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MICROSTRUCTURAL STUDY OF THE INTERFACIAL ZONE BETWEEN EXPANSIVE SULPHOALUMINATE CEMENT PASTES AND LIMESTONE AGGREGATES

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ABSTRACT

The hydration products, the crystal sizes, the morphology and the thickness of the interfacial zone between expansive sulphoaluminate cement pastes and limestone aggregates are examined systematically by using XRD, SEM/EDAX, TGA. etc.. The effects of the levels of gypsum blended into sulphoaluminate cement clinkers (25% and 45% gypsum contents) and the restraining condition of the specimens on the microstructures of the interfacial zone and the bond strength between the cement pastes and the aggregates are investigated. The mechanism of the interfacial zone formation is discussed.

Introduction

The microstructuralcharacteristics of the interfacial zones between sulphoaluminate cement clinker pastes and limestone aggregates were discussed in the reference(1). In order to systematically understand the interfacial behaviors of the different categories of the sulphoaluminate cements, the investigations are concentrated on expansive sulphoaluminate cement in this paper. microstructural variations in the synthetic interfacial zones between the cement pastes and the aggregates are observed, when the levels of gypsum blended into cement are changed and the measures to improve the weak microstructures of the interfacial zones of the expansive sulphoaluminate cement concrete is investigated.

Experiments

1. Raw Materials. Sulphoaluminate cement clinkers are made in Hebei Province and the industrial gypsum is made in Shanxi Province. Their chemical compositions are listed in Table 1.

The clinkers and the gypsum is ground respectively and are homogenized by machine at the gypsum levels of 25% and 45% to prepare the two kinds of expansive sulphoaluminate cements which are numbered by SA-25 and SA-45.

2. Specimen Preparation and Methods for Microstructural Analysis.
2.1 Specimen preparation and analytical instruments. The preparation of the synthetical interfacial zones and the instruments for the analysis of the microstructures and composition of the interfacial zone are same as in reference (1).

2.2 Preparation of the specimens restrained in three dimensions. The synthetic aggregates with polished surfaces are symmetrically put into the steel cylinder mold (Φ20 × 25 cm) with a steel bottom which can be disassembled. Steel (Φ2cm) stands vertically in the center of the cylinder. The percentage of reinforcement is 1.4% in the axial direction. The cement is mixed with water at 0.3 water cement ratio and cast into the steel cylinder with the aid of vibration. A steel cover seals the cylinder with screws and contacts the cement pastes . Then the paste is put under water until the ages required.

2.3 Measurement of bonding strength. The bonding strength between the cement pastes and the aggregates are tested by 3-point bending(1). The aggregates are cut into 4 × 4 × 2cm pieces and put into 4 × 4 × 16cm molds. The cements mixed with water are cast into the molds and aged by the standard procedure(20°C).

Results and Analysis

3.1 Relative Contents and Crystal Size of Aft in the Interfacial Zones Between Expansive Sulphoaluminate Cement Pastes and Limestone Aggregates. The relative contents of AFt in the interfacial zones were examined by XRD analysis(2). The following phenomena can be observed from FIG. 1.

When gypsum contents blended into the sulphoaluminate cement are 25%, AFt phase can not be detected by XRD in the interfacial zones between 0 and 30 microns from the surface of the aggregate. The contents of AFt increase gradually with the distance from the surface of the aggregate and finally keep constant about over 70 microns from the aggregate surface. Under

TABLE 1

Chemical Compositions of Materials (%)

	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
SAC clinker	1.84	9.78	29.49	1.58	42.81	2.49	10.02
Gypsum	22.98	0.53	0.35	0.11	32.05	2.43	41.11

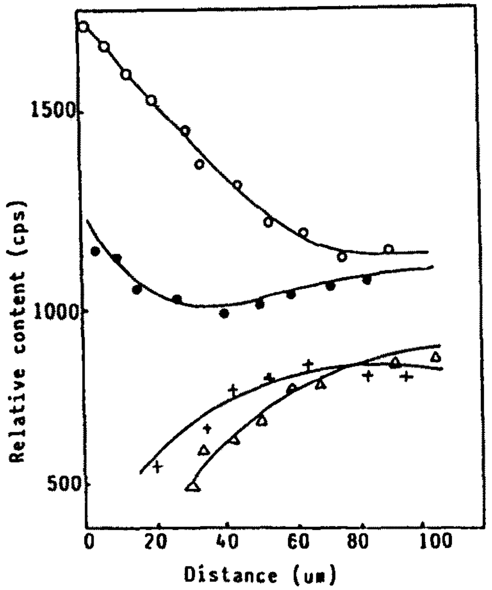


FIG. 1.
Relationship between relative contents of AFt and distance from limestone surface. Added amount of gypsum: Δ –25; O–45; + –25 (restrained); • –45 (restrained).

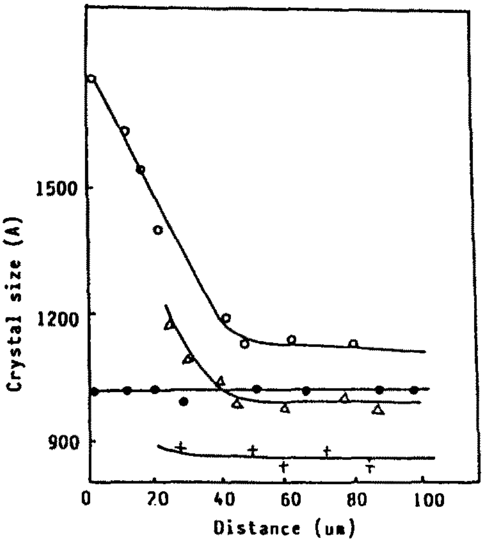


FIG. 2.
Relationship between mean size of AFt and distance from limestone surface. Added amount of gypsum: Δ –25; O–45; + –25 (restrained); • –45 (restrained).

the 3-dimensional restraint condition, the interfacial zone, in which AFt phases disappear, reduces to 0–20 microns from the surface of the aggregate. The distance from the surface of the aggregate, over which AFt phases begin to keep constant, reduces to 40 microns.

When gypsum contents in the sulphoaluminate cement are 45%, AFt phases concentrate in the interfacial zone between the cement paste and the aggregate. The zone concentrated by AFt phases is about 80 microns thick from the surface of the aggregate. Under 3-dimensional restraint, this zone decreases to about 40 microns.

FIG.2 shows the variation of the crystal size of AFt phases in the interfacial zone which is determined by X-ray line-profile analysis. In the bulk cement pastes, the average crystal size of AFt increases with the addition of gypsum in the sulphoaluminate cement. The average crystal size is about 980Å and 1180Å respectively corresponding to 25% and 45% addition of gypsum. The average crystal size will be fined for the 3-dimensionally restrained specimens in both the cases of 25% and 45% gypsum addition. In the interfacial zones, AFt crystals are finer than in the bulk paste for the specimens with 25% gypsum addition. The crystal size increases with the distance from the surface of the aggregate. For the specimens with 45% gypsum addition, the average crystal size of AFt is larger than in the bulk paste and reduces with the distance from the aggregate. The interfacial zones with AFt crystal size different from the bulk paste are about 60 microns and 50 microns thick for the cases of 25% and 45% gypsum addition. Their thickness will reduce as the specimens are restrained.

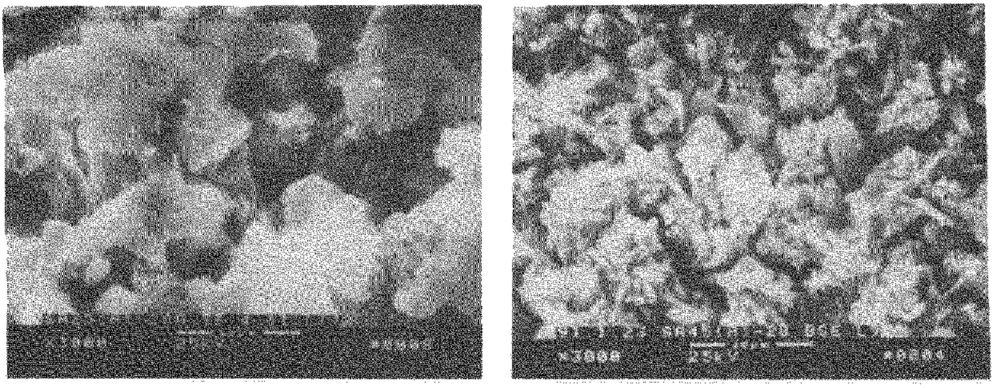


FIG. 3.
SEM photographs against the hardened paste (28d). (a) 25% CSH_2, SE, (b) 45% CSH_2, BSE.

3.2 Morphologies of Hydration Products in the Interfacial Zone Between Expansive Sulphoaluminate Cement Pastes and Limestone Aggregates. The specimens with a synthetic interface are split along the interfaces between the cement pastes and the aggregates. The profiles on the paste side are put under SEM for microstructure observation.

As the addition of gypsum is 25% and the specimens are hydrated for 28 days, the hydrates growing in the interfacial zone close to the surface of the aggregate appear to be gel-like hydrates (FIG.3a); but as the addition of gypsum is 45% and hydration ages are 28 days, much well crystallized AFt phases, which are plum-blossom AFt bars, form in the interfacial zone (FIG.3b).

EDAX (FIG.4) indicates that the chemical composition of the gel-like hydrates is Ca, Al and S. Only AFt peak appears at temperature 134°C on the DTA curve (FIG.5), but no crystalline AFt can be detected by XRD in the 0–30 Micron area from the surface of the aggregate.

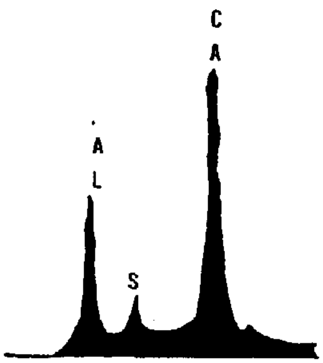


FIG. 4.
The energy dispensive X-ray curve of hydrates.

FIG. 5.
The TGA curve of hydrates.

Therefore, it is justified in basis of the above evidences that the gel-like hydration products are AFt gel.

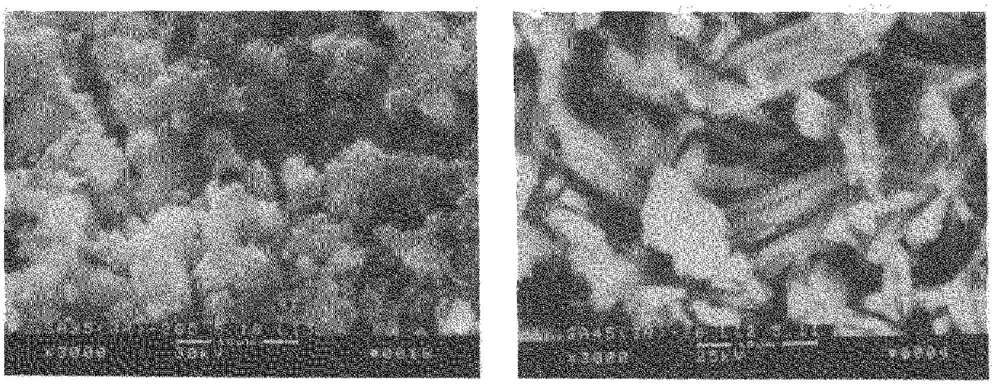
Under the condition of 3-dimensional restraint, the hydrate grains in the interfacial zone will be finer in the both cases of gypsum additions (FIG.6a and 6b). Particularly as gypsum addition is 45%, the plum-blossom AFt phases in the interfacial zone become thin and long AFt bars (FIG.6).

4. Bond Strength between Expansive Cement Pastes and Limestone Aggregates. Table 2 lists the effects of the added gypsum contents and the 3-dimensional restraint on the interfacial bond strength between expansive sulphoaluminate cement pastes and limestone aggregates tested by 3-point bending . The increase of gypsum addition tends to weaken the interfacial bond strength. 3-dimensional restraint improves the interfacial bond strength.

Discussion

5.1 Definition of the Interfacial Zone. According to analysis of XRD and SEM/EDAX, it was found that a porous interfacial zone exists between the cement pastes and the limestone aggregates. AFt phases concentrate in the interfacial zone. The average crystal size of AFt is also different from that in the bulk pastes. These differences of AFt crystal size and AFt contents reduce with increasing distance from the surface of the aggregate. The distance from the aggregate surface at which the differences of the microstructures and compositions between the interfacial zone and the bulk pastes begin to disappear is defined as the thickness of the interfacial zone. Table 3 shows the thickness between expansive cement pastes and limestone.

5.2 Formation Mechanism of the Interfacial Zone. There are apparent microstructural differences between the interfacial zones and the bulk cement pastes. The formation of these differences are influenced by the properties of the aggregates, the solubility's and the degrees of hydration of the sulphoaluminate cement minerals and the migrating speed of the different



(a) (b)

FIG. 6.

SEM photographs against the hardened paste under 3-dimensional restraint. (6a) 25% CSH_2, (6b) 45% CSH_2.

TABLE 2

Flexural Bond Strength Between Expansive Cement Pastes and Limestone Aggregate

	SA25	SA45	SA25*	SA45*
Bond strength (MPa)	0.52	0.390	1.31	0.989

Note: * — 3-dimensional restraint

ions. Once a limestone aggregate comes into contact with the fresh cement paste, a water film with a certain thickness forms between the cement paste and the aggregate. The ions dissolved from the cement grains diffuse into the water film around the aggregate due to the difference of the ionic concentrations between the water film and the cement paste. In the current experiments, the major minerals of the sulphoaluminate cement are C_4A_3S, C_2S and gypsum. Firstly, gypsum dissolves to produce Ca^{2+} and SO_4^{2-}. These ions are easy to react with the ions dissolved from C_4A_3S forming AFt and AH_3, C_2S hydrates slowly to produce C-S-H gel and CH. These chemical reactions obey the following formulae:

$$C_4A_3S + 2CSH_2 + 34H_2O = C_3A{\cdot}3CS{\cdot}32H + 2AH_3 \quad (1)$$

$$\alpha\text{-}C_2S + 2H_2O = C\text{-}S\text{-}H + CH \quad (2)$$

$$3CH + 3CSH_2 + AH_3 + 20H_2O = C_3A{\cdot}3CS{\cdot}32H_2 \quad (3)$$

The order of the migrating speed of the ions is $SO_4^{2-} > Al^{3+} > Ca^{2+} > SiO_4^{4+}$. These ions migrate into the water film around the limestone from the cement pastes in the above order. SO_4^{2-}, Al^{3+} and Ca^{2+} ions react with each other in the interfacial zone to form AFt. Only a little amount of C-S-H gel forms in the interfacial zone, which is attributed to the low migrating speed of SiO_4^{4+}. The hydrates in the interfacial zone grow well because there is enough space available.

5.3 Microstructuralcharacteristics of the Interfacial Zone.

5.3.1 Under the condition offree expanding. When the addition of gypsum is 25%, the degree of hydration of C_4A_3S in the cement paste hydrated for 28 days is about 84%(3). It is assumed that the ratio of Al/S in this situation may be especially beneficial to AFt growth. Too much formation of AFt nuclei affects its crystal only forms in the pastes away from the aggregate. Its contents and size gradually rise with increasing the distance from the surface of aggregate. The interfacial zone is mainly concentrated by gel-like AFt. The thickness of the interfacial zone is about 70 microns. The average crystal size of AFt is finer than in the bulk cement pastes. The

TABLE 3

Thickness of Interfacial Zone Between Expansive Cement Pastes and Limestone Aggregate

	SA25	SA45	SA25*	SA45*
Interface zone (μm)	60-70	70-80	30-40	30-40

Note: * — 3-dimensional restraint

interfacial zone is also more porous and contains less amount of C-S-H gel and gypsum than the bulk paste.

As the addition of gypsum is 45%, almost all C_4A_3S is hydrated in the sulphoaluminate cement paste cured for 28 days(3). The interfacial zone is concentrated by well crystallized AFt phases which are coarse plum-blossom clusters of AFt bars. A small quantity of C-S-H gel and gypsum exists in the interfacial zone. The thickness of the interfacial zone is about 80 microns.

5.3.2 Under the condition of 3-dimensional restraint. It is verified that 3-dimensional restraint can effectively improve the microstructures of the interfacial zone. The thickness of the water film around the aggregate are compressed under the expanding compression exerted by the expanding sulphoaluminate cement paste. The concentration of AFt nucleus increases relatively in the interfacial zone and the space available for AFt growth is diminished so that AFt crystal is relatively difficult to form. Therefore, the morphologies of AFt in the interfacial zone are changed. The concentration of Aft crystal is weakened and crystal grains of AFt are fined. The interfacial zone becomes denser than in the case of free expanding.

5.4 Effects of the Interfacial Microstructures on the Mechanical Properties. It is found that the interfacial microstructures correlate with the bond strength. The bond strength reduces with the addition of gypsum. The bond between sulphoaluminate cement pastes and limestone aggregates is enhanced after the specimens are restrained. The gel phase of the sulphoaluminate cement hydrates have a good ability to fill the voids and dense structures itself. In the interfacial zone, the gel phases possess larger contact surface area with the aggregate and produce denser structures easily than the crystalline hydrates. It is demonstrated in Table 2 that the interfacial zone containing high contents of gel phase corresponds to high bond strength.

On 25% addition of gypsum, the main hydrate in the interfacial zone is AFt gel. Relatively high bond strength between cement paste and aggregate can be observed. If the addition of gypsum is 45%, AFt crystal concentrates in the interfacial zone so as to decrease the contact area with the aggregate and to form porous structures. The mechanical behavior corresponding to this interfacial microstructure is low bond strength. 3-dimensional restraint can make the hydrate grains finer and compress the thickness of the interfacial zone so as to improve the interfacial bond properties.

Conclusion

1. The main hydrate AFt of expansive sulphoaluminate cement concentrates in the interfacial zone between the cement pastes and the limestone aggregates.
2. The morphologies of hydration in the interfacial zone are varied from gel-like AFt aggregates to plum-blossom AFt bars as the addition of gypsum is from 25% to 45% and hydration ages are 28 days.
3. The thickness of the interfacial zone increases with addition of gypsum. 3-dimensional restraint can markedly improve the interfacial microstructures, compressing the thickness of the interfacial zone and fining the crystal grains.
4. Increasing the proportion of gel phases in the interfacial zone and exerting restraint on the expanding sulphoaluminate cement concrete are effective measures to enhance the interfacial bond.

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