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EXTERNAL CHEMICAL SHRINKAGE OF PASTES CONTAINING FLUE GAS DESULPHURISATION (FGD) WASTE

ABSTRACT

The effect of including flue gas desulphurisation (FGD) waste on total chemical shrinkage of cement paste up to 7 days is reported. The FGD wastes were obtained from different plants located in different countries which vary in compositions. Also simulated FGD wastes were prepared in the laboratory which is a blend of fly ash and gypsum. Pastes were prepared with water to binder ratio of 0.5. The binder consists of cement and FGD. Cement was replaced with 25% (by weight) of different FGD materials. The results reported show varying trend depending upon chemical composition. Using calcium sulphate based FGD waste in cement paste, both the short and long-term total chemical shrinkage were reduced. For paste containing SiO_2-Al_2O_3-$CaSO_4$ based waste the total chemical shrinkage was reduced.

Keywords: Chemical Shrinkage, Desulphurised Waste, FGD Waste, Fly Ash, Gypsum, Waste

BACA GAZI DESÜLFÜRÜZASYON ATIĞI HAMURUNUN HARİCİ KİMYASAL BÜZÜLMESİ

ÖZET

Baca gazı desülfürüzasyon atiğinin (FGD) 7 günlük çimento hamurunun kimyasal büzülmesi üzerine etkileri araştırılmıştır. FGD atığı farklı ülkelerden farklı oranlarda elde edilmiştir. Bununla beraber benzetilmiş FGD atıkları uçucu kül ve alçının karışımıyla laboratuarda elde edilmiştir. Hamur su-bağlayıcı oranı 0.5 olarak sabit tutulmuştur. Bağlayıcı çimento ve FGD'den oluşmaktadır. Çimento, FGD atığının ağırlıkça %25 oranında yer değiştirilmiştir. Sonuçlar değişik yaklaşımlar göstermektedir. Kalsiyum sülfat kullanarak oluşturulan FGD atığının çimento hamuru üzerine kısa ve uzun sürede kimyasal büzülmeyi azaltmıştır. SiO_2-Al_2O_3-$CaSO_4$ içeren hamurda toplam kimyasal büzülme değeri azalmıştır.

Anahtar Kelimeler: Kimyasal Büzülme, Kükürt Atığı, FGD Atığı, Uçucu Kül, Alçı, Atık

1. INTRODUCTION (GİRİŞ)

Cement hydrates in the presence of water. Reactions between the anhydrous material (cement) and water result in the formation of new products (CH, C-S-H) that form the structure of cement-based materials. The volume of the new products formed during hydration is smaller than the volume of the original reactants. This volume change (reduction) is commonly referred to as chemical shrinkage **[1]**. A common technique used to evaluate the progress of hydration is the amount of non-evaporable water present in the system. The non-evaporable water is chemically bound within the hydration products, and its volume is dependent on the amount and type of hydration products formed. Therefore, the measure of non-evaporable water can be used as an indicator of setting and hardening [2]. Several researchers [2,3 and 4] have reported that chemical shrinkage possesses a linear relationship with non-evaporable water. The measurement of chemical shrinkage is simpler, more cost effective, and allows continuous monitoring of samples on an unlimited time scale. Therefore, the measurement of chemical shrinkage can provide a less complicated method of evaluating the hydration properties of cement-based materials. Geiker [3] reported a direct linear relationship between chemical shrinkage and compressive strength. Therefore, the measurement of chemical shrinkage could be used to evaluate and predict the strength of cement-based materials. Alternatively, the evaluation of chemical shrinkage could provide a useful method of evaluating the performance of blended cements in practical situations, which often require longer curing periods than normal cements. The chemical shrinkage of pastes was evaluated based on two measurable quantities total chemical shrinkage (TCS) [5]. TCS is the total change in volume due to the hydration of cement. This incorporates both the external volume changes, and the internal volume change caused by hydration products filling the open capillary pores.

2. RESEARCH SIGNIFICANCE (ARAŞTIRMANIN ÖNEMİ)

Dimensional stability of a concrete material affect its performance construction application. Chemical shrinkage is a measure of dimensional stability. Therfore, this paper reports the results on chemical shrinkage of cement paste containing actual and simulated desulphurised waste.

3. EXPERIMENTAL STUDY (DENEYSEL ÇALIŞMA)

Cement paste mixes consists of 42.5N Portland cement (C), selected actual desulphurised waste materials: PL-P, SL-G, PL-RP, PL-ZP, SL-F, and G were used. Materials Pl-P, SL-G and G are predominantly gypsum based whereas materials Pl-RP, PL-ZP and SL-F are silca-alumina-gypsum based.

Table 1 shows the binder proportion of mixes. The water/binder was kept constant at 0.5. Mix 1 represents a reference mix containing 100% C. Mixes 2 to 7 contain different materials as 25% replacement of cement by weight. Mixes 8 to 11 contain different simulated desulphurised wastes blended from fly ash and gypsum. The basis for the proportions of the SDW and chemical compositions of materials can be found elsewhere [**6**].

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

		Proportions (% weight of binder)		
Mix No	Mix ID	Cement (C)	Replacement Material (RM)	Replacement Material Type
1	REF (100_C)	100	0	-
		Calcium Sulphate Based Waste		
2	75_C25_{PL-P}	75	25	PL-P
3	75_C25_{SL-G}	75	25	SL-G
4	75_C25_G	75	25	G
		SiO_2-Al_2O_3-$CaSO_4$ Based Waste		
5	75_C25_{SL-F}	75	25	SL-F
6	75_C25_{PL-RP}	75	25	PL-RP
7	75_C25_{PL-ZP}	75	25	PL-ZP

The experimental procedure used to measure chemical shrinkage was based on work carried out by earlier investigators [5, 7 and 8]. After mixing, external chemical shrinkage (ECS) samples were prepared as follows:

- The weight of the rubber membrane (standard commercial condom) was weighed.
- The paste was then placed into the rubber membrane. The amount of paste used in each sample was approximately 300 to 350g. Three samples per mix were prepared.
- Once filled the membrane was lightly vibrated to remove as much air from the sample as possible.
- The membrane was then tied off with two knots and the loose end of the membrane removed.
- Once sealed, the surface was wiped clean to remove any surface material and the weight of the paste and membrane was recorded.

External chemical shrinkage (ECS) was measured by observing the change in submerged weight of the paste enclosed within the airtight membrane and by comparing it with the original weight of the paste in air. After preparation, the weight of the paste sample in air (W_A) was recorded, and then placed in the basket, which was suspended from a balance and submerged in water. Any bubbles present on the membrane surface were removed so as not to affect the submerged readings. The basket was allowed to settle before the initial submerged weight of the sample was recorded (W_0, at time = 0). The initial submerged weight was a resultant of the buoyancy force produced by the sample.

The initial submerged reading was taken approximately 20 minutes after the addition of water to the dry material during the mixing process. This was represented on the plots as zero hours (days). However, for typical cements during the first 20 minutes the hydration process has gone through the pre-induction phase and is entering the dormant phase. During this period, a large amount of heat is produced, which is accompanied by some initial shrinkage. The initial shrinkage is not measurable with the technique used in this investigation. This was also applicable for the total chemical shrinkage (TCS) test.

Once the initial submerged weight had been recorded, the samples were placed in water between measurements. To avoid or minimise the effects of bleeding, which results in higher ECS than normal **[1]**, the samples were regularly rotated between readings for the first twelve hours. Care was taken not to damage the samples during measurements and while rotating. The change in submerged weight (W_t, **Hata! Başvuru kaynağı bulunamadı.**) was taken every 2 hours for the first 10 to 12 hours and then every 24 hours until a constant weight was achieved. The increase in submerged weight was a result of the decrease in buoyancy due to the reduction in the external volume of the sample (Archimedes Principle). When the binder had achieved sufficient stiffness to resist the internal contracting forces, a constant external volume was reached. After this stage, the submerged weight remained constant. The change in submerged weight (g), with respect to the original weight in air was used to calculate external chemical shrinkage, as shown in Equation 1.

$$ECS = \frac{W_t - W_0}{W_A} 100 \qquad \textbf{Equation 1}$$

Where: ECS = External chemical shrinkage (ml/kg paste)
W_A = weight of paste sample in air (g)
W_0 = initial weight of paste sample submerged in water at time =0 (g)
W_t = weight of paste sample submerged in water at time ‘t’ (g)

Chemical shrinkage is generally interpreted as ml/100g cement, where the 100g is the weight of the dry material, i.e. cement + replacement material. The use of ml/kg of paste assesses the chemical shrinkage of the whole system, i.e. water + dry material. This will have more significance in practical situations, and will allow the correlation of chemical shrinkage with other properties such as compressive strength. Calculation of absolute chemical shrinkage in terms of either the dry material (cement + replacement material) or the paste (water + dry material) will give the same relationship, however, the magnitude of the relationship will change. For instance, if a cement paste with a water/binder of 0.5 has an ECS of 50ml/kg paste, the same mix will have an ECS with respect to the dry material of 33ml/kg cement. This is simply a reduction based on the water/binder, where the binder includes the cement or cement + replacement material.

4. RESULTS AND FINDINGS (SONUÇLAR VE BULGULAR)

Figure 1 shows the change in external chemical shrinkage (ECS) with time for pastes containing the materials G, SL-G or PL-P as partial cement replacement (25%). During the first twelve hours, material PL-P increased the rate of change in ECS compared to the reference mix, whereas, replacing cement with G and SL-G reduced the rate of change in ECS. The final ECS was similar for the reference mix and the mix containing PL-P. The replacement of cement with G and SL-G, in mixes 75_C25_G and 75_C25_{SL-G} respectively, increased the ECS by approximately 50% compared to the reference mix. Material SL-G appeared to increase the time taken to achieve a constant ECS from 24 hours to 48 hours.

Figure 2 shows the change in external chemical shrinkage (ECS) with time for pastes containing PL-RP, PL-ZP and SL-F. During the first twelve hours, the paste containing PL-RP exhibited a similar ECS as the reference mix, whereas, the pastes containing PL-ZP and SL-F increased the ECS during the same period. All pastes achieved a constant ECS at approximately 24 hours. The final ECS for pastes containing the materials PL-ZP, PL-RP and SL-F was 35%, 60% and 60% higher than the reference mix respectively at 24 hours.

The reduction in the rate of chemical shrinkage during the first twelve hours associated with the calcium sulphates G and SL-G is most likely due to changes in the hydration process. Both G and SL-G are predominantly gypsum based, which is commonly used in cement manufacture to retard setting. The gypsum content in plain cement depends on the C_3A content, fineness, and alkali content (K_2O, Na_2O). C_3A is highly reactive, and without any retardation, a flash set is likely to occur **[9]**. When gypsum is added it dissolves into the solution and combines with the lime. The gypsum-lime solution suppresses the rate at which alumina is broken down, therefore, retarding the formation of early hydration products [10 and 11]. Therefore, if the hydration process is retarded, the volume of hydration products formed is reduced resulting in a reduction in chemical shrinkage. The calcium sulphate material PL-P does not significantly affect the early chemical shrinkage like the calcium sulphates G and SL-G. In fact PL-P did not appear to retard early hydration. This maybe due to the presence of hannebachite and the low SO_3 content of PL-P compared to materials G and SL-G. Hannebachite, unlike gypsum, is a calcium sulphite and is generally assumed non-reactive [12]. Therefore, material PL-P may be acting as an inert replacement material. Material PL-P has a much higher specific surface area than the cement (664 m^2/kg, compared to 376 m^2/kg). This increase in fineness may have a deflocculating effect on the cement particles, which increases the available minerals for reaction due to the increase in specific surface area of the cement in contact with water.

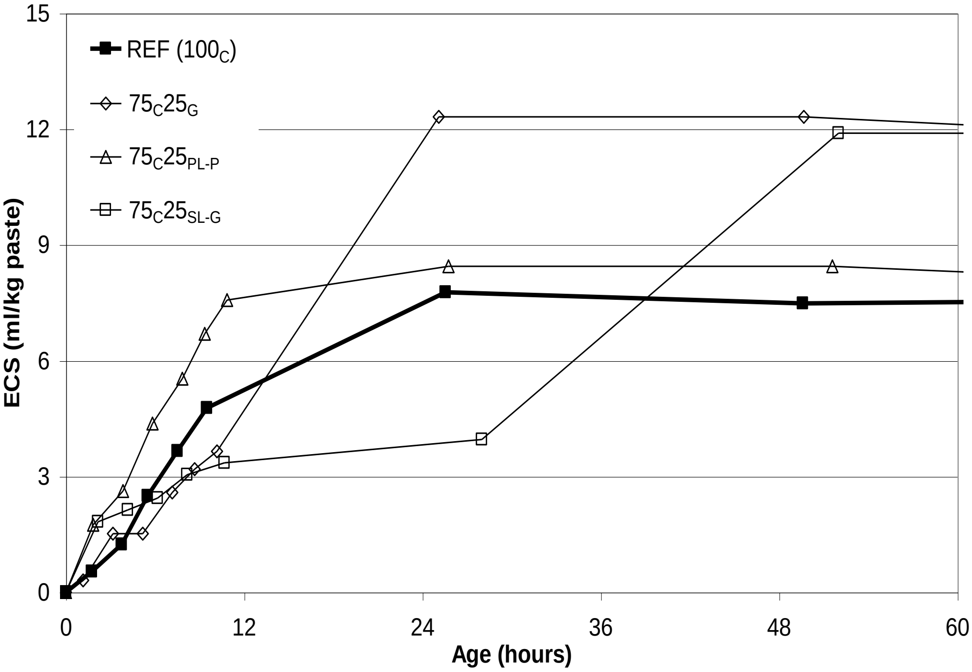

Figure 1. ECS of pastes containing the materials G, PL-P and SL-G
(Şekil 1. G, PL-P and SL-G malzemelerden oluşan ECS hamuru)

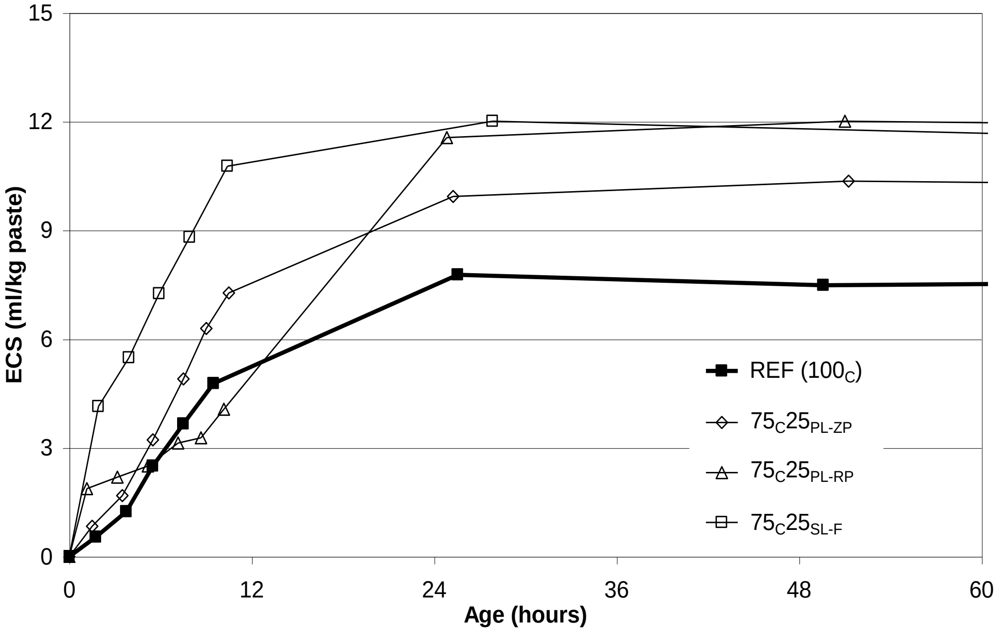

Figure 2. ECS of pastes containing the materials PL-ZP, PL-RP and S-FAG
(Şekil 2. PL-ZP, PL-RP and S-FAG malzemelerden oluşan ECS hamuru)

The TCS for all pastes was generally similar to the reference mix. However material PL-RP showed a decrease in TCS during the first 12 hours, after which the rate on increase in TCS was similar to the other mixes. The slight decrease in TCS may be due to the presence of small amounts of SO_3, which may retard the hydration process however this does not appear to affect the mixes containing SL-F and PL-ZP. Therefore some other factors such as particle size, etc. In similar pozzolanic materials, such as fly ash, longer setting times and low strengths compared to reference cements have been reported [13]. The influence of fly ash on cement has been shown to retard early C_3S and C_3A hydration, which is responsible for setting and hardening [14].

5. CONCLUSIONS (SONUÇLAR)

Replacing cement with 25% calcium sulphate based desulphurised wastes (G, SL-G and PL-P) generally increased external chemical shrinkage (ECS) compared to the reference mix. Increasing the SO_3 content of the desulphurised waste appeared to decrease ECS. Replacing cement with SiO_2-Al_2O_3-$CaSO_4$ based desulphurised wastes (PL-ZP, PL-RP and SL-F) resulted in a similar increase in ECS as the reference mix.

NOTICE (NOT)

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

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