Effect of Blast Furnace Slag on Environmentally Friendly Fly Ash Based Geopolymer Bricks

Çevre Dostu Uçucu Kül Tabanlı Geopolimer Tuğlalara Yüksek Fırın Cürufunun Etkisi

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ABSTRACT

In this study, the objective is to produce fly ash based geopolymer bricks by using blast furnace slag, which is the waste of Karabük Iron and Steel Plant, and Seyitömer thermal power plant waste fly ash. Study, it is aimed to produce a geopolymer brick with superior physical and mechanical properties compared to regular bricks and better thermal properties. In accordance with this purpose, geopolymer bricks were produced based on fly ash (20%) and different proportions (10%, 30%, 50% and 70%) of blast furnace slag and 8 - 10 M sodium hydroxide and 4 - 8% calcium hydroxide concentrations. The samples were subjected to unit volume weight, water absorption (by weight), compressive strength and flexural tensile strength tests. SEM images of the samples were also taken for microstructure analysis. As a result of the study, it was determined that with the increase in the ratio of sodium hydroxide and calcium hydroxide, a more amorphous structure was obtained, the amount of water absorption decreased and the compressive strength increased. Furthermore, it was determined that waste can be used in the production of geopolymer bricks, which is a very proper method for waste disposal.

Keywords: Geopolymer brick, blast furnace slag, fly ash, sodium hydroxide, calcium hydroxide

ÖZET

Bu çalışmada Karabük Demir Çelik Fabrikası atığı olan yüksek fırın cürufu ve Seyitömer termik santrali atık uçucu külü kullanılarak uçucu kül bazlı geopolimer tuğlaların üretilmesi hedeflenmektedir. Çalışmada normal tuğlalara göre üstün fiziksel ve mekanik özelliklere sahip, ısıl özellikleri daha iyi olan bir geopolimer tuğla üretilmesi amaçlanmaktadır. Bu amaç doğrultusunda, uçucu kül (%20) ve farklı oranlarda (%10, %30, %50 ve %70) yüksek fırın cürufu ve 8 - 10 M sodyum hidroksit ve %4 - 8 kalsiyum hidroksit konsantrasyonları esas alınarak geopolimer tuğlalar üretilmiştir. Numuneler birim hacim ağırlığı, su emme (ağırlıkça), basınç dayanımı ve eğilmede çekme dayanımı testlerine tabi tutulmuştur. Mikroyapı analizi için numunelerin SEM görüntüleri alınmıştır. Çalışma sonucunda sodyum hidroksit ve kalsiyum hidroksit oranının artmasıyla daha amorf bir yapı elde edildiği, su emme miktarının azaldığı ve basınç dayanımının arttığı belirlenmiştir. Ayrıca atık bertarafı için çok uygun bir yöntem olan geopolimer tuğla üretiminde atıkların kullanılabileceği belirlenmiştir.

Anahtar Kelimeler: Jeopolimer tuğla, yüksek fırın cürufu, uçucu kül, sodyum hidroksit, kalsiyum hidroksit

INTRODUCTION

Brick is one of the most important components of the construction industry [1] and its production is one of the oldest industries dating back to 8000 BC [2,3]. Brick is a burnt block achieved after clay is burnt in a kiln [4]. Despite advances in technology, more than half of the world's population still builds their load-bearing structures from clay, which is fired into bricks. It is a large-scale building material generally used in the construction of exterior and interior walls in buildings [5]. They are also widely used in low and medium-rise building construction in many parts of the world [3].

In recent years, the use of these materials has increased due to the rapid increase in urbanization and population growth. Population growth puts a great pressure on the construction industry and the increasing demand for building materials [6]. Waste materials are often used in the literature to produce building materials due to cost reduction, energy saving and possibly better products [6,7,8].

One of the waste materials used in the study is blast furnace slag. Blast furnace slag is produced in the furnaces of iron and steel plants as molten coke, iron ore gangue, etc. after iron production at temperatures between 1400-1600 °C. Blast furnace slag can have different properties depending on the type of main material and manufacturing method [9,10,11]. This waste, which is generally used in cement and concrete production [12], has also started to be used in brick production [13].

Another waste is fly ash. Fly ash is the pozzolanic waste generated by the combustion of coal in thermal power plants. In 2020, a total of 24,400,000 tons of fly ash is released in all thermal power plants of 100 MW and above in our country. Out of this, 10,000 tons are considered hazardous. Of the non-hazardous waste, 79.5% is ash and slag waste and 20.5% is metal, paper, etc. waste. 85.9% of the waste is disposed of in ash dams or landfills, while 13.2% was sent to twenty-three licensed facilities. The returned waste was used for backfilling in stone or mine quarries. The remaining 0.9% was disposed of in different ways [14].

In this study, it was aimed to produce geopolymer bricks with better physical and mechanical properties than normal bricks by using blast furnace slag and fly ash. In the study, firstly, normal brick production, then blast furnace slag and fly ash added geopolymer brick production, and finally, physical and mechanical tests were used on the produced samples. When the study was completed, it was observed that the water absorption decreased with the increase in the amount of blast furnace slag, and the optimum mixing ratio for mechanical experiments was 30%. In addition, it has been concluded that the use of wastes in brick production will decrease the use of fertile soil.

MATERIAL AND METHOD

Material

Clay Soil; The clay soil, which is the raw material of the geopolymer brick produced, was taken from Kırşehir province. The mineralogy of the soil is given in Table 1.

When the table is examined, it is shown that the highest element value is Silicon (Si) with 38.35%. Additionally, there are oxygen, aluminum and iron elements in the soil.

Table 1. Weight percentages of the elements in the soil used in the production of geopolymer bricks

Element	Weight (%)
Si	38.35
Al	9.22
Fe	7,45
O	21,78
Nb	5.62
K	2.70
Ca	15.92

Blast Furnace Slag; Blast furnace slag, which is the waste of Kardemir Iron and Steel Plant, was used in the study. The mineralogy of blast furnace slag is given in Table 2. When the table is examined, it is determined that the highest value was SiO2 with 41.97% and a high percentage of CaO, Al2O3 and MgO compounds were also found.

Table 2. Mineralogy of blast furnace slag

Compound	SiO_2	Al_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	Mn_2O_3	K.K
%	41,97	10,51	35,66	6,78	1,47	0,35	0,79	0,53	2,20	0,58

K.K: Ignition Loss

Fly Ash; The fly ash used in the testal study was supplied from Seyitömer Thermal Power Plant and its mineralogy is given in Table 3. When the table is analyzed, SiO2 has the highest value with 51.74%. In addition, CaO, MgO, Fe2O3 and Al2O3 compounds are also found in fly ash. F class fly ash was preferred in the study.

Table 3. Chemical compounds of fly ash

Compound	SiO_2	CaO	MgO	Fe_2O_3	Al_2O_3	Na_2O	K_2O	SO_3	Na_2O (eşd)	Free CaO
(%)	51,74	7,29	5,90	9,08	18,87	0,75	2,35	2,74	1,85	0,25

Sodium Hydroxide; Sodium hydroxide (NaOH) is frequently used in many industrial fields, especially in the chemical industry. One of these fields is construction. Sodium hydroxide is slippery, odorless and white in color. It has high moisture retention properties. The sodium hydroxide used in the testal study, whose chemical value is given in Table 4, was procured from Mikro Teknik.

Table 4. Chemical values of Sodium Hydroxide [15]

Chemical Name	Sodium Hydroxide
Chemical Formula	NaOH
Molecular Weight	39,997 g/mol
Density	2.13 g/cm^3
Melting Point	318 ^{o}C

Calcium Hydroxide; Calcium hydroxide, which is obtained by adding water to quicklime, has a wide range of uses in construction. Its color is white and powdery. When it interacts with water, it forms a pasty consistency. Chemical values of calcium hydroxide are given in Table 5.

Table 5. Chemical values of calcium hydroxide [15]

Chemical Name	Calcium Hydroxide
Chemical Formula	$Ca(OH)_2$
Molar Mass	74,093 g/mol
Density	2,21 g/cm^3
Melting Point	580 ^{o}C

Mixing Water; Kırşehir province's city water supply was used in the geopolymer brick samples produced within the scope of the study.

Method

Production of Geopolymer Brick Samples

In the experimental study, firstly, the solution was prepared for the production of sodium hydroxide with a concentration of 8 and 10 M and calcium hydroxide to be used at 4% and 8%. 8 moles of sodium hydroxide 320 g and 10 moles of sodium hydroxide 400 g were used. To make the solution, 1 liter of water was made into a solution separately in a glass beaker. The same process was applied for 4% and 8% calcium hydroxide.

In the second stage, clay soil, which is the raw material of geopolymer brick, was taken from the furnace by the quartering method and ground in a roller crusher grinding machine to achieve 1 mm undersize material. The same process was applied for blast furnace slag from Kardemir iron and steel plant and fly ash from Seyitömer thermal power plant.

After the solid materials were prepared, production was started using the recipe quantities given in Table 6. In the table, REF means reference sample, YFC10 means 10% blast furnace slag doped geopolymer brick, YFC30 means 30% blast furnace slag doped geopolymer brick, YFC50 means 50% blast furnace slag doped geopolymer brick, YFC70 means 70% blast furnace slag doped geopolymer brick. Fly ash ratio was fixed at 20% in the study. Clay / blast furnace slag ratios were planned as 70:10, 50:30, 30:50 and 10:70. When the literature is analyzed, NaOH ratio is recommended as 2.5 in geopolymer brick production [16-19]. Based on these studies, NaOH 2.5% was used in this study. Mixing water was determined as 20% of the mixture. Geopolymer brick production scheme is given in Figure 1.

Table 6. Mixture recipe

	Clay (%)	Blast Furnace Slag (%)	Fly Ash (%)	Sodium Hydroxide (M)	Calcium Hydroxide (%)
REF	100	--	--	--	--
YFC10-8-4	70	10	20	8	4
YFC30-8-4	50	30	20	8	4
YFC50-8-4	30	50	20	8	4
YFC70-8-4	10	70	20	8	4
YFC10-8-8	70	10	20	8	4
YFC30-8-8	50	30	20	8	4
YFC50-8-8	30	50	20	8	4
YFC70-8-8	10	70	20	8	4

	Clay (%)	Blast Furnace Slag (%)	Fly Ash (%)	Sodium Hydroxide (M)	Calcium Hydroxide (%)
YFC10-10-4	70	10	20	10	8
YFC30-10-4	50	30	20	10	8
YFC50-10-4	30	50	20	10	8
YFC70-10-4	10	70	20	10	8
YFC10-10-8	70	10	20	10	8
YFC30-10-8	50	30	20	10	8
YFC50-10-8	30	50	20	10	8
YFC70-10-8	10	70	20	10	8

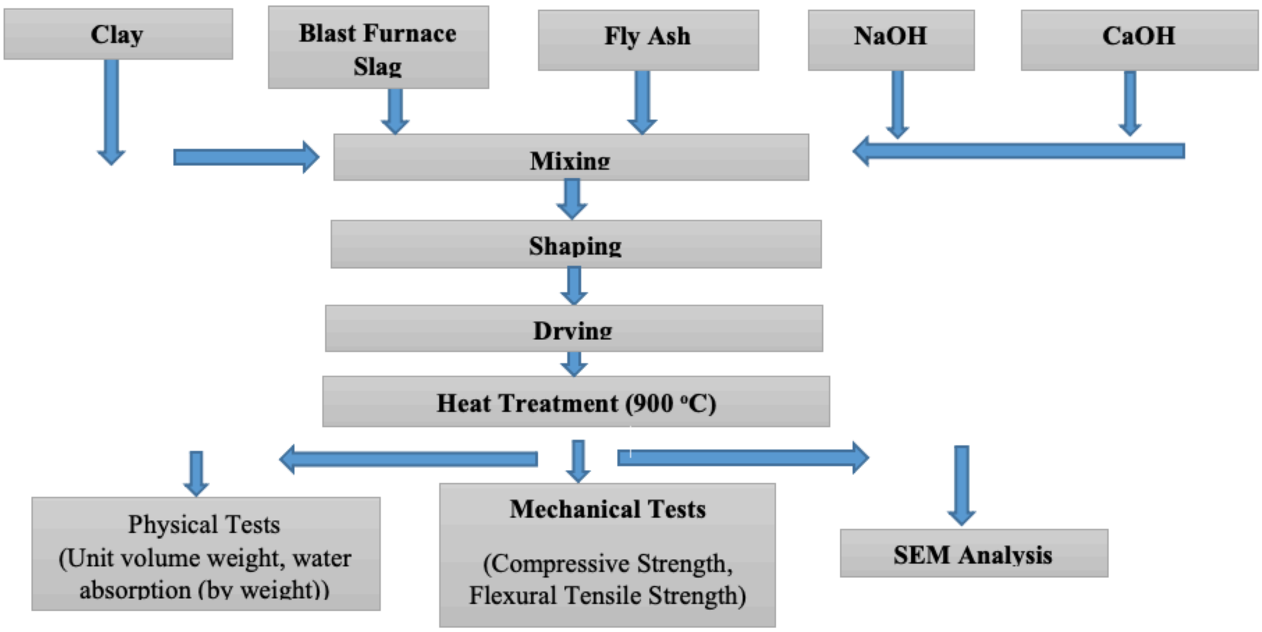

Figure 1. Geopolymer brick production scheme

In the production stage of the study, firstly, the dry materials clay, fly ash and blast furnace slag were mixed in a mixer for 60 seconds at the ora setting to achieve a dry homogeneous mixture.

After mixing, NaOH and CaOH in aqueous solution were poured into the dry mixture consisting of clay, fly ash and blast furnace slag and mixed at low setting for 90 seconds. It was then mixed at high setting for 90 seconds. The produced brick dough was cast into 4x4x16 cm molds after the mold was greased. For the compression process, 60 hits were applied.

Geopolymer brick samples were kept in the mold for one day. The semi-finished brick samples were then left to dry in a semi-open space to dry out the water. After the drying process was completed, they were fired in high temperature electric furnaces by gradually increasing the temperature.

After firing, the samples were allowed to cool slowly in the furnace. The reason for not removing the samples from the furnace immediately after firing is to avoid problems such as cracking or breakage due to sudden temperature changes on the samples. The cooled geopolymer brick samples shown in Figure 2 were removed from the furnace and subjected to physical and chemical tests and SEM analysis.

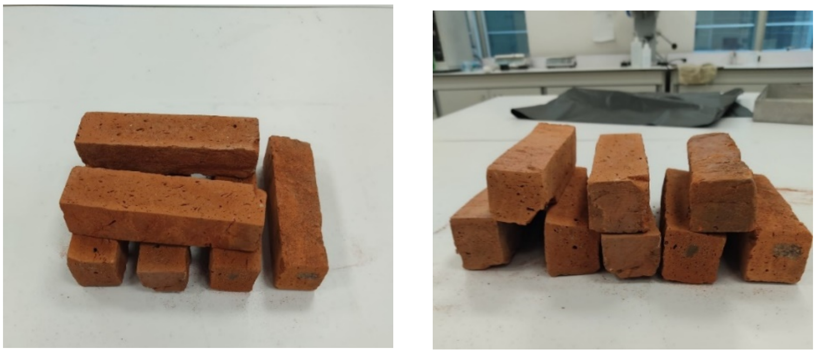

Figure 2. Produced geopolymer brick samples

Physical Tests on Geopolymer Brick Samples

Unit Volume Weight

The unit volume weight test is based on TS 699 [20] standard. As a result of this test, density and unit volume weight values are calculated. The values obtained are substituted in the formula given in 3.1 and 3.2. In the formula p: Density (g/cm^3), ɣ: Unit volume weight (kN/m), W: Sample weight (g), V: Sample Volume (cm^3).

$$p = W V \qquad (3.1)$$

$$ɣ = 9{,}81 \times p \qquad (3.2)$$

Water Absorption (Weight)

Water absorption test was carried out based on TS 699 standard. In this test, it is applied to determine the amount of water that the pores in the structures of the samples can absorb as a ratio. The values obtained at the end of the test were calculated by substituting them in formula 3.3. In the formula, Aw : Water absorption rate by weight (%), ws : Water saturated sample weight, wd : Dry sample weight (g).

$$Aw = ws{-}wd \; wd \times 100 \qquad (3.3)$$

Mechanical Tests on Geopolymer Brick Samples

Compressive Strength

The computer-aided compressive strength measurement device shown in Figure 3 was used for the test. The test was conducted based on TS EN 772-1, 2012 [21] standard. In the first stage of the test, the samples were placed in the device. Then the device was operated and the strength was measured under the pressure applied to the sample. The values obtained in the test were calculated by substituting them in formula 3.4.

Compressive strength: Breaking load / surface area (3.4)

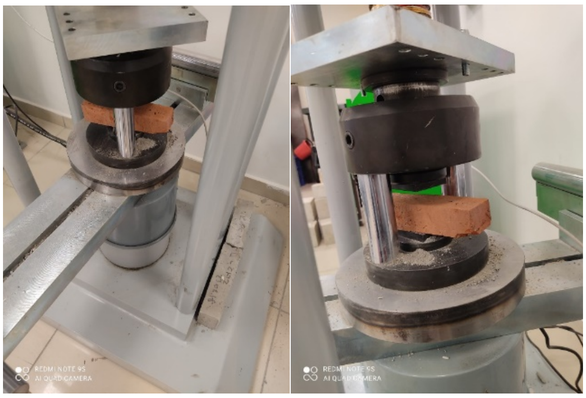

Figure 3. Compressive strength device

Flexural Tensile Strength

The flexural tensile strength test applied to the samples was based on TS EN 772-6 [22] standard. The samples were subjected to flexural tensile strength test by applying pressure in the right angle and from three points.

Analyzing the Microstructure of Geopolymer Brick Samples (SEM Analysis)

Scanning Electron Microscopy (SEM) is an analysis for a more detailed study of the sample microstructure. The electrons sent from the device interact with the sample atoms to produce different signals that contain data related to the composition and topography of the sample surface. The signals are collected by detectors and transferred to the screen of a computer to create an image.

RESEARCH RESULTS AND EVALUATION

Unit Volume Weight

The data obtained as a result of the unit volume weight test are shown in Figure 4. When the graph is analyzed; it is seen that the unit volume weight value of all samples varied between 1.82 and 2.05 g/cm^3. The lowest unit volume weight was obtained from YFC10 sample doped with 10 M (NaOH) + 4% (CaOH) with 1.82 g/cm^3 and the highest unit volume weight was obtained from YFC70 sample doped with 8M (NaOH) + 8% (CaOH) with 2.05 g/cm^3. In samples with 8 M (NaOH) concentration, it was determined that the unit volume weight increased with the increase in the amount of blast furnace slag. It was also determined that the unit volume weight values of YFC10 samples decreased with the increase of sodium hydroxide ratio and then the unit volume weight values increased with the increase of blast furnace slag substitution. According to TS 705 [23], there is no limit on the unit volume weight value. However, it is believed that bricks with low unit volume weight (light weight) will be more useful.

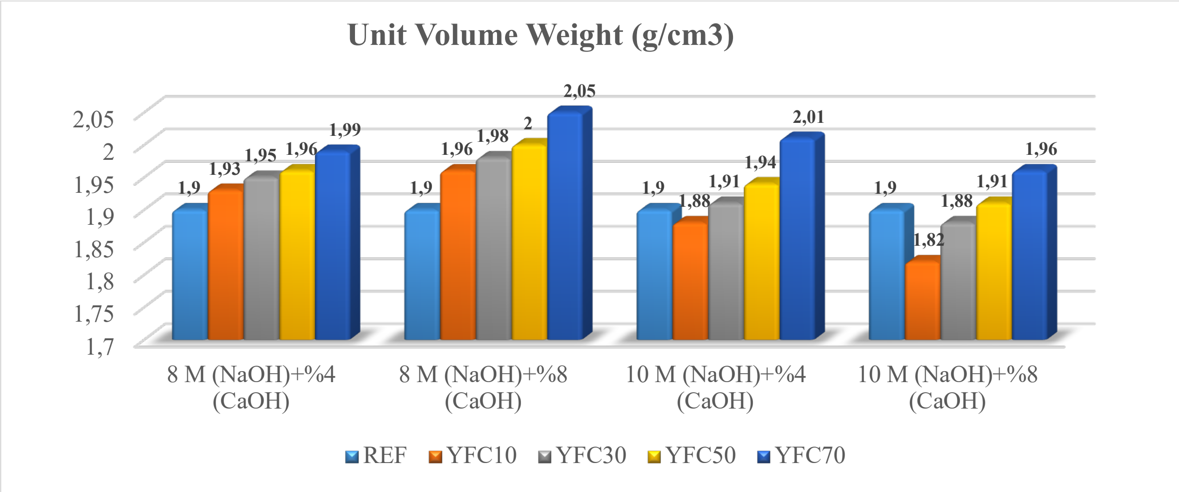

Figure 4. Graph of unit volume weight values

Water Absorption (by weight)

The water absorption test results applied to the samples produced within the scope of the study are given in Figure 5. When the graph is analyzed, it is seen that the amount of water absorption decreases as the blast furnace slag content increases. It was observed that the reference sample had the highest water absorption rate with 20.3%. The water absorption values of the doped samples were below the limits of ASTM C62-10 [27] requirements and ranged between 19.7% and 16.8%. It was determined that the water absorption rate decreased with increasing blast furnace slag content. Furthermore, it was determined that the water absorption value decreased with the increase in the ratio of sodium hydroxide and calcium hydroxide. This resulted in a higher degree of geopolymerization, a less porous matrix and a lower water absorption rate in mixtures containing high concentrations of sodium hydroxide. This value is confirmed by the study of Madani et al., 2020 in the literature.

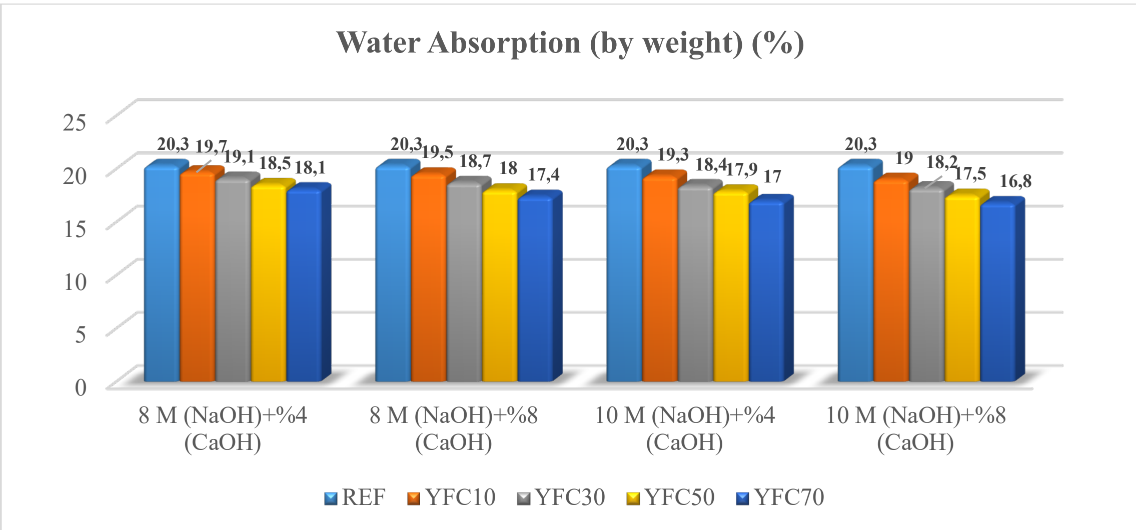

Figure 5. Graph of water absorption values

Compressive Strength

The compressive strength values of the samples produced within the scope of the study are given in Figure 6. When the graph is analyzed; it is seen that the compressive strength values of the reference sample vary between 4.3 MPa and the compressive strength values of the doped samples vary between 5.1-7.8 MPa. The lowest compressive strength of the doped samples was obtained from 8 M (NaOH) + 4% (CaOH) doped YFC10 samples with 5.1 MPa and the highest compressive strength was obtained from 10 M (NaOH) + 8% (CaOH) doped YFC30 samples with 7.8 MPa. The lowest compressive strength increased by 18.6% and the highest compressive strength increased by 81.4%. It was determined that the compressive strength increased as the sodium hydroxide and calcium hydroxide ratios increased. Al_2O_3 in the clay, CaO in fly ash and blast furnace slag interact with SiO_2 and contribute to the increase in compressive strength of 10 M (NaOH) + 8% (CaOH) doped YFC30 samples. These values obtained are similar when compared with other studies [24-26].

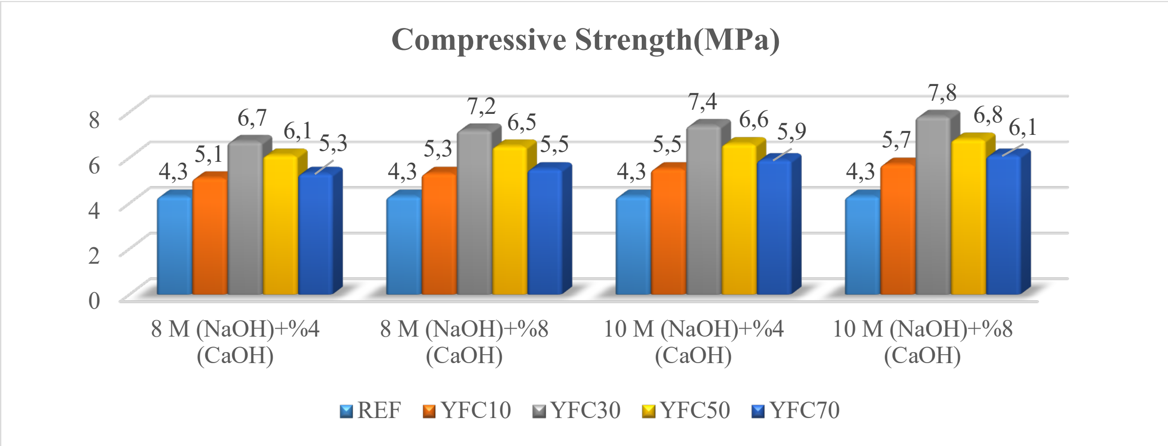

Figure 6. Graph of compressive strength values

Flexural Tensile Strength

The flexural tensile strength values of the samples produced within the scope of the study are given in Figure 7. When the graph is analyzed; it is seen that the flexural tensile strength values vary between 0.68 and 0.53 MPa. It was determined that the reference sample had the highest flexural tensile strength value with 0.68 MPa, while the samples with 10 M (NaOH) + 8% (CaOH) YFC30 additives had the lowest flexural tensile strength value with 0.53 MPa. As a result of the mechanical tests of the produced samples, it was determined that the optimum blast furnace slag additive was 30%.

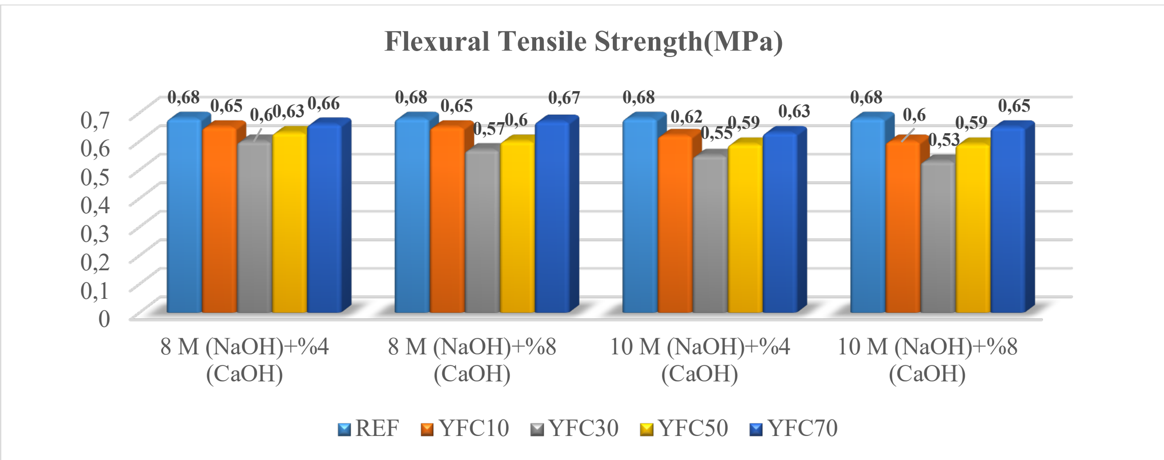

Figure 7. Graph of flexural tensile strength values

Analysis of SEM Images

SEM images showing the microstructure of the reference sample and YFC30 sample with 10 M (NaOH) + 8% (CaOH) concentration are given in Figure 8 and Figure 9. Since the sample with the highest compressive strength was the YFC30 sample with 10 M (NaOH)+8% (CaOH) concentration, the interpretation of the SEM image of this sample was preferred.

When Figure 8 is analyzed, it is seen that amorphous structures are dense and crystalline structures are rare. Dense amorphous structures transform into crystalline structures over time.

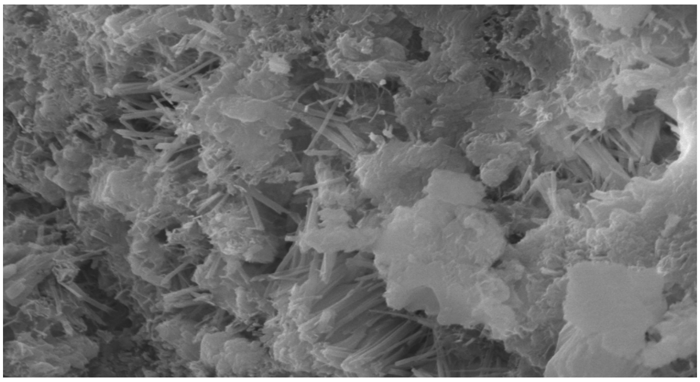

Figure 8. SEM image of the reference sample

Figure 9 shows that the waste material consists of coarse crystalline particles with irregular shapes and clear microstructure. The homogeneity in the microstructure of the geopolymer is clearly understood from the microstructure analysis as a dense and homogeneous matrix is formed. Also, the presence of air bubbles confined in the geopolymer can be seen. With the substitution of sodium hydroxide concentration, it can be seen that the coarse particles turn into finer particles and stick together. A well-formed, confined microstructure is developed, resulting in an amorphous microstructure. Calcium hydroxide shows that it forms a finer and homogeneous microstructure. The compressive strength test results and SEM images support each other. It was also revealed that the concentration of sodium hydroxide and calcium hydroxide contributed to the stability of the samples.

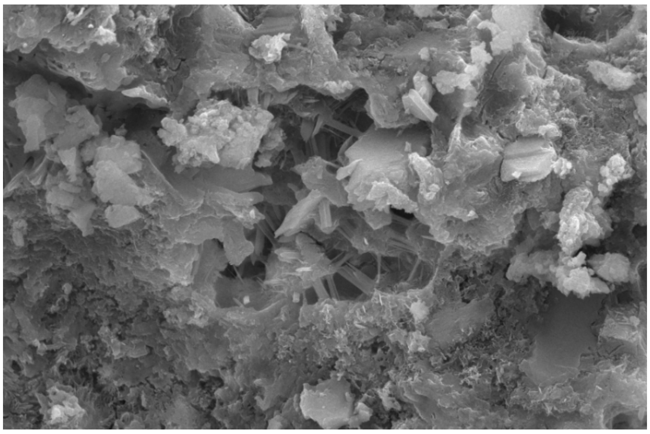

Figure 9. SEM image of YFC30 sample with 10 M (NaOH) + 8% (CaOH) concentration

CONCLUSIONS AND RECOMMENDATIONS

In this study, the objective is to produce fly ash based geopolymer bricks by using blast furnace slag, which is the waste of Karabük Iron and Steel Plant, and Seyitömer thermal power plant waste fly ash. It is aimed to produce a geopolymer brick with superior physical and mechanical properties compared to regular bricks and better thermal properties. In accordance with this purpose, geopolymer bricks were produced, related tests were carried out and the results obtained are listed below.

- In the samples with 8% M (NaOH) + 4% (CaOH) concentration, the lowest unit volume weight was obtained from the reference and the highest unit volume weight was obtained from the YFC70 samples. At this concentration, it was determined that the unit volume weight value increased with the increase of blast furnace slag.
- At 8% M (NaOH) + 8% (CaOH) concentration, the lowest unit volume weight was obtained from the reference samples and the highest unit volume weight was obtained from the YFC70 samples. At this concentration, it was determined that the unit volume weight value increased with the increase of blast furnace slag.
- In the samples with 10% M (NaOH) + 4% (CaOH) concentration, the lowest unit volume weight was obtained from YFC10 and the highest unit volume weight was obtained from YFC70 samples. At this concentration, the use of 10% blast furnace slag decreased the unit volume weight value, then the value increased as the blast furnace slag increased.
- In the samples with 10% M (NaOH) + 8% (CaOH) concentration, the lowest unit volume weight was obtained from YFC10 and the highest unit volume weight was obtained from YFC70 samples. At this concentration, the use of 10% blast furnace slag decreased the unit volume weight value, then the value increased as the amount of blast furnace slag increased. The unit weight values of YFC10 and YFC30 samples are below the value of the reference sample.
- At all concentrations, the water absorption rate decreased with increasing blast furnace slag substitution.
- At all concentrations, the compressive strength of geopolymer brick samples increased up to 30% blast furnace slag substitution, and the compressive strength decreased with further increase in the proportion of blast furnace slag.
- The flexural tensile strength values of geopolymer brick samples at all concentrations decreased up to 30% blast furnace slag substitution, and the flexural tensile strength continued to increase with further increase in blast furnace slag content.
- The optimum mix ratio for mechanical tests was determined to be 30%.
- In SEM images, it was seen that the reference sample, which had a crystalline structure, turned into an amorphous structure with the substitution of waste material.
- It is also believed that the waste materials stick to each other with the effect of sodium hydroxide, which may contribute to the compressive strength.
- The use of blast furnace slag and fly ash as brick making materials was found to be an economically viable option.
- It was determined that it is possible to produce geopolymer bricks using waste from aggregate industries by using appropriate preparation conditions (sodium hydroxide concentration, calcium hydroxide content).
- The use of waste as aggregate in brick production will be a very convenient and feasible method for waste disposal in terms of both environment and human health.

- Disposal of waste will reduce storage costs, which will benefit the economy of the enterprises.
- The use of waste as aggregate in brick production will ensure less consumption of soil that takes centuries to form.

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