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Utilization of phosphogypsum as raw and calcined material in manufacturing of building products

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Abstract

The main objective of this research was to investigate the utilization potential of phosphogypsum with fly ash and lime in construction industry. Phosphogypsum was used as raw and calcined material for making the cementitous binder. A series of the tests were conducted to determine the compressive and flexural strength, water absorption and unit weight after 28 days of the specimen preparation. On the basis of the test results, it was concluded that the curing conditions have an important influence on the compressive and flexural strength of the binder specimens. It was also concluded that the cementitous binder obtained can be used for the production of interior wall materials such as bricks and blocks.

Keywords: Fly ash; Phosphogypsum; Lime; Cementitious binder

1. Introduction

Phosphogypsum and fly ash are industrial by-products that are generated by the phosphorus fertilizer industry and by thermal power plants, respectively. Approximately 15 million tons of fly ash and 3 million tons of phosphogypsum are generated each year in Turkey; these waste products are discarded in landfills, rivers and ponds.

Phosphogypsum consists primarily of calcium sulphate and contains some impurities, such as phosphate, fluorides, organic matter and alkalies. The presence of impurities puts restrictions on the use of phosphogypsum in building materials. Relatively little of this by-product is currently used by the cement and gypsum industries as a set retarder for cement and for making gypsum plaster and bricks [1–8].

The main way to reuse of fly ash and phosphogypsum is the manufacture of building products. Singh and Garg [9], studied the cementitous binder from flourogypsum, phosphogypsum and fly ash. They concluded that the cementitous binders are eminently suitable for use in masonry mortars and making concrete. In the study of Marinkovich et al. [10], the possible uses of fly ash and fgd gypsum were investigated in manufacturing of building products. It was concluded that FaL–G binder obtained in their study can be used for the production of interior wall materials. Kostich-Pulek et al. [11] studied a binder composed of two industrial wastes; calcined nitrogypsum and bottom ash with water, both with and without lime addition. These mixtures gave solidified products at room temperature and atmospheric pressure after 28 days and had satisfactory compressive strength for application in the civil industry. Kumar made [12] a perspective study on fly ash–lime–gypsum bricks and hollow blocks for low cost housing development. In another research by Kumar [13], the durability of FaL–G hollow blocks in sulfate environments was also determined. It was reported that these blocks have sufficient strength for their use in general building construction.

The enormous volume of unused phosphogypsum can be re-used by combining fly ash and Portland cement in

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the building industry. However, environmental concerns have developed in the past 10 years due to the presence of radionuclides in phosphogypsum. This material contains naturally occurring radioactivity and ^{226}Ra is a major source of radioactivity. Phosphogypsum that exceeds 370 Bq kg^{-1} (10 pCi g^{-1}) of radioactivity has been banned from all uses by the Environmental Protection Agency (EPA) since 1992. EPA revised the standard to permit use but a safe limit was set 10 pCi g^{-1} and the international limit prescribed by European Atomic Commission (EURATOM) is 500 Bq kg^{-1} (13.5 pCi g^{-1}) [14,15].

There is no unanimity on the safe limit for the radioactivity exposure due to phosphogypsum. The phosphate industry has been looking into different ways of reducing the size of stacks. Researchers have also been seeking new application areas for phosphogypsum use as research has indicated that it would be more environmentally sound to use by-products rather than to dump them.

The aim of this study was to investigate the possibility of the utilization of two industrial wastes, fly ash and phosphogypsum with lime to produce the cementitous binder. The unit weight, water absorption, volume stability, compressive strength and flexural strength of the binder specimens were determined after 28 days of their preparation. These cementitous binders can be used in civil industry, primarily for use in masonry and for the manufacture of bricks and blocks.

2. Experimental

The basic ingredients of the cementitous binder were fly ash (FA), hydrated lime (L), phosphogypsum (PG) and water. Phosphogypsum as a by-product of the phosphoric acid process was procured from the Bagfas fertilizer factory in Bandirma, Turkey. The specific gravity of phosphogypsum is 2.89, the optimum moisture content is 13% and the maximum dry density is 14.70 kN/m^3, based on the standard Proctor compaction. Phosphogypsum is a damp, powdery material that is predominantly silt-sized and has little or no plasticity. The maximum size range is 0.5–1.0 mm. The results of radioactivity analyses of phosphogypsum determined by the Turkish Atomic Energy Association (Cekmece Nuclear Research and Training Center) are ^{226}Ra: 22 Bq kg^{-1}, ^{238}U: 9.0 Bq kg^{-1}, ^{232}Th: 1.0 Bq kg^{-1} and ^{40} K: 11 Bq kg^{-1}. Measures carried out on the radioactivity of phosphogypsum obtained from Bagfas Fertilizer Plant permit its classification as a weakly radioactive material.

Fly ash used in this study was procured from Soma Seas Thermal Plant in Manisa, Turkey. The Soma fly ash was produced from lignite coal and contains a significant amount of CaO with a lime content of 15.34%. Based on chemical characteristics, Soma fly ash can be classified as class-C fly ash according to ASTM C 618 [16]. The total amount of SiO_2, Al_2O_3 and Fe_2O_3 is 74.32%, which was a larger quantity than the value given by ASTM as the standard for a type C class fly ash. Free lime content of fly ash complies with TSI (Turkish Standard Institute) [17] and EN [18] standards because it is present in 1.90%. The amount of SO_3 (at 0.99%) is less than the value given by the standards. Pozzolanic activity index (PAI) of Soma fly ash is 88% at 28 days; this value satisfies the ASTM C 618 limit (75%). PAI also meets the TSI and EN criteria of 75% and 85% at 28 days and 90 days, respectively. The remaining on the 45-μm sieve was 16%, which was less than the 40% requirement of the TSI and of EN, and less than 34% of the ASTM standards.

Hydrated lime was a commercial hydrated lime and it was procured in paper sacks from local suppliers. The chemical composition and physical properties of fly ash, phosphogypsum and lime used in production of the cementitous material is given in Table 1.

The mixtures were composed of varying percentage of fly ash and phosphogypsum by holding the lime ratio constant as 10%. The mix proportions of the binders are given in Table 2. Phosphogypsum was used as raw and calcined materials for making the cementitous binder. A suitable amount of phosphogypsum was air dried and sieved through a 4.75 mm sieve before using. In order to obtain calcined gypsum, phosphogypsum was heated in an electric oven at 150 °C for 2 h. The calcined material was desiccated in a closed vessel to room temperature to avoid any contamination.

The weighed quantity of fly ash, phosphogypsum and lime passing through 4.75 mm sieve were thoroughly mixed in dry state. The dry compositions were then mixed in Hobart mixer with addition of water for 60 s. The water content for each mix was determined by flow test. The flow table was used to adjust the flow within 110–115 mm. The water was regular tap water. The mixed cementitous binders were cast in two layers into three-gang molds compacting by a vibration table for 60 s.

Table 1
Chemical composition and physical properties of FA, L and PG

Constituent (%)	FA	L	PG
SiO_2	45.98	1.1	3.44
Al_2O_3	23.75	–	0.88
Fe_2O_3	4.59	0.5	0.32
CaO	15.34	–	32.04
MgO	2.10	1.5	–
SO_3	0.99	–	44.67
K_2O	1.19	–	–
Na_2O	0.21	–	0.13
P_2O_5	–	–	0.50
F	–	–	0.79
$CaCO_3$	–	5.90	–
$Ca(OH)_2$	–	90.80	–
Loss on ignition	1.62	2.15	21.06
Specific gravity	2.24		2.96
Blaine (m^2/kg)	390		467
Retained on			
# 200 (75 μm) sieve (%)	16.00	8.00	20.13
# 325 (45 μm) sieve (%)	31.20	14.00	38.00

Table 2
The mix proportions of the cementitous binders

Constituent materials (%)				Water absorption (%)		Unit weight (kN/m^3)	
Mix designation	FA	L	PG	Raw PG	Calcined PG	Raw PG	Calcined PG
M-1	90	10	0	28	10	14.64	13.60
M-2	80	10	10	30	12	14.32	13.54
M-3	70	10	20	37	15	13.60	13.12
M-4	60	10	30	38	17	13.56	12.48
M-5	50	10	40	40	19	13.44	12.16
M-6	40	10	50	40	23	12.92	12.08

After casting all specimens were stored in a moisture room for 24 h at relative humidity of 90–95% at 20 °C. After demolding, the specimens were cured for 28 days under two different curing conditions, wet curing (in water) and dry curing (in air). Curing temperature was 20 ± 2 °C.

The flexural and compressive strength tests of investigated the cementitous binder were performed at 28 days in conformance with TS EN 196 [19]. For flexural strength test, three specimens from each mix and curing conditions were prepared and tested by one-point loading configuration with span of 10 cm. The flexural strength test was performed in ELE model testing machine with a capacity of 10 kN at a loading rate of 5 N/mm^2/s. The results indicated are the average of three specimens.

Compressive strength tests were performed using six broken pieces of test prisms left flexural strength test. Compressive strength measurements were carried out using ELE International ADR 3000 hydraulic press with a capacity of 3000 kN, the loading rate was 20 N/mm^2/s. The test results indicated the average of the six specimens.

The evaluation of the water absorption for 24 h in water and unit weight was performed on cubes of 5 cm. The specimens were dried at the age of 28 days in an oven at 105 °C and then allowed to cool to room temperature. For the determination of water absorption by total immersion, the dry mass for each specimen was recorded and then totally immersed in water at 20 °C until achieved a constant mass. The gain in weight expressed as a percentage of the dry weight was of the water absorption of the specimens. The volume stability of the binders kept in water or in air was measured on $25 \times 25 \times 285$ mm prismatic specimens.

3. Results and discussion

A large number of the cementitous binder specimens were made with different proportions of fly ash, lime and phosphogypsum (Fig. 1). Raw and calcined phosphogypsum was used in preparing of the cementitous binders.

The compressive strength value of the cementitous binders prepared raw and calcined phosphogypsum are reported in Figs. 2 and 3. Compressive strength value decreased as the percentage of raw phosphogypsum was increased. This behavior is observed at all specimens for both curing conditions. Specimens containing 50% of phosphogypsum seem to be weaker than the others. The lowest compressive strength was obtained as 2.29 MPa at 28 days for 50% of raw phosphogypsum addition. On the contrary, the addition calcined phosphogypsum increased the mechanical properties of test specimens. The same value

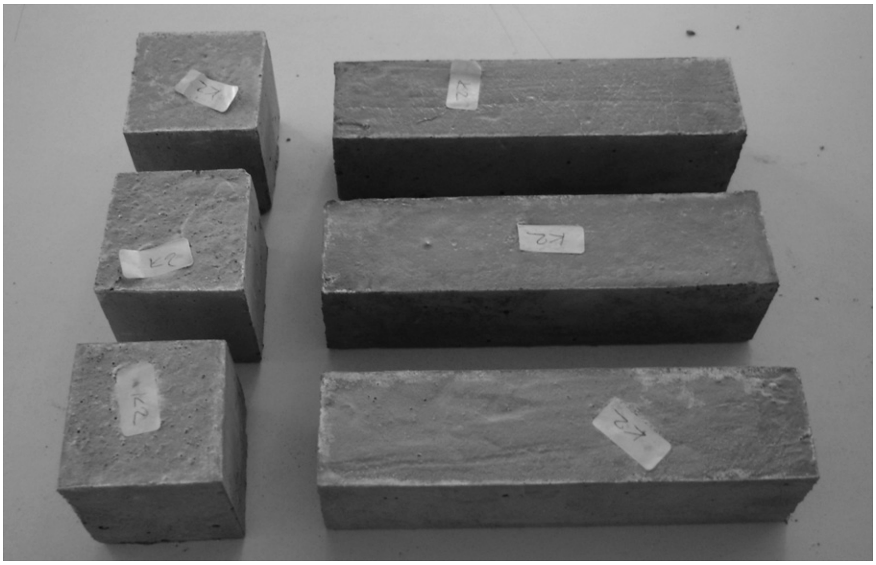

Fig. 1. A view of test specimens.

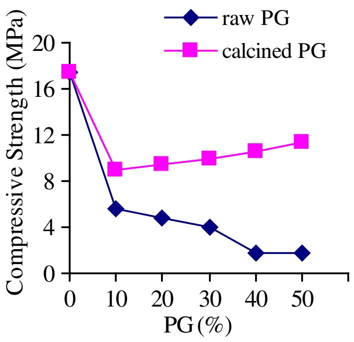

Fig. 2. The compressive strength of the cementitous binders cured in water.

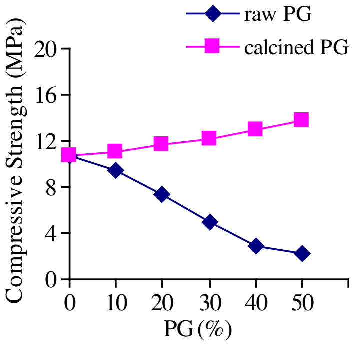

Fig. 3. Compressive strength of the cementitous binders cured in dry state.

of 13.76 MPa was obtained for 50% of calcined phosphogypsum addition. Heat treatment of phosphogypsum in preparing of the binders has resulted in improvement of mechanical properties compared to those of binders prepared with untreated phosphogypsum. The effect of two different curing conditions on compressive strength of the cementitous binders prepared with raw phosphogypsum is presented in Fig. 4. Curing conditions have an important influence on the strength development of these binders. It seems that curing in water decreases the strength values except the specimens prepared without phosphogypsum addition. The compressive flexural strength of the cementitous binders cured in water and air at 20 °C is shown in Fig. 5. The lowest flexural strength was obtained as 0.92 MPa for dry curing and 0.31 MPa for wet curing at 28 days.

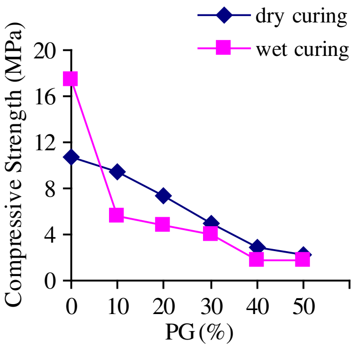

Fig. 4. The compressive strength of the cementitous binders prepared with raw PG.

Water absorption and unit weight of these mixtures are shown in Table 2, Figs. 6 and 7 respectively. It was observed that water absorption of the binders in the present investigation is between 28% and 40% for the raw phosphogypsum addition. The same values are obtained as to be between 10% and 23% for calcined phosphogypsum addition. The cementitous binder made with calcined phosphogypsum shows low water absorption and better compressive strength. The increase in the amount of phosphogypsum addition causes a reduction in the unit weights of specimens. This indicates that the use of the cementitous binder as building materials will reduce the weight of structures considerably.

The expansion or shrinkage values of the specimens cured in water or in air are shown in Fig. 8. The expansion

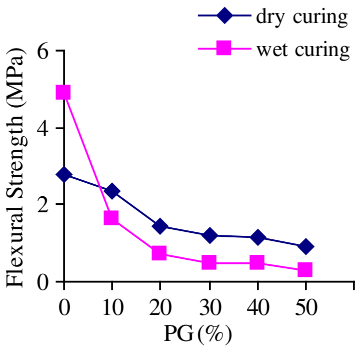

Fig. 5. The flexural strength of the cementitous binders prepared with raw PG.

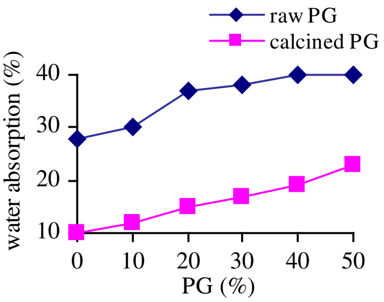

Fig. 6. Water absorption of the cementitous binders.

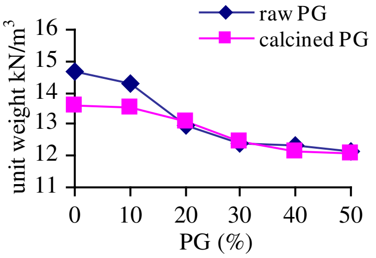

Fig. 7. Unit weight of the cementitous binders.

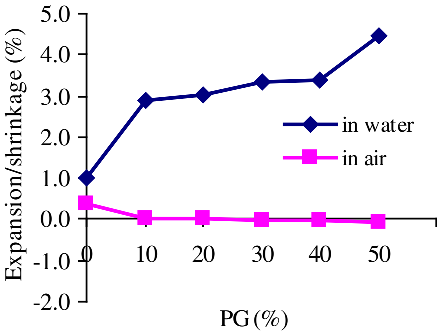

Fig. 8. Expansion or shrinkage of the cementitous binders prepared with raw PG.

of the binders prepared with 50% raw phosphogypsum is also given in Fig. 9. It can be seen from Fig. 8, when specimens were kept in water considerable expansion values were measured on the test specimens. These specimens also exhibited crack formation. This behavior can be attributed to sulfate reaction between gypsum and lime. Yazici [20] investigated the composite materials consisted of flue gas desulfurization sludge, fly ash, bottom ash, cement and lime. He reported that these composite materials kept in water exhibit crack formation and bending. He suggested that steam curing improves the mechanical properties and durability to against water effect. It can be seen from Fig. 9, the specimens that were kept in air generally showed negligible expansion or shrinkage values.

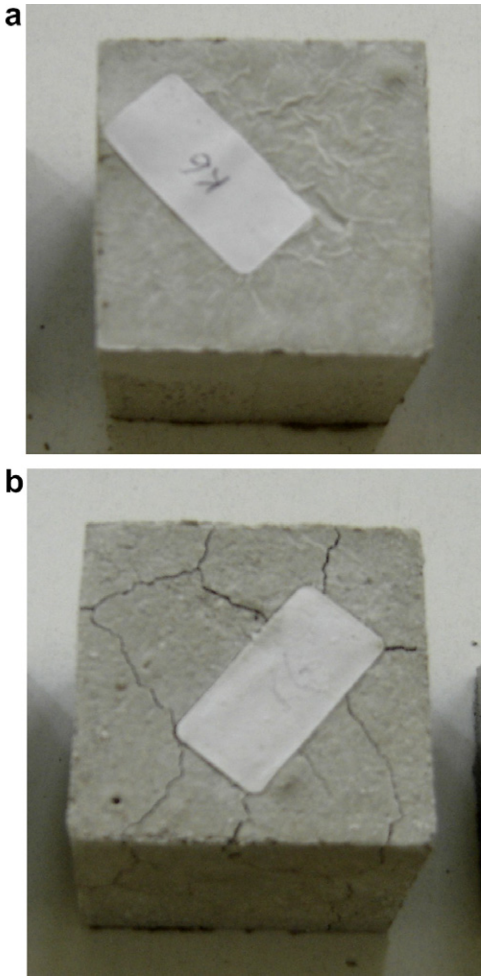

Fig. 9. The specimens cured in air (a) and in water (b).

4. Conclusions

Based on the experimental results of this investigation, the following conclusions can be drawn;

- In general, incorporating phosphogypsum into the cementitous binder caused a reduction in the mechanical properties. On the contrary, the calcined phosphogypsum addition increased the compressive strength values.
- Heat treatment of phosphogypsum has resulted in the highest improvement in compressive and flexural strength of the binders.
- The curing method has affected significantly the strength of the binders; binder specimens cured in water showed lower strengths than those cured in air.
- Water absorption increased with increasing phosphogypsum content.
- The unit weights decreased with increasing phosphogypsum ratio in the binders.
- The cementitous binders have generally volume stability in air, however they showed great expansion and crack formation when exposed to water due to sulfate attack caused by phosphogypsum sludge. This problem could be overcome by steam curing. Steam curing may be an alternative way to improve the mechanical properties and durability. Otherwise these binders should be used interior applications.

The cementitous binders find extensive application in manufacturing of building components and materials. The utilization of fly ash and phosphogypsum as by product waste in construction industry could not only provide low cost material but also help to decrease environmental hazards.

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