

USABILITY OF FLY ASH AND PHOSPHOGYPSUM IN MANUFACTURING OF BUILDING PRODUCTS

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ABSTRACT

In this study, the class-C fly ash, lime and phosphogypsum were used with water to produce fly ash-lime-phosphogypsum (FaL-G) based binders. The dry unit weight, water absorption, compressive and flexural strength of the specimens was determined after 28 days of their preparation. On the basis of the test results, it was concluded that phosphogypsum decreased the compressive and flexural strength while fly ash increased. It was also concluded that the curing conditions have an important influence on the strengths of FaL-G specimens. These binders gain further strength after 28 days. For the strength requirements, phosphogypsum content should be constant as 20%. The water absorption and thermal conductivity of the specimens increases with the increase in phosphogypsum content. Also the increase in the amount of phosphogypsum addition caused a reduction in the dry unit weight of the specimens. The test results show that these binders may be utilized in production of construction elements such as blocks, masonry mortars and controlled low-strength materials.

Key Words : Fly Ash, Phosphogypsum, Lime, Compressive strength.

UÇUCU KÜL VE FOSFOALÇININ YAPI ELEMANI ÜRETİMİNDE KULLANIM OLANAKLARI

ÖZET

Bu çalışmada uçucu kül, kireç ve fosfoalçı kullanılarak uçucu kül-kireç-fosfoalçı esaslı bir bağlayıcı üretilmiştir. 28 günlük numunelerin su emme, kuru birim ağırlık, basınç ve çekme dayanımları tayin edilmiştir. Deney sonuçlarına göre fosfojips basınç ve çekme dayanımını azaltırken, uçucu kül dayanımları arttırmaktadır. Kür koşulları da dayanımlar üzerinde etkili olmaktadır. Uçucu kül-kireç-fosfoalçı esaslı bu bağlayıcı 28 günden sonra dayanım kazanmaktadır. Dayanım gerekliliği nedeniyle fosfoalçı oranı %20 olarak sabit tutulmalıdır. Numunelerin su emmesi ve ısı iletkenliği fosfoalçı oranı ile artmaktadır. Aynı zamanda fosfoalçı oranındaki artış birim ağırlığın azalmasına neden olmaktadır. Deney sonuçları geliştirilen bağlayıcının blok eleman, harç ve düşük dayanımlı malzeme üretiminde kullanılabileceğini göstermektedir.

Anahtar Kelimeler : Uçucu kül, Fosfoalçı, Kireç, Basınç dayanımı.

1. INTRODUCTION

Phosphogypsum (PG) and fly ash (FA) are industrial by-products that are generated by the phosphorus

fertilizer industry and by thermal power plants, respectively. Approximately 15 million tons of FA and 3 million tons of PG are generated each year in Turkey; these waste products are discarded in landfills, rivers and ponds. PG consists primarily of calcium sulfate and contains some impurities, such

as phosphate, fluorides, organic matter and alkalies. The presence of impurities puts restrictions on the use of PG in building materials and soil amendments. 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 (Smadi et al., 1999; Singh and Garg, 2000; Singh, 2002; Altun and Sert, 2004; Verbeek and Plesis, 2005).

FA is a pozzolanic material and has been classified into two classes, F and C, based on the chemical composition. Class-F fly ash is produced from burning anthracite and bituminous coals. Class-C fly ash is produced from lignite and sub-bituminous coals and usually contains a significant amount of lime. The major difference between class-F and class-C FA is in the amount of calcium and the silica, alumina and iron content in the ash. Class-C FA, in addition to be having pozzolanic properties, also has some cementitious properties and it has been successfully used as cement replacement in concrete and as additive in cement production and as part of the binder in stabilized base applications (Atiş et al., 2004; Oner et al., 2005; Yazıcı et al., 2005; Yazıcı et al., 2006).

The enormous volume of unused PG can be re-used by combining FA and Portland cement in the building industry. Kumar studied fly ash-lime-gypsum bricks and hollow blocks for low cost housing (Kumar, 2002; 2003). It was reported that these blocks have sufficient strength for their use in building construction. Singh and Garg studied the cementitious binder from flourogypsum, phosphogypsum and fly ash. They concluded that the binders are suitable for use in masonry mortars and making concrete (Singh and Garg, 1999).

The phosphate industry has been looking into different ways of reducing the size of stacks. Researchers have also been seeking new application areas for PG 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 to produce so-called Fal-G cementitious binder. Physical and mechanical properties of Fal-G binders were also determined. This binder can be used in civil industry, primarily for the manufacture of bricks and blocks.

2. EXPERIMENTAL STUDIES

2. 1. Materials

The chemical composition and physical properties of FA, lime (L) and PG used in production of FaL-G cementitious material is given in Table 1.

Table 1. Chemical Composition and Physical Properties of FA, L and PG.

| Constituent (%) | FA | L | PG |
|------------------------------------|-------|-------|-------|
| SiO ₂ | 45.98 | 1.1 | 0.44 |
| Al ₂ O ₃ | 27.75 | - | 0.88 |
| Fe ₂ O ₃ | 4.59 | 0.5 | 0.32 |
| CaO | 15.34 | - | 32.04 |
| MgO | 2.10 | 1.5 | - |
| SO ₃ | 0.99 | - | 44.67 |
| K ₂ O | 1.19 | - | - |
| Na ₂ O | 0.21 | - | 0.13 |
| Free CaO | 1.90 | - | - |
| P ₂ O ₅ | - | - | 0.50 |
| F | - | - | 0.79 |
| CaCO ₃ | - | 5.9 | - |
| Ca(OH) ₂ | - | 90.80 | - |
| Loss on Ignition | 1.62 | 2.15 | 21.06 |
| Specific gravity | 2.24 | | 2.96 |
| Blaine (m ³ /kg) | 390 | | 467 |
| Retained on # 200 (75µm) sieve (%) | 16.00 | 8.00 | 20.13 |

FA was obtained from Soma Seas Thermal Plant in Manisa, Turkey. The Soma FA was produced from lignite coal and contains a significant amount of CaO with a lime content of 15.34 %. According to ASTM C 618 (Anon., 1994a), Soma FA can be classified as class-C FA due to its chemical composition. This FA, in addition to having pozzolanic properties, also has some cementitious properties. The total amount of SiO₂, Al₂O₃ and Fe₂O₃ is 74.32 %, which was a larger quantity than the value given by ASTM as the standard for a type C class FA. Free lime content of FA complies with TSI (Anon., 1998) and EN (Anon., 1994b) standards because it is present in 1.90 % of the FA. The amount of SO₃ (at 0.99 %) is less than the value given by the standards. Pozzolanic activity index (PAI) of Soma FA 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 FA 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.

PG as a by-product of the phosphoric acid process was obtained from the Bagfas Fertilizer Factory in Bandirma, Turkey. The major constituent in PG is calcium sulfate and, as a result, PG exhibits acidic properties (pH less than 3). The specific gravity of PG 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. PG 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. PG can be classified as a silty soil, an A-4 or ML soil, with little or no plasticity. Phosphogypsum is generated as a filter cake in the wet process and is pumped in slurry form to holding ponds. The resulting product should be allowed to dry somewhat before being used.

2. 2. Mix Proportion

The mixtures were composed of varying percentage of FA and PG by holding the lime ratio constant as 10%. The mix proportions of FaL-G binders are given in Table 2. The basic ingredients of the cementitious binder were dry mixed manually until obtaining homogeneous appearance and dry compositions were then mixed in Hobart mixer with addition of water for 60 sec. The amount of mixing water was determined using a flow table. The flow table was applied to get a flow 110-115 mm. Each specimen was cast in two layers into three-gang molds compacting by a vibration table for 60 sec. After casting all specimens were stored in a moisture room for 24 h. After demolding, part of the specimens were cured under in water at 20°C and the rest of the specimens were stored in laboratory air of 20°C , 65 % RH until testing age.

Table 2. The Mix Proportions of FaL-G Cementitious Binders.

| Mix designation | Constituent Materials (%) | | |
|-----------------|---------------------------|----|----|
| | FA | L | PG |
| M-1 | 90 | 10 | 0 |
| M-2 | 80 | 10 | 10 |
| M-3 | 70 | 10 | 20 |
| M-4 | 60 | 10 | 30 |
| M-5 | 50 | 10 | 40 |
| M-6 | 40 | 10 | 50 |

2. 3. Tests

Prismatic specimens with $40 \times 40 \times 160$ mm dimensions and cube specimens with $50 \times 50 \times 50$ mm dimensions were prepared from each mix for the strength measurements and water absorption respectively. For the flexural strength tests, three specimens for each mix were prepared and tested by one-point loading based on TSI procedure (Anon., 2002). The flexural strength was measured using middle point loading with a span of 100 mm. The compressive strength measurements were carried out using the broken pieces of the prism specimens. The reported results are the average of six specimens. The compressive strength was carried out using a hydraulic universal testing machine of 3000 kN

capacity at a rate of loading of 90 kN/mm/s . The compressive and flexural strength values of the specimens are given in Figures 1 and 2, respectively.

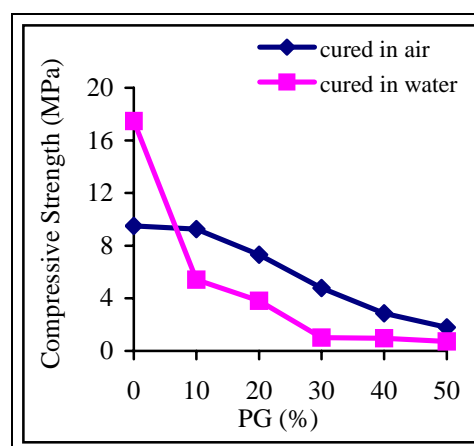


Figure 1. Compressive Strength of FaL-G Binders at 28-days.

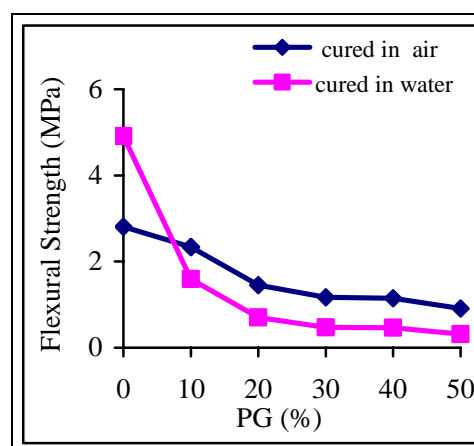


Figure 2. Flexural Strength of FaL-G Binders at 28-days.

The water absorption behavior of FaL-G binders was also determined. The water absorption test was conducted at $20 \pm 2^\circ\text{C}$ and $60 \pm 5\%$ RH by using cube specimens after curing 28 days. The cube specimens were predried at 105°C until a constant weight, cooled to room temperature and weighed before immersion in water. After dry to constant mass, the specimens were immersed in water. The water level in the tank was kept constant during the test period. The specimens were taken out from the water tank and were weighed on a 0.01 g balance after being wiped with a dry paper towel. Their weight increase was measured until complete saturation of the specimens. Water absorption was calculated as percentage of dry weight of the test specimen. The test values of water absorption and dry unit weight of test specimens are presented in Table 3 and Figure 3.

Table 3. The Properties of FaL-G Cementitious Binders.

| Mix Designation | Water absorption (%) | Dry unit weight (KN/m ³) | Compressive str. (MPa) | | Flexural str. (MPa) | |
|-----------------|----------------------|--------------------------------------|------------------------|----------------|---------------------|----------------|
| | | | Cured in air | Cured in water | Cured in air | Cured in water |
| M-1 | 29 | 14.64 | 9.49 | 17.47 | 2.81 | 4.91 |
| M-2 | 31 | 14.32 | 9.26 | 5.43 | 2.34 | 1.59 |
| M-3 | 38 | 12.96 | 7.31 | 3.81 | 1.45 | 0.70 |
| M-4 | 40 | 12.40 | 4.78 | 1.01 | 1.17 | 0.47 |
| M-5 | 41 | 12.28 | 2.87 | 0.97 | 1.15 | 0.46 |
| M-6 | 41 | 12.12 | 1.81 | 0.73 | 0.91 | 0.31 |

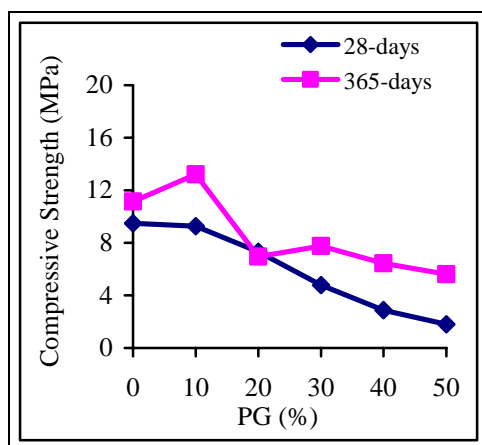


Figure 3. Compressive Strength of FaL-G Binders Cured in Air.

Thermal conductivity test was employed on 40×40×160 mm prismatic specimens by using 'hot wire' method in the mechanical engineering, thermal laboratory in Dokuz Eylül Üniversitesi. A shotherm QTM-D2 apparatus has been used to determine the thermal conductivity.

3. RESULTS AND DISCUSSIONS

Several mixtures were prepared by mixing a commercial hydrated lime with fly ash and phosphogypsum. These mixtures were cured in water and laboratory air at 20°C until testing age. The compressive and flexural strength values of the 28 day FaL-G specimens are given in Figures 1 and 2. It was observed that the increase of the percentage of phosphogypsum decreased the compressive and flexural strength. This behavior is observed on all specimens for both curing conditions. Specimens containing 50 % and 40 % of phosphogypsum seem to be weaker than the others. The lowest compressive strength was obtained as 1.81 MPa at 28 days for 50 % of phosphogypsum addition. Also the curing method was found to greatly affect the strengths. The specimens, which cured in water,

showed lower strength as compared to those cured in laboratory air. The lowest compressive strength was obtained as 0.73 MPa of 50 % of phosphogypsum addition for water curing.

For economy and strength requirements, phosphogypsum content of FaL-G binders should be kept constant as 20 %. The compressive strength of FaL-G binders with 20 % phosphogypsum, mix-3, was obtained as 7.31 MPa after 28-days curing in air. The compressive strength values of FaL-G binders with 10% phosphogypsum, mix-2, were obtained as 9.26 MPa and 5.43 MPa after curing in air and in water respectively. The minimum average of compressive strength prescribed in Turkish standard (Anon., 1977) for class-C mortar is 5.0 N/mm². The FaL-G binders having 7.31 MPa of compressive strength can be classified as class C mortar for masonry applications according to TSI procedure. Therefore these binders with 20 % and 10 % phosphogypsum content have sufficient strength for masonry applications.

FaL-G binders can be used for the production of controlled low-strength materials (CLSM). To be classified as CLSM, the material must have a compressive strength between 450 kPa (65 psi) and 8400 kPa (1200psi) according to ACI report (Anon., 1994c) FaL-G binder satisfies the strength requirements for production of controlled low-strength materials.

The average and minimum compressive strength of solid bricks prescribed in Turkish standards (Anon., 1979; 1985) are 5.0 N/mm² and 4.0 N/mm², respectively. The bricks made with FaL-G binders (up to 20 % phosphogypsum) replace the burnt clay bricks as they have sufficient strength for their use in low-cost housing.

The FaL-G binders gain further strength after 28 days of casting. There is need to carry out long-term study of the properties of FaL-G binders beyond the age of 28 days. For this purposes, the compressive strength of these binders was also determined at 365

days. Figure 3 shows the compressive strength of FaL-G binders after 28 and 365 days of casting. It was observed that the strength of these binders increases with age.

Water absorption and dry unit weight of these mixtures are shown in Table 3 and Figures 3 and 4 respectively. Water absorption of FaL-G binders in the present investigation was obtained to be between 29 % and 41 %. The water absorption of these binders increases with the increase in phosphogypsum content. It was observed that water absorption and compressive strength is closely related each other. It also observed that the binders with a higher percentage of water absorption have lesser compressive strength. According to Turkish standard, the water absorption of solid bricks should not be more than 20 % by weight. The water absorption of FaL-G binders with phosphogypsum is more compared to traditional solid bricks. This aspect certainly needs further investigation. As can be seen from Figure 5, the increase in the amount of PG addition causes a reduction in the dry unit weights of the specimens.

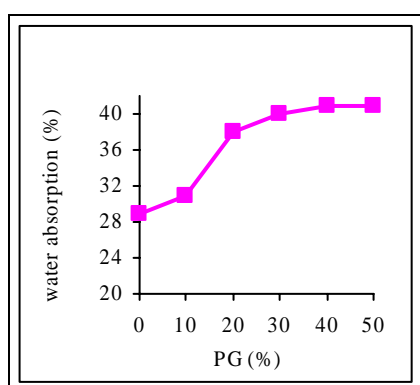


Figure 4. Water Absorption of FaL-G Binders Cured in Air

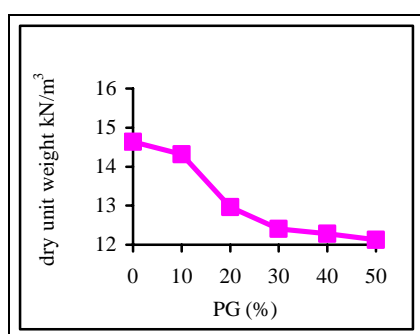


Figure 5. Dry Unit Weight of FaL-G Binders.

The dry unit weight of specimens varied from 14.64 to 12.12 kN/m³. The maximum unit weight of solid bricks is given as 14.00 kN/m³. The increase in the amount of PG addition causes a reduction in the dry

unit weights of the specimens. This indicates that the use of these binders will reduce the weight of structures considerably. These binders may find an extensive application in the manufacturing of building materials.

Thermal conductivity of the test specimens calculated between the ranges of 0.360 W/mK and 0.378 W/mK. Phosphogypsum content increases the thermal conductivity values. Test specimens have very low thermal conductivity by comparison to other building materials.

4. CONCLUSIONS

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

- The compressive strength of the specimens increases with increasing of ratio of FA. The flexural strength development of FaL-G mixtures is similar to that for compressive strength. PG decreases flexural and compressive strength while FA increases. For strength requirements, phosphogypsum content of FaL-G binders should be kept constant as 20%. These binders gain further strength after 28 days. There is a need to carry out long-term study of the properties of these binders.
- The curing conditions have an important influence on the strength values of FaL-G binders. It seems that curing in water, decreases the strength values.
- Water absorption increases with increased phosphogypsum content. The water absorption of FaL-G binders with phosphogypsum content is more compared to traditional solid bricks. This aspect certainly needs further investigation.
- Dry unit weights decreased with increasing phosphogypsum ratio in the binders. The reduced weight will provide the reduction in dead weight of structures.
- Thermal conductivity of specimens increases with increasing phosphogypsum content.

Phosphogypsum can be used with fly ash as alternative material in production of masonry mortar, controlled low-strength materials and solid bricks to bring economy, conserve energy and to reduce environmental pollution.

Utilization of various industrial wastes produced such as phosphogypsum and fly ash not only solve

the environment problems but also provides a new resource for construction.

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