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Utilization of weathered phosphogypsum as set retarder in Portland cement

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Abstract

In this study, usability of weathered phosphogypsum (PG) from residue areas as set retarder in Portland cement was investigated. The effects on the setting and mechanical properties of PG added in ratios 1, 3, 5, 7, 10, and 12.5 wt.% to Portland cements were studied and compared with a Portland cement containing natural gypsum (NG). It was found that PG can be used in place of NG for Portland cement according to Turkish standards. The highest 28-day compressive strength was found in the sample with 3 wt.% PG.

Keywords: Phosphogypsum; Waste management; Cement

1. Introduction

Phosphogypsum (PG) is a kind of gypsum that occurs as a by-product and is obtained from phosphate rock during the production of phosphoric acid. PG contains some impurities such as P_2O_5 and F, so in order to use it as a cement retarder instead of natural gypsum (NG), purification, drying, and calcination processes must be applied [1–4]. If these impurities are not removed, PG causes retarding (delay) in setting time and decreases the strength of Portland cement. The usage of the PG as a retarder replacement of NG provides both economical and ecological profits. There are several researches on the usage of phospho-, citro-, and borogypsum as a retarder in the manufacturing of cement [1–11]. According to Singh, it was reported that the purified PG may be used in place of gypsum in cement because P_2O_5 and F present in PG decreases after treatment with aqueous citric acid [1]. In a study by Erdoğan et al. [2], it was reported that untreated PG retards the setting time in Portland cement and decreases its strength. The use of unrefined PG in trass cement after washing and calcination processes were reported. Smadi et. al. [3] calcined PG at 170, 600, 750, 850, and 950 °C after washed and not washed with water. The amount of P_2O_5 in the calcined and washed samples was 0.41% after the calcination at 170 °C; however, it decreased to 0.32% after the calcination at 950 °C, and also F amounts decreased from 0.89% to 0.27% at the same temperatures. In the samples that were not washed with water, no significant decrease in P_2O_5 at the same calcination temperatures was observed, but the F decreased from 2.12% to 0.16% with increasing the calcinations temperature from 170 to 950 °C. In the study of Smadi et al. [3], the setting times increased with using PG for calcined and uncalcined samples. Heat treatment of PG has resulted in the highest improvement in latter's flexural strengths and the lowest improvement in compressive strengths. Also, the curing method was found to greatly affect the strengths. The samples, which were cured in damp room, showed lower strength as compared to those cured in air [3].

In another research by Muramaki [4], impurities in PG retarded the setting time of Portland cement but did not an effect the strength growth, except for the 3-day strengths. Mehda and Brady [5] reported that addition of 2% SO_3 to raw mixture decreased temperature of clinkering and the retarding effect but increased early strengths.

In this study, usability of PG residues obtained from BAGFAŞ in Turkey as a set retarder in Portland cement was investigated. Every year, such residues occupying increas-

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Table 1
Composition of the samples (%)

Samples	Clinker (C)	NG	PG
C+NG1	99	1	–
C+PG1	99	–	1
C+NG3	97	3	–
C+PG3	97	–	3
C+NG5	95	5	–
C+PG5	95	–	5
C+NG7	97	3	–
C+PG7	97	–	3
C+NG10	90	10	–
C+PG10	90	–	10
C+NG12.5	87.5	12.5	–
C+PG12.5	87.5	–	12.5

ingly large space were investigated more and disturb the environment.

2. Experimental

2.1. Materials and methods

PG, which may be added to clinker, is obtained as a by-product during the production process of phosphoric acid from phosphate rocks in the Bandırma-Turkey Fertilizer Factory. In this study, PG that was stored in open-air (weathered) residue areas for several years was used. The clinker, NG, and sand, which were used in the present experimental study, have been brought from Bursa Cement Factory. The percentage compounds of the experimental samples are given in Table 1. The clinker used in this study had a silica ratio of 2.13, alumina ratio of 1.7, and lime saturation factor of 94.32. Its phases and their percentages amounts as calculated from the Bogue analysis method are as follows: C_3S 58.24%, C_2S 16.52%, C_3A 10.42%, and C_4AF 11.1%. The chemical compositions of the three materials are given Table 2. The fineness, specific gravity, and specific surface of all samples are given in Table 3. The test of mixes was performed according to the Turkish Standards Institute TS 19 [12]. The setting times were measured on cement pastes with a Vicat needle in accordance with TS 24 [12]. Mortar bars were prepared ($40 \times 40 \times 160$ mm) such that cement/sand/water ratio was 1:3:0.5. Mechanical tests were applied to samples in accordance with the Turkish Standard TS 24. The samples initial and final setting times and volume expansions are

Table 2
Chemical composition of clinker, NG, and PG

Constituents (%)	Clinker	NG	PG
SiO_2	21.37	3.54	3.34
Al_2O_3	6.32	0.98	0.88
Fe_2O_3	3.70	0.57	0.23
CaO	65.74	30.51	29.11
MgO	0.87	1.09	–
SO_3	0.98	40.22	44.27
Na_2O	0.47	0.05	0.13
K_2O	0.55	0.14	–
P_2O_5	0.09	0.03	0.45
Cl^-	0.014	0.250	0.004
CaO_{free}	1.17	0.86	0.82
F	–	–	0.81
Loss of ignition	0.74	21.57	21.06
Insoluble matter	0.54	0.048	0.53

Table 3
Physical characteristics of the samples

Samples	Fineness (wt.%)		Specific gravity (g/cm^3)	Specific surface (m^2/kg) (Blaine)
	+90 μm	+45 μm		
C+NG1	2	14	3.14	332.7
C+PG1	2.5	15.6	3.15	341.9
C+NG3	2.7	15	3.12	347.7
C+PG3	2.3	15.2	3.13	357.5
C+NG5	2.1	18	3.13	342.2
C+PG5	2.4	18	3.14	338.7
C+NG7	2.3	16	3.12	340.3
C+PG7	2.5	16	3.11	337.8
C+NG10	2.4	16	3.11	363.9
C+PG10	2.6	16	3.12	359.1
C+NG12.5	2.5	15	3.11	371.9
C+PG12.5	2.4	15.4	3.12	369.0

Table 4
Physical characteristics of the samples

Samples	Water (%)	Setting time (h:min)		Volume expansion (total)
		Initial	Final	
C+NG1	26.5	1:40	3:30	3
C+PG1	26.5	1:50	3:35	2
C+NG3	27.0	2:30	3:40	5
C+PG3	27.0	2:35	3:50	4
C+NG5	27.5	2:20	4:25	5
C+PG5	27.5	2:25	4:25	4
C+NG7	27.5	2:25	4:35	4
C+PG7	27.5	4:40	6:55	4
C+NG10	27.5	3:55	5:20	5
C+PG10	27.5	4:10	6:00	5
C+NG12.5	28.0	4:05	6:25	6
C+PG12.5	28.0	4:30	6:50	6
TS 19		Min 1	Max 10	Max 10

Table 5
Compressive strengths of the samples (N/mm^2)

Samples	2 days	7 days	28 days
C+NG1	17.9	33.7	41.7
C+PG1	10.6	30.3	36.8
C+NG3	16.8	41.7	55.8
C+PG3	18.2	41.1	58.7
C+NG5	22.3	42.9	55.7
C+PG5	20.0	41.7	55.4
C+NG7	23.3	31.8	42.2
C+PG7	26.9	36.6	47.5
C+NG10	19.7	27.0	44.2
C+PG10	20.0	29.0	46.4
C+NG12.5	14.5	20.8	25.1
C+PG12.5	14.9	21.0	26.2
TS 24	Min 10	Min 21	Min 32.5

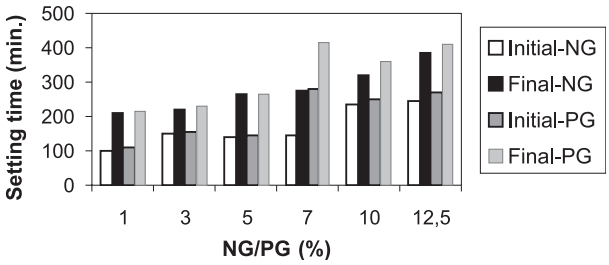

Fig. 1. Setting time of the samples with NG and PG.

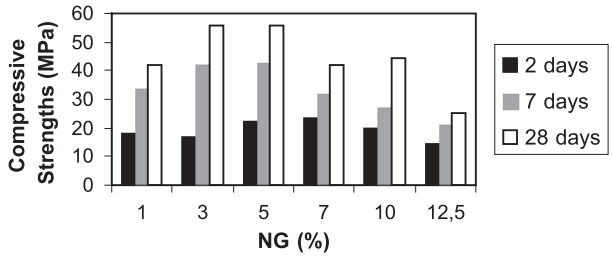

Fig. 3. Compressive strength of the samples with NG.

given in Table 4. The 2-, 7-, and 28-day compressive strengths are given in Table 5.

3. Results and discussion

As shown in Table 4, the required water content for normal consistency related to different cement types complies with TS 19, which limits the amount of water to 20–30% water. Due to the high water content for consistency, an increase in initial and final setting times was reported for the C + NG12.5 and C + PG12.5 samples.

The setting times of samples are within the requirements of TS 19 as shown in Table 4. These setting times show that the PG, which was added (3–5%) according to standards, is being a strong retarder. The longer setting time was obtained for specimens containing 7%, 10%, and 12.5% PG as shown in Fig. 1. The PG, which was used in this study, contains 0.45% amount of P_2O_5 and 0.69% amount of F, noting that the PG was placed outside for aging and was naturally washed by rain. In spite of this, PG and NG added to all samples resulted in setting times and volume expansions, which were appropriate to the Turkish Standards TS 19 [12].

The much longer retarder effect of PG was related to the surfaces of cements particular surfaces coating with inactive materials such as calcium phosphate and fluorides during mixing [1]. In this study, P_2O_5 amount of PG had decreased from 0.95% to 0.46% after heat treatment with aqueous citric acid. In the same way, F had decreased from 1.5% to 0.65%; while for cleaned samples, the initial, and final setting times were according to the impure samples [1].

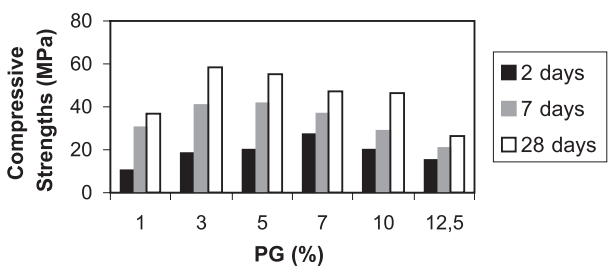

Fig. 2. Compressive strength of the samples with PG.

Erdoğan et.al. [2] indicated that PG containing 1.05% total P_2O_5 (0.25% water soluble) and 0.79% total F (0.24% water soluble) retarded the setting time of Portland cement and reduced its strength. As the percentage of PG addition was increased there by the amount of impurities increased, the setting times were reported by Smadi et.al [3] to increase. In other studies also, it was reported that the fluorides retarded the setting times [6–9].

For PG-added samples, 2-day compressive strengths were found to increase for samples containing 1%, 3%, 5%, and 7% PG but decreased for those with 10% and 12.5% PG (Table 5 and Fig. 2). A similar tendency was observed in the NG-added samples (Fig. 3). When the 2-day strength samples were compared, it was seen that C + PG7 sample has the highest compressive strength.

For the 7-day compressive strengths, it was noted that samples with 1%, 3%, and 5% PG had higher strengths while those with 7%, 10%, and 12.5% PG had lower strengths. For the PG-added samples, the 7-day compressive strengths decreased when the addition amount increased (Fig. 2). The same tendency was seen in the NG-added samples (Fig. 3). As for the 28-day samples, the compressive strengths increased in only the PG-added 1% and 3% samples (Fig. 2). In the 5%, 7%, 10%, 12%, and 12.5% PG-added samples, it was observed that as the PG amount increased, the strengths decreased. The same tendency was observed for the NG-added samples as shown in Fig. 3. The 2-, 7-, and 28-day compressive strengths of all samples, except C + NG12.5 and C + PG12.5 samples, were appropriate for TS 24 Standard (Table 5).

4. Conclusions

The weathered PG can be used as a retarder in place of NG for Portland cement.

The highest 28-day compressive strength was found in the sample with 3 wt.% PG.

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