AAS contents of 0.5% or less increases with an increase in the polymer-cement ratio, and reaches the maximum at a polymer-cement ratio of 10%.

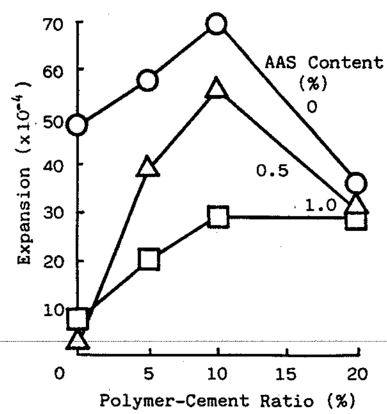

Fig. 2 Effects of Polymer and AAS Modifications on Expansion of Mortars Containing Reactive Aggregate.

By contrast, the expansion of the polymer-modified mortars containing the reactive aggregate with an AAS content of 1.0% increases with increasing polymer-cement ratio, and becomes nearly constant at a polymer-cement ratio of 10%. The effectiveness of AAS addition to the polymer-modified mortars for the expansion reduction is remarkable at lower polymer-cement ratio. The most effective polymer and AAS modifications in reducing expansion are achieved at polymer-cement ratios of 5 to 20% and an AAS content of 1.0%. The mechanism of the expansion reduction due to the polymer modification is found to be based on the restraint due to the network structures of polymer films formed in the mortars as seen in a large crack in Photo 3. However, the polymer and AAS modifications are not so effective techniques for reducing the expansion due to the alkali-aggregate reaction in comparison with the additions of Na_2SiF_6 and AAS.

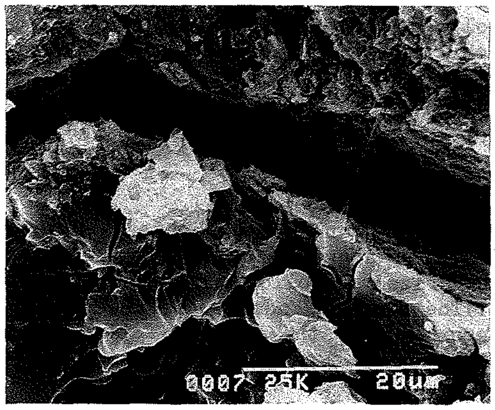

Photo 3 Microstructure of Polymer Films in Large Crack of Polymer-Modified Mortar.

Figure 3 illustrates the effect of chemical admixture content on the relative compressive strength of mortars containing a reactive aggregate. The relative compressive strength of the mortars containing the reactive aggregate increases with increasing Na_2SiF_6 content. This tendency corresponds well to the Na_2SiF_6 content-expansion reduction relationship of the mortars as seen in Figure 1. It seems that the addition of Na_2SiF_6 causes the strengthening of the gel produced by the alkali-aggregate reaction. An idea of the addition of Na_2SiF_6 as a hardener for the gel for inhibiting the alkali-aggregate reaction is clearly explained to be reasonable from the results. On the other hand, the effects of the additions of AAS and lithium compounds on the relative compressive strength of the mortars containing the reactive aggregate are hardly recognized.

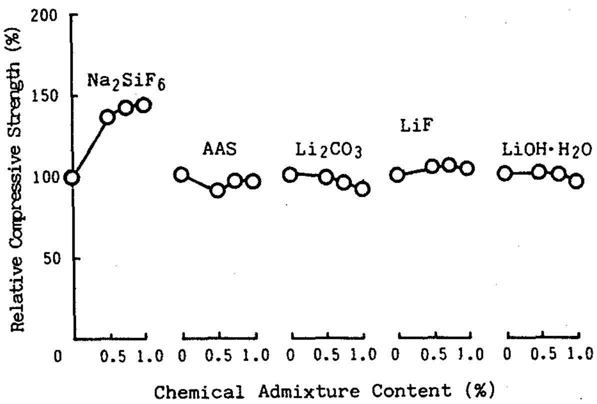

Fig.3 Effect of Chemical Admixture Content on Relative Compressive Strength of Mortars Containing Reactive Aggregate.

Figure 4 indicates the effect of polymer-cement ratio on the relative compressive strength of polymer-modified mortars containing a reactive aggregate with AAS. Regardless of AAS addition, the relative compressive strength of the polymer-modified mortars containing the reactive aggregate is increased with a raise in the polymer-cement ratio. It appears that this trend does not correspond to the polymer-cement ratio-expansion reduction relationship of the polymer-modified mortars as shown in Figure 2.

5. CONCLUSIONS

The conclusions obtained from the above test results are summarized as follows:

(1)The chemical admixtures which appear to be the most effective in reducing expansion resulting from the alkali-aggregate reaction are Na_2SiF_6 and AAS. In particular, the addition of Na_2SiF_6 causes a considerable increase in mortar strength. The recommendable Na_2SiF_6 and AAS contents are 0.7 to 1.0% and 0.5 to 1.0% respectively.

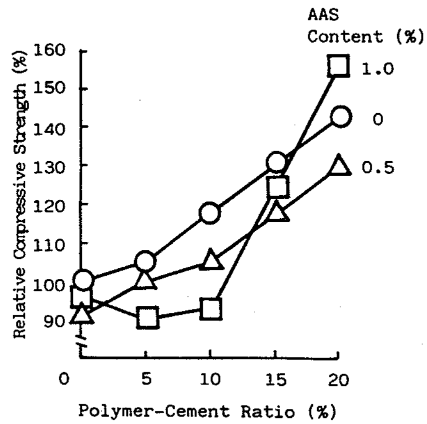

Fig.4 Effect of Polymer-Cement Ratio on Relative Compressive Strength of Polymer-Modified Mortars Containing Reactive Aggregate with AAS.

(2)The inhibiting effects of lithium compounds and polymer dispersions on the expansion due to the alkali-aggregate reaction are inferior to those of Na_2SiF_6 and AAS.

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