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## Effect of Alkali Modulus on the Compressive Strength and Ultrasonic Pulse Velocity of **Alkali-Activated BFS/FS Cement**

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Abstract: Portland cement, which has been used as an unrivaled binder material since its development has become one of major sources of greenhouse gas emission. Compared with the conventional cement, alkali-activated materials which based on the principle of activating precursor materials by means of alkali activators have comparable engineering properties and lower CO<sub>2</sub> emission during its production. In this study, the effect of alkali modulus on the compressive strength and ultrasonic pulse velocity of granulated blast furnace slag (BFS)/ferrochrome slag (FS)based alkali-activated cement was investigated. Alkali-activated cement was produced from the mixture of a blast furnace slag and ferrochrome slag in proportion 80% and 20% respectively. Alkali modulus of 0.8, 1.0, 1.2, 1.4 were adopted in the test. Mortar specimens with the alkali modulus of 0.8 and 1 had a compressive strength of 6.43 MPa and 9.75 MPa, respectively, while specimens with the modulus of 1.2 and 1.4 gained approximately half of their 28-day strength in the first three days. The 28-days UPV values of the specimens with alkali modulus of 0.8, 1, 1.2 and 1.4 were 4117, 4032, 3831 and 3697 m/s, respectively.

# Alkali Modülünün Alkali-Aktif YFC/FC Çimentosunun Basınç Dayanımı Ve UPV Hızı Üzerindeki Etkisi

Anahtar Kelimeler Alkali-aktif cimento, Yüksek fırın cürufu, Ferrokrom cürufu, Alkali modülü

Öz: Geliştirildiği günden bu yana rakipsiz bir bağlayıcı malzeme olarak kullanılan Portland cimentosu, sera gazi emisyonunun baslıca kaynaklarından biri haline gelmistir. Geleneksel cimento ile karşılaştırıldığında, öncü malzemelerin alkali aktivatörler vasıtasıyla etkinleştirilmesi prensibine dayanan alkali-aktif malzemeler, benzer mühendislik özelliklerine sahip olmalarının yanısıra üretiminden kaynaklanan CO2 emisyonu çok daha düşüktür. Bu çalışmada, alkali modülünün yüksek fırın cürufu/ferrokrom cürufu esaslı alkali-aktif çimentonun basınç dayanımı ve ultrasonik geçiş hızı üzerindeki etkisi araştırılmıştır. Alkali-aktif çimentonun bağlayıcı malzemesi %80 oranında yüksek firin cürufu, %20 oranında ferrokrom cürufundan oluşmaktadır. Test edilecek alkali modülleri 0.8, 1.0, 1.2, 1.4 olarak belirlenmiştir. Alkali modülü 0.8 ve 1 olan harç numunelerinin basınç dayanımları sırasıyla 6,43 MPa ve 9,75 MPa iken alkali modülü 1.2 ve 1.4 olan numuneler ilk üç günde 28 günlük dayanımlarının yaklaşık olarak yarısını kazanmıştır. Alkali modülü 0.8, 1, 1.2 ve 1.4 olan numunelerin 28 günlük UPV değerleri sırasıyla 4117, 4032, 3831 ve 3697 m/s olarak ölçülmüştür.

### **1. INTRODUCTION**

Cement, used as a binding material in concrete, constitutes around 10% of conventional concrete by mass and is manufactured at a rate of around 4 gigatonnes (Gt) per year [1]. Over the more than past half century, cement consumption has increased tenfold, while steel production has only increased by a factor of three [1], [2]. Cement is responsible for 36% of the 7.7

Gt of CO<sub>2</sub> released globally by construction activities in 2010 [1], [3].

With the increase in infrastructure activities throughout the world, especially in developing countries, the demand for cement has continuously been increasing. Many concerns regarding CO<sub>2</sub> emission, raw materials consumption and energy are incorporated with Portland cement (PC) productions [4]. Although developments in PC production technology provide a reduction in energy

consumption and harmful emissions, PC manufacturing produces approximately 0.8 tons of  $CO_2$  per ton of PC [5], [6]. These reasons have motivated researchers to study on alternative materials to substitute PC. Alkaliactivated materials (AAM) are potential alternatives to the traditional cement [5].

The main benefit of AAM is that it significantly reduces CO2 emissions [7]. Besides having good mechanical properties, its chemical resistance is better than PC [4], [8]–[10]. AAMs are manufactured by activating the precursor with alkali activators. High alkalinity conditions are required for AAM production. Some of the precursor materials used in alkali activation systems are blast furnace slag (BFS), fly ash, metakaolin etc. Sodium hydroxide (NaOH) and sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) are most used activators to activate these precursor materials. Under high alkali conditions, aluminosilicates dissolve in water and decompose into alumina and silica units. Then these units combine to form polymeric bonds [4], [11], [12].

Alkali-activated slag are considered as alternative binder material to PC that can be activated by alkali activator such as Na<sub>2</sub>SiO<sub>3</sub> and NaOH [5]. Early mechanical strengths, low porosity, lower heat of hydration and superior durability are some advantages of alkaliactivated slag [13], [14]. The main reaction product formed by alkali activation of blast furnace slag is an aluminum-substituted C-A-S-H-type gel which has a disordered tobermorite-like structure. Regardless of the activator used, the C-A-S-H-type gel has a lower calcium content than a hydrated PC system, whose Ca/Si ratio is usually between 1.5 and 2.0 [15]. There are several factors affecting the properties of alkali-activated slag such as raw materials used, activator type, liqiud to solid ratio, the curing temperature, alkali dosage and modulus etc. [5].

There are many studies [4], [16]–[18] investigating the impact of silicate modulus (Ms) and alkali dosage on the strength of alkali-activated slag. Compressive strength generally increases as the alkali dosage increases, provided that it is between 2% and 8% by slag mass [19]-[21]. The impact of Ms on the strength is more complex. At a constant dosage as the Ms increases the compressive strength increases because of the formation of more silica gel. The optimum Ms is found to be lower when the alkalinity of slag is lower. Above the optimum modulus compressive strength may decrease as the Ms increases [16], [20]. There are several studies [22]-[24] on the usage of ferrochrome slag (FS) to produce alkaliactivated cements. Karakoç et al. [25] investigated the effect of silicate modulus on alkali-activated cement produced with FS. More research are needed to investigate the effect of the alkali modulus on the ferrrochrome based alkali-activated cement.

Within the scope of this study, AAM mortars were produced by using 80% BFS and 20% FS as the precursor material. The effect of the alkali modulus on the compressive strength and ultrasonic pulse velocity (UPV) of the mortar specimens was investigated.

## 2. MATERIAL AND METHOD

#### 2.1. Material

BFS and FS were used in this study as the precursors of alkali-activated cement (AAC) production. The chemical composition of the BFS and FS were given in Table 1.

Table 1. C	Themical	composition	of BFS	and FS
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Constituent	BFS (%)	FS (%)
$SiO_2$	40.52	33.8
$Al_2O_3$	13.74	25.48
Fe <sub>2</sub> O <sub>3</sub>	1.74	0.61
CaO	33.86	1.1
MgO	7.72	35.88
$SO_3$	0.17	-
Na <sub>2</sub> O	0.66	-
K <sub>2</sub> O	0.81	-
$Cr_2O_3$	-	2.12
Specific gravity	2.8	2.85

The aggregate used for mortar production was natural river sand. The size distribution of the aggregate used is shown in Figure 1.



Figure 1. Size distribution of the aggregate

The mixture of NaOH and Na<sub>2</sub>SiO<sub>3</sub> were used as an activator for the activation of BFS and FS. The NaOH in the form of pellets with 99% purity was used. NaOH solution was prepared by dissolving NaOH pellets in water. Na<sub>2</sub>SiO<sub>3</sub> solution consisted of 28% SiO<sub>2</sub>, 9% Na<sub>2</sub>O, and 63% H<sub>2</sub>O content by mass with a silica modulus of 3.11.

#### 2.2. Mortar preparation and test procedure

A total of four mortar mixtures were prepared to investigate the effect of alkali modulus on BFS/FS based alkali activated cement. The mixture proportions are presented in Table 2.

#### Table 2. Mix proportions of the produced mortars

	Codes	Modulus	w/b	Sand/binder	Na <sub>2</sub> O (%)	BFS (%)	FS (%)	
•							/	_
	M0.8	0.8	0.45	2.75	6	80	20	
	M1.0	1.0	0.45	2.75	6	80	20	
	M1.2	1.2	0.45	2.75	6	80	20	
-	M1.4	1.4	0.45	2.75	6	80	20	

BFS and FS precursor were used in a mass ratio of 80:20. The precursor-to-aggregate ratio was 1:2.75 and the water-to-precursor (binder) ratio was 0.45. The alkali dosage (Na<sub>2</sub>O by mass of the precursor materials) of all mixtures was 6 wt%. A set of mixtures were prepared with four alkali modulus. Alkali modulus refers to the ratio of total SiO<sub>2</sub> (wt %) to total Na<sub>2</sub>O (wt %) in the activator mix. Figure 2 shows one of the fresh mortars prepared.



Figure 2. Fresh mortar mixture

Initially, precursor materials and aggregate were blended together for half a minute. Afterward, NaOH and Na<sub>2</sub>SiO<sub>3</sub> solutions were added to the dry mixture after mixing together. Mixing continued until a homogeneous mixture (2 minutes) was obtained. Mortar mixtures were poured into steel molds of 50 mm cube. After the fresh mortars were casted, the molds were wrapped with stretch film to prevent water evaporation (Figure 3). Mortar specimens were cured at 50 °C for 24 hours and then kept at room temperature until days of testing. Literature review and preliminary experiments revealed that 50 °C curing temperature was the most suitable curing temperature in terms of compressive strength [26], [27].



Figure 3. Wrapped mold

The compressive strength test was carried out according to ASTM C109 [28]. The ultrasonic pulse velocity test was performed in accordance with ASTM C597 [29]. Figure 4 shows the compressive strength and UPV tests, respectively.



Figure 4. Compressive strength and UPV tests, respectively

### **3. RESULTS**

#### **3.1.** Compressive strength results

3-day compressive strength results of mortar specimens are given in Figure 5. The compressive strength increased with the increase of alkali modulus.



Figure 5. 3-day compressive strength results

The compressive strengths of the specimens with alkali modulus of 0.8 and 1 were considerably lower than the compressive strengths of the specimens with alkali modulus of 1.2 and 1.4. The compressive strengths of the specimens for 0.8, 1, 1.2 and 1.4 modules were measured as 6.43, 9.75, 35.56 and 36.32 MPa, respectively. When the alkali modulus was increased from 1 to 1.2, the 3-day compressive strength increased 2.45 times. It was understood that 1.2 alkali modulus is the critical value in terms of 3-day compressive strength. There was no significant difference between the 3-day compressive strength of the samples with alkali modulus of 1.2 and 1.4. The strength of the sample with an alkali modulus of 1.4 was 2.1% higher than the specimen with a modulus of 1.2. Fang et al. [17] stated that compressive strength increased with the increase of alkali modulus. The increase in compressive strength can be attributed to the high alkalinity of the exposure solution [4]. In the study conducted by Fang et al. [17] it was stated that the difference between the 28-day compressive strength and the 7-day compressive strength generally increased as the alkali modulus decreased. The fact that the 3-day compressive strength is much lower can be attributed to

the absence of a strong reaction between the precursor materials and the activator at low alkali modulus.

28-day compressive strength results of mortar specimens are given in Figure 6. As can be seen from the figure, the compressive strength increased as the alkali modulus increased.



Figure 6. 28-day compressive strength results

The compressive strengths of the specimens for 0.8, 1, 1.2 and 1.4 alkali modules were measured as 40.76, 48.28, 52.44 and 54.4 MPa, respectively. The compressive strength of M1.4 specimen, which the highest strength was obtained, was 33.5% more than the M0.8 specimen, which the lowest compressive strength was obtained. This difference was 464.9% for 3-day compressive strengths. When the alkali modulus of alkali-activated BFS/FS mortar was below 1.2, the 3-day compressive strength was very low compared to the 28-day strength. It was understood that compressive strength development of the specimens with alkali modulus of 0.8 and 1 was quite slow.

Figure 7 represents the changes of the 28-day compressive strength of the mortar specimens compared to the 3-day strength.



Figure 7. Changes in compressive strength

The 28-day compressive strength of the specimens with alkaline modulus of 0.8 and 1 increased considerably compared to the 3-day strengths. The 28-day strength of the specimens with an alkali modulus of 1.2 and 1.4 was approximately 50% higher than the 3-day strength. Mortar specimens with 1.2 and 1.4 alkali modules gained a very important part of their strength in the first 3 days.

#### 3.1. UPV results

3-day UPV values of mortar specimens are given in Figure 8. The highest UPV value was obtained when the alkali modulus was 1.2.



Figure 8. 3-day UPV results

The UPV values of the specimens coded M0.8, M1, M1.2 and M1.4 were 2336, 2616, 3731 and 3556 m/sec, respectively. Consistent with the results measured in the compressive strength test, the UPV values of the M0.8 and M1 coded specimens were considerably low compared to the M1.2 and M1.4 coded samples. While the highest compressive strength was obtained from the specimen coded M1.4, the highest UPV value was measured in the M1.2 coded sample. The UPV value of the M1.2 coded sample was 4.9% higher than that of the M1.4 coded sample.

28-days compressive strength results of mortar specimens are given in Figure 9.





The UPV values of the specimens coded M0.8, M1, M1.2 and M1.4 were 4117, 4032, 3831 and 3697 m/sec, respectively. The UPV values of all specimens increased compared to those obtained after 3 days. At the end of 28 days, the highest UPV value was obtained from the M0.8 coded specimen, while the highest compressive strength was obtained from the M1.4 coded specimen. The specimen with the highest UPV value at the end of 28 days had the lowest 3-day UPV value.

Figure 10 shows the changes of the 28-day UPV values of the mortar specimens according to the 3-day UPV values.



Figure 10. Changes in compressive strength

The 28-day UPV values of the mortar specimens coded M0.8, M1, M1.2 and M1.4 increased by 76.2%, 54.3, 2.7 and 4, respectively, compared to the 3-day UPV values. While the 28-day UPV values of the M1.2 and M1.4 coded mortar specimens did not change notably compared to the 3 days, the UPV values of the M0.8 and M1 coded mortar specimens increased significantly.

## 4. CONCLUSION

In this study, the effect of alkali modulus on the compressive strength and ultrasonic pulse velocity of granulated blast furnace slag/ferrochrome slag-based alkali-activated cement was investigated. Mortar specimens with alkali modulus 0.8 and 1 had very low compressive strength after 3 days, while mortar specimens with alkali modulus 1.2 and 1.4 gained most of their 28-day strength in the first three days. Especially in cases where early strength is required, the alkali modulus of 1.2 is the limit value in terms of compressive strength. In accordance with the result obtained in the compressive strength test, the 3-day UPV values of the samples with alkali modulus of 0.8 and 1 were lower than the samples with alkali modulus of 1.2 and 1.4. In contrast to the compressive strength results, the 28-day UPV values of the samples with 0.8 and 1 alkali modulus were higher.

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