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Engineering Characteristics of Geopolymer Mortars Manufactured with Ground Granulated Blast Furnace Slag

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Abstract: Geopolymers are obtained by various methods in different alkaline environments by changing compositions and crystal structures of pozzolans, which have Al and Si oxide compounds in their structures and carry little or no hydraulic characteristics. In this study, mechanical and physical characteristics of geopolymer mortars manufactured with ground granulated blast furnace slag (GGBFS) and activated with sodium silicate (water glass) were determined and also their SEM-EDS analyses were performed. As a result of the study, it was determined that geopolymers prepared with GGBFS can also be used in the areas where blast furnace slag cement would be used.

Öğütülmüş Yüksek Fırın Cürufu ile Üretilen Geopolimer Harçların Mühendislik Özellikleri

Anahtar Kelimeler
Geopolimer,
Yüksek fırın cürufu,
Aktivatör,
Sodyum silikat (cam suyu)

Özet: Geopolimerler, yapısında Al ve Si oksit bileşiği bulunduran, hidrolik özelliği olmayan veya çok az olan puzolanların, farklı alkali ortamlarda kompozisyonları ve kristal yapılarının çeşitli yöntemlerle değiştirilmesi sonucu elde edilirler. Bu çalışmada, Sodyum silikat (Cam Suyu) ile aktive edilmiş, öğütülmüş yüksek fırın cürufu (YFC) ile üretilen geopolimer harçların mekanik, fiziksel özelliklerinin belirlenmesinin yanı sıra SEM-EDS analizleri yapılmıştır. Çalışmanın sonucunda; yüksek fırın cüruflu çimentonun kullanılacağı alanlarda YFC ile hazırlanan geopolimerlerin de kullanılabileceği belirlenmiştir.

1. Introduction

As its raw materials are abundant in every geographical place, cement is widely used in building activities and it is the most widely produced material worldwide. The cement production in the world had increased 2.5 times in the last twelve years, and reached to 4.3 billion tones in 2014 from 1.8 billion tones in 2002. More increase in cement demand is also predicted in the following years. Within the next years, it is likely to have problems in supply of raw materials used in cement production. In production of one ton of cement, about one ton of carbon dioxide releases to the atmosphere, which is a big threat for environment. Also, a large amount of energy is required for cement production [1, 2]. Due to such reasons, in order to develop an alternative binder instead of cement by decreasing cement cost, altering or enhancing some cement characteristics, usage of pozzolans increase day by day.

Slags, which are a kind of pozzolans, are in the group of waste materials obtained from various metallurgical facilities. Their chemical compositions and characteristics differ from each other based on the main product type and the manufacturing method of the industry organization they were obtained from [3]. For instance, the slags of metals such as nickel or copper have only pozzolanic characteristics, whereas blast furnace slags (GGBFS) obtained by iron-steel production have the self-binding characteristics [4]. There are many places of use for GGBFS in cement and concrete industries [5]. Blast Furnace Slag has little hydraulic characteristics and its reaction with water is too slow and less effective compared with Portland cement. Therefore, GGBFS has to be activated with alkaline activators (NaOH, Na_2CO_3, KOH etc.) [6-8].

Materials produced as a result of changing compositions and crystal structures of natural minerals that has Al and Si oxide compounds in their structure are called geopolymers or inorganic

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polymers. Prof. Dr. J. Davidovits has defined and classified geopolymers for the first time in 1978 [9]. Geopolymers are formed by polycondensation of silicon molecules with aluminates at high pH alkaline environments. The crystal structure to be formed is effected by the raw materials in geopolymer reaction and Si/Al molar ratio of sialate and aluminate in the alkaline solution. Briefly, it affects the characteristics of the geopolymer material that would be formed. The geopolymer reaction starts at room temperature and after the desired mixture is provided, to increase the polymerization process, the mixture is exposed to heat processes by using different temperatures and different methods. By this way, several types of geopolymer materials can be produced [10, 11].

In literature, it can be seen that attempts on activating ground granulated blast furnace slag by using alkaline continues for over 70 years [12]. There are many studies investigating physical and mechanical characteristics and strength of mortars and concretes with slags that are activated by using different types of activators [6, 12-18], and use of slags as raw materials in geopolymer cement production [19-21].

In this study, it was aimed to produce ground granulated blast furnace slag geopolymer mortars that are activated with Sodium Silicate (Water glass). The mechanical and physical characteristics and microstructural properties of the produced geopolymer mortars were examined.

2. Material and Method

2.1. Materials

Ground Granulated Blast Furnace Slag (GGBFS): Chemical characteristics of fine ground granulated blast furnace slag supplied by Bolu Çimento A.Ş., which is produced in accordance with TS EN 15167-1 [22] standard, are given in Table 1 (Figure 1).

Table 1. Chemical characteristics of fine ground granulated blast furnace slag.

Chemical Composition (%)					
SiO_2	40.52	**Al_2O_3**	14.59	**Na_2O**	0.58
Fe_2O_3	1.10	**CaO**	34.18	**K_2O**	1.10
TiO_2	0.98	**MgO**	7.29	**SO_3**	0.16

Cement: CEM III/A (S) 32.5 N type Blast Furnace Slag Cement produced in accordance with TS EN 197-1 [23] standard was used (Figure 1).

Silica Sand: 40-45 AFS silica sand was used as sand in the tests. Particle size distribution and standard limit values of silica sand are given in Table 2 (Figure 1).

Table 2. Particle size distribution and standard limit values of silica sand

Sieve Size (Micron)	Acceptance Range (%)	Analysis Results (%)
+1000	0-1	0.3
710-1000	1-8	3.8
500-710	7-25	12.5
355-500	10-35	25.3
250-355	25-45	32.4
180-250	5-30	20.6
125-180	0-7	3.3
90-125	0-1	0.7
0-90	0-0.3	0.1
AFS	40-45	43.6 AFS
Clay	max: 0.25	0.19

Activator: In the production of samples, sodium silicate solution (Water Glass) was used as activator. The characteristics of the used activator are listed in Table 3 (Figure 1).

Table 3. Characteristics of Sodium Silicate (water glass) solution

Characteristics			
Physical State	Liquid	**Evaporation Rate**	>1 (ether=1)
Appearance	Not Available	**Viscosity**	Not Available
Odor	None reported	**Boiling Point**	100.6 deg C
pH	11.2	**Melting Point**	-0.6 deg C
Vapor Pressure	14 mm Hg	**Solubility**	Soluble in water
Vapor Density	0.7	**Specific Density**	1.4 g/cm^3
Chemical Formula		$Na_2O(SiO_2)x.\ (H_2O)x$	

Water: Potable water taken from municipal water system was used as water for mixture.

Figure 1. A) Ground Granulated Blast Furnace Slag (GGBFS) B) CEM III/A (S) 32.5 N Blast Furnace Slag Cement C) Silica Sand D) Activator

2.2. Method

2.2.1. Preparation of geopolymer mortars

Geopolymer mortars were produced by using GGBFS, activator, water and silica sand without cement. Activator was dissolved in water with the ratios given in Table 4 and different mixtures were obtained. Amount of substances that were included in the mixture and the codes given to the samples are listed in Table 4.

Table 4. Amount of substances that were included in the mixture for Geopolymer mortars (g)

batches	Cement (g)	GGBFS (g)	Activator (ml)	Water (ml)	Activator /Water	Silica Sand (g)
Mix1 (Ref)	450	0	0	225	0:3	1350
Mix2	0	450	225	0	3:0	1350
Mix3	0	450	150	75	2:1	1350
Mix4	0	450	75	150	1:2	1350
Mix5	0	450	0	225	0:3	1350

For preparation of mixtures, mixing procedure in TS EN 196-1 [24] standard was applied. To prepare the mixtures, firstly water and/or activator were placed into the mixing container and GGBFS or cement was added. The mixer was started to work at low speed and after 30 sec. sand was continuously added within 30 sec. The mixer was set to high speed and mixing was continued for 30 seconds more. The mixer was stopped after 1 minute 30 seconds and with the rubber stripper, the mortar adhered to the walls and bottom of the container were stripped and gathered into the middle of the container. Mixing was continued at high speed for 60 seconds more.

Initially, the prepared mortars were filled into the molds up to their half volume. Molds filled up to their half volume were kept at shaking table for 1 minute. After shaking procedure, the molds were completely filled and again put on the shaking table to be shaken for 1 min. Obtained mortar samples were placed into 50×50×50 mm cubic and 40×40×160 mm dimensioned molds.

48 hours after pouring, the samples were taken out form their molds and they were cured in air under laboratory conditions until the test day. No thermal processing was applied on the samples.

2.2.2. Tests on fresh geopolymer mortars

Consistency and density of fresh blast furnace slag geopolymer mortars activated with alkaline were determined by TS EN 1015-3 [25] and TS EN 12350-6 [26] standards, respectively.

2.2.3. Tests on hardened geopolymer mortars

Physical (density (TS EN 12390-7) [27], water absorption (ASTM C642 [28], capillary water absorption, porosity) and mechanical (compressive strength (TS EN 196-1) and flexural strength) tests were performed on hardened blast furnace slag geopolymer mortar samples activated with alkaline.

2.2.4. Examination of microstructure of hardened geopolymer mortar samples

To examine the physicochemical and structural changes on the reference sample and the geopolymer mortar with the best physical and mechanical characteristics, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analysis were made and their surface and mineral structure characteristics were determined.

3. Results

3.1. Consistency and workability values of fresh geopolymer mortar samples

Flow diameters and fresh density values obtained by the samples in the study are given in Table 5.

Table 5. Flow diameters and density values of fresh geopolymer mortars

	Mix1	Mix2	Mix3	Mix4	Mix5
Flow diameter (cm)	11.7	12.5	12.5	14.05	12.1
Change %	0	6.8	6.8	20.1	3.4
Density (kg/m^3)	2195	2322	2224	2196	2196
Change %	0	5.8	1.3	0.1	0.1

When table 5 is examined, the minimum flow diameter was found as 11.7 cm and this value was obtained by Mix1 (reference) mortar mixture. Other series has been evaluated with Mix1. Although Mix1 and Mix5 mixtures had similar flow diameters, other mixtures had greater flow diameters. This is considered to be due to the activators introduced to the mixtures. When the density values of the mixtures are compared, it is observed that the density values were similar except for Mix2. As water was not used but only activator was used, it is observed that the density value increased in Mix2 mixture.

3.2. Density, water absorption and capillary water absorption values of hardened geopolymer mortars

Density and water absorption values for geopolymer mortar samples for 28 days are given in Table 6.

Table 6. Density and Water absorption test results

	Mix1	Mix2	Mix3	Mix4	Mix5
Density (kg/m^3)	2144.0	2241.2	2219.2	2216.9	0.0
Water absorption (%)	8.43	5.84	6.70	7.99	0.00
Porosity %	16.70	12.39	13.97	16.44	0.00
Water absorption/ Porosity	0.50	0.47	0.48	0.49	0.00

As any strength could not be obtained for Mix5 batch, samples broke into pieces when handled. Therefore, in tests carried out with water, no values were obtained for this batch.

When Table 6 is examined, it can be seen that density values of samples (Mix2, Mix3 and Mix4) were between 2216.9 kg/m^3 and 2241.2 kg/m^3. In respect of density values with fresh mortars, the values were close to each other in every batch, excluding Mix2. However, for hardened geopolymer mortars, it can be seen that the density values were increased between 3.3-4.5% compared with reference sample. It is considered that the strength products formed due to polymerization caused this change.

The water absorption values of mortars depend on the porosity ratio as well as the status of the pores in both the mortar and the sand particles. In other words, if the pores were half-open or totally closed, the mortars would absorb less water. If the pores in the mortar or sand particles were open, they would be able to have the water absorption ability as much as the porosity ratio [29]. When the porosity values were examined, it is found that it had values changing between 12.39% and 16.70%. As it can be seen, the water absorption ratios were about 50% of the porosity values. In that case, it can be concluded that half of the pores were half open or totally closed.

Capillary water permeability test were performed in accordance with ASTM C 1585 standard [30]. Capillary permeability tests were made on 3 samples of each and initial rate capillary permeability coefficients of the mortars were found (Figure 2).

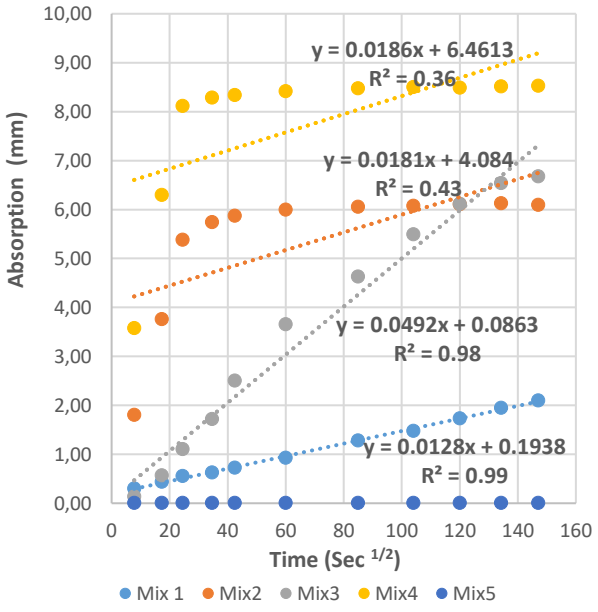

Figure 2. Capillary water permeability values of geopolymer mortars

When Figure 2 is examined, it was found that initial rate capillary permeability coefficients of Mix1 and Mix3 were 1.28×10^{-2} and 4.92 ×10^{-2}, respectively. In the related standard, in determination of initial rate capillary permeability coefficients, it is stated that if a linear correlation cannot be found for the data between 1 minute to 6 hours (a correlation coefficient smaller than 0.98) and a systemic curve is demonstrated, the initial absorption rate cannot be determined. [30]. Therefore, as Mix2, Mix4 and Mix5 batches could not provide the correlation coefficient condition (0.98) in the standard, their capillary water permeability coefficients couldn't have been determined. When Mix2 and Mix4 batches were examined, it was seen that they reached saturation in the first 30 minutes and the curve progresses as a straight line. It can be said that Mix2 and Mix4 batches have greater diameters of capillary water channels and the air voids captured in the samples are connected to each other with the capillary water channels.

3.3. Compressive strength and flexural strength values of hardened geopolymer mortars

In accordance with TS EN 196-1, graphical demonstrations of 7 and 28 days of mean compressive and flexural strength values of geopolymer mortars are given in Figure 3.

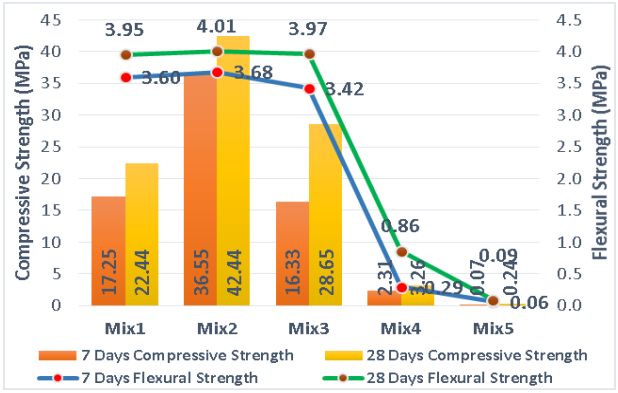

Figure 3. Mean compressive and flexural strength values of geopolymer mortars

When obtained results are examined, it can be seen that as the water amount increased in the solution prepared by adding water to the activator, the compressive strength values decreased. Also, it is observed that based on the sample age, the compressive strength values increased. When 7 days of compressive strength were examined, compared with the reference sample (Mix1), Mix2 (36.55 MPa) batches had the highest strength value with 111.93% strength increase. Smaller values than the reference (Mix1) batch were obtained by other batches. When 28 days of compressive strength were examined, compared with the reference sample (Mix1), Mix2 (42.44 MPa) batches had the highest strength value with 89% strength increase and Mix5 batches had the minimum strength value (0.24 MPa). Mix3 batches had shown similar strength characteristics as reference (Mix1). As a result, when water glass is

used as activator, it was observed that the mortar samples prepared with 100% water glass and GGBFS achieved the maximum strength. To produce geopolymer mortar, the ratio of water glass and water mixture solution should be selected to be greater than ½. In mortar batches that were obtained by only water and GGBFS (Mix5), a value smaller than 0.25 MPa was obtained. This case is in accordance with the pozzolan definition which describes that it has very little or no binder characteristics by its own. [31].

As it can be seen in Figure 3, flexural strength of samples showed similar characteristics as their compressive strengths. 7 days of flexural strength values of Mix1, Mix2 and Mix3 batches were 3.60 MPa, 3.68 MPa and 3.42 MPa, respectively whereas 28 days of flexural strength values of Mix1, Mix2 and Mix3 batches were 3.98 MPa, 4.01 MPa and 3.97 MPa, respectively. For Mix4 and Mix5 batches no significant strength could be obtained.

3.4. Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) Analysis

SEM and EDS analyses of Blast Furnace Slag cement (Mix1) and geopolymer paste prepared with blast furnace slag (Mix2) on 28th day of hydration, are given in Figure 4, 5, 6 and 7.

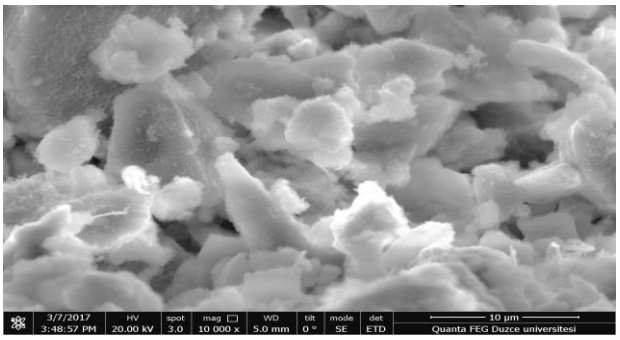

Figure 4. SEM image of Mix1 batch

The main structure of blast furnace slag is made up of crystallized and locally acicular C-S-H phase. Amorphous gel had been the major phase throughout the whole structure, formed a link between hydration products, and tried to fill up the voids, however local voids having 1 to 5 microns of lengths had been seen.

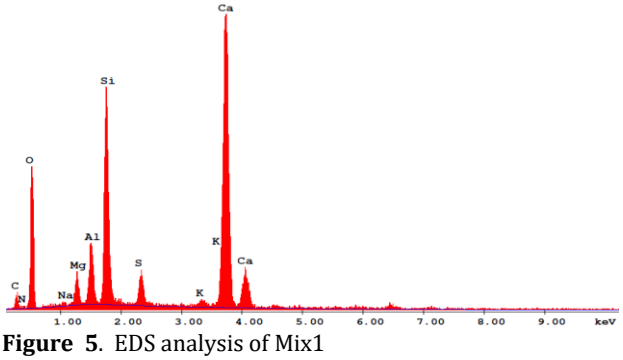

Figure 5. EDS analysis of Mix1

EDS spectrum on the surface of the hydrated blast furnace slag cement paste showed that the composition of the layers on the surface was mainly consisted of Ca and Si.

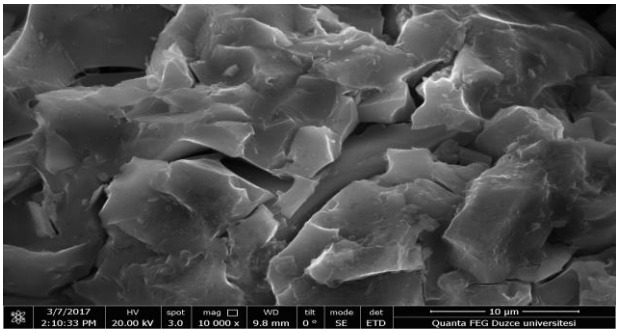

Figure 6. SEM image of Mix2 batch

In SEM image of Mix2 coded paste, C-S-H phase, which dominates to the structure, was seen. This phase tried to fill up the voids, but though there were a few of them, there were seen local voids having lengths of 1-2 microns.

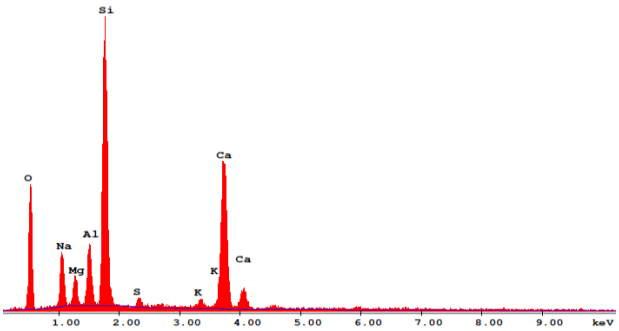

Figure 7. EDS analysis of Mix2

EDS spectrum had shown that the composition of surface layer was consisted of mainly Si and Ca, respectively.

4. Discussion and Conclusion

In this study, physical, mechanical and inner structural characteristics of geopolymer mortars with ground granulated blast furnace slag activated with sodium silicate (water glass) were investigated. The following results were obtained as a result of this study;

- As the water amount in the solution obtained by adding water on sodium silicate solution (water glass) increased, the compressive strength decreased.
- When sodium silicate solution (water glass) is used as activator, the mortar samples prepared with 100% water glass solution and GGBFS had obtained the maximum strength (42,44 MPa).
- To produce geopolymer mortar, the ratio of water glass and water mixture solution should be selected to be greater than ½.

- In mortar batches that were obtained by only water and GGBFS (Mix5), a value smaller than 0.25 MPa was obtained. This case is in accordance with the pozzolan definition which describes that it has very little or no binder characteristics by its own.
- When SEM images were examined, it was seen that compared to reference (Mix1) sample, Mix2 batch had a more compact structure. This was also supported with less density and water absorption amount of Mix2.
- When SEM and EDS analysis of Mix1 and Mix2 were analyzed, it was observed that they had similar compositions having Si and Ca, and C-S-H phases were dominant.
- As geopolymer mortars can be produced without the need for curing process, it can be said that they are favorable compared with mortars produced with blast furnace slag cement. So, in hot days, without getting extra precautions, the cement can be poured.
- GGBFS, which is an industrial waste, can be used in mortar or concrete production.
- With its shown performance, geopolymers prepared by GGBFS can also considered to be used in the areas where blast furnace slag would be used.

References

[1] Aleem, M. I. A., Arumairaj, P. D. 2012. Geopolymer Concrete-A Revıew. International Journal of Engineering Sciences & Emerging Technologies. 1(2), 118-22.

[2] Köleli, Y. 2015. TR63 Bölgesi Çimento Sektör Raporu. Doğu Akdeniz Kalkınma Ajansı: Doğu Akdeniz Kalkınma Ajansı.

[3] Tokyay, M., Erdoğdu, K. 2009. Cüruflar ve Cüruflu Çimentolar. TÇMB / AR-GE / Y 972. Ankara: TÇMB.

[4] Baradan, B., Yazıcı, H., Aydın, S. 2012. Beton. İzmir: Dokuz Eylül Üniversitesi Mühendislik Fakültesi Yayınları.

[5] Dorum, A., Koçak, Y., Yılmaz, B., Uçar, A. 2009. The Effects of Blast Furnace Slag on the Cement Surface Properties and Hydration. Journal of the Institute of Science and Technology of Dumlupinar University. 19, 47-58.

[6] El-Didamony, H., Amer, A. A., El-Sokkary, T. M., Abd-El-Aziz, H. 2013. Effect of substitution of granulated slag by air-cooled slag on the properties of alkali activated slag. Ceramics International. 39(1), 171-81.

[7] Praveen, J. A., Senthilkumar, P., Sridhar, J., Nickson, S. 2015. A Comparative Study of Alkali Activated Slag and Fly Ash-Based Geopolymer Concrete. International Journal of Innovative Research in Science, Engineering and Technology. 2001, 10151-10156.

[8] Universit, B., Benbouali, H. 2009. Some Parameters Affecting the Heat of Hydration of Blast-Furnace Slag. SBEIDCO – 1st International Conference on Sustainable Built Environment Infrastructures in Developing Countries ENSET. (Durability of materials and structures), 8-16.

[9] Davidovits, J. 1991. Geopolymers: Inorganic Polymeric New Materials. Journal of Thermal Analysis. 37, 1633-1656.

[10] Xu, H., Van Deventer, J. S. J. 2000. The geopolymerisation of alumino-silicate minerals. International Journal of Mineral Processing. 59(3), 247-266.

[11] Görhan, G., Kürklü, G. 2014. Alkali Tuz İçeriğinin Geopolimer Cephe Kaplama Malzemesi Özelliklerine Etkisi. 7 Ulusal Çatı & Cephe Sempozyumu. İstanbul, 51-58.

[12] Altan, E., Erdogan, S. T. 2012. Alkali activation of a slag at ambient and elevated temperatures. Cement Concrete Comp., 34(2), 131-139.

[13] Chi, M. 2012. Effects of dosage of alkali-activated solution and curing conditions on the properties and durability of alkali-activated slag concrete. Construction and Building Materials. 35, 240-245.

[14] Dutta, D., Ghosh, S. 2014. Durability Study of Geopolymer Paste Blended with Blast Furnace Slag. IOSR Journal of Mechanical and Civil Engineering, 11(2), 73-79.

[15] Madheswaran, C. K., Gnanasundar, G, Gopalakrishnan, N. 2013. Effect of molarity in geopolymer concrete. International Journal of Civil and Structural Engineering, 4(2), 106-115.

[16] Krishnan, L., Karthikeyan, S., Nathiya, S., Suganya, K. 2014. Geopolymer Concrete an Eco-Friendly Construction Material. IJRET: International Journal of Research in Engineering and Technology, 2319-2322.

[17] Ramani, P. V., Chinnaraj, P. K. 2015. Geopolymer concrete with ground granulated blast furnace slag and black rice husk ash. GRAĐEVINAR, 67, 741-748.

[18] Mathew, B. J., Sudhakar, M., Natarajan, C., Ash, B. 2013. Strength, Economic and Sustainability Characteristics of Coal Ash – GGBS Based Geopolymer Concrete. International Journal of Computational Engineering Research, 3, 207-212.

[19] Bakharev, T., Gnananandan, J., Cheng, Y. B. 1999. Alkali activation of Australian slag cements. Cement and Concrete Research, 29, 113-120.

[20] Allahverdi, A. L. I., Kani, E. N., Yazdanipour, M. 2011 Effects of Blast-Furnace Slag on Natural

Pozzolan-Based Geopolymer Cement. Ceramics – Silikáty, 55(1), 68-78.

[21] Angulo-ramírez, D. E., Mejía, R., Gutiérrez, D., Puertas, F. 2017. Alkali-activated Portland blast-furnace slag cement : Mechanical properties and hydration. Construction and Building Materials, 140, 119-28.

[22] TS EN 15167-1. 2006. Ground granulated blast furnace slag for use in concrete, mortar and grout - Part 1: Definitions, specifications and conformity criteria. Turkish Standards Instituion, 23.

[23] TS EN 197-1. 2012. Cement - Part 1: Composition, specifications and conformity criteria for common cements: Turkish Standards Instituion, 2012.

[24] TS EN 196-1. 2016. Methods of testing cement - Part 1: Determination of strength. Turkish Standards Instituion, 35.

[25] TS EN 1015-3/A2. 2007. Methods of test for mortar for masonry - Part 3: Determination of consistence of fresh mortar (by flow table) Turkish Standards Instituion, 5.

[26] TS EN 12350-6. 2010. Testing fresh concrete - Part 6: Density Turkish Standards Instituion, 12.

[27] TS EN 12390-7. 2010. Testing hardened concrete - Part 7: Density of hardened concrete. Turkish Standards Instituion, 11.

[28] ASTM C 642-13. 2013. Standard Test Method for Density, Absorption, and Voids in Hardened Concrete. West Conshohocken, PA,: ASTM International.

[29] Uygunoğlu, T. 2008. Properties of Self-Compacting Concrete with Lightweight Aggregate. Isparta: Süleyman Demirel University.

[30] ASTM C1585 - 04. 2004. Measurement of Rate of Absorption of Water by Hydraulic- Cement Concretes. West Conshohocken, PA,: ASTM International, 6.

[31] Newman, J., Choo, B. S. 2003. Advanced Concrete Technology 1: Constituent Materials: Elsevier Science.