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Microstructure and properties of the binder of fly ash-fluorogypsum-Portland cement

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Abstract

The hydration process, mortar microstructure, and properties of the binder consisting of fly ash, fluorogypsum, and Portland cement were investigated with X-ray diffraction, differential thermal analysis, scanning electron microscopy with energy dispersing spectrum, and mercury intrusion porosimetry. Its major hydrates are hydraulic gypsum solid solution, CSH gel, and ettringite. The addition of alum activator enhanced the formation of ettringite and the transformation of anhydrite into gypsum. They intermix uniformly to form a dense mortar structure with very low porosity and low proportion of large pores. The binder shows high strength, good volume stability, and excellent water resistance. The properties of the binder can be adjusted by the quantity of alum added to prepare shrinkage-free or microexpansive concrete. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Fly ash; Fluorogypsum; Hydration; Microstructure; Physical Properties

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Chemical gypsum is a major industrial by-product that occupies considerable land and contaminates air and water sources if it is not utilized appropriately. The main way to use chemical gypsum is to manufacture building materials [1,2]. A serious shortcoming of gypsum products is their poor water resistance, which limits their utilization to only indoor wall elements. Attempts were made to improve this issue [3–5]. Some composite binders and prefabricated building elements based on chemical gypsum and pozzolanic materials were studied [6–8]. Among them, a novel binder with excellent hydraulic properties has been developed [9,10]. It used mainly fly ash and fluorogypsum, two industrial by-products; thus, it is an energy-saving and environmentally friendly binder with a satisfactory developing prospect. It has some faults, such as long initial setting time and low early strength. Alum was added to the binder as an activator to improve its properties. The microstructure and properties of the binders cured in different conditions were investigated.

1. Experiments

The chemical compositions of the raw materials used in this study are listed in Table 1. They were same as those described previously [9]. X-ray diffraction (XRD) investigation showed that the dominant phase in fluorogypsum was anhydrite with minor phases of gypsum and calcium fluoride. The Bogue calculation of P-II 525 Portland cement gave 53% C_3S, 23% C_2S, 6% C_3A, and 12% C_4AF. The Chinese standard silica sand was used for the cement strength test. According to earlier work [9], superior hydraulic properties can be obtained when the composition of the binder has the proportions of fly ash:fluorogypsum:Portland cement of 53:31:16. In the present study, three binders were prepared. One was normal binder with superior composition as the control sample (G); the other two were the regulated binders with superior composition and extra 3% or 5% alum (GA1 and GA2, respectively). The alum added is a commercial product.

The mortars with binder-to-sand ratio of 1 were prepared for the strength test, and the pastes were prepared for investigation of the hydration process. The designations, water-to-binder ratios, and curing conditions of mortars and pastes are listed in Table 2.

Fluorogypsum, fly ash, Portland cement, and alum were blended. The mixture was ground in a ball mill to a fineness similar to that of Portland cement. The mortars were mixed by machine for 3 min, cast into 40 × 40 × 160 mm moulds for the strength test or 40 × 40 × 140 mm moulds with 4-mm diameter steel limiting frame for the volume variance test, and then vibrated for 2 min. The samples were kept in hu-

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Table 1
Chemical composition of the raw materials

	CaO	Fe_2O_3	Al_2O_3	SiO_2	MgO	SO_3	R_2O	CaF_2	LOI at 1000°C
Fluorogypsum	42.53	0.38	0.27	1.29	0.09	46.42		4.35	1.54
Fly ash	4.42	9.56	19.78	58.64	2.08	0.41	3.51		0.25
Portland cement	61.44	3.63	4.39	20.82	1.37	2.51	1.12		1.31

mid air at 20°C ± 2°C for 24 h. After demoulding, the initial length of the restrained mortar prisms was measured. Then, the samples were cured at the different conditions listed in Table 2 until the day of testing. The restrained mortars were cured only in air. The corresponding pastes were prepared and cured in the same conditions.

The strength of mortars was determined at the scheduled ages. Crushed pastes were washed with alcohol and dried at 80°C for 5 h to stop hydration at the same ages. The dried paste powder was used for determination of hydrate phases by XRD and differential thermal analysis (DTA). The porosities of pastes were measured using mercury intrusion porosimetry (MIP). The morphologies and compositions of the hydrates were investigated on the fresh fracture surface of the pastes using scanning electron microscopy with energy dispersing spectrum (SEM-EDS).

2. Results and discussion

2.1. Mechanical properties and volume variance of the binders

The addition of the alum as an activator accelerated the setting of the binder. The initial and final setting times were shortened from 8.5 h and 13.0 h for sample G to 2.8 h and 4.7 h for sample GA1, and then 1.25 h and 2.6 h for sample GA2. The setting time of the binder can be adjusted with the quantity of alum added.

Table 3 shows the strength of the mortars cured in air or under water. The early strengths of the binders are not very high because of the low content of Portland cement and the slowness of the pozzolanic reaction of fly ash. The strengths of all the mortars increased significantly as the hydration proceeded due to the continuous pozzolanic reaction of the fly ash and rose to a high level. Curing mortar GH at 60°C for 6 h increased its early strength to a great extent, but its increasing rate of strength was lower than that of mortar G cured at 20°C. The early strength of binder GA1 was slightly higher, but increased less in the later period of the hydration than that of binder G. GA2 had the lowest strength among the binders. Elevating the curing temperature enhanced the development of its strength, but the effect was limited. Mortars GA1 and GA2H had similar strengths that were lower than that of mortar G after 91 days of hydration. The compressive strengths of the mortars cured under water for 28 days were higher than that of corresponding mortars cured in air. Thus, the binders have good water resistance.

Fig. 1 shows the longitudinal variance of the mortars during 1 year of hydration. There are two expansive reactions in the hydration process of the binder of fly ash-fluorogypsum-Portland cement: the formation of ettringite and the transformation of anhydrite into gypsum by a topochemical process because the water-to-binder ratios of mortars are very low. The volume expansion caused by these reactions compensates for most of the chemical shrinkage caused by hydration of the cement clinker. Comparing the large amount shrinkage during the initial hydrating period and the mild developing rate of ordinary Portland cement, the binder of fly ash-fluorogypsum-Portland cement has a

Table 2
Water-to-binder ratio and curing conditions of the mortars and pastes

Sample	Water-to-binder ratio	Curing conditions
G	0.24	20°C in air or under water
GH	0.24	Initially steam curing at 60°C for 6 h, then at 20°C in air or under water
GA1 and GA2	0.25	20°C in air or under water
GA2H	0.25	Initially steam curing at 60°C for 6 h, then at 20°C in air or under water

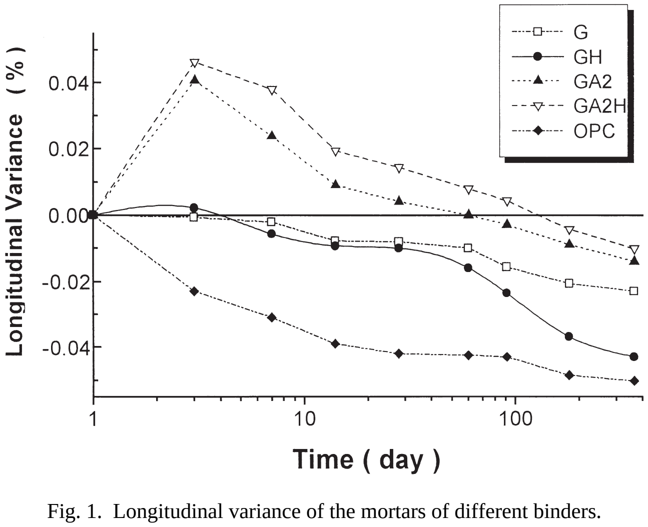

Fig. 1. Longitudinal variance of the mortars of different binders.

Table 3
Strength (MPa) of mortars with binder-to-sand ratio of 1

	Cured in air								Cured under water	
	Flexural strength				Compressive strength				Flexural strength (28 days)	Compressive strength (28 days)
	3 days	7 days	28 days	91 days	3 days	7 days	28 days	91 days		
G	3.31	4.48	8.81	10.48	15.8	24.8	54.6	69.4	6.64	59.0
GH	6.67	8.51	9.17	10.71	40.3	44.5	58.6	71.1	9.33	58.8
GA1	3.34	5.96	8.98	9.64	18.0	34.0	55.5	60.7	8.08	55.8
GA2	2.31	3.95	7.03	8.69	10.7	23.8	37.8	54.3	5.67	41.1
GA2H	3.38	5.18	7.90	9.45	13.8	26.8	43.4	60.9	7.06	46.3

small amount of shrinkage after the beginning of hydration and a stable developing rate.

Mortar GA2 cured at 20°C has an obvious volume expansion during the initial hydrating period because of the formation of larger quantities of gypsum and ettringite. Mortar volume shrinks gradually to a constant value after 28 days of hydration when the pozzolanic reaction of fly ash dominates over other reactions. A coeffect of the activator and the elevated curing temperature results in the largest expansion during the early hydrating period and the smallest shrinkage after 1 year of hydration. The volume expansion of the mortars can be maintained for a long time if there is rich water supply. The expansive rate of the mortars can be modified by regulating the quantity of activator added.

2.2. Identification of hydration products

The XRD patterns of paste G are shown in Fig. 2. Portland cement hydrates quickly during the early hydration period. The characteristic peaks of $Ca(OH)_2$ appear after 3 days of hydration. Strong peaks of gypsum and remaining anhydrite exist, but those of clinker are very weak. With progressive hydration, more anhydrite transforms into gypsum, and some $Ca(OH)_2$ and gypsum are consumed to activate the pozzolanic reaction of the fly ash. At 28 days, the peak intensity of anhydrite and $Ca(OH)_2$ decreases, and that of gypsum increases slightly in the XRD pattern of sample G. When curing the samples under water, there is enough water supply to enhance the formation of gypsum and the pozzolanic reaction of the fly ash, which consumes

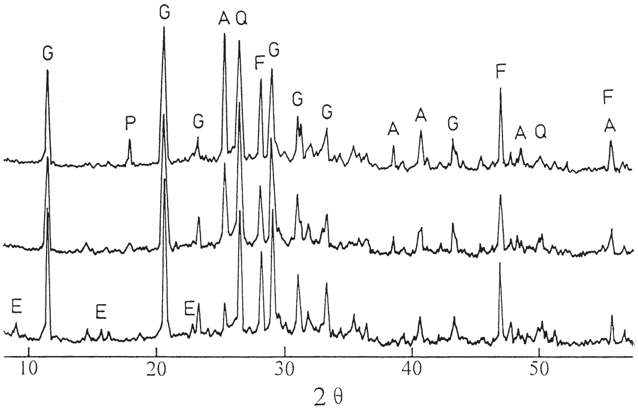

Fig. 2. XRD patterns (CuKα) of paste G. *(Upper pattern)* cured in air for 3 d; *(middle pattern)* cured in air for 28 days; *(lower pattern)* cured under water for 28 days. A: anhydrite; E: ettringite; F: CaF_2; G: gypsum; P: portlandite; Q: quartz.

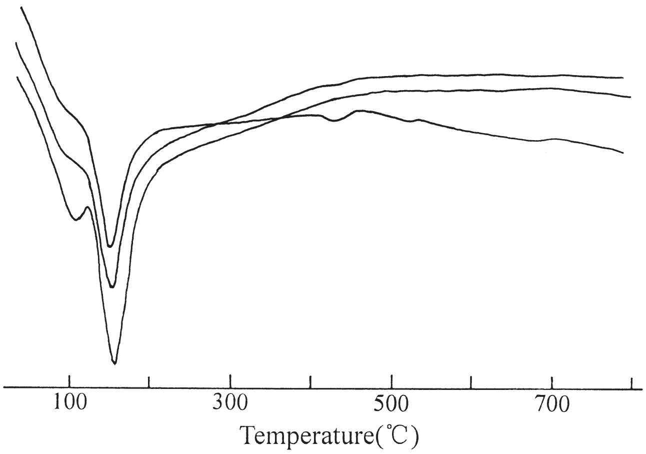

Fig. 3. DTA curves of paste G. *(Upper pattern)* cured in air for 3 days; *(middle pattern)* cured in air for 28 days; *(lower pattern)* cured under water for 28 days.

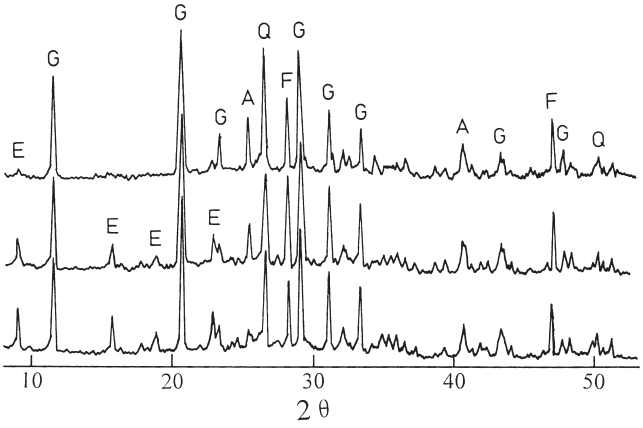

Fig. 4. XRD patterns (CuKα) of paste GA2. *(Upper pattern)* cured in air for 3 days; *(middle pattern)* cured in air for 28 days; *(lower pattern)* cured under water for 28 days. A: anhydrite; E: ettringite; F: CaF_2; G: gypsum; Q: quartz.

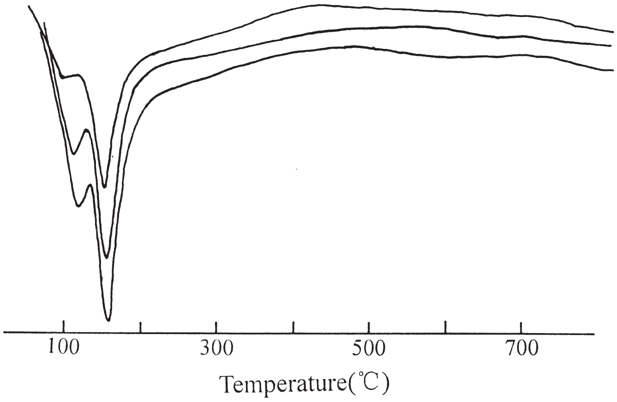

Fig. 5. DTA curves of paste GA2. *(Upper pattern)* cured in air for 3 days; *(middle pattern)* cured in air for 28 days; *(lower pattern)* cured under water for 28 days.

$Ca(OH)_2$ and gypsum to form CSH gel and ettringite. Thus, in the XRD pattern of paste G cured under water for 28 days, the $Ca(OH)_2$ peaks disappear, those of anhydrite weaken greatly, and those of ettringite appear.

The DTA curves of paste G are shown in Fig. 3. A quantity of gypsum whose endothermic effect is located at about 150°C and some $Ca(OH)_2$ whose endothermic effect is located at about 430°C can be detected during the early hydration period. The overlapping endothermic effect of CSH gel and ettringite in the region between 100° and 110°C is very weak. At 28 days of hydration, the endothermic effects of gypsum, CSH gel, and ettringite increase slightly and that of $Ca(OH)_2$ weakens in paste G; however, in paste G cured under water for 28 days, the endothermic effects of CSH gel and ettringite increase significantly, that of $Ca(OH)_2$ disappears, and that of gypsum does not change. The results are the same as those of the XRD investigations.

Addition of alum accelerates the transformation of anhydrite into gypsum, the pozzolanic reaction of fly ash, and the formation of ettringite, especially in the paste cured under water. The solution of alum contains ions K^+, Al^{3+}, and SO_4^{2-}, which easily react with $Ca(OH)_2$ to increase the quantity of nuclei in the paste and aggress on the surface of fly ash particles after the beginning of hydration. This enhances the hydration of Portland cement and the pozzolanic reaction of fly ash. The $Ca(OH)_2$ yielded during the hydration of Portland cement is consumed quickly by the pozzolanic reaction of fly ash. Thus, the characteristic peak of $Ca(OH)_2$ in the XRD patterns of paste GA2 at 3 or more days of hydration is not present (Fig. 4). The characteristic peaks of gypsum are the strongest ones. The peaks of anhydrite weaken with prolongation of hydration in the paste cured in air and almost disappears in the paste cured under water after 28 days of hydration. Ettringite can be detected in paste G only in the XRD pattern at 28 days of hydration (Fig. 2). It is identified in paste GA2 at 3 days of hydration and strengthens at 28 days of hydration in the pastes cured both in air and under water. Fig. 5 shows the DTA curves of paste GA2. There is a strong endothermic effect of gypsum and a mixing endothermic effect of CSH gel and ettringite, but not one of $Ca(OH)_2$ in the DTA curve of paste GA2 at 3 days of hydration. The endothermic effect of gypsum changes little, whereas the endothermic effect of CSH and ettringite increases obviously when the sample hydrates for 28 days regardless of curing in air or under water. A similar result was obtained from XRD and DTA investigation of paste CA2H.

2.3. Morphologies and porosities of the mortars

Difference from the control binder G whose hardened paste consisted of amorphous CSH gel, gypsum microcrystals, remainder anhydrite, and a little ettringite, the hardened pastes of the regulated binder GA cured both in air and under water consisted of a large amount of crystalline ettringite and gypsum, remainder anhydrite, and some amorphous CSH gel (Fig. 6). A dense structure was formed in both pastes. When the percentage of alum added was high, some ettringite clusters formed (Fig. 7). It could produce local stress that is harm to the mechanical properties of the binder. The typical gypsum has high solubility; thus, gyp-

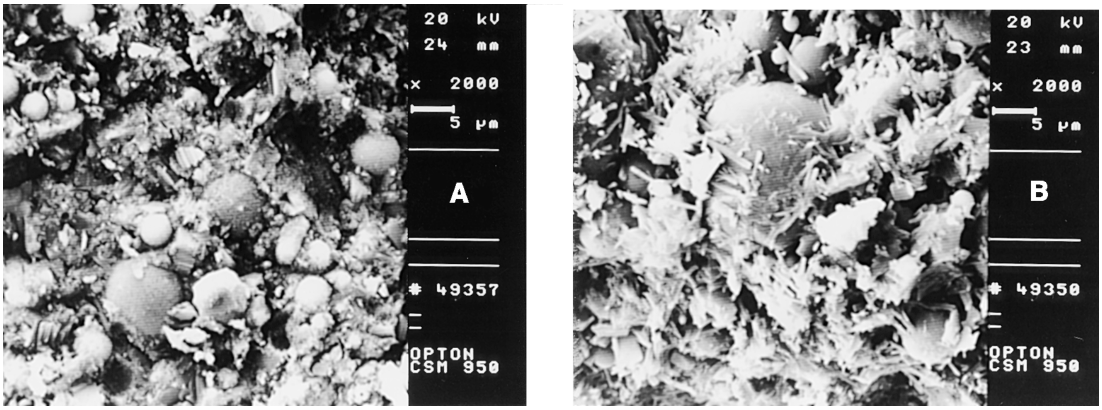

Fig. 6. Morphology of the hardened paste cured in air for 91 days. *(A)* paste G; *(B)* paste GA1.

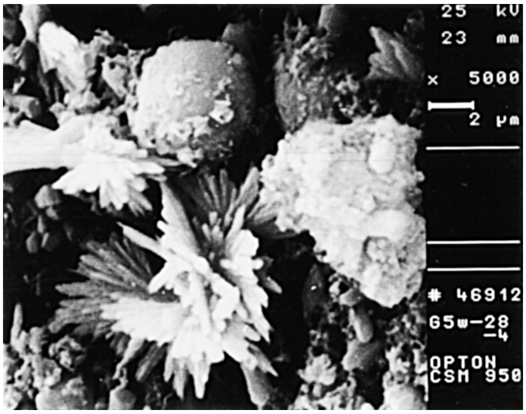

Fig. 7. Ettringite cluster in paste GA2 cured in air for 28 days.

Table 4
Chemical composition of the different phases in the mortars (wt%)

	Na	Mg	Al	Si	S	K	Ca	Fe
Gypsum microcrystal	1.8	0.9	7.4	8.8	26.2	3.2	48.0	3.9
Amorphous phase	0.3	—	9.2	24.1	15.1	1.7	47.1	2.8

sum products possess poor water resistance. The results of EDS analysis shows that the gypsum crystals in mortars G and GA comprised about 10% Si and Al ions to form a solid solution. They were round tablets that had lower solubility (Fig. 8). Some of the gypsum microcrystals and anhydrite residue was dispersed uniformly in the amorphous phase (Table 4). They were engulfed by CSH gel densely, which hindered their contact with water; therefore, the binder possesses very good water resistance (Table 3).

Figs. 9 and 10 show the porosities of the hardened pastes with or without alum activator hydrating for 91 days. They have very low porosities of about 0.02–0.06 mL/g, which is only about half of the porosity of ordinary Portland cement paste. Although the samples cured under water have higher porosities than those cured in air, they have a larger portion in the range of pore size distribution <10 nm than the samples cured in air. The pore whose size distribution is <10 nm in the hardened paste rarely influences the mechanical properties and permeability of the binder [11]. This is an important reason why the binder has good strength and water resistance. Adding the alum activator to the binder increased the total porosities of the pastes, especially that of the paste cured in air, and enlarged the most possible radius of the pore in the pastes. The more alum activator is added, the larger are the porosity and the most possible radius of the pore in the pastes and the lower the strength of the mortars. There is volume expansion in the mortars of the regulated binders. The overexpansion could decrease the strength and water resistance of the mortars. If the regulated binder is used to prepare concrete in the confining condition, this expansion can compensate for the volume shrinkage to prevent cracking of the concrete during hydration. It is favorable to preparation of massive concrete.

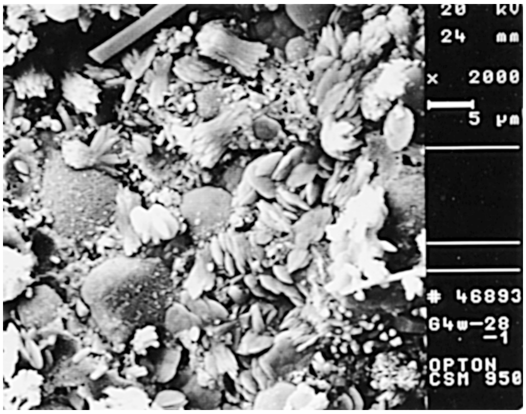

Fig. 8. Less soluble gypsum crystals in paste G cured under water for 28 days.

3. Conclusion

The major hydrates of the binder of fly ash-fluorogypsum-Portland cement are hydraulic gypsum solid solution, CSH gel, and ettringite. The addition of alum activator enhances the formation of ettringite and the transformation of

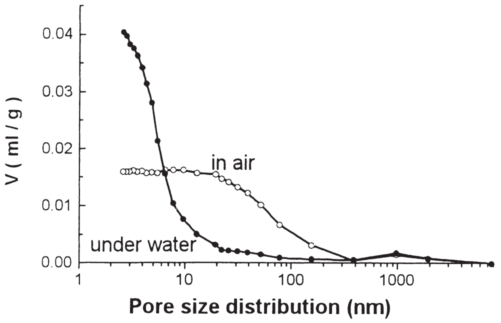

Fig. 9. Porosities of paste G.

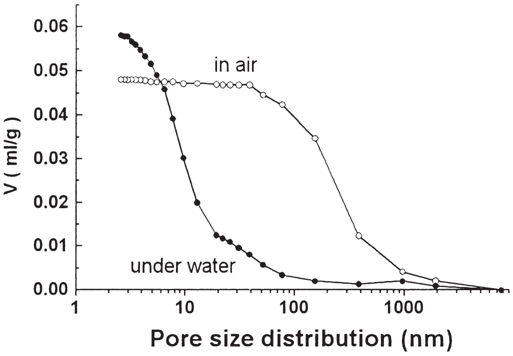

Fig. 10. Porosities of paste GA1.

anhydrite into gypsum during the early period of hydration of the binder. They intermix uniformly to form a dense structure with very low porosities and low proportions of large pores. Thus, the binder has high strength and good water resistance.

The properties of the regulated binder can be adjusted by the amount of activator added. The more alum is added into the binder, the shorter is the setting time and the larger the volume expansion of the mortars. The regulated binder can be used as the shrinkage-compensate binder or the microexpansive agent to prepare massive concrete.

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