

## Microstructures Investigation of Mineral Additive Concretes

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### Abstract

Concrete is the most widely used building materials today's world. Production methodology and using of different types of materials affect the cost of concrete. The most important of these materials is cement. The low cost to be realized in cement will directly affect the economic efficiency of the concrete. Pozzolanic materials such as mineral admixtures can be used by replacing with cement in concrete production. In this study, three different types of pozzolanic materials (fly ash, silica fume, blast furnace slag) were replaced with cement in %10, %20 and %30 ratios and concrete samples were produced. The specimens were tested for compressive strength after curing in laboratory conditions for 7, 28 and 90 days. The highest compressive strength data were obtained in 10% silica fume replaced series. Microstructure studies were carried out on the specimens using SEM analysis technique and relations between strength values and microstructures were tried to be established. Ettringite formation was observed in fly ash replaced series. It has been determined that this situation may cause a decrease in compressive strength.

**Key Words:** Concrete, Microstructure, Physical and mechanical properties

### Mineral Katkılı Betonların Mikroyapılarının İncelenmesi

#### Öz

Beton, günümüz dünyasında en çok kullanılan yapı malzemesidir. Üretim metodolojisi ve farklı malzemelerin kullanılması betonun maliyetini etkiler. Bu malzemelerin en önemlisi çimentodur. Çimentoda gerçekleştirilecek düşük maliyet, betonun ekonomik etkinliğini doğrudan etkileyecektir. Mineral katkıları gibi puzolanik malzemeler beton üretiminde çimento ile değiştirilerek kullanılabilir. Bu çalışmada üç farklı puzolanik malzeme (uçucu kül, silis dumanı, yüksek fırın cürufu) %10, %20 ve %30 oranında çimento ile değiştirilmiş ve beton numuneleri üretilmiştir. Numuneler, 7,28 ve 90 gün boyunca laboratuvar koşullarında sertleştirildikten sonra basınç dayanımı değerleri ölçülmüştür. En yüksek basınç dayanımı sonuçları %10 silis dumanı ikameli serilerde tespit edilmiştir. Numuneler üzerinde SEM analiz tekniği kullanılarak mikroyapı çalışmaları yapılmış ve mukavemet değerleri ile mikroyapı arasındaki ilişkiler belirlenmeye çalışılmıştır. Uçucu kül ikameli serilerde etrenjit oluşumu gözlenmiştir. Bu durumun basınç dayanım değerlerindeki düşüşe sebep olduğu belirlenmiştir.

**Anahtar Kelimeler:** Beton, Mikroyapı, Fiziksel ve mekanik özellik

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## 1. INTRODUCTION

Concrete is a manmade building material that looks like stone. The word “concrete” is derived from the Latin *concretus*, meaning “to grow together.” [1]. The most widely used construction material is concrete, commonly made by mixing portland cement with sand, crushed rock, and water [2]. Initially obtaining the desired mold shape since it is fluid at the beginning, and after hardening it can provide the necessary strength for a certain carrying force with high durability [3].

Concrete is not a new building material. The first known concrete formed the foundation of a club in Yugoslavia at 5600 BC [4]. Ancient Romans were probably the first of use concrete—a word of Latin origin—based on hydraulic cement that is a material which hardens under water [5]. The concrete produced in the last 20-30 years is much more than the produced in all human history [4]. Building concrete material made of cement is the most consumed basic material after water per man in the world. In the 2007, the cement consumed per person in the world is about 420 kg; consumption in Turkey is higher than in the world, 601 kg/person-year in 2007 and 585 kg/person-year in 2009 [6]. As the end of 2013, the production capacity of the Turkish cement sector was 107.4 million tons/year and its production was 70.4 million tons. According to data from the year 2014, production was 69.7 million tons [7]. It has been estimated that the rate of the world’s population will increase explosively from 1.5 to 9 billion by the year 2050, then will result in an increased demand for energy, housing, food and clothing as well as the demand for concrete is forecasted to grow up approximately 18 billion tons annually by 2050 [2]. Therefore, concrete technology has focused on other alternatives that can be used as cement replacement materials in concrete [8].

The amount of cement in the concrete is generally 12-15% [9]. Pozzolanic materials are used to reduce costs in cement and concrete production [9]. Pozzolans are siliceous or siliceous and aluminous materials [10] that consist

predominantly of silica and alumina and are able to combine with portlandite in the presence of water to produce new reaction products exhibiting a binding character [11]. Pozzolans which do not have non-binding values on their own or can demonstrate very little binding are defined as siliceous or siliceous and aluminous materials that have fine-grained and hydraulic bonding properties when combined with calcium hydroxide in an aqueous medium [9]. Pozzolans are now classified depending on their origins. Accordingly pozzolans are divided into two basic groups, natural and artificial. Volcanic glasses, tuff, trass and certain clays and shales, creates natural pozzolan, fly ash, blast furnace slag, silica fume creates an artificial pozzolan class [12]. It is widely accepted the use of pozzolanic materials such as fly ash and microsilica as partial replacement of Portland cement to produce mortars and concretes [13]. Pozzolans are known to increase the durability, lower the hydration heat, increase the resistance to sulphate attack and reduce the energy cost per cement unit [14].

Fly ash is a solid, fine-grained material resulting from the combustion of pulverized coal in power station furnaces [15]. Fly ashes (FA) used as a mineral admixture in cement and concrete, is a product of the pulverized coal firing system, through conventional boilers, mostly used in the thermal power plants [16]. Fly ash is composed of fine dusty tufts which are mostly glassy or filled with voids [17]. The fly ash particle shape is spherical and the diameter varies between 1-200  $\mu\text{m}$ . Specific surface area of the fly ash is conveniently close to cement fineness, it could be used without grinding [18].

Silica fume is a by-product of the silicon metal and alloy industries. Silicon metal and alloys are produced in electric arc furnaces in which quartz is reduced at temperatures above 1.700 °C [19]. The size of the particles forming the silica fume is 0.1-0.2  $\mu\text{m}$  [20]. The average size of individual silica fume particles is approximately 100 times smaller than those of portland cement [21]. When a 45  $\mu\text{m}$  sized mesh is sieved, the remaining particles on the sieve are considered to be oversized particles. Since the silica fume is very

fine grained, the water need is very high. It also shows a very strong pozzolanic binding [22].

Blast furnace slag (BFS) is produced as a by-product during the manufacture of iron in a blast furnace. Iron sprouts gangue, coke and scraps of the burned limestone produce the blast furnace slag [23]. The binding character of BFS has been known since 1774. The first use of BFS as an additive in cement production began in Germany in 1892 and in the United States in 1896. It has been since 1950's years to participate as a concrete additive [24].

In this study, concrete specimens with mineral admixtures were produced and more economical concrete production was aimed and relations between microstructures and mechanical properties were tried to be established.

## 2. MATERIALS AND METHOD

In this study, portland cement CEM I 42.5 R type in accordance with TS EN 197-1 [25] was used binder material. Chemical properties of cement and additives are given in Table 1 and physical properties of cement are given in Table 2.

**Table 1.** Chemical components of materials

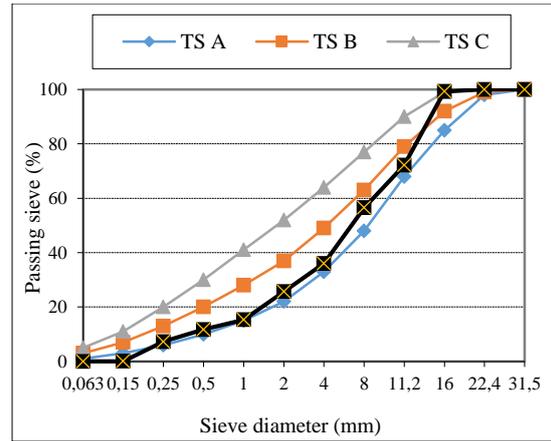
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Li
CEM	19.29	3.88	4.25	62.63	3.42	2.58	0.34	2.86
SF	93.6	0.28	0.58	0.27	0.25	-	0.49	4.36
BFS	40.1	7.83	0.92	39.69	4.2	2.11	1.24	0.63
FA	28.84	9.44	6.65	30.29	1.61	14.83	0.85	6.90

**Table 2.** Physical properties of cement

Physical Properties		Results
Density (g/cm <sup>3</sup> )		3.09
Set time	Firstly (minute)	125
	Finally (minute)	190
Specific Surface Area (cm <sup>2</sup> /g)		3420

The maximum particle diameter of the aggregate used in concrete mixtures is 22 mm. The water absorption capacity and specific gravity of the

aggregates are determined according to TS EN 1097-6 [26] and the aggregate granulometry are determined according to TS 706 EN 12620 [27] (Figure 1).



**Figure 1.** Experiment aggregate granulometry

The calculation of the amount of mixture is made according to TS 802 [28]. Mineral additive mixtures were used with 10%, 20% and 30% ratios substitution with cement. The amounts of the materials in one cubic meter of concrete are given in Table 3.

Ultrasound pulse velocity transit speed measurements were made according to ASTM C 597 [29]. 7, 28, and 90 days after curing, ultrasonic measurements were applied to the 3 samples. While each sample was in dry state, 2 different surface readings were performed and the average of these values was taken. Concrete compressive strength tests were carried out in accord with TS EN 12390-3 [30] standard on 3 specimens cured for 7, 28 and 90 days at 15 cm sizes prepared.

## 3. FINDINGS

### 3.1. Ultrasound Pulse Velocity Findings

The results of the ultrasound pulse velocity measurements for the added and witnessed concrete are given in Table 4.

**Table 3.** Approximate amounts of material for one cubic meter of concrete mixture (kg/m<sup>3</sup>)

Components	Fine Aggregate (0-5 mm)	Middle Aggregate (5-12 mm)	Coarse Aggregate (12-22 mm)	Cement	Additive	Water	Air
Witness	668	618	444	371	-	204	20
%10 FA	668	618	444	334	37	204	20
%20 FA	668	618	444	297	74	204	20
%30 FA	668	618	444	260	111	204	20
%10 BFS	668	618	444	334	37	204	20
%20 BFS	668	618	444	297	74	204	20
%30 BFS	668	618	444	260	111	204	20
%10 SF	668	618	444	334	37	204	20
%20 SF	668	618	444	297	74	204	20
%30 SF	668	618	444	260	111	204	20

Ultrasonic transit speed values of concrete with mineral admixture were higher than those of witness samples. Mineral pozzolanic admixtures may have influenced these values by forming additional binding gel structures during the subsequent hydration periods and thus being more packed than the witness samples.

**Table 4.** Ultrasound pulse velocity results (km/sn)

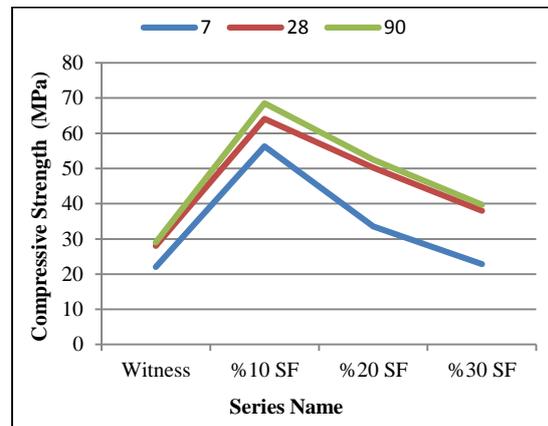
Experiment Samples	7 Days	28 Days	90 Days
Witness	4.52	4.33	4.07
%10 FA	1.74	2.02	2.21
%20 FA	3.39	4.53	4.64
%30 FA	3.08	4.15	4.59
%10 BFS	3.15	3.44	4.85
%20 BFS	3.04	4.76	4.52
%30 BFS	2.91	4.62	4.61
%10 SF	2.76	3.30	5.09
%20 SF	2.26	4.98	4.86
%30 SF	1.40	4.61	4.29

### 3.2. Compressive Strength Findings

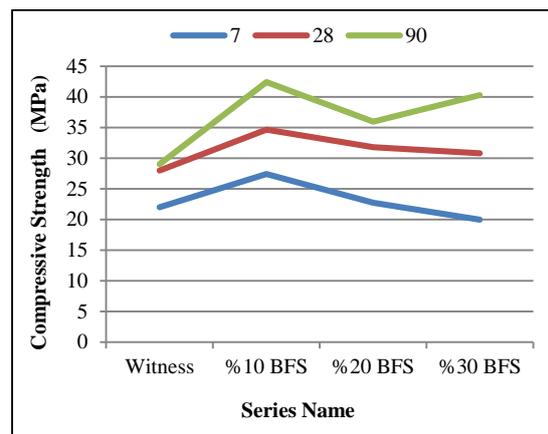
In concrete prepared from different pozzolanic admixtures, compressive strengths values were determined under standard curing conditions for 7, 28 and 90 days and the obtained results are presented in Figure 2-4.

When observed Figure 2, the compressive strengths of the test specimens increase with SF additions compared to the witness samples at 28 and 90 days. When the additive rates were compared among themselves, the highest compressive strength values were obtained for each day of the day with the addition of 10% SF

ratios. In this case, it can be said that optimum SF addition yields 10% good results.

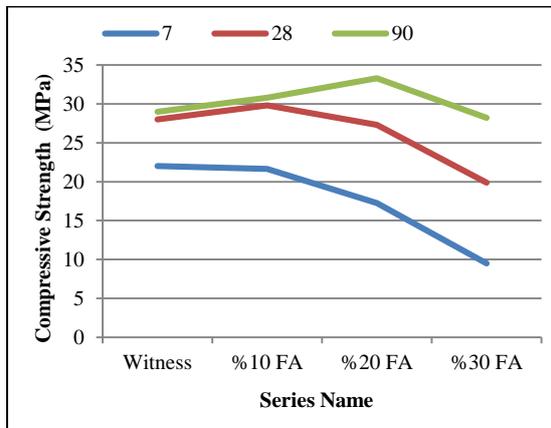


**Figure 2.** Compressive strength graph with SF added concrete



**Figure 3.** Compressive strength graph with BFS added concrete

When we examine Figure 3, it can be said that the BFS additive has a positive effect on the compressive strength. Especially in 10% ratios addition series, higher strength values were obtained compared to witness sample and other additive ratios. In the 7 day series, we observed a decrease in the strengths values in the 20% and 30% BFS-added series. A decrease in the amount of cement during the early hydration period can be attributed to this decrease in strength values.



**Figure 4.** Compressive strength graph with FA added concrete

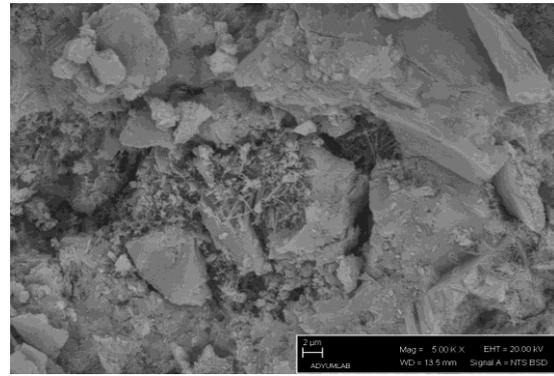
When Figure 4 is examined, it can be said that the FA additive plays a negative role in the strength in the 7<sup>th</sup> and 28<sup>th</sup> day series, which has a positive effect on 20% strength in 90 day series. When the chemical composition of the used FA is examined, it can be said that the presence of  $SO_3$  in it may play a role in the formation of ettringite, and the strength tends to decrease with this reason.

When the general effect of the additives is examined, it is found that the highest resistance values are obtained in the SF-added series, lower than the SF-added series in the BFS-added series, and the lowest resistance values are obtained in the FA-added series.

### 3.3. Microstructure Studies

Microstructure studies of the test specimens were performed using the SEM technique. SEM examinations were made on 90 days samples

together with witness and additives concrete samples. When the SEM analysis of the 90 day witness samples was examined (Figure 5), C-S-H gel structure and ettringite formation were observed from the cement hydration phases. In some regions, intense C-S-H is observed while gaps are observed in some regions. It has been determined that the ettringite pellets have developed as needle-like structures towards the cavities.



**Figure 5.** SEM images of witness samples

SEM images of fly ash-added series are given in Figures 6,7. When Figures 6 and 7 are examined, it was observed that the formation of C-S-H gel structure and the formation of ettringite and tobermorite plates. Ettringite plates are observed around the fly ash deposits in the 20% FA-added series. It can be said that higher strength values are obtained in 30% FA-added series, because the tobermorite plates are observed more intensively in these series.



**Figure 6.** SEM images of 10%FA-added series

The chemical composition of the fly ash is observed, the presence of  $SO_3$  is quite high. The following reaction of the sulphate-containing compounds and the cemented  $C_3A$  phase forms the resulting ettringite phase. The presence of this structure affects the strength and durability of the concrete.

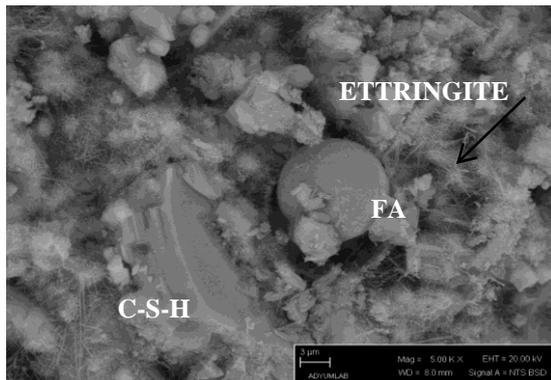


Figure 7. SEM images of 20% FA added series

The SEM images of SF and BFS added series are given Figure 8a and 8b. It was observed that formation of tobermorite plates and C-S-H gel structure in these series. In the BFS-added series, the tobermorite plates do not appear as clearly as in the SF-added series. Since SF is finer than BFS, may be the affect that form to strong gel structure in concrete. The fact that the pozzolanic reactivity of silica fumes is stronger than that of BFS also caused the differences in strength.

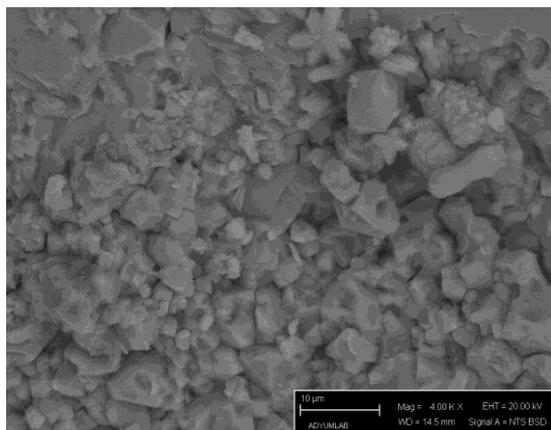


Figure 8a. SEM images of 10% BFS added series



Figure 8b. SEM images of 10% SF added series

#### 4. CONCLUSION

In this study, in order to reduce of cement costs in concrete admixtures we obtained different compressive strength values in 3 different additive types. According to the ultrasound pulse velocity findings all series belong to quality concrete class. When the strength values were examined, the highest strength values were obtained in silica fume added series. However, the best strength value in the series with silica fume was observed in the 10% added series. In the series with addition of 20%SF and 30%SF, the compressive strength also decreased. The fact that the silica fume is finer than the cement may have adversely affected the adherence of the cement-aggregate adherence and may have caused the loss of strength.

The lowest strength values were obtained in the fly ash added series. The formation of ettringite plates in these series was clearly observed in SEM examinations. This might be due to the loss of strength of concrete materials.

It was observed that the best added ratio was 10% of BFS added series. The strength values show a decreasing tendency on the other added ratios. As the amount of cement required for hydration decreases as a result of BFS substitution, it can be said that the strength values have decreased. However, according to the witness samples, high strength values were still observed.

As a result of using 10% SF and 10% BFS added concrete, it is possible to added value to waste materials as well as to be economical in cost of concrete. From the viewpoint of ecology and environmental protection, it would be appropriate to use of these materials as a concrete additive.

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