Research Letter

Properties of Cement Mortar with Phosphogypsum under Steam Curing Condition

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The purpose of this study is to utilize waste PG as an admixture for concrete products cured by steam. For the study, waste PG was classified into 4 forms (dehydrate, β -hemihydrate, III-anhydrite, and II-anhydrite), which were calcined at various temperatures. Also, various admixtures were prepared with PG, fly-ash (FA), and granulated blast-furnace slag (BFS). The basic properties of cement mortars containing these admixtures were analyzed and examined through X-ray diffraction, scanning electron microscopy, compressive strength, and acid corrosion resistance. According to the results, cement mortars made with III-anhydrite of waste PG and BFS exhibited strength similar to that of cement mortars made with II-anhydrite. Therefore, III-anhydrite PG calcined at lower temperature can be used as a steam curing admixture for concrete second production.

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1. INTRODUCTION

Phosphogypsum (PG) is an industrial by-product of the phosphoric acid process involved in manufacturing fertilizers [1]. PG consists mainly of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and contains impurities such as free phosphoric acid, phosphates, fluorides, and organic substances that adhere to the surface of gypsum [2–4]. Efficient recycling and disposal countermeasures for PG are essential. The purpose of this study is to utilize PG as an admixture for steam-cured high-strength concrete.

For the study, the PG was calcined at different temperatures to see what effects it had on the finished product. Admixtures for steam cured concrete were manufactured by mixing fly ash (FA) and granulated blast-furnace slag (BFS). By partially substituting them for ordinary Portland cement (OPC), we prepared mortars which were then subjected to compressive strength and acid corrosion resistance tests.

2. EXPERIMENTATION

2.1. Raw materials

The chemical composition, density, and pH of the raw materials are listed in Table 1. The OPC and sand used were specified by Korean Standard KS L 5100 for mortar specimens. A mineral admixture was prepared from BFS and FA to im-

prove strength. The blast furnace slag was a ground pelletized slag (Blaine 4600 g/cm²). The FA was an ASTM Type F fly ash (Blaine 3300 g/cm²). The PG was collected from the storage yard of the fertilizer plant of N Company. After dry refining, the PG was calcined at 140°C, 170°C, and 450°C thus transforming the original $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (D) into the forms β - $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ (H), III- CaSO_4 (A3), and II- CaSO_4 (A2), respectively. Figures 1 and 2 present the results of XRD and SEM analysis of the PG.

2.2. Experimental method

2.2.1. Manufacturing of specimens

The cement pastes were manufactured specifically to undergo scanning electron microscope examination and X-ray diffraction analysis. Mortar specimens were prepared according to the mixing proportions given in Table 2. All specimens were cast in 50 × 50 × 50 mm mold for compressive strength on cement mortar, then steam cured at 65°C for 6 h. After steam curing, the specimens were dry-cured.

2.2.2. Acid corrosion test

The acid corrosion test was performed as specified in ASTM C 267 and 579. In order to evaluate the acid corrosion resistance of these cementing materials, the cement mortar

TABLE 1: Chemical compositions of raw materials.

Type	Oxide composition (%)								Density	pH
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	SO ₃	Ig. Loss		
OPC	21.00	6.00	2.80	62.10	3.50	—	2.10	2.50	3.15	12.50
BFS	34.76	14.50	0.48	41.71	6.87	0.03	0.13	0.23	2.91	11.70
FA	46.9	25.40	8.2	3.70	1.00	0.02	0.90	9.50	2.22	9.30
D	1.53	0.08	0.08	32.50	0.01	0.40	44.19	22.12	2.63	3.65
H	1.69	0.05	0.08	35.68	—	0.43	48.83	13.24	2.75	3.06
A3	2.06	0.93	0.03	39.31	—	0.42	54.00	3.25	2.86	3.65
A2	1.72	1.45	0.07	39.17	—	0.45	56.24	0.90	3.03	3.52

FIGURE 1: X-ray diffraction of unrefined PG.

FIGURE 2: Scanning electron microscopy of unrefined PG.

specimens were tested in three-type acid solutions. The specimens were cured for 14 days and then immersed in 5% solution of hydrochloric acid (HCl) and a 5% and 10% solution of sulfuric acid (H₂SO₄) for 14, 28 and 56 days. The mass reduction rates and compressive strength were measured for each immersion period.

3. RESULTS AND DISCUSSION

3.1. Microstructure and X-ray diffraction patterns

Figures 3 and 4 show the microstructure and X-ray diffraction patterns of the cement paste containing PG at a 28-day curing period. In the OPC paste analyzed by SEM, very little ettringite was observed and monosulfate was observed in

FIGURE 3: Scanning electron microscopy of hardened paste containing PG calcined at various temperatures for 28 days.

TABLE 2: Mixing proportion (by mass) of binder for mortar specimens.

OPC	Binder (%)			Sand/binder	Water/binder
	PG	FA	BFS		
100	—	—	—	2.0	0.45
95.0	5.0	—	—		
92.5	7.5	—	—		
90.0	10.0	—	—		
87.5	12.5	—	—		
90.0	7.5	2.5	—	2.0	0.45
90.0	7.5	—	2.5		
90.0	7.5	1.5	1.0		

FIGURE 4: X-ray diffraction of hardened paste containing PG calcined various temperatures at 28 days.

small amounts. On the contrary, there was an abundance of ettringite, of several μm in size and in the form of needle-shaped crystals, found in the pastes containing PG. In addition, X-ray diffraction analysis showed strong ettringite peaks in all the pastes containing PG up to 28 days.

3.2. Compressive strength of mortar

Figure 5 shows the 28-day compressive strength of the cement mortar containing PG calcined at 140°C , 170°C , and 450°C and replacing cement in amounts of 5%, 7.5%, 10%, and 12.5% by mass. Regardless of the crystal form of the PG, the strength was the highest with a PG addition of 7.5%. As the incorporation rate increased above 7.5%, the strength began to show a downward tendency. In addition, the compressive strength of the cement mortar, in which 7.5% of cement by mass had been replaced with PG of different calcination temperatures, was 22–53% higher (depending on the

FIGURE 5: Compressive strength of cement mortar admixed with PG at various calcination temperatures for 28 days.

FIGURE 6: Compressive strength of cement mortar substituted various admixtures to OPC for 28 days.

form of PG) than the strength of cement mortars containing OPC only. The strength of mortar containing PG in the D form was 55.2 MPa, which was 12.1 MPa lower than the strength of mortar containing PG in the A2 form. However, the compressive strength of mortars containing PG in the H and A3 forms were 68.8 MPa and 69 MPa, respectively, which is higher than mortar of the A2 form. Therefore, when using PG as an admixture for steam-cured concrete, it may be possible to use H and A3 forms rather than A2 forms for their lower calcination temperature.

Figure 6 shows the compressive strength of the mortar made with OPC replaced with a 10% by mass admixture containing BFS and FA with PG. In all cases, except the H form, mortars containing BFS and FA with PG appeared to be stronger than those containing only PG. In particular the case of A2, where the strength of mortar containing PG and FA was 72.2 MPa, this was higher than any other mortar containing the admixture. Thus, when PG is used as a concrete admixture for steam curing, the addition of small amounts of BFS and FA effectively enhance strength.

3.3. Acid corrosion resistance

Figure 7 shows the mass reduction rate of mortar specimens containing PG in different crystal forms immersed for different periods in the acid solutions. Throughout all ages, the mortars containing A2 and A3 were superior to the other admixtures in their resistance to HCl and to H₂SO₄. In particular, the mass reduction rate of mortar specimens containing A2 and A3 immersed in 5% H₂SO₄ solution for 14 days was less than 10%, indicating that it had been slightly corroded away. When the immersion period was longer than 14 days, however, the mass of the specimens decreased gradually and then decreased rapidly after 28 days. Compared to those specimens containing A2 and A3, the mortars containing D and H appeared to have low acid corrosion resistance.

(a) 5% HCl

(b) 5% H₂SO₄

(c) 10% H₂SO₄

FIGURE 7: Mass reduction rate of mortar containing PG of different crystal form according to the immersion period.

4. CONCLUSION

(1) According to SEM examinations, pastes containing PG have a much denser microstructure than OPC paste and a larger quantity of ettringite which reduce voids and makes the internal structure dense and, consequently, increases compressive strength.

(2) The optimal mixing rate, depending on the type of PG, was 7.5% and a noticeable strength increase was observed at both early and later ages when compared to OPC.

(3) In the case where PG was classified according to the calcination conditions, the strength of H and A3 was similar to A2. However, the H and A3 forms appear to be more convenient than the A2 form since they require a lower calcination temperature.

(4) The result of the acid corrosion resistance test shows that mortars containing PG have a higher acid corrosion resistance than those using only OPC, as their microstructure becomes dense after the production of ettringite.

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