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A reuse study from Niğde, Turkey: the conversion of industrial ash to geopolymer

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ABSTRACT

Coal is used to generate power for industrial operations. Two types of industrial ashes, including fly and bottom ash, which are solid residues arising from coal burning, are dumped to the landfill of Niğde from a selected large-scale international firm named as Göknur A.Ş in Niğde, Turkey with no care for reuse. Geopolymer production was chosen from different alternatives of productive reuse of these waste materials. The properties of the geopolymers are dependent on source materials. Therefore, the first part included elemental analysis of ashes, sieve analysis of them, compacted bulk density analysis of them, and reaction affinity of them. The chemical composition of industrial ash used in this study contained Si and Al accompanied by Ca and Fe. This character has important implications on the potential for productive reuse and reaction potential of these waste materials. The second part of the research is planned to include ashes analysis for calculation of efficiency of combustible matter, experiment of obtaining samples from ashes in different thermal processes, activation of ashes with sodium hydroxide and sodium silicate, activation of ashes with Portland cements, pressure and resistance evaluations for geopolymer samples, water absorption experiment to them, and porosity experiment for them. Considering pressure and resistance, water absorption and porosity experiments, by only a few studies in the literature, higher-strengthened geopolymer is produced at temperatures of 100 and 150°C.

Keywords: Ash; Cement; Concrete; Environment; Geopolymer; Industry; Reuse

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1. Introduction

In industrial applications, the process of raw material and production is based on a single support and waste generations in most industrial organizations are an inevitable result. Fly ash (FA) and bottom ash (BA) as industrial wastes are released during combustion of coal used for the energy required to meet the needs of industrial companies. These wastes consist of environmental and technical issues which are needed to be resolved.

Depositing or disposal of these wastes leads to significant environmental pollution. Some environmental problems of the FA are dust, damaging agricultural products, rain and wind erosion, radiation, and infiltration of toxic substances in soil. Therefore, environmentally undesirable results occur concerning agricultural products, water and air quality, wildlife, and the region's economic status [1–3]. Using FAs in various areas and gaining them to the country's economy seem to be possible if solutions to these problems are found. Due to its fine formation, pozzolan property, and the one-dimensional spherical structure, the FA is resistant to freezing and thawing and is preferred as building material [4]. Therefore, construction industry mainly comes first among the sectors using the FA [2,5–7]. The FAs are used in the production of cement, concrete, aggregates, adobe, brick, gas concrete and insulation material and in the construction of dam and road, and in geotechnical applications. The production of cement is one of the areas most commonly used in the construction industry due to cost reduction, energy conservation, and environmentally friendly behavior. The FAs are used as additive and substitute material in both normal and lightweight concrete as well as in ready-mix concrete whose use is increasingly getting widespread in the production of pre-production and pre-stressed concrete elements [5,8–10], as a water trapping additive in concrete [11–13].

Regarding the use of the FAs in the construction industry, studies usually focus on cement and concrete in the world [14–17]. When the FA is used in concrete mixtures, both durability and increase in strength of the concrete are obtained [4,18]. In order to reduce the heat of hydration of the concrete, the FA is used in the construction of many dams in Turkey and in the world [4,13,19–21]. The examples of using the FA in the constructions are Castor and Pollux skyscrapers in Frankfurt and Picasso skyscrapers in Madrid (between 20 and 40% FA were used in various parts of them), building of Caixa Gérai Deposite Bank in Lisbon, Great Bell East Bridge in Denmark, Permantokoski Hydroelectric Power Plant in Finland, Puylaurent Dam in France, runways of Eindhoven Airport in the Netherlands, underground railway tunnels in Austria, aboveground utility poles in Italy, and Tornes Nuclear Power Plant in Scotland [22].

It is estimated that 600 million tons/year FA are produced in the world. Less than 25% of this total amount is used; only 10% of it is used in concrete technology [23]. More than 95% of the FAs produced are used by Germany, the Netherlands and Belgium, and almost 50% of the FAs produced are used in the UK [24,25]. On the other hand, the FA is produced in large quantities in the USA and the Republic of China, almost 40 and 32% of them are used, respectively [25]. Utilization rate of the FA is less than 1% in Turkey [16].

Nowadays various industrial wastes, particularly ashes are used as pozzolanic material in concrete [26]. Pozzolana is a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form and in the presence of water, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. The broad definition of pozzolana imparts no bearing on the origin of the material, only on its capability of reacting with calcium hydroxide and water [27,28]. Pozzolanic material addition in concrete or cement obtains many known benefits such as reduction of heat of hydration, providing high strength and low permeability, control of alkali–silica reaction and sulfate effect, and obtaining more porous bricks [29,30].

In his study done in 1998, Bayat compares mineralogical, morphological, physical, and chemical properties of seven different FA samples obtained from lignite and bituminous coal fields of east-central and western parts of Turkey. He investigates the FA's distribution of density, solubility, and pH characteristics in water and suggests the FA can be used as a binder in cement [31].

According to Yiğiter and the study of his working group in 2004, it was found that compressive strength of standard curing concrete specimens for 1 d decreased when the FA ratio increased, but the next stages (3 d after) this difference had disappeared and compressive strength of standard curing concrete specimens increased with increasing the FA ratio. Compressive strength and modulus of elasticity of air curing samples were found significantly lower than those of standard curing samples in water. This indicated that the FA containing mixtures has sensitivity of the cure [32].

In their study in 2005, Ural and his colleagues determined that the FAs released from Afşin Elbistan Thermal Power Plant included mainly CaO, SiO_2, Fe_2O_3, and Al_2O_3 (74–85%). Hematite, quartz, and anhydrides were found in the ashes of bottom part of coal, limestone, and anhydrite were found in the ashes of middle part of the coal, gehlerit and melilit crystals were found in the ashes of upper part of the coal. C_3A, C_4AF, and βC_2S minerals -also existed in cement- were determined in all three ashes. As a result, they suggested the ashes of bottom part of the coal could be used to produce low-calcium oxide content class F cement, ashes of middle and upper part of the coal could be used to produce high-calcium oxide content class C cement, ashes of bottom part of the coal could be used in glass–ceramics industry, all of the ashes could be used in soil stabilization [33].

Karahan and Atış (2007) reported that the FAs were used in the production of cement as pozzolanic additives and with the cement as the secondary binder to concrete, in the production of brick and building block, in the production of artificial aggregate, in injection practices, as filling material, and in soil improvement. They investigated availability of the FAs of the Sugözü Thermal Power Plant as a concrete additive [34].

It was determined in Zeybek's (2009) study that compressive strengths of geopolymeric bricks produced using class C FA of thermal plant were between 8 and 13 N/mm^2 (MPa). Only 7 d compressive strengths were measured 11, 12, and 11 MPa, respectively, in geopolymer bricks produced as a result of heat treatment in the oven of 60˚C at 2, 24, and 72 h to Class C FA-sodium hydroxide-sodium silicate mixture [35].

In terms of environmental technologies, in the pyramid of waste management hierarchy, conversion of waste to another product is named as reuse. Each year very large quantities of ashes are released as waste from power plants and various industrial organizations during coal burning. Therefore, development of new using areas for these wastes is required under the concept of industrial ecology. Instead of dumping of these industrial wastes, converted them to geopolymer would be a minimized existing pollution in the environment.

In terms of new and advanced technology, conversion of waste ash to geopolymer has acquired an important place in recent years. Geopolymer is a good alternative to the solution of environmental problems based on the waste ashes in the national and international scale. In addition to its economic benefits, it is suitable for industrial symbiosis.

In this study, geopolymer production was chosen from different alternatives of productive reuse of the waste ashes. Because geopolymer is a form of cementitious materials using silicon and aluminum activated in high alkali solution based on ash as source material and it is an environmentally friendly choice against Portland cement releasing a large amount of greenhouse gas to the atmosphere during energy intensive manufacturing process. Geopolymer has thermoset polymer structure resulting from polycondensation. Found in high amounts in the material, the oxide compounds of Al and Si compose monomers that provide binding and volume. Process of geopolymer is polymerization process that is not fusion, sintering, or melting process. Geopolymer has reached monolithic ceramic structure after the heat treatment. Geopolymers exhibit many excellent properties such as high compressive strength, low creep, good acid resistance, and low shrinkage [36,37].

The objective of this study is the conversion of industrial ashes that include BA and class F FA to higher strengthened geopolymer. In the study, geopolymeric concretes were produced using these industrial ashes. Compressive strengths of these geopolymer concretes were measured in a larger time interval (1, 7, and 28 d).

2. Materials and methods

2.1. Material

The materials, which are aimed to be investigated by this study, were supplied from a large-scale international firm named as Göknur A.Ş in Niğde, Turkey. Approximately four tons/d (1,500 tons/year) of industrial ashes (both FA and BA) are released due to burning of coal used to generate power for industrial operation and are dumped to the landfill of Niğde Municipality from this firm. The materials used in geopolymer production are given in Table 1.NaOH of 10–20% and Na_2SiO_3 mixing samples were loaded into the mold by fogging. As 30–40% mixing samples formed plastic consistency, they were placed directly into the mold.

Elemental analysis of these industrial ashes was done in accredited laboratory based on standard test methods of EPA 3051A (microwave digestion "pre-processing") and EPA 2007 (ICP-OES analysis) and the results are given in Table 2.

After reaching to an oven dry condition, samples of both FA and BA were sieved with 500 μm and then filled and hit until no changes were observed in 500 mL measuring cylinder to 200 g sample ± 0.1 g accuracy. Therefore, the volume of the sample was obtained in this measuring cylinder. On the other hand, the compacted bulk densities of the samples were determined by dividing volume to weight [38]. 10 ± 0,05 g samples that passed from 500 μm pore sized sieve were weighed in pre-dried and already tared crucibles. The crucibles were placed in

Table 1
The amount of industrial ashes (FA and BA) and mixing ratios of NaOH and Na_2SiO_3 used in this study

Sample mold (cm)	FA by volume (cm^3)	FA by weight (g)	NaOH mixing by volume (cm^3)				NaOH mixing by weight (g)			
			10%	20%	30%	40%	10%	20%	30%	40%
16 × 4 × 4	350	206.5	35	70	105	140	45.5	91	136.5	182
			Na_2SiO_3 mixing by volume (cm^3)				Na_2SiO_3 mixing by weight (g)			
16 × 4 × 4	350	206.5	35	70	105	140	50.4	100.8	151.2	201.6
			NaOH mixing by volume (cm^3)				Na_2SiO_3 mixing by volume (cm^3)			
16 × 4 × 4	350	206.5	35	70	105	140	35	70	105	140

Table 2
The percentage of chemical composition of industrial ashes (FA and BA) used in this study

Elements	FA (%)	BA (%)
Al_2O_3	12.68	2.44
CaO	39.31	90.77
Fe_2O_3	8.23	2.50
K_2O	0.43	0.54
MgO	0.74	1.53
Na_2O	1.88	0.34
SiO_2	27.36	0.79
SO_3	5.94	0.32
Other	3.43	0.77

controlled electric oven at 800 ± 25°C and kept there for one hour. The crucibles were cooled to room temperature in the desiccator and weighed to find combustible materials of the samples [39,40]. Experiments were conducted three times and arithmetic means were calculated. Bulk density and combustible materials of both FA and the BA were found as $\gamma = 0.59\ t/m^3$, 43% and $\gamma = 1.21\ t/m^3$, 14%, respectively. Sieve analysis of these industrial ashes was given in Figs. 1 and 2. Accordingly, particle distribution of 75% of FA is below 500 μm and particle distribution of 95% of BA is above 500 μm. The percentage of combustible material was calculated by this equation: Combustible material % = First weight − Last weight/First weight × 100.

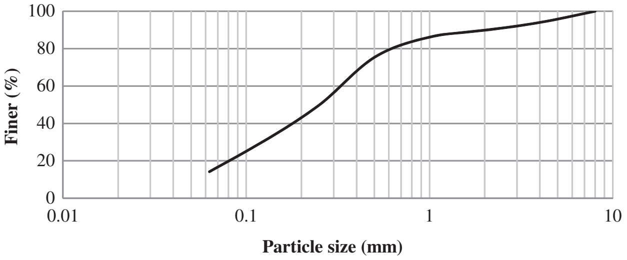

Fig. 1. Sieve analysis for the FA.

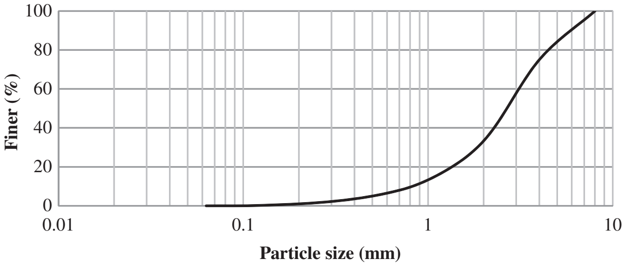

Fig. 2. Sieve analysis for the BA.

In this study, sodium silicate and sodium hydroxide were used as chemical activators. Sodium silicate is $1.44\ g/cm^3$ in density while sodium hydroxide is $1.30\ g/cm^3$ in density. The molar ratio of SiO_2/Na_2O is 13.34 for the sodium silicate and the molarities of the sodium silicate and sodium hydroxide are 11.40 and 52.72, respectively. TS EN 771-2 standard series [41–44] were used in the experiments done for geopolymer lightweight building material.

2.2. Method

After receiving from industry, the ashes were used without any treatment. Producing steps are mixing, forming the samples, drying, and determination of baking properties, respectively. Sodium hydroxide and sodium silicate were used as chemical activators (binding chemicals). In a mixture of the sample volume calculation was made because activators and filled material for the ashes were very different from each other. Viscosity of the mixture was not taken into account in the mixture. Plastic form was obtained from the mixture by adding water in 30% by volume. Water was not added in samples of 40% ratio. Mixing for 5 min was made in table-type mixer on low speed, then the samples were formed in sample containers measuring 4 × 4 × 16 cm. After setting the oven to dry condition, dried samples that were placed into molds were removed from the molds and were subjected to baking (heat treatment). Preliminary studies determined that baking time did not affect physical properties for the product; therefore baking processing time for all samples was fixed at 24 h. In the study, 15 samples for each mix were produced. Arithmetic mean was calculated to determine physical properties of the three samples. Producing and mixing parameters for the samples are given in Table 3.

3. Obtaining the sample

Depending on the used coal type, BA was used in obtaining the samples which contain high amount of lime (CaO). Two classes of FAs have been defined by American Society for Testing and Materials (ASTM) C618: Class F FA and Class C FA [45]. The main difference between these two classes is related to the amounts of calcium, silicon, aluminum, and iron content in the ash. The chemical properties of the FA are largely influenced by the chemical contents of the burnt coal (i.e. anthracite, bituminous, and lignite). The FA is pozzolanic in nature, and contains less than 20% lime. Possessing pozzolanic properties, the glassy silicon, and aluminum of Class F FA require a cementing agent, such as Portland cement, quick lime, or hydrated lime, with the presence of water in order to react and produce cementitious compounds. Alternatively, the addition of a chemical activator such as sodium silicate to a Class F ash can lead to the formation of a geopolymer [46]. In this study, Class F FA that requires a cementing agent such as Portland cement or chemical activator like sodium silicate was used.

Each sample stirred at the same condition was poured into the molds in size of 4 × 4 × 16 cm. After setting the oven to dry condition it was realized that conformational integrity of the samples were preserved and then each set was enumerated. Heat

Table 3
Mixing parameters for the samples

Type of ash	Sample no.[a]	NaOH (%)[b]	Sample no.[a]	Na_2SiO_3 (%)[b]	Baking temperature (°C)	Sample number
FA	FA_{H1-100}	10	FA_{S1-100}	10	100–150–200–250–300–350–400–450–500–550–600–650	180 pieces + 180 pieces
	FA_{H2-100}	20	FA_{S2-100}	20	100–150–200–250–300–350–400–450–500–550–600–650	180 pieces + 180 pieces
	FA_{H3-100}	30	FA_{S3-100}	30	100–150–200–250–300–350–400–450–500–550–600–650	180 pieces + 180 pieces
	FA_{H4-100}	40	FA_{S4-100}	40	100–150–200–250–300–350–400–450–500–550–600–650	180 pieces + 180 pieces
BA	BA_{H1-100}	10	BA_{S1-100}	10	100–150–200–250–300–350–400–450–500–550–600–650	180 pieces + 180 pieces
	BA_{H2-100}	20	BA_{S2-100}	20	100–150–200–250–300–350–400–450–500–550–600–650	180 pieces + 180 pieces
	BA_{H3-100}	30	BA_{S3-100}	30	100–150–200–250–300–350–400–450–500–550–600–650	180 pieces + 180 pieces
	BA_{H4-100}	40	BA_{S4-100}	40	100–150–200–250–300–350–400–450–500–550–600–650	180 pieces + 180 pieces

[a] FA and BA refers to fly ash and bottom ash, H ve S in subscribe refers to mixing of NaOH ve Na_2SiO_3, 1 refers to percentage of mixing, 100 refers to baking temperature.

[b] Percentage of mixing NaOH and Na_2SiO_3 for the FA and the BA.

treatment on the samples was carried out in an oven of 200 dm^3. For baking of FA_H, FA_S, BA_H, and BA_S samples in equal conditions, 16 × 15 = 240 samples were placed in the oven that provide heat circulation and cured for 24 h. In this study, the temperature was increased in every 4˚C/min for each sample to minimize thermal stresses until the baking temperature and this time was not included in the baking time.

In this study, thermal heat process was scheduled up to 650˚C. There was no observed deformation in the samples of FA and BA from 100 to 300˚C. Partial shedding was started and cracks were observed in the samples baked at 350˚C. Breakup in 80% ratio was observed in 400˚C in two samples from the FA and the BA. Samples produced at baking temperatures of 500 and 600˚C were completely broken up and converted to ashes again.

The samples from the FA and the BA were baked at 850˚C in the period of 12 and 24 h considering positive results reported in the literature at 850˚C. The samples were not broken up at both temperatures, but they melted and underwent large deformations without conformational integrity.

4. Experimental study

The experiments were conducted at temperatures below 100˚C, as well, but no activations were observed due to raw material that was used. Each sample in chemical composition of FA_H, FA_S, BA_H, and BA_S produced in baking temperatures from 100 to 300˚C was evaluated in experimental studies. Because it was observed that other samples did not provide sufficient conformational integrity. Physical properties were determined by making experimental studies on the samples displayed solid. Obtained results were summarized in Table 4.

Formal appearance of the samples produced from the FA is extremely smooth and have high compactness. Bulk density of fly ash is low, so the bulk densities of the samples were found in lightweight construction materials standard. Since granulometry of the FA that has particle diameter of greater than 95% 500 μm and has not been compressed under press during production, porous material is formed. Unlike thoughts, bulk density of the material was more, but bulk density of product came quite close to bulk density of the FA samples and became as standard in lightweight construction materials.

The samples were brought to the oven dry condition. After obtaining experimental data, water absorption percentages of the samples by weight were calculated using the formula below: water soaked sample weight − oven dry sample weight oven dry sample weight × 100. On the other hand, weights of the samples in water were found in the Archimedes scale. Water absorption percentages of the samples by volume were calculated, which were also apparent porosity [47]. Although the water absorption percentages of the FA samples were expected to be low as they appeared, it was determined to absorb water in high-rate percentages. The water absorption percentages of the BA samples were higher as expected from their appearance. However, they released water entering their body in very short time.

The BA contains 39% calcium and this calcium converts to quicklime (CaO) during sample production; therefore, complete disintegration was observed where the samples were water saturated. The resulting product did not withstand external effects. As shown in Table 4 it was not achieved the appropriate samples from the BA.

After brought to air dry condition, samples were placed as flat surfaces facing the press jaw. Loading was performed in 2% loading speed of bearing surface area. Breaking load was determined and then compressive strength was calculated by dividing breaking load to bearing surface area [48]. Taking compressive strength values into account, it was observed that the material could be used as construction material for wall elements. The samples were brought to water saturated condition for 24 h. Having been kept at −15˚C for 2 h, they dissolved in water in an hour. This process was repeated for 50 times. Pressure loss value of freezing test was calculated using the formula below: compressive strength − compressive strength after freezing compressive strength × 100. After subjected to the freezing test [49], capillary cracks were observed in the samples. After the test, compressive strength was measured again and any value was found (The press used in the experiment was not read values below 1 MPa). Visually optimized FA values are given from Figs. 3–15 to interpret the values given in Table 4.

The samples produced from the BA, not having even compressive strength (minimum 2.5 MPa) of constructive light building materials standards and not resisting from outside influences even water, were not shown graphically.

Shown in Figs. 3 and 4, as parallel to mixing ratio of the samples, bulk density increase was found in the samples prepared with the FA and NaOH and Na_2SiO_3 activators. It was also shown that bulk density was not affected by the baking temperature.

As shown in Figs. 5 and 6, optimum compressive strength [48] were found in the samples having 20% mixing ratio at the value of 11.26 MPa (for samples preparing with NaOH activator) and 9.11 MPa (for

Table 4
Physical properties of the obtaining samples

Type of ash	Sample no.[a]	Bulk density $(\gamma = g/cm^3)$[b]	Water absorption (%)[c]	Compressive strength (MPa)[d]	Sample no.[a]	Bulk density $(\gamma = g/cm^3)$[b]	Water absorption (%)[c]	Compressive strength (MPa)[d]
FA	FA_{H1-100}	0.58	58	4.90	FA_{S1-100}	0.61	68	3.00
	FA_{H2-100}	0.62	54	7.30	FA_{S2-100}	0.64	64	9.00
	FA_{H3-100}	0.72	52	5.45	FA_{S3-100}	0.88	64	7.65
	FA_{H4-100}	0.74	45	5.00	FA_{S4-100}	0.92	62	4.80
	FA_{H1-150}	0.60	56	5.85	FA_{S1-150}	0.71	66	5.85
	FA_{H2-150}	0.64	58	11.26	FA_{S2-150}	0.76	62	9.11
	FA_{H3-150}	0.74	46	7.75	FA_{S3-150}	0.86	60	4.37
	FA_{H4-150}	0.81	40	7.12	FA_{S4-150}	0.90	56	3.00
	FA_{H1-200}	0.61	52	3.35	FA_{S1-200}	0.64	65	3.59
	FA_{H2-200}	0.78	50	6.39	FA_{S2-200}	0.70	63	3.00
	FA_{H3-200}	0.84	48	5.96	FA_{S3-200}	0.85	55	1.96
	FA_{H4-200}	0.88	42	5.00	FA_{S4-200}	0.90	52	1.15
	FA_{H1-250}	0.64	56	2.62	FA_{S1-250}	0.62	66	5.08
	FA_{H2-250}	0.72	49	5.14	FA_{S2-250}	0.72	62	7.12
	FA_{H3-250}	0.88	47	2.85	FA_{S3-250}	0.82	58	1.20
	FA_{H4-250}	0.92	42	2.10	FA_{S4-250}	0.88	50	–
	FA_{H1-300}	0.52	52	2.11	FA_{S1-300}	0.60	62	1.65
	FA_{H2-300}	0.58	50	3.00	FA_{S2-300}	0.68	58	2.15
	FA_{H3-300}	0.61	48	1.56	FA_{S3-300}	0.81	52	1.20
	FA_{H4-300}	0.80	42	1.22	FA_{S4-300}	0.86	50	–
	Standard deviation (SD)	0.12	5.5	2.5		0.11	5.5	2.7
BA	BA_{H1-100}	0.85	–	2.20	BA_{S1-100}	0.90	–	1.10
	BA_{H2-100}	0.92	–	2.42	BA_{S2-100}	0.94	–	1.40
	BA_{H3-100}	0.96	–	2.00	BA_{S3-100}	0.99	–	1.15
	BA_{H4-100}	1.06	–	1.20	BA_{S4-100}	1.05	–	1.05
	BA_{H1-150}	0.88	–	2.10	BA_{S1-150}	0.92	–	1.25
	BA_{H2-150}	0.94	–	2.60	BA_{S2-150}	0.97	–	1.45
	BA_{H3-150}	0.97	–	2.22	BA_{S3-150}	1.05	–	1.30
	BA_{H4-150}	1.09	–	1.10	BA_{S4-150}	1.10	–	1.22
	BA_{H1-200}	0.86	–	1.36	BA_{S1-200}	0.90	–	1.05
	BA_{H2-200}	0.93	–	1.88	BA_{S2-200}	0.95	–	1.50
	BA_{H3-200}	0.98	–	1.65	BA_{S3-200}	1.03	–	1.12
	BA_{H4-200}	1.07	–	1.10	BA_{S4-200}	–	–	–
	BA_{H1-250}	–	–	–	BA_{S1-250}	–	–	–
	BA_{H2-250}	–	–	–	BA_{S2-250}	–	–	–
	BA_{H3-250}	–	–	–	BA_{S3-250}	–	–	–
	BA_{H4-250}	–	–	–	BA_{S4-250}	–	–	–
	BA_{H1-300}	–	–	–	BA_{S1-300}	–	–	–
	BA_{H2-300}	–	–	–	BA_{S2-300}	–	–	–
	BA_{H3-300}	–	–	–	BA_{S3-300}	–	–	–
	BA_{H4-300}	–	–	–	BA_{S4-300}	–	–	–
	SD	0.08	–	0.53		0.07	–	0.16

[a] H and S represent NaOH ve Na_2SiO_3 mixing, respectively. 1 and 100 represent mixing ratio (%) and baking temperature, respectively.

[b] Bulk density was not measured because of breakup of the BA above 200°C.

[c] Water absorption percentage was not measured because of breakup of the BA in water.

[d] Compressive stress was not measured because of breakup of the BA samples above 200°C.

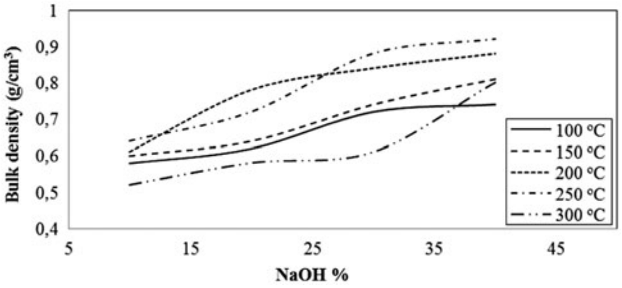

Fig. 3. Considering baking temperature and mixing ratio, bulk density of the samples prepared with the FA and NaOH activator.

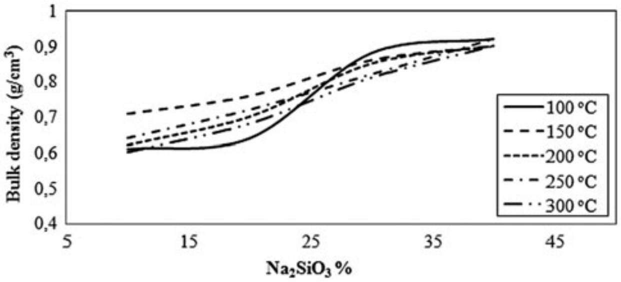

Fig. 4. Considering baking temperature and mixing ratio, bulk density of the samples prepared with the FA and Na_2SiO_3 activator.

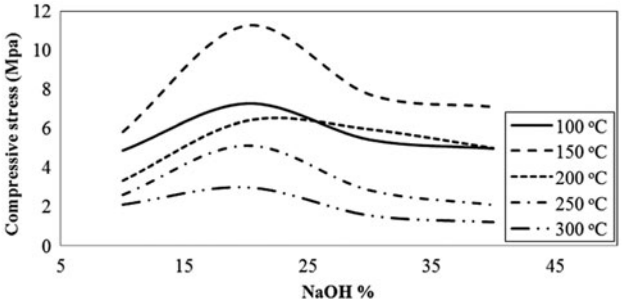

Fig. 5. Considering baking temperature and mixing ratio, compressive stress of the samples prepared with the FA and NaOH activator.

samples preparing with NaOH activator). In the samples, loss in strength was observed when baking temperature was increasing. Considering compressive strength values, it was determined that optimum baking temperature was in the range from 100 to 150˚C.

As shown in Figs. from 7 to 10, according to baking temperature for both activators, compacted bulk densities [38] showed a similar behavior in the samples prepared with NaOH and Na_2SiO_3 activators. However, a slight decrease in compacted bulk densities was observed for the samples prepared with NaOH activator at 300˚C. This could be resulted from almost 43% flammable materials in the fly ash and combustion of these materials at 300˚C. Vitrification occurred at 300˚C in the samples prepared with Na_2SiO_3 activator, so this could prevent the decrease in compacted bulk density.

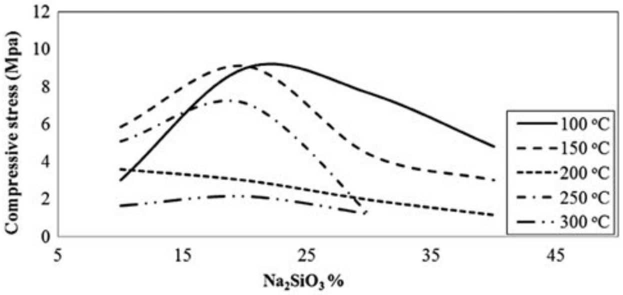

Fig. 6. Considering baking temperature and mixing ratio, compressive stress of the samples prepared with the FA and Na_2SiO_3 activator.

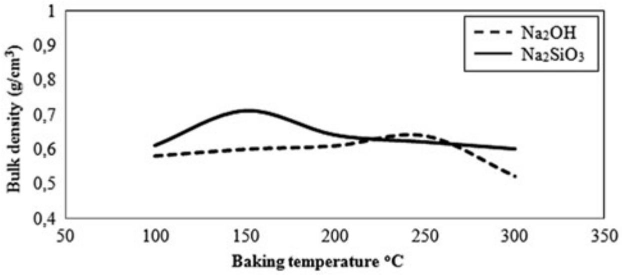

Fig. 7. According to baking temperature, bulk density of the samples prepared with the FA and 10% NaOH and Na_2SiO_3 activators.

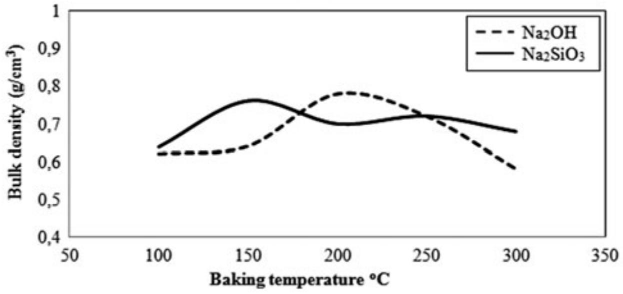

Fig. 8. According to baking temperature, bulk density of the samples prepared with the FA and 20% NaOH and Na_2SiO_3 activators.

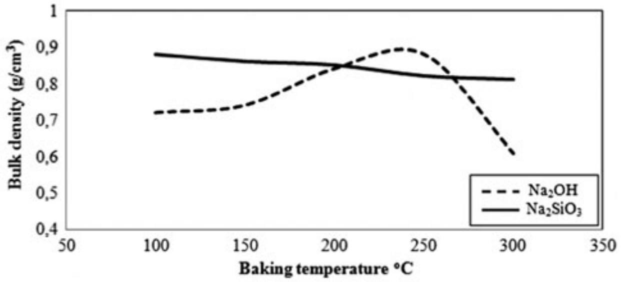

Fig. 9. According to baking temperature, bulk density of the samples prepared with the FA and 30% NaOH and Na_2SiO_3 activators.

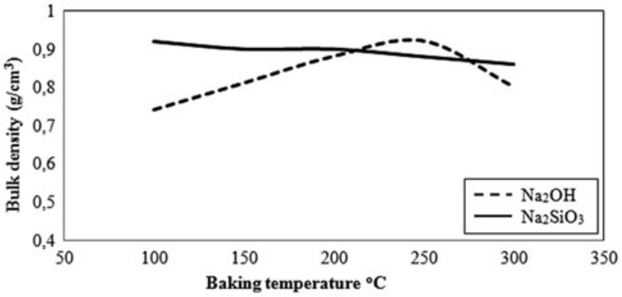

Fig. 10. According to baking temperature, bulk density of the samples prepared with the FA and 40% NaOH and Na_2SiO_3 activators.

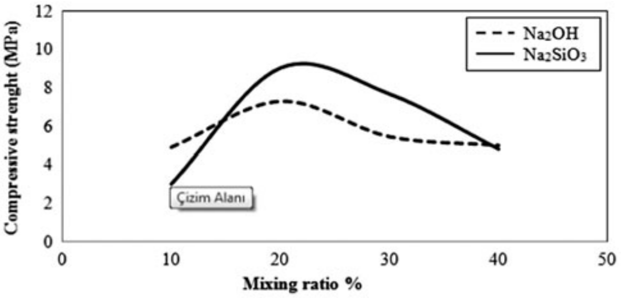

Fig. 11. Compressive strength of the samples prepared with the FA at 100°C.

As shown in Figs. between 11 and 15, according to mixing ratios, samples preparing with NaOH and Na_2SiO_3 activators showed a similar behavior for each mixing ratios percentage. The ideal mixture for each activator was 20%. Baking temperature did not play an important role on compressive strength value of the samples. It was observed that the key factor on compressive strength is mixing ratio percentages of activators.

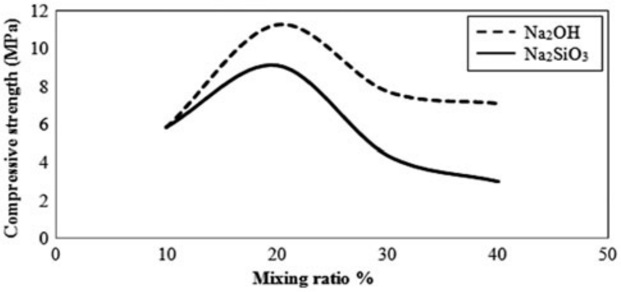

Fig. 12. Compressive strength of the samples prepared with the FA at 150°C.

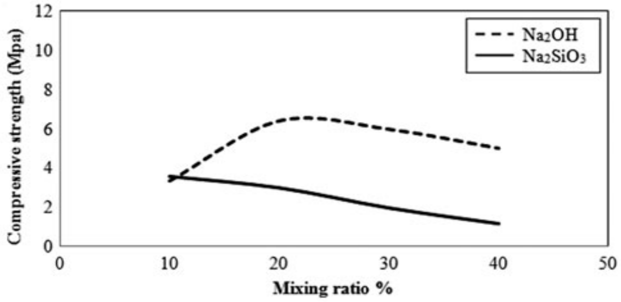

Fig. 13. Compressive strength of the samples prepared with the FA at 200°C.

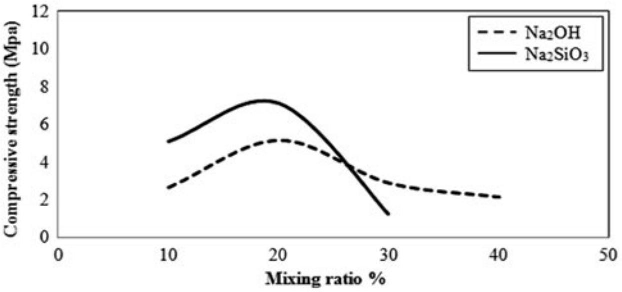

Fig. 14. Compressive strength of the samples prepared with the FA at 250°C.

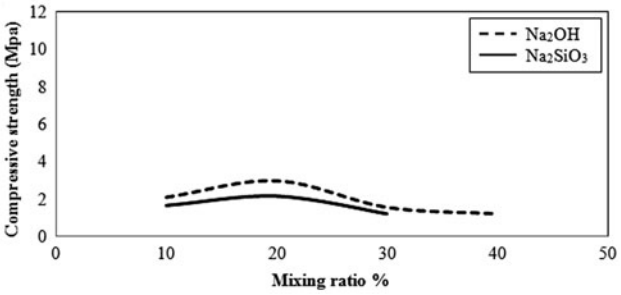

Fig. 15. Compressive strength of the samples prepared with the FA at 300°C.

5. Discussions and conclusions

Geopolymer has thermoset polymer structure which results from polycondensation. In the geopolymer formation, at low-temperatures kaolin reacts with NAOH as hydration soda undergoes polycondensation. In general, oxidic compounds of aluminum “Al” and silicon “Si” existing in the material in high amounts allow binding and form monomers which provide volumetric stiffness. Geopolymer process is not a fusion, sintering, or melting process, it is a polymerization process. After heat treatment, geopolymer reaches monolithic ceramic structure in the result.

Davidovits identified nine types of available geopolymer materials [36]. One of these definitions is fly ash-based geopolymer. According to this definition, being polymerized at temperatures below 100˚C is related to chemical structure of the raw material. Experiments of this study were conducted at temperatures below 100˚C, as well, but no activation was observed due to the raw material used. The possible reasons for this:

(1) SiO_2/Al_2O_3 compound ratio in the FA composition is not between 2 and 3.5 by weight.
(2) Unburned material ratio in the FA composition (should not exceed 5%) is much higher.
(3) Particles in the glass phase are not in higher amounts in the raw material.
(4) The fineness of particles of the FA should be below 50 μm, but in our study these particles were below 500 μm; therefore they cannot provide toughness of the material.
(5) Excessive amount of Fe_2O_3 compound slows geopolymer reaction and gives low-compression strength.
(6) Most importantly, the excessive amounts of unburned carbon in the coal adversely affect the material properties.

For these reactions activation has been due to heat treatment. In this manuscript, waste is reused directly and further studies are not done.

The production of cheap and high quality material seems possible when waste ash is reused as well as protection of natural raw material and ecological balance, prevention of environmental pollution, contributing to national economy by reusing of waste materials in the world and in Turkey. In this context, this study identified the following conclusions were reached as a result.

(1) In this study, the FA and the BA having two different chemical structures were used. When added chemical activators (sodium hydroxide, sodium silicate), conversion to geopolymer concrete from particularly the FA is possible.
(2) Adding chemical activators to the FA creating environmental problems for the Niğde region, constructional material for lightweight products are manufactured.
(3) According to compressive strength values in the FA, in both activator, ideal mixture, and optimum baking temperature were 20% by volume and 150˚C, respectively.
(4) In the samples prepared with the FA at baking temperature of 150˚C with 20% mixture, compressive strength were 9.11 and 11.26 MPa for the samples prepared with NaOH and Na_2SiO_3 activators.
(5) In the mixtures prepared with the FA with NaOH and Na_2SiO_3 activators, minimum compacted bulk densities were found 0.52 g/cm^3 and 0.50 g/cm^3, respectively, in 10% mixing ratio at 300˚C baking temperature. The reason for that is the activation of some combustible material at 300˚C.
(6) In optimum compressive strength in the products prepared with the FA, compacted bulk densities were found 0.64 and 0.76 g/cm^3, respectively, to the products with NaOH and Na_2SiO_3 activators.
(7) In the mixtures of the FA with NaOH and Na_2SiO_3 activators, samples were not affected by external influences and water absorption of them was identified. But after freezing experiments, the capillary cracks were observed and load carrying capacity was lost.
(8) In both activators, at 350˚C and above the product could not be obtained and breakup was observed in the samples prepared with the FA. Activation at low temperatures is to be a positive feature. In both activators, at 250˚C and above the product also could not be obtained and breakup was observed in the samples prepared with the BA.
(9) The BA includes 90% Ca. During the curing of the mixture, this calcium converts to quicklime (CaO) and therefore it released some heat due to the moment of contact with water. This causes to breakup of the products.
(10) Sufficient compressive strength could not be obtained from the samples prepared by mixing BA with NaOH and Na_2SiO_3 activators.

As a result of these measurements, the best resulting geopolymer concrete products were obtained at a baking temperature of 150°C with maximum 11.26 MPa compressive strength and at a baking temperature of 100°C with maximum 10.82 MPa compressive strength from the class F FA samples activated with sodium hydroxide and sodium silicate activator, respectively. It was found that the class F FA was more suitable than the BA to produce geopolymer concrete.

This study is an indicator of conversion of waste ashes to geoplymer product by alkaline activator and it sheds light on the problem of industrial waste ashes that needs an answer. In the subsequent studies, new products can be tested by mixing certain proportions of the FA and the BA. Thus, the wastes creating environmental problems will be reused in the industry.

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