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Research on the hydration, hardening mechanism, and microstructure of high performance expansive concrete

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Abstract

High performance expansive fly ash concrete (HPEC) was prepared and the differences of mechanical properties between the high performance concrete and HPEC were compared under free- and confined-curing conditions. By means of XRD and SEM methods, the hydration progress and microstructure of HPEC were investigated. The results show that an expansive agent is useful and the confinement action could improve the microstructure of hardened expansive concrete.

Keywords: Hydration; Microstructure; Expansion; High performance concrete

With many positive properties, high performance concrete (HPC) is increasingly applied in many fields and it has become an object of development of modern concrete technology. However, the shrinkage of HPC is usually larger than that of common concrete due to the application of water reducer and low water cement ratio, which influences the quality and durability of HPC [1,2]. At present, the main method of reducing HPC shrinkage is the addition of an expansive agent into HPC, which can make the concrete expand and compensate for shrinkage, thus improving the density and durability of HPC [3]. However, research on the mechanism of hydration and the microstructure of high performance expansive concrete is absent. It is therefore necessary to further study the above-mentioned problems.

1. Methods

1.1. Raw materials

1.1.1. Cement

Number 525 portland cement was used; its chemical composition and properties are shown in Table 1.

1.1.2. Aggregate

Coarse aggregate used was 5–31.5 mm crushed stone with a smashing index of 10.6%, silt content less than 1%, and needle and slice-shaped grain content of 11.8%. Fine aggregate was river sand with a fineness module 2.6 and a silt content of 1.2%.

1.1.3. Fly ash

The chemical compositions and properties of fly ash are given in Table 1. The XRD analysis of the fly ash is shown in Fig. 1.

1.1.4. United expansion agent

The united expansion agent (UEA) was made of alunite and gypsum. Its chemical composition and properties are given in Table 1. The XRD pattern is showed in Fig. 1.

1.1.5. Superplasticizer

FDN, the naphthalene series water-reducing agent, was used and its water reduction rate was 20%.

1.2. Methods

The compressive strength of concrete specimens was tested at 3 and 28 days according to Chinese National Standard GBJ 107-87. The size of the specimens was 150 × 150 × 150 mm. Free-curing condition was employed: the concrete specimens were demolded after 24 h of being cast, and then cured without molds for 28 days in standard condition (20°C, underwater). Confined-curing condition was also employed: the concrete specimens were cured with molds for 28 days in standard conditions.

2. Results and discussion

First, we prepared high performance C60 concrete without expansive agent, then 10% (wt.) UEA was substituted

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Table 1
Characteristics of raw materials

Materials	Chemical compositions (%)								Specific surface ($m^2 \cdot kg^{-1}$)	Ratio of water demand (%)	Compressive strength at 28 days (MPa)
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Loss			
Cement	21.47	5.80	4.04	–	59.64	3.24	2.08	2.44	319	–	57
UEA	29.50	7.76	2.82	–	17.93	1.83	24.79	20.67	331	–	–
Fly ash	50.11	26.15	4.68	6.41	2.39	1.93	0.43	7.8	286	105	–

for cement. Under free- and confined-curing conditions, the physical properties of the two kinds of concrete were measured and the results are given in Table 2.

It can be seen from Table 2 that under the free-curing condition, the 3- and 28-day compressive strengths of concrete specimens with UEA (specimen no. 2) is lower than that of usual concrete (specimen no. 1). For expansive concrete, when it is cured under the confined condition the 3- and 28-day compressive strengths both are higher than those cured under the free condition. Compared with control HPC (no. 1), the 3-day compressive strength of expansive concrete is basically equal to that of control HPC and 28-day compressive strength is slightly lower. We think the strength enhancement of confined-cured expansive concrete was caused by the improvement of the concrete microstructure. So we further studied the hydration, hardening mechanism, and microstructure of high performance expansive concrete.

2.1. X-ray diffraction analyses on hydration products

Fig. 2 shows the X-ray diffraction (XRD) patterns of different samples hydrated for 28 days. The water/cement ratios of every sample were the same (0.28) and the samples were free-cured underwater at 20°C. We can see that the main hydrated products of pure cement are C-S-H gel, $Ca(OH)_2$, and AFt, with unhydrated C_3S and C_2S still existing (Fig. 2a). When 15% (wt) fly ash was substituted for cement, the hydration products of the mixture were the same as that of pure cement. All crystal minerals of fly ash can be seen in Fig. 2b. The diffraction peak strengths of AFt and $Ca(OH)_2$ basically were the same as that of pure cement, and the diffraction peak strengths of C_3S and C_2S clearly decreased. The main reason is that the addition of fly ash to portland cement may cause a significant dilution effect and increase the relative water/cement ratio of paste. Therefore, the hydration degree of fly ash cement has been increased more than that of pure cement. For fly ash cement concrete, this kind of dilution effect will still take effect although the aggregates might affect the dilution effect. Fig. 2c is the XRD pattern of cement with 10% (wt) UEA hydrated for 28 days. Comparing Fig. 2c with Fig. 2a and Fig. 2b, we find that the counts of AFt and $Ca(OH)_2$ obviously increased and respectively reached to 85.6 and 186.7, with the increasing ranges respectively being 71.2 and 77.8%. The mineral components of UEA are $K_2SO_4 \cdot Al_2(SO)_3 \cdot 4Al(OH)_3$ and $CaSO_4 \cdot 2H_2O$, which can react with $Ca(OH)_2$ to form AFt. The reaction equation is expressed as shown in Eq. (1):

$$K_2SO_4 \cdot Al_2(SO)_3 \cdot 4Al(OH)_3 + 13Ca(OH)_2 + 5CaSO_4 + 78H_2O \rightarrow 3(C_3A \cdot 3CaSO_4 \cdot 32H_2O) + 2KOH \quad (1)$$

Because the $Ca(OH)_2$ is the hydration product of C_3S and C_2S, the formation of AFt also causes vast consumption of $Ca(OH)_2$. The expansion will cause the paste to crack under the free-curing condition. The curing water is rather easy to bleed into, so the hydration degree of expansive cement paste is relatively higher than that of portland cement paste under the free-curing condition. The amount of AFt and $Ca(OH)_2$ also increases to a certain degree. It is an important characteristic of expansive cement that the vast amount of AFt enables the concrete to expand and compensate for shrinkage. In addition, because it forms a vast amount of $Ca(OH)_2$, the pozzolanic effect of fly ash is increased greatly and the strength-developing rate of fly ash concrete is obviously enhanced. Therefore, acting as an expansive mineral with its addition into concrete, UEA cannot only compensate for the concrete shrinkage and make the concrete expand, but it can also increase the early strength of fly ash concrete.

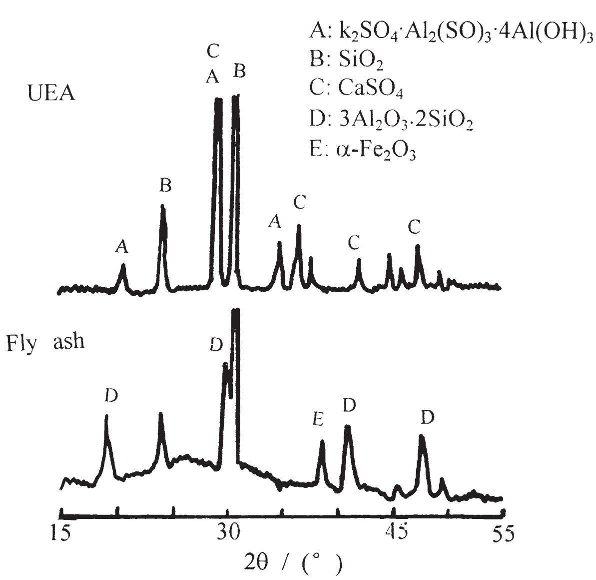

Fig. 1. XRD patterns of fly ash and UEA.

Table 2
Composition proportion and test results of HPC

Specimen no.	Composition proportion of HPC ($kg \cdot m^{-3}$)						Slump (mm)	Compressive strength at 3 days (MPa)		Compressive strength at 28 days (MPa)	
	Water	Cement	UEA	Fly ash	Sand	Stone		Free-curing condition	Confined-curing condition	Free-curing condition	Confined-curing condition
1	156	460	0	60	655	1069	195	46.5	–	69.3	–
2	156	414	46	60	655	1069	210	43.1	46.6	62.7	66.8

2.2. SEM research

Compared with usual concrete, the microstructure of HPC paste has quite different characteristics, such as relatively less porosity, finer and denser C-S-H gel, and closer paste-aggregate interface. But when an expansive agent is added into HPC, the concrete microstructure becomes quite different under free- or confined-curing conditions. By means of SEM, we observed the change of the microstructure of high performance expansive concrete.

2.2.1. SEM research on hardened paste

Figs. 3, 4, and 5 respectively show the microstructures of pure cement paste, cement + 15% fly ash paste, and cement + 10% UEA paste hydrated for 28 days. The curing conditions are the same as that of XRD analyses. It can be seen from Fig. 3 that at 28 days the hydration products were C-S-H gel, $Ca(OH)_2$, and AFt, with the paste structure being quite dense. Fig. 4 shows that in the microstructure of fly ash cement, the fly ash beads were easily wrapped up by C-S-H gel and $Ca(OH)_2$. Some beads surfaces were coarse, which is due to the hydration reaction between $Ca(OH)_2$ and fly ash. This kind of reaction easily occurs in fly ash pores and defects. Comparing Fig. 3 to Fig. 4, we find that the density of fly ash cement paste was similar to that of pure cement paste within 28 days. This kind of microstructure also explains why the cement hydration degree increases by mixing fly ash. After 28 days, the glass phase on the fly ash surface will be continually corroded by $Ca(OH)_2$ and form C-S-H gel. Therefore the porosity becomes smaller and smaller and the pore distribution is modified. The amount and size of pore distribution is obviously lower than that of pure cement paste. So the long-term strength of fly ash concrete is higher than that of pure cement concrete. Fig. 5 reflects the microstructure of expansive cement paste. Due to the free-curing condition, the particles in the expansive concrete deviated from each other, which lengthened the distance between concrete particles. Thus the structure tissue became loose, with more cracks existing. Therefore, with expansive agent added into cement, the paste mechanical properties will decrease under free-curing conditions.

2.2.2. SEM research on the paste-aggregate interface

Research on the paste-aggregate interface is a hot topic in material science at present. Some research results show that although the interface zone only holds a small ratio to the total volume, it plays an important role in concrete me-

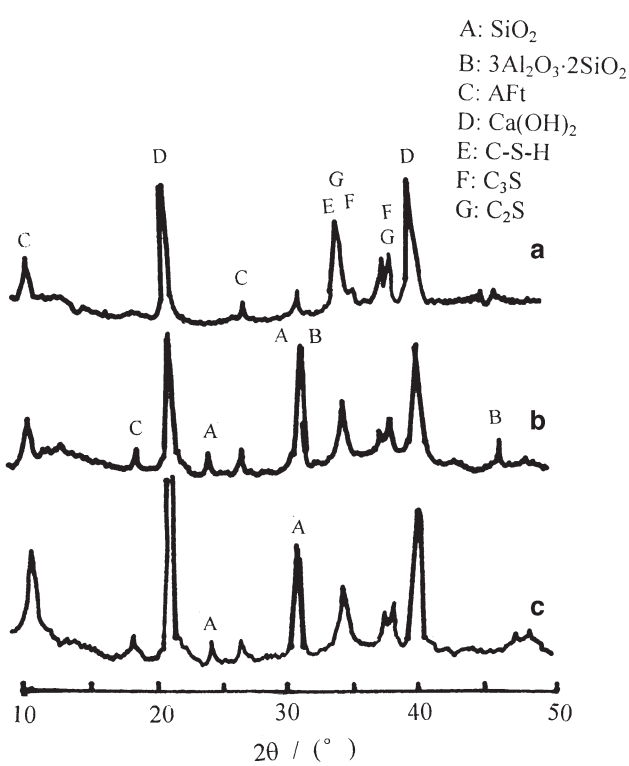

Fig. 2. XRD patterns of different samples hydrated for 28 days. (a) cement; (b) cement + 15% fly ash; (c) cement + 10% UEA.

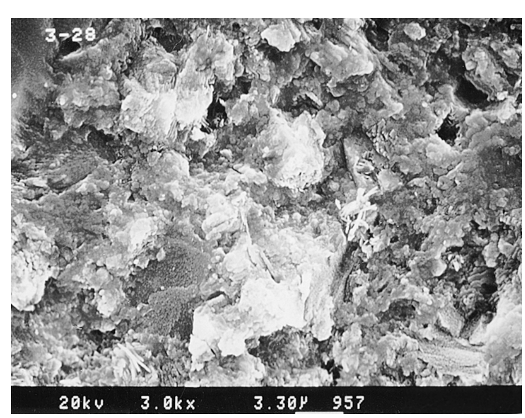

Fig. 3. SEM of pure cement paste.

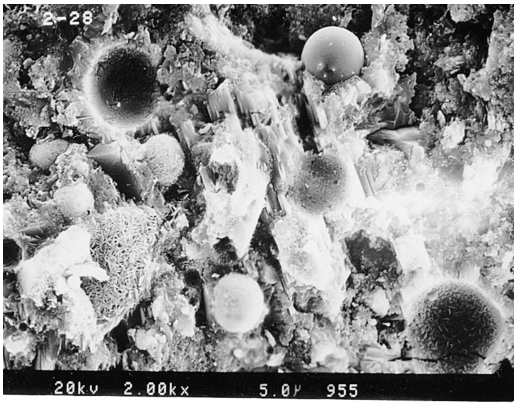

Fig. 4. SEM of cement + 15% fly ash paste.

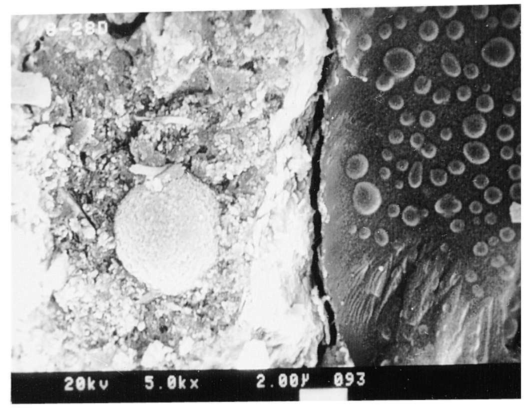

Fig. 6. SEM of expansive concrete paste-aggregate interface under free-curing condition.

chanical and physical properties. Usually the paste-aggregate interface is considered as a weak zone in structure. At present, there are two main methods to improve the interface structure [4]. One method is to add pozzolanic active material (such as fly ash, silica fume, slag, etc.) to the concrete. This method is effective in increasing hardened paste density and interface binding strength. The other method is to change the aggregate surface constituent to get good interface binding properties, such as using an artificial material like clinker or corundum with hydrated surface as aggregate. Although this method can make the interface zone closer, it is hard to apply to actual concrete technology. In order to design a new method to improve the interface, we added expansive agent to concrete and observed the changes of the microstructure of the paste-aggregate interface under different conditions.

Figs. 6 and 7 are SEM photographs of paste-aggregate interface in expansive concrete at 28 days under free- and confined-curing conditions, respectively. It can be seen from Fig. 6 that the structure of the matrix is closer and more even than that of interface. Clear cracks exist between the paste and aggregate, and fly ash beads easily assemble near the interface zone. Because of inner bleeding in fresh concrete, a large amount of water fills around the aggregate to form a water film on the surface of aggregate. If the water film is thick enough, cracks will appear. Under usual conditions, ions such as Ca^{2+}, SO_4^{2-}, and Al^{3+} can penetrated into the water film by diffusion. When these ions reach the oversaturation condition, they will crystallize and grow to form large crystals. For expansive concrete under confined condition, the volume expansion of paste will reduce the thickness of the water film and make the paste come close to the aggregates, which causes the cement hydration products such as C-S-H gel to have more opportunities to connect with aggregates, and the contact is effectively increased. In addition, the reduction of crystal growth space limited the free growth of AFt and $Ca(OH)_2$. So instead of a large $Ca(OH)_2$ and AFt crystal, the main components in the interface zone are dense C-S-H gel and fine AFt crystal. The density of paste matrix and interface is approximately the same. All these factors have guaranteed the paste-aggregate interface will bind effectively. Therefore, with the expansive agent added into concrete under confined-curing conditions, the paste-aggregate interface is intensified and densified, which is an effective method to improve the interface microstructure.

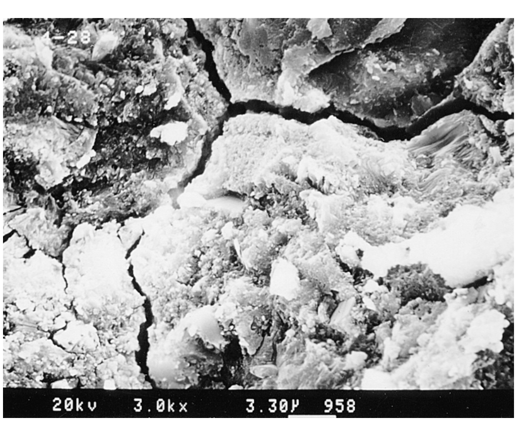

Fig. 5. SEM of cement + 10% UEA paste.

Fig. 7. SEM of expansive concrete paste-aggregate under confined-curing condition.

3. Conclusions

1. An expansive agent consisting of alunite and gypsum can obviously increase the amount of AFt, which can make concrete expand and compensate for shrinkage.
2. Under the free-curing condition, the inner microstructure of expansive cement paste and concrete is loose, with many cracks in the paste and paste-aggregate interface. Confined-curing condition could improve the microstructure of expansive concrete, especially by intensifying and densifying the paste-aggregate interface.

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