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STUDIES ON THE BINDER OF FLY ASH-FLUORGYPSUM-CEMENT

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ABSTRACT

A new binder with high strength, good volume stability, and excellent water resistance has been developed using fly ash and fluorgypsum as main raw materials, as well as Portland cement as stimulator. The hydration process and microstructure of the binder were investigated with X-ray diffraction and scanning electron microscopy. The continuously pozzolanic reaction of fly ash, the transformation of anhydrite into gypsum, in appropriate quantity, and the homogeneous mixing of CSH gel, gypsum microcrystal, and the remaining anhydrite results in the formation of a dense paste structure, and consequently the good properties of the binder. © *1998 Elsevier Science Ltd*

Introduction

Portland cement is the most used construction material. Production of Portland cement consumes huge energy, destroys the ecological environment, and brings us a serious greenhouse effect. The development of clinker cement production must be limited.

Industrial production creates a quantity of by-products. In China, about 100 million tons of fly ash is discharged annually from coal-burning electric-generating plants, and only about a fourth of it is utilized. Chemical gypsum is another great source of industrial waste residue. Fluorgypsum, one kind of chemical gypsum, is the by-product theof production of hydrofluoric acid. Its annually discharged magnitude is as high as 10,000 tons for a middle-scale plant. Though some of the fluorgypsum is used in the cement industry as a set regulator of Portland cement, its main part is still placed in disposal areas. Fly ash and fluorgypsum occupy considerable land and contaminate air and water sources. They produce troublesome problems for environmental protection.

The major mineral phase in fluorgypsum is anhydrite. The anhydrite plaster is not suitable for external application on account of its solubility in water. Otherwise, it sets too slowly to directly produce building elements. When applying a suitable stimulator such as cement or lime, the potential cementitious properties of the mixture of fluorgypsum and pozzolanic materials, for example fly ash, can be excited to produce stable hydration products (1). This is a way to utilize industrial waste residue in large quantity and to develop non-contaminating substitute for clinker cement. M. Singh et al. developed a water-resistant gypsum binder by blending calcined phosphogypsum, granulated blast furnace slag, and Portland cement (2–4).

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TABLE 1
The chemical composition of fluorgypsum and fly ash.

	CaO	Fe_2O_3	SiO_2	Al_2O_3	MgO	SO_3	R_2O	CaF	LOI
Fluorgypsum	42.53	0.38	1.29	0.27	0.09	46.42		4.35	1.54
Fly ash	4.42	9.56	58.64	19.78	2.08	0.41	3.51		0.25

Ikeda and Tomisaka studied a slip casting process (5) and Coppola et al. developed a pressure forming process (6) to fabricate building elements with a mixture of calcined flue gas desulphurization gypsum, fly ash, and Portland cement or lime. Use of an expensive and complex calcining process is not beneficial to decrease the production cost. In this study, a new kind of binder containing fly ash, fluorgypsum, and cement is developed using a simple grinding process. The mechanical properties, hydration mechanism, and microstructure of the binder paste are investigated.

Experiments

Materials

The chemical compositions of the fly ash and fluorgypsum are shown in Table 1. First class fly ash complying with Chinese National Standard GB1596–91 came from a Generating Plant in Inner Mongolia. Fluorgypsum came from a fluoride plant in Shanxi Province. X-ray diffraction (XRD) investigation showed that in fluorgypsum, anhydrite was the main phase with lesser phases of gypsum and calcium fluoride. In fly ash, quartz was the main crystalline phase. Scanning electron microscopy (SEM) investigation showed that the fluorgypsum particles were polyhedral and finer than the fly ash particles that were spherical and had a geometric mean diameter of 7.68 μm. There was only less than 0.4% of soluble F^- and no radioactivity in the fluorgypsum.

Sample Preparation and Investigation

Fluorgypsum, fly ash, and cement were blended according to the proportion shown in Table 2. The mixture was ground in a ball mill to fineness similar to Portland cement. The water-binder ratios of pastes are shown in Table 2. The pastes were mixed by machine for

TABLE 2
Proportions (%) and water-binder ratios of binders.

	Fluorgypsum	Fly ash	Portland cement	Aluminate cement	W/B
G1	36	64			0.22
G2	36	60	4		0.22
G3	35	57	8		0.22
G4	31	53	16		0.22
A4	31	53		16	0.20

TABLE 3
Strength of studied binders (MPa).

	Samples Cured in Air						Samples Cured in Water			
	Compr. Strength			Flex. Strength			Compr. Strength		Flex. Strength	
	3 d	28 d	91 d	3 d	28 d	91 d	28 d	91 d	28 d	91 d
G1		very low			very low					
G2	4.4	28.1		0.90	4.41					
G3	7.5	31.5		1.37	4.84					
G4	15.4	52.7	72.7	3.54	7.32	7.75	59.3	77.3	5.99	7.11
A4	14.8	40.8	44.3	3.05	4.28	4.56	38.9		4.24	

3 min, cast into 4 × 4 × 16 cm moulds for test of strength or 4 × 4 × 14 cm moulds with a steel limiting frame for test of volume variance, and then vibrated for 2 min. The samples were kept in air at 20 ± 2°C for 24 h. After demoulding, part of samples were cured in air at 20 ± 2°C, and the rest were cured in water at 20 ± 2°C until the date of testing. The restrained samples were cured only in air.

After strength determination, the sample residue was washed with alcohol and dried at 80°C for 5 h to stop hydration. The dried sample powder was used for determination of hydrate phases with XRD. The quantity of chemically combined water was determined by ignition of dried sample powder at 900°C to indicate the degree of hydration. The line expansion rate was measured by a restrained prism at different ages to show the volume change. The morphologies of paste were investigated on the fresh fracture of pastes with SEM.

Results and Discussion

From Table 3, it can be seen that the plain mixture of fluorgypsum and fly ash does not gain cementitious property. Some stimulator must be added to the mixture to excite its potential cementitious property. This binder sets slowly. The initial setting came in 8.5 h, and the final setting came in 13 h for paste G4. The less the percentage of cement in the binder was, the longer the setting time. The strengths of pastes in the early age were not high, but accompanying the continuous development of hydration, the strengths increased continuously. When the proportion of cement that is both the stimulator and hydraulic component in the binder increased from 8% in G3 to 16% in G4, the properties of the binder were improved greatly. G4 had satisfactory early strength and excellent later strength. It eliminated the shortcoming of normal gypsum plaster that loses its strength in humid environment due to its low water resistance. G4 gained even higher compressive strength because the pozzolanic reaction of fly ash proceeded more fully, and more CSH gel yielded in the paste cured in water than in air.

The XRD patterns of G4 and A4 at early and later hydrating ages are shown in Figure 1. After the beginning of hydration, Portland cement in paste G4 hydrated quickly, and a high alkaline pore solution formed. Anhydrite dissolved and precipitated into gypsum microcrystals in large quantity. Some $Ca(OH)_2$ microcrystals and CSH gel formed, too. The charac-

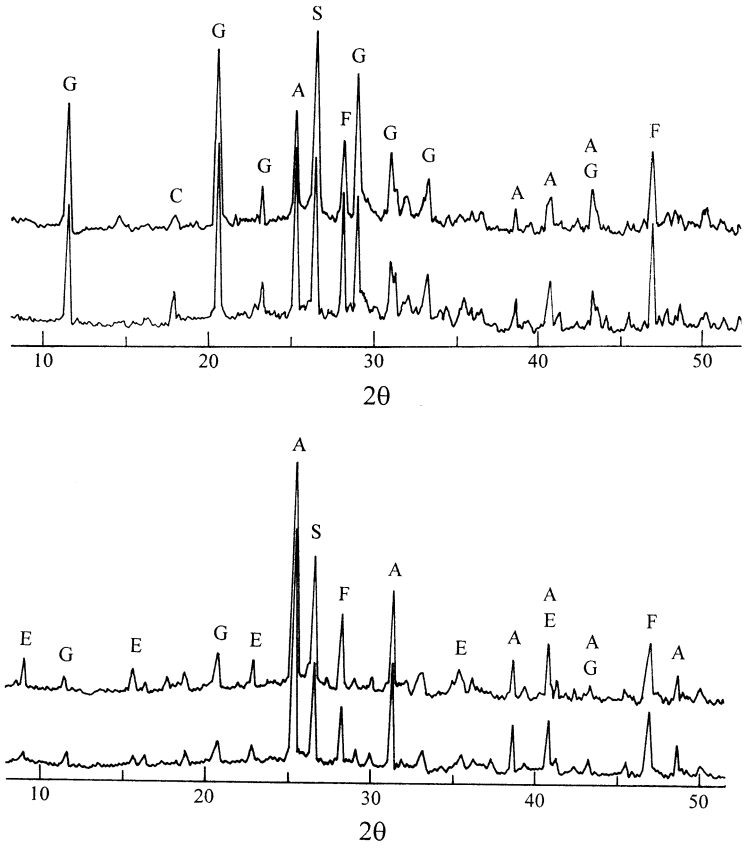

FIG. 1.
XRD Patterns (Cu Kα) of Selected Pastes: *A*, Anhydrite; *G*, Gypsum; *S*, Quartz; *F*, CaF_2; *C*, $Ca(OH)_2$; *E*, Ettringite.

teristic peaks of formed gypsum, $Ca(OH)_2$, and the remaining anhydrite could be seen in the XRD pattern of paste hydrating for 3 days. The peaks of clinker were very weak. After 28 days of hydration, the peak intensity of anhydrite and $Ca(OH)_2$ decreased; and that of gypsum increased slightly. Inert quartz and CaF_2 remained constant. Hydrous SO_4^{2-} and Ca^{2+} ions greatly stimulated the pozzolanic reaction of fly ash. After 3 days of hydration, there was much hydrate on the fly ash particles (Fig. 2a). Gypsum and $Ca(OH)_2$ crystals detected by XRD were too small to be seen. Polyhedral anhydrite particles were seldom found. The gypsum microcrystals and remaining anhydrite particles were blended homogeneously with CSH gel to form a dense paste structure that had good water resistance. Along with the development of hydration, more and more hydrate formed mainly through the pozzolanic reaction of fly ash (Fig. 2b). The paste structure was increasingly strengthened. Therefore, the strength of G4 increased continuously.

In the paste A4, aluminate cement with super-high early strength hydrated very quickly to form low alkaline ettringite and aluminate hydrates (Fig. 1). The characteristic peaks of ettringite could be identified after 3 days of hydration and were strengthened in the later hydrating period. The peak intensity of anhydrite was strongest but that of gypsum was very

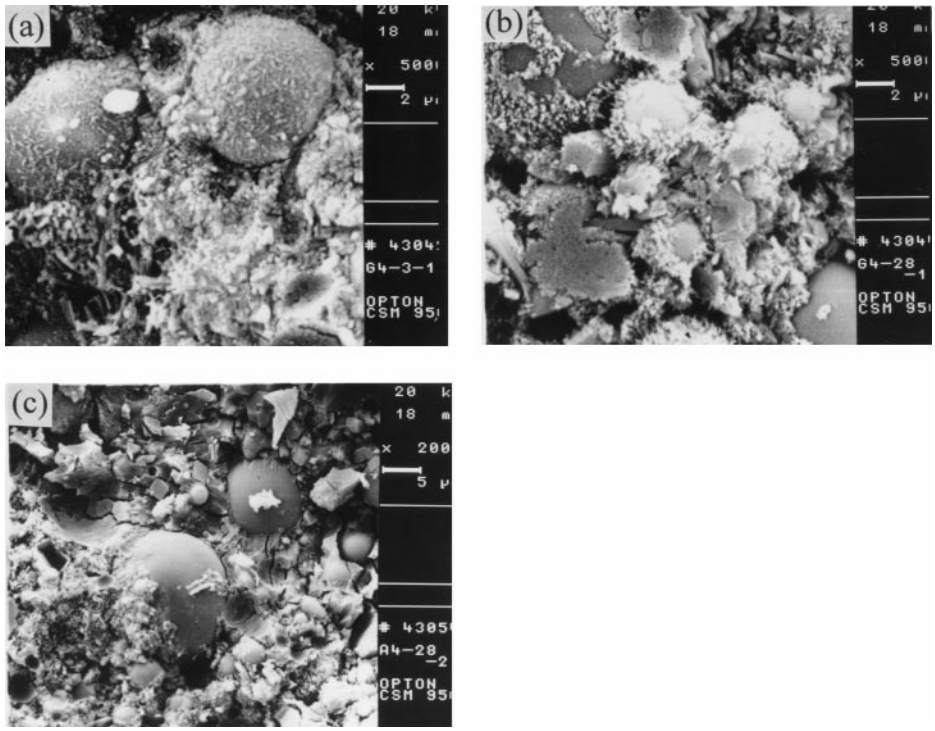

FIG. 2.
The microstructure of hardened pastes: (*a*) G4 hydrating in air for 3 days, (*b*) G4 hydrating in air for 28 days, (*c*) A4 hydrating in air for 28 days.

weak during the entire hydration period. This meant that only little anhydrite was transformed into gypsum. In low alkaline pore solution, the dissolution of anhydrite and the formation of gypsum were impeded. The pozzolanic reaction of fly ash was not also fully stimulated. Until 28 days of hydrating age, the surface of fly ash particles was smooth and little hydrate formed (Fig. 2c). There was only "microfiller" effect but less pozzolanic effect to strengthen the microstructure of paste A4. Therefore, A4 gained early strength due to the fast hydration of aluminate cement, but its strength did not increase much in later hydrating age.

In the initial hydrating age, the binder pastes gain strength due to the hydration of cement and the formation of gypsum; in the later hydrating age, the strength increase is mainly attributed to the continuous pozzolanic reaction of fly ash. The reaction degree is higher and formed paste microstructure is better in a high alkaline environment than in a low one. Thus, G4 has similar early strength as A4, but the later strength of G4 is much higher than that of A4 because aluminate cement with low alkaline hydrates results in very poor excitation of the pozzolanic reaction. The strength of G4 increases considerably until 91 days, but the strength of A4 increases little after 28 days.

The amount of chemically combined water of G4 and A4 (Table 4) increased along with the development of hydration. This indicated that their hydrating degree increased gradually. The amount of chemically combined water in initial hydrating age was higher for A4 than that for G4 because the main hydrate ettringite in A4 contains more water than CSH gel and

TABLE 4
Chemically combined water and volume changes of selected pastes.

	Chemically combined water (%)					Longitudinal variance (%)			
	3 days	28 days		91 days					
	Cured in air	Cured in air	Cured in water	Cured in air	Cured in water	3 days	7 days	28 days	91 days
G4	7.15	8.22	10.74	14.44	14.37	+0.001	−0.004	−0.006	−0.019
A4	8.51	10.48	11.14	11.72	11.76	−0.001	−0.021	−0.055	−0.064

$Ca(OH)_2$ in G4. The hydrating degree of G4 rose more in the later age than that of A4 due to its full pozzolanic reaction. The samples cured in water gained higher hydrating degree because of the full water supply than ones cured in air. Both of them reached the similar level after 91 days of hydrating age when the hydration was nearly ended.

Transformation of anhydrite into gypsum brings about a 60% increase of solid phase volume. If the transformation amount is suitable, this volume increase can compensate the chemical and drying shrinkage of pastes. Therefore, G4 had good volume stability (Table 4). Anhydrite transformed little into gypsum but ettringite formed much in the paste A4. Ettringite formed through solution does not yield volume expansion. It may bring large chemical shrinkage (7). Thus, A4 had poor volume stability.

Conclusion

A new binder with high strength, good volume stability, and excellent water resistance has been developed using industrial waste residue, fluorgypsum, and fly ash as the main raw materials. As a stimulator, Portland cement has better excitation than aluminate cement because the high alkaline environment in the paste containing Portland cement enhances the transformation of anhydrite into gypsum and the pozzolanic reaction of fly ash. The binder sets slowly and does not attain high strength in initial hydrating age. The strength of the binder increases continuously and reaches a high level in the later age due to the continuously pozzolanic reaction of fly ash. Homogeneously mixing of CSH gel, gypsum microcrystal, and remaining anhydrite ensures good water resistance of the binder. Satisfactory volume stability of the binder is obtained with the formation of gypsum in appropriate quantity.

References

1. H. Wang and Z. Zhang, China Concr. Cem. Products 1, 5 (1996).
2. M. Singh and M. Garg, Cem. Concr. Res. 26, 449 (1996).
3. M. Singh, M. Garg, and S.S. Rehsi, Cem. Concr. Res. 20, 271 (1990).
4. M. Singh and M. Garg, Constr. Build. Mater. 6, 52 (1992).
5. K. Ikeda and T. Tomisaka, J. Jap. Ceram. Soc. 97, 468 (1989).
6. L. Coppola, G. Belz, G. Dinelli, and M. Collepandi, Mater. Struct. 29, 305 (1996).
7. P. Yan and I. Odler, Adv. Cem. Res. 7, 125 (1995).