

STUDY ON ALKALI AGGREGATE REACTION FOR CONCRETE
WITH ANTI-FREEZING ADMIXTURES

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ABSTRACT

The influence of anti-freezing admixture on the alkali aggregate reaction of mortar is analyzed with accelerated methods. This study confirms that the addition of sodium salt ingredients of anti-freezing admixture accelerate the alkali silica reaction to some extent, whereas calcium salt ingredient of anti-freezing admixture reduce the expansion of alkali silica reaction caused by high alkali cement. It was also found that addition of the fly ash considerably suppress the expansion of alkali silica reaction induced by the anti-freezing admixtures.

Key words: Anti-freezing admixture, Alkali silica reaction, Reactive aggregates, Fly ash

In china, the use of anti-freezing admixture has rapidly been increasing to construct concrete structure during winter season. It has recently been pointed out that calcium salt and sodium salt are widely used as ingredients of anti-freezing admixture. These ingredients may cause serious damage to concrete [1]. The damage to concrete is attributed to a detrimental effect that happened in the chemical and physical process when the steel corroded and the formation of a complex salt. However, it is ambiguous whether the anti-freezing admixtures accelerate the expansion of mortar containing reactive aggregate in the same way as high alkali cement.

In this paper, the effects of the calcium salt and sodium salt on the deterioration of Portland cement mortar due to the alkali aggregate reaction were evaluated based on the method of accelerated expansion test and microscopic analysis. Such approach is to elucidate effect of added anti-freezing admixture and fly ash on the alkali silica reaction in mortar.

1. MIX PROPORTION OF MORTAR

The opal and Chinese standard quartz sand were used as a reactive aggregate and non-reactive aggregate respectively. The cement used was Type I Portland cement, which was supplied by Harbin

Cement Industries in China, with an equivalent 0.85% Na₂O. Reagents of NaCl、NaNO₂、Ca(NO₂)₂、CaCl₂ were used as ingredients of anti-freezing admixtures. Mortar was prepared with a 0.2 ratio of a total aggregate to cement. In the mortar, as reactive aggregate the opal and standard sand were introduced at a pessimum proportion of 10% and 90% respectively, which had been determined in advance by chemical method [2-5]. In order to investigate the effect of fly ash on expansion, grade I fly ash was introduced in mortar which sodium chloride addition level was 3% by mass of cement. Its physical property and chemical composition is given in Table 1.

2. EXPERIMENTAL METHODS

In this study, the characteristics of alkali silica reaction progressing within reactive aggregate grains in mortar are revealed by the combined methods of accelerated expansion test and microscopic method. Accelerated expansion test was conducted according CECS48-93 (A rapid test method for determining the alkali reactivity of sands and rocks). Further, in order to investigate changes in micro structural features and reaction products in the interfacial zone of reactive aggregate, SEM and XRD were carried out at selected stages.

Table 1 Physical property and chemical compositions for fly ash

| Surface area (m ² / kg) | The ratio of water demand (%) | Loss on ignition (%) | Density (g/cm ³) | SO ₃ (%) | CaO (%) | Na ₂ O _{eq} (%) |
|---------------------------------------|----------------------------------|-------------------------|---------------------------------|------------------------|------------|--|
| 460 | 92 | 2.78 | 2.41 | 0.48 | 2.78 | 0.88 |

3. RESULTS AND DISSCUSSION

3.1 Expansion test

Fig.1 shows changes of expansion of mortar with and without reactive-aggregate. In Fig.1, RA represents reactive aggregate, while NRA represents non-reactive aggregate. The results indicating the expansion in all the mortar with reactive aggregate were above 0.2% caused by high alkali cement used. However the expansion of mortar with non-reactive aggregate was below 0.1%. For addition of 5% NaCl and 5% NaNO₂, the expansion was 0.03% and 0.042%, indicating the expansion of mortar was caused by alkali-silica reaction but not by re-crystallization. The addition of NaCl and NaNO₂ increased the expansion of mortar compared with control mortar without anti-freezing admixture, which indicated that alkali-silica reaction was accelerated by increasing the alkali content of pore solution in mortars. Whereas, the addition of CaCl₂ and Ca(NO₂)₂ reduced the expansion of mortar containing reactive aggregate, suggesting the reduction of the alkali content of pore solution in mortar and formation of complex salt [6].

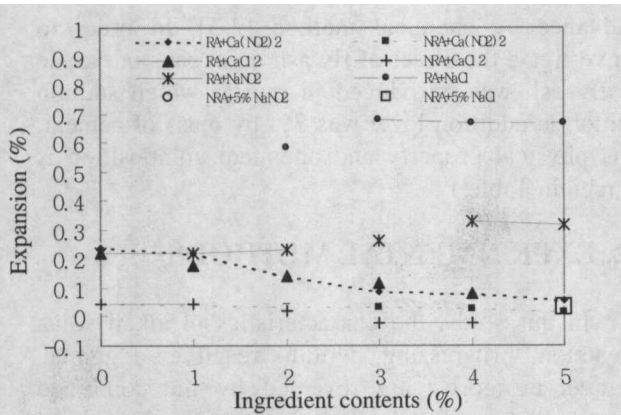


Fig.1 Relationship between ingredient contents of anti-freezing admixtures and expansion

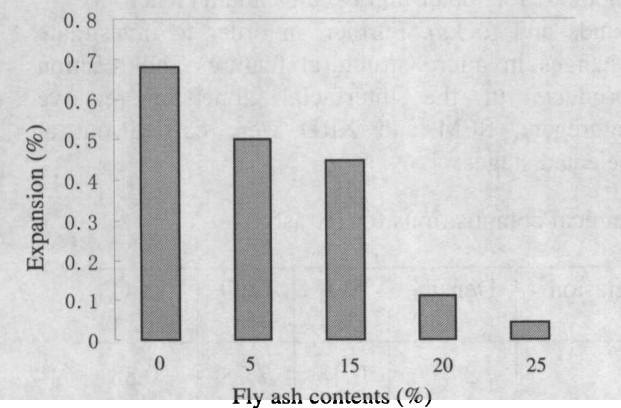


Fig.2 Effect of fly ash on the alkali-silica reaction

In order to reveal the effects of fly ash on the behavior of mortar with 3% NaCl, the expansion was plotted against fly ash content, as shown in Fig.2. The behavior of expansion of mortar with fly ash suggesting the addition of fly-ash suppress the expansion of mortar containing reactive aggregate. The expansion of mortar with reactive aggregate was reduced to 0.1% by about 20%, when fly ash was added.

3.2 Microscopic analysis

The analyses of SEM and XRD were made on interfacial zone of mortar in order to elucidate effects of anti-freezing admixtures on the alkali-aggregate reaction.

3.2.1 3% NaCl bearing specimen

Fig.3 shows SEM micrographs of interfacial zone for reactive aggregate bearing mortar. White substance of massive alkali-silica gel was found to be sticking to the surface of reactive aggregate, and markedly cracked as shown in Fig.3. The dominant spectra peak of Si, K and Na in Fig.4 shows that the white gel was a alkali-silica gel.

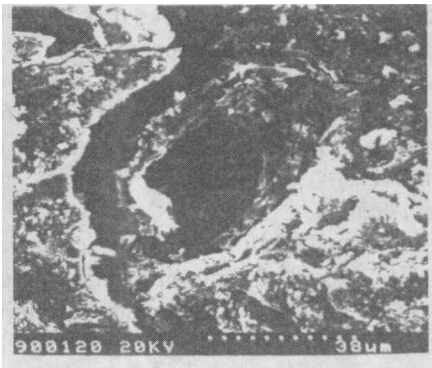


Fig.3 SEM micrograph of alkali-silica gel layers for reactive aggregate-bearing mortar at 3% NaCl

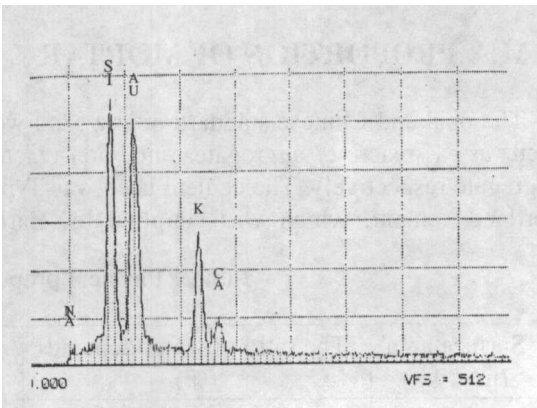


Fig.4 XRD spectra of alkali-silica gel layers for reactive aggregate-bearing mortar at 3% NaCl

3.2.2 3% NaNO₂ bearing specimen

Fig.5 shows SEM micrographs of interfacial zone for reactive aggregate bearing mortar at 3% NaNO₂. This white substance seen on the surface of reactive aggregate was found to be the massive alkali-silica gel determined by dominant spectra peak of Si, Ca, K and Na in Fig.6.

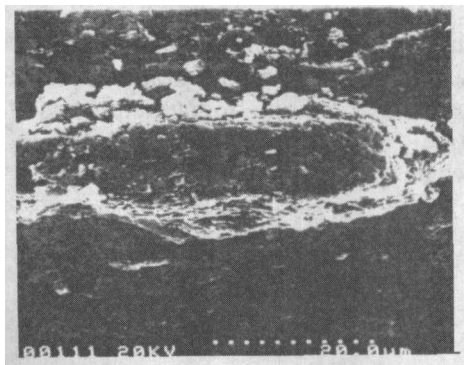


Fig.5 SEM micrograph of alkali-silica gel layers for reactive aggregate-bearing mortar at 3% NaNO₂

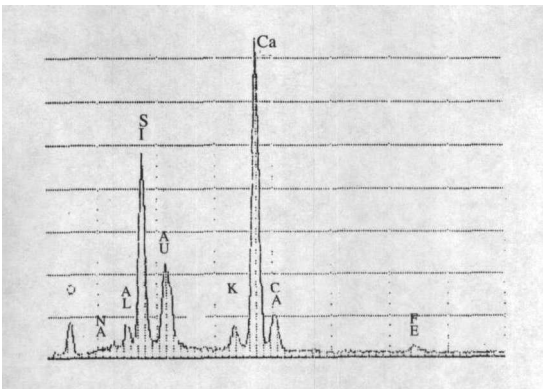


Fig.6 XRD spectra of alkali-silica gel layers for reactive aggregate-bearing mortar at 3% NaNO₂

3.2.3 3% Ca(NO₂)₂ and 2% CaCl₂ bearing specimen

Fig.7 and Fig.8 show SEM micrographs of interfacial zone for reactive aggregate-bearing aggregate at 3% Ca(NO₂)₂ and 2% CaCl₂. In this micrograph, it is difficult to see any gel or crack in surface of reactive aggregate particles and seems to be consolidated and uniform. Fig.9 shows the SEM micrograph of hydration products for mortar containing 3% Ca(NO₂)₂. The needle shaped net work formation of the CSH layer precipitated on the surface of reactive aggregate grains and the CH hexagonal plates is detected. Accordingly, these textures of mortar show a considerable increasing in compressive strength at early stages.

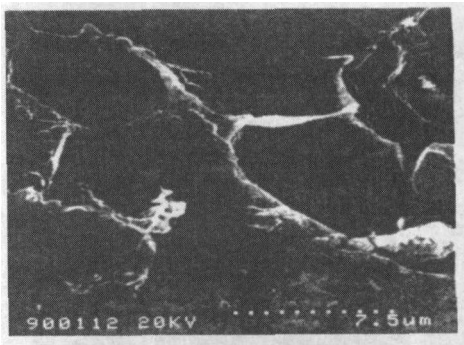


Fig.7 SEM micrograph of interfacial zone for reactive aggregate-bearing mortar at 3% Ca(NO₂)₂



Fig.8 SEM micrograph of interfacial zone for reactive aggregate-bearing mortar at 2% CaCl₂

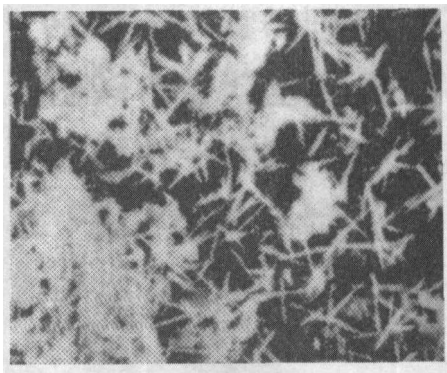


Fig.9 SEM micrograph of hydration products at 3% Ca(NO₂)₂

3.2.4. Effect of the fly ash on AAR

Fig.10 shows SEM micrograph of interfacial zone for reactive aggregate bearing mortar containing 3% NaCl and 25% fly ash. As shown in Fig.10, the most abundant CSH on the surface of reactive aggregate indicated the effect of the CH-pozzolana reaction. This suggests that the pozzolanic reaction produces new CSH phases. It is interesting to note that alkali-silica reaction gel was not detected on the surface of reactive aggregate, which confirms suppress effect of fly-ash on

alkali-silica reaction.

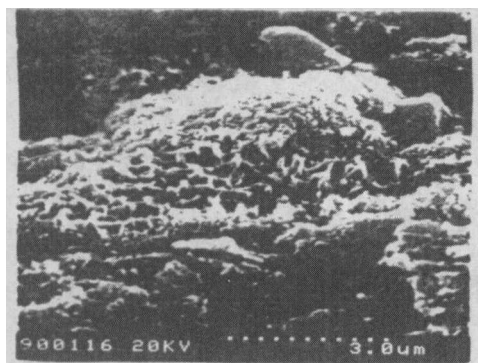


Fig.10 SEM micrograph of interfacial zone for reactive aggregate bearing mortar containing 3% NaCl and 25% fly-ash

4. CONCLUSIONS

(1) Compared to the control mortars, the addition of sodium salt considerably increased the harmful expansion of alkali-silica reaction for reactive aggregate bearing mortars, whereas calcium salt reduced the expansion of alkali-silica reaction caused by high alkali cement.

(2) The addition of 3% $\text{Ca}(\text{NO}_3)_2$ consolidated the interfacial zone of mortars by formation of CSH and CH. This is a reason why did compressive strength increase at early stages.

(3) In this study the fly ash reduced the expansion of mortars compared with control mortars without fly ash. More fly ash, less expansion. The expansion of mortar with reactive aggregate was reduced to 0.1% by about 20%, when fly ash was added.

(4) In construction in winter stage, it is preferable to avoid the use of a high content of sodium salt as a anti-freezing admixture. Hereafter, it is clearly necessary to search for a harmless and inexpensive anti-freezing admixture to replace sodium-bearing materials such as NaCl and NaNO_2 .

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