



ISSN:1306-3111

e-Journal of New World Sciences Academy
2011, Volume: 6, Number: 4, Article Number: 1A0273

ENGINEERING SCIENCES

Received: March 2011
Accepted: October 2011
Series : 1A
ISSN : 1308-7231
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**INFLUENCE OF INCORPORATING FLUE GAS DESULPHURISATION (FGD) RESIDUES ON
POROSITY AND PORE SIZE DISTRIBUTION OF CEMENT PASTE**

ABSTRACT

This paper reports results on the porosity and pore size distribution of cement paste containing varying amounts of simulated desulphurised waste (SDW). The water to binder ratio was 0.5. The binder consists of cement and SDW. The SDW is a combination of fly ash and gypsum ranging from 0-100%. Cement in the pastes was partially replaced with 25% SDW (by weight). The porosity and pore size distribution of cement pastes at 90 days of curing is reported. Increasing the amount of gypsum up does not change the pore volume, however, there is tendency of obtaining coarser pore structure in the presence of gypsum.

Keywords: Desulphurised Waste, Fly Ash, Gypsum, Porosity,
Pore Size Distribution, Threshold Diameter

**KÜKÜRT ATIKLARI (FGD) İLE HAZIRLANAN ÇİMENTO HAMURUNUN POROZİTE VE
BOŞLUK ORANI DEĞERLERİ ÜZERİNE ETKİLERİ**

ÖZET

Bu makalede değişik oranlarda kükürt atıklarından hazırlanan çimento hamurunun porozite ve boşluk oranı değerleri araştırılmıştır. Su bağlayıcı oranı 0.5 olarak alınmıştır. Bağlayıcı çimento ve kükürt giderme atıklarından oluşmaktadır. Kükürt giderme atığı uçucu kül ve alçının karışımından %0-100 oranlarında elde edilmiştir. Çimento kükürt giderme atığının ağırlıkça %25 oranında yer değiştirilmiştir. Çimento hamurunun porozitesi ve boşluk oranı değerleri 90 günlük kür değerlerinde bulunmuştur. Alçı değerinin yükseltilmesi boşluk hacminde herhangi bir değişime neden olmamış ancak daha geniş boşluk yapısına sebep olmuştur.

Anahtar Kelimeler: Kükürt Atığı, Uçucu Kül, Alçı, Porozite,
Boşluk Oranı Dağılımı, Sınır Çap

1. INTRODUCTION (GİRİŞ)

The materials used in the construction industry are generally porous and the measure of porosity and the sizes of pores would normally give a useful idea on the engineering performance of such materials. The strength and durability properties of materials such as concrete depend heavily on the amount of pores present as well as the size and distribution of such pores. The influence of porosity and pore size distribution on areas such as physical and mechanical development [1, 2 and 3], and durability properties [4 and 5] is well documented. Many attempts have been made to correlate porosity and pore structure with the performance of paste, mortar and concrete [6 and 7]. The main relationships tend to indicate that strength is related to total porosity, whereas, durability tends to be influenced more by pore structure.

2. RESEARCH SIGNIFICANCE (ARAŞTIRMANIN ÖNEMİ)

There is a wealth of information in the literature on the effects of mineral admixtures on porosity and pore structure of blended cement paste [8,9 and 10]. This paper reports the results on porosity and pore size distribution at the age of 90 days of curing of blended cement paste containing different combinations of fly ash and gypsum.

3. EXPERIMENTAL METHODS (DENEYSEL YÖNTEM)

Cement paste mixes consists of 42.5N Portland cement (C), fly ash (FA), gypsum (G) and water. Further information regarding composition is given elsewhere [11]. The water/binder was kept constant at 0.5. Mix M1 represents the reference paste containing 100% C. Mixes M2 to M8 contain different simulated desulphurised wastes blended from fly ash and gypsum (FA-G blends). The cement was replaced with 25% fly ash and/or gypsum. The gypsum content in the FA-G blends ranged from 0 to 100%. Shows the binder proportion of the mixes. The basis for the proportions of the SDW is reported elsewhere [11].

Table 1. Binder constituents
(Tablo 1. Bağlayıcı bileşenleri)

Mix No	Mix ID	Proportions (% weight of binder)		
		Cement (C)	Gypsum (G)	Fly Ash (FA)
M1	REF (100 _C)	100	0	0
M2	100 _{FA} 0 _G	75	0	25
M3	85 _{FA} 15 _G	75	3.75	21.25
M4	50 _{FA} 50 _G	75	12.5	12.5
M5	0 _{FA} 100 _G	75	25	0

The paste samples consisted of cubes of 50mm in size. All samples were placed in a mist curing room at 20°C±1°C and 95%±5% relative humidity for 24 hours. After that demoulding took place and cubes were placed in water at 20°C until testing. At 90 days, the cubes were crushed and samples were taken from the middle of specimen. A suitable sample size used for the analysis was between 0.9 and 1.2g. The samples were dried in an oven at 70°C to remove moisture until a constant weight was achieved. This usually took approximately 48 hours. After drying, the samples were placed in an airtight bottle until testing. Silica gel crystals were added to the bottle to absorb any moisture. Mercury intrusion porosimetry was then used to determine total porosity and pore size distribution. Further information on the testing technique is found elsewhere [11].

The threshold diameter (TD) corresponds to the pore width, which has the highest rate of mercury intrusion per change in pressure, i.e. the steepest part of the cumulative pore volume slope. The TD has been reported as being a boundary between surface and internal porosity [12]. As hydration proceeds the TD reduces as the capillary pores are filled with hydration products. The dominant pore diameter (DPD) is the pore range, which corresponds to a maximum volume of intruded mercury.

4. RESULTS AND DISCUSSION (SONUÇLAR VE TARTIŞMA)

The total pore volume (TPV) of paste containing different FA-G blends at 56 is approximately 28-37% higher than that exhibited by the reference (M1).

Figures 1-5 to Figure show the PSD for pastes M1, M2, M3, M4 & M5 respectively at 90 days of curing. There was a significant difference between the reference mix, FA-G blends that were predominantly fly ash (gypsum less than 25%), and the FA-G mixes that were predominantly gypsum (gypsum greater than 25%). An increase in the gypsum content of the FA-G blend increased the pore diameter relating to the initial peak. The reference mix exhibited a well-defined initial peak at 0.1 μ m, and a narrow distribution of pores. Pastes containing FA-G blends exhibit a much wider distribution of pores and a less definable initial peak. For FA-G blends with gypsum contents up to 15%, the initial peak appeared to diminish giving way to a second more rounded peak at approximately 0.1 μ m. Although this was not observed with the reference mix, it might be a transition point, which was made more apparent by the relatively slow hydration of pastes containing FA-G blends. As the gypsum content in the FA-G blend exceeded 15%, both the initial and secondary peak were clearly defined at approximately 1.0 μ m and 0.08 μ m (in diameter) respectively.

The threshold diameter (TD) for mixes containing different FA-G blends show that as the gypsum in the mix increases the threshold diameter increases indicating coarser pores (i.e. a decrease in pore refinement) in the presence of increasing amounts of gypsum. The determination of threshold diameter is reported elsewhere [11].

The pores in Figures 1-5 were split into large pores (pores whose diameter is larger than 0.1 μ m and small pore with diameter less than 0.1 μ m). The replacement of cement with FA-G blends decreased the percentage of small pores (SP) in the paste compared to the reference mix. Replacing fly ash with increasing levels of gypsum decreased the percentage of SP, i.e. decreased pore refinement.

The partial replacement of cement (25%) with different blends of fly ash and gypsum (FA-G blends) generally leads to an increase in the TPV Of cement paste compared to the reference mix. At 90 days the TPV of cement pastes containing the FA-G blends were similar, however, increasing the fly ash content in the blend did appear to increase the TPV. With respect to total porosity (%), a difference of approximately 4% was observed between the mixes. The increase in TPV during at 90 days was accompanied by a decrease in pore refinement, i.e. an increase in the threshold diameter (TD) and a decrease in the percentage of small pores below 0.1 μ m (SP).

Manmohan and Mehta [13] reported that replacing cement with fly ash increased porosity and decreased pore refinement at 90 days, compared to a reference mix of 100% cement. This was attributed to the pozzolanic properties of the fly ash, i.e. delayed hydration. The CH released during cement hydration increases the pH of the pore solution, which then reacts with the silica and alumina components of the fly ash to form additional C-S-H and C-A-H. These products fill

the open capillary pores, which result in an improvement in the pore structure [14].

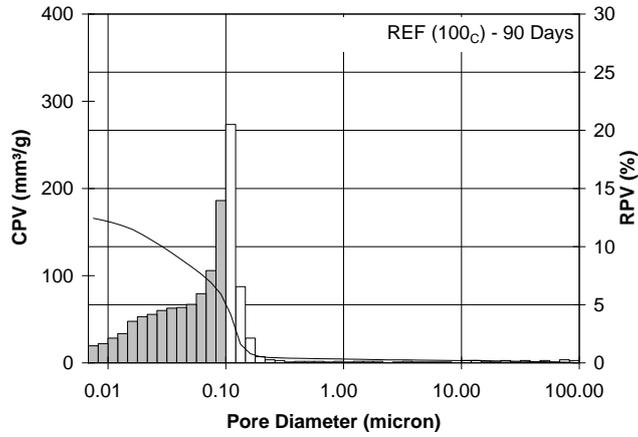


Figure 1. Pore size distribution of the reference paste M1
(Şekil 1. Referans hamur M1 için boşluk oranı dağılımı)

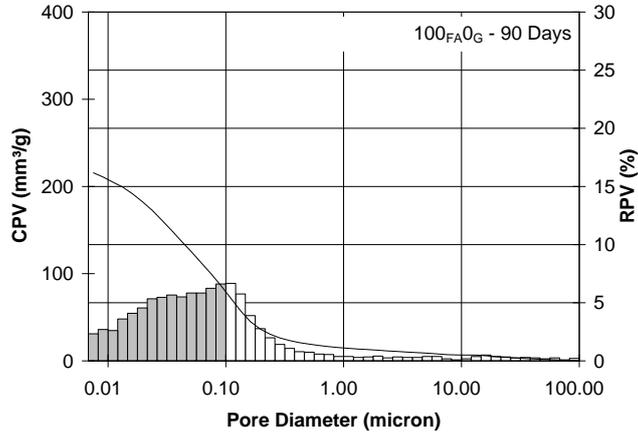


Figure 2. Pore size distribution of paste M2
(Şekil 2. Referans hamur M2 için boşluk oranı dağılımı)

Other researchers [15 and 20] have reported that the reactivity of fly ash could be improved by adding sulphate, by increasing the reactivity of the fly ash or the formation of sulphate containing C-A-S-H products that form around the fly ash particles. However at 28 days this was not evident In the present study. Long term data is reported elsewhere [11]. Excessive gypsum replacement can result in a retardation of the hydration process as the ettringite formed on the fly ash particles increases, which temporally retards the reaction with lime [20]. This did appear to be the case, especially in the mix containing just gypsum as replacement.

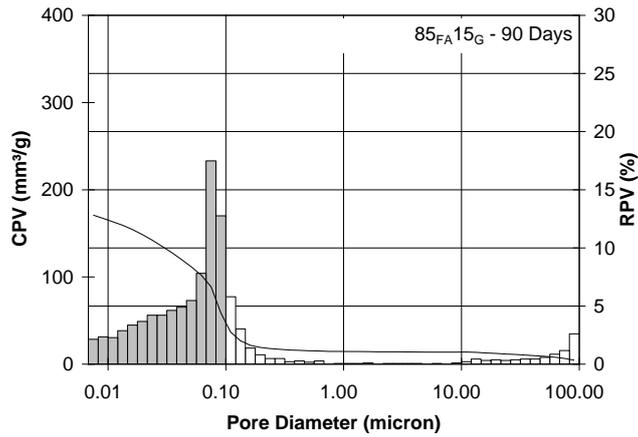


Figure 3. Pore size distribution of paste M3
(Şekil 3. Referans hamur M3 için boşluk oranı dağılımı)

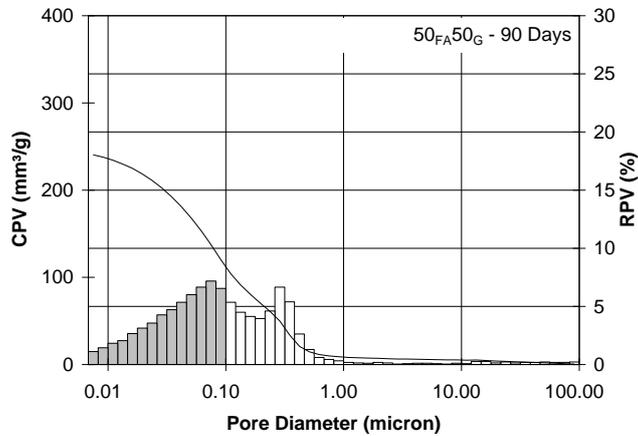


Figure 4. Pore size distribution of paste M4
(Şekil 4. Referans hamur M4 için boşluk oranı dağılımı)

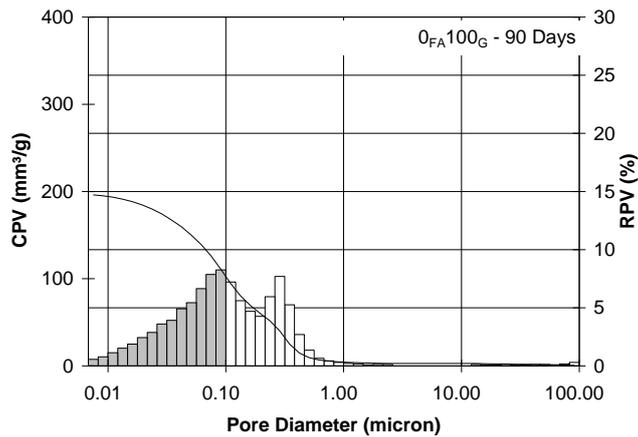


Figure 5. Pore size distribution of paste M5
(Şekil 5. Referans hamur M5 için boşluk oranı dağılımı)

One possible indication to the alteration of the pore structure is the appearance of a secondary rounded peak on the pore size distributions (PSD). The initial peak corresponds to a transition point between surface and internal porosity, normally defined by the

threshold diameter. The secondary peak indicated a bimodal distribution. This could be due to the fineness of the fly ash introduced, or a modification of the pore structure through pozzolanic reactions occurring that fill the capillary pores with ettringite [5]. The pores then become blocked and inaccessible creating a discontinuous pore structure until the pressure is great enough to break through the formed barriers. Therefore, the pore diameter represented on the PSD may actually correspond to the breakthrough pressure.

5. CONCLUSIONS (SONUÇLAR)

Replacing 25% of cement with different simulated desulphurised waste (FA-G Blends) increased the total pore volume (TPV) of cement pastes at 28 days of curing. Increasing the gypsum content in the FA-G blend generally increased TPV. Replacing cement with different FA-G blends increased the threshold diameter (TD) and decreased the percentage of small pores below 0.1µm (SP), which indicated a decrease in pore refinement compared to the reference paste.

NOTICE (NOT)

Bu makale, 28-30 Eylül 2011 tarihleri arasında Elazığ Fırat Üniversitesinde yapılan "International Participated Construction Congress" IPCC11'de tebliğ sunulmuştur.

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