Shahrood University of Technology

Journal of Mining and Environment (JME)

Journal homepage: www.jme.shahroodut.ac.ir

Iranian Society of Mining Engineering (IRSME)

Evaluation of Pozzolanic Activity of Two Different Types of C and F Fly Ashes with Fineness Factor

Demet Demir Sahin[1*], Ibrahim Cavusoglu[2], and Ali Osman Yilmaz[3]

1. Department of Mining and Mineral Extraction, Mining Technology Program, Gümüşhane Vocational School, Gümüşhane University, Gümüşhane, Turkey
2. Department of Mining Engineering, Faculty of Engineering and Natural Science, Gümüşhane University, Gümüşhane, Turkey
3. Department of Mining Engineering, Karadeniz Technical University, Trabzon, Turkey

Article Info

Received 2 March 2023
Received in Revised form 24 March 2023
Accepted 11 April 2023
Published online 11 April 2023

DOI:10.22044/jme.2023.12795.2324

Keywords

Fly ash
Grinding time
Pozzolanic activity index
Fineness
Grinding

Abstract

Today, energy produced from coal is economical compared to other sources but it faces a very serious waste problem. However, these wastes are evaluated by using them as mineral additives in cement, which leads to lower cement costs, saving resources, producing environmentally friendly cement, reducing CO2 gas, and producing high-strength cement. In this work, the pozzolanic properties of different types of fly ash (Afşin Elbistan C type and Çayırhan F type) are investigated. The fly ashes used in the study are first subjected to the milling process (10, 20, 30, 45, and 60 minutes), and then the 28 and 90-day pozzolanic activity index tests of the milled and unmilled ashes are performed. The results obtained show that the 28-day pozzolanic activity value of the ashes subjected to 20-, 30-, 45-, and 60-minute milling times are higher than the value specified in the standard, compared to the unmilled and 10 min milled fly ash. In addition, for all fly ash samples, the 90-day pozzolanic activity index results show that while the pozzolanic activity index value of Çayırhan (ÇYH) fly ash is higher than the standard value, that of Afşin Elbistan (AE) fly ash is lower than standard. The outcomes of the present study show that the mechanical properties of the fly ash are generated by the burning of coal increase after milling process, and thus can be used as a mineral additive. With the effect of grinding, both fly ash increase the pozzolanic activity. The results are determined with the experimental results obtained.

1. Introduction

Fly ashes are known as waste materials generated after the combustion of coal obtained as a result of mining activities carried out especially in areas with low-calorie coal to generate electrical energy [1, 2]. Although it is a waste product, fly ash is mostly used as a by-product in the construction industry. The utilization of fly ash as a by-product in the construction industry depends on its puzzolanic properties [3].

Pozzolan is defined in the study ASTM C125 [4] as "a siliceous and aluminous material that has little or no cementitious value in itself but in the presence of moisture, in a finely divided form, reacts chemically with calcium hydroxide at normal temperature to form compounds with cementitious properties". Pozzolans are produced naturally in nature such as tuffs with acidic and basic properties or artificially such as fly ash collected from chimneys as a result of burning coal in thermal power plants [5]. In addition, obsidian, another naturally occurring mineral of volcanic origin, has pozzolanic properties, is used as a cement component, and, most importantly, has pozzolanic properties. In the studies, the use of obsidian reduces the need for water in the cement, contributes to the regulating the set start and end time and balances the hydration temperature with its pozzolanic feature [6]. Fly ashes are materials with pozzolanic properties, but such properties vary depending on the source of the fly ash and the way it is collected and burned. In other words, fly ashes obtained from different sources generally have different chemical and pozzolanic properties.

Corresponding author: demetsahin@gumushane.edu.tr (D. Demir Shahin)

The pozzolanic activity of fly ashes generally varies depending on the chemical composition, morphology and fineness of the fly ash. While it is possible to determine the chemical composition and fineness at the macro-level with the experimental method, which affects the pozzolanic activity, the grain structure is determined morphologically by the microscope image. The effect of physical and chemical properties on the pozzolanic property of silicon fly ash was determined by the results of the experiment, and SEM images revealed its morphological structure. It has been determined that the grain structure has different effects on the pozzolanic property, such as physical and chemical properties [7]. In another study, fly ash was produced artificially. This produced fly ash is intended to be similar to the properties of naturally produced fly ash. Pozzolanic properties were taken into account as the most important feature to be developed to use the obtained synthetic fly ash instead of cement. It has been stated that it is possible to change the pozzolanic properties with fineness, chemical component and crystal properties in synthetic fly ash [8]. Therefore, some fly ashes may have low pozzolanic activity. It is known that the pozzolanic properties of fly ashes with low pozzolanic activity are increased by mechanical activation through grinding process [9, 10-12]. Furthermore, it is possible to increase the pozzolanic activity with different fineness values obtained by sieving in different sizes of fly ash [13].

In this study, the formation mechanism and the fineness (blaine) of the pozzolanic activity of fly ashes were discussed, and the change in pozzolanic activity of two different types of fly ashes were investigated by applying different grinding times. The study investigated the chemical composition of fly ash and the effect of fineness changes due to grinding effect on the effect of gradual pozzolanic properties. The effect of fineness, especially the use of fly ash instead of cement, mechanical properties such as short and long-term compressive strength, and pozzolanic change were observed on fly ash with two different chemical compositions. After the values obtained, at the end of the 28-day curing period, the limit value of pozzolanic activity in fly ash named AE and ÇYH was determined as $\geq 75\%$ and above. At the end of the 90-day curing period, it was concluded that AE fly ash did not meet the requirement of $\geq 85\%$ and above for all fineness values, but ÇYH fly ash did not meet the requirement for all fineness values. According to the results, fly ash with different chemical compositions causes different fineness values and different pozzolanic properties after the same grinding time.

1.1. Properties of fly ashes

In this study, a study was conducted on the effect of the chemical and physical properties of fly ash on pozzolanic properties. Therefore, the physical, chemical, mechanical, morphological, and pozzolanic properties of fly ash were considered but mainly physical and chemical properties were examined. Specific surface area values of each of the physical properties of fly ash were determined and compared with cement. In many studies, the higher the fineness, the higher the pozzolanic activity [14-16]. Optimum results in Portland pozzolan cement, the specific surface area value should not exceed 2500 cm^2/g [17]. Its chemical composition consists of components such as silica, alumina, iron oxide, calcium oxide, magnesium oxide, sulfur trioxide, loss of ignition and carbon in fly ash. Each component has a particular importance in the development of the pozzolanic reaction. It contains silica and alumina, the main components in fly ash, and is primarily glassy in nature. The amount of SiO_2 or $SiO_2 + Al_2O_3$ in the fly ash contributes to improving the pozzolanic activity and increasing the strength at the end of the long curing period of the fly ash [18, 19]. Iron can be in crystalline and non-crystalline composition in fly ash. Glassy fly ash has magnetic properties. The studies determined that the iron content as a component of fly ash and magnetic separation increased the pozzolanic activity [20]. It has been determined that it improves the pozzolanic activity by improving the strength developed in the sulfur lime-fly ash mixtures [21]. Calcium (CaO) and magnesium (MgO) oxides vary in their proportions in fly ash, depending on their being obtained from coal of different origins. It has been determined that the amounts of magnesium (MgO) and free lime (CaO) up to 5% do not cause any harm. It has been emphasised that the presence of free lime and/or alkali content in some products is necessary for the cementation and strength of fly ash [22]. It was stated that silica, alumina, iron and lime and other components in the fly ash composition had no effect on the pozzolanic property.

Actually, the carbon in the fly ash represents the non-combustible part of the fly ash, and there are ideas that high carbon content reduces the pozzolanic activity [18]. However, it was stated in different studies that it did not have any harmful effects [19]. It is considered an undesirable component because the carbon composition creates a diluting effect on the pozzolanic substance in the fly ash. The fact that the carbon content is between 5% and 12% allows the use of fly ash as pozzolan [23].

1.2. Occurrence mechanism of pozzolanic activity in fly ashes

The compounds required for pozzolanic activity in fly ashes are SiO_2 and Al_2O_3, and the reaction of these compounds with $Ca(OH)_2$ leads to the formation of the expressed activity [24]. The pozzolanic activity occurs after the combination of water and $Ca(OH)_2$. With the formation of the reaction, portlandite ($Ca(OH)_2$ reacts and the amount of this component decreases. The portlandite composition decreases, on the other hand, the increase in the calcium silica hydrate (CSH) component gives a binding structure [25]. As the composition of the product reacted for pozzolanic reaction changes, there is definitely a change in the products released. For example, calcium alumina hydrate is formed with $Ca(OH)_2$ + natural and artificial pozzolans + water. $Ca(OH)_2$ + natural and artificial pozzolans + calcium silica hydrate with water. It is not common in different chemical components in fly ash but in previous studies, it has been determined that chemical components increase the pozzolanic properties [26]. The pozzolanic properties of fine-grained fly ash were determined by different parameters and different studies. However, some of these studies require a long time and various procedures, while others can achieve effective results in a shorter time. For example, the pozzolanic activity of fly ash, fly ash/slaked lime or fly ash/cement paste, and time-dependent compressive strength development of mortar or concrete was determined as a result of a long process and is among the commonly used methods. However, a very simple, fast and bright method based on electrical conductivity measurements has been demonstrated by the studies that have been determined based on the theoretical definition of the pozzolanic property and suggested as short-term methods [27]. In another study, pozzolanic properties were determined by the compressive strength test used in both artificial and natural pozzolans, such as fly ash. While testing the cement in the determination, the air contents in the tested mortars are compared with the effect of other factors. However, it has been mentioned that it is difficult to interpret this method [28].

Both the composition of the reacting products and the degree of pozzolanic activity after hydration of cement depend on the formation of products of a material with different chemical composition but close morphological structure [29, 30]. Although the reaction of fly ashes is similar to the reaction of cement with alkalis, it is slower than cement in terms of reaction rate [31, 32]. In fly ashes, the pozzolanic reaction starts at the top of the grain, that is, on the surface or closest to the surface, and the solubility of the CSH structure released after the reaction is low. The initiation of the reaction on the surface of the grain starts with the breaking of the glassy structure in the fly ash and then its dissolution. The glassy phase causes the concrete to decompose due to the alkali (OH-) ion in the pore solution. With the realization of the decomposition event, the molecules in the aluminium and silica structure are separated from each other and dissolved in the pore solution. After the different formations formed due to the reaction, Ca ion reacts with water in the pore to form calcium-silica-hydrate and calcium-alumina-hydrate, which are more durable structures. It depends on the pH of the pore solution and the diffusion distance of the main ions and the CSH structure formed. The CSH structure formed prevents the pozzolanic reaction and the inflow and outflow of the compounds participating in the process, thanks to a dense layer formed on the surface of the fly ash. The pozzolanic reaction in fly ash depends on the grain fineness, grain shape and structure, amount of glassy structure, OH^-, Ca^{+2} ion exchange and pH of the pore solution formed, as well as the glassy property of the fly ash. The effects of each of these parameters on the pozzolanic reaction are as follows [33].

The fineness parameter on pozzolanic activity in fly ashes is expressed as the effect on grain and particle size. Calcium hydroxide (CH) ion plays an active role in the formation of pozzolanic activity and contributes to the reaction. In cases where there is an excess of alkaline ions in the pore solution and a decrease in the amount of fly ash, it causes a decrease in the amount of CH ion. This means that the ion has no effect on the early stages of the pozzolanic reaction but has an effect on the hydration reaction. Because adding CH ion in the early stage can increase cement hydration, however, it does not contribute to the pozzolanic reaction since fly ash has not started to dissolve. In the early stage of hydration, the CH structure is effective but does not affect the development of pozzolanic activity. This indicates that fly ash has not yet dissolved. Cement hydration is enhanced by adding CH in the early stage.

Another parameter affecting pozzolanic activity is the pH value in the pore water. This value has an indirect but not direct effect on the reaction (pozzolanic reaction). Increasing the water/cement ratio leads to dilution of the pore solution and decreases in the pH value. Different phase structures of fly ash such as amorphous or crystalline have a slightly different effect on pozzolanic activity. For example, having an amorphous or glassy structure rather than a crystalline structure facilitates the dissolution process and contributes to an increase in the reactivity day. OH^- ion again has an indirect effect on the reaction. Since this effect initiates the dissolution of the glassy structure of fly ash, it causes the silicon ion and silica present as atoms in the solution [34].

The improvement of the pozzolanic activity with the grinding of fly ash contributes to both the reaction rate and the development of the amorphous structure, which affects the development of this reaction. For example, the relationship between the glassy chemical composition and structure of siliceous fly ash is analysed depending on its pozzolanic activity. In fly ash rich in siliceous content, calcium silicate hydrates (called C-S-H) and calcium aluminate, and calcium aluminosilicate hydrates are active chemical components (SiO_2 and Al_2O_3) that react with $Ca(OH)_2$ to produce. Among these components, fly ash with higher depolymerisation of $[SiO_4]^{4-}$ anions in glass mesh accelerates cement hydration and contributes to the development of pozzolanic activity by increasing the strength of cement mortars [35].

By grinding, fly ash gains a finer structure and the grain size increases. However, in addition to the effect of grinding on grain size change, it is also provided by classification and separation method. While the pozzolanic activity is changed by grinding, the specific surface area, grain shape and morphology and mineralogical content of fly ash, which are different parameters, also have an effect [36]. In terms of its chemical composition, the fact that fly ash has aluminum-reactive silica and calcium-rich composition in its content enables the development of pozzolanic activity and binding properties like cement. In fact, different parameters contribute to the development of pozzolanic activity. However, the combination of a few of these parameters is even more effective in the development of pozzolanic activity. For example, the use of fly ash with a fine spherical grain size of less than 45µm reduces the water requirement of the cement paste. While the decreasing water requirement is due to the fact that the fly ash used in fine grain size fills the spaces between the cement grains, this situation causes the water need to be higher in coarse grain fly ash [37]. The effect of fly ash fineness, physical properties, and chemical composition on pozzolanic reaction has been investigated in many studies. These effects are divided into short and long term. In the work [38], examined the effect of fly ash and cement with different chemical compositions on pozzolanic activity. They stated that especially the rate and capacity of the reaction were affected by calcium hydroxide from the cement composition and aluminosilicates in pozzolan. In addition to the effect of chemical composition, they mentioned that fly ash being in amorphous phase and showing fineness in terms of grain size improve pozzolanic activity. They conducted a detailed study on the short and long term effects of these parameters on pozzolanic activity. The surface area of the fly ash provided the increase in the pozzolanic activity in the short term, while the chemical and mineralogical composition led to such increase in the long term. Self hardening and of the fly ash due to increase in its surface area after grinding -contrary to its original condition before grinding- and its reaction with with calcium hydroxide $Ca(OH)_2$ enabled the formation of calcium silicate and calcium aluminate compounds with a more solid structure. In the work [39], investigated the effect of physical and chemical properties on the pozzolanic activity of fly ashes, the development of pozzolanic activity and strength, the ratio of fly ash in cement and the effect of fineness. They stated that calcium silica hydrate and calcium silica aluminate compounds that form the hydration of clinker are formed by the reaction of $Ca(OH)_2$ from cement and fly ash with amorphological glassy structure (Eqs. 1 and 2).

Pozzolanic reaction:

$$Ca\,(OH)_2 + SiO_2 \rightarrow CSH - gel \quad (1)$$

Cement hydration: $$Cement\ (C_3S;\ C_2S) + H_2O \rightarrow CSH - gel + Ca\,(OH) \quad (2)$$

The long-term exposure of the above-mentioned reactions causes a slow pozzolanic activity in the short-term. In the short term, the reaction is accelerated by grinding fly ash.

1.3. Specific surface area (Blaine) representing fineness in fly ash

Specific surface area in fly ash is a parameter that numerically indicates the fineness value. In admixed cements, specific surface area is an effective parameter in changing the strength properties of cement and concrete. The formation process and grinding mechanism of fly ash are effective on this parameter. This grain structure of coarse-grained fly ashes depends on the composition of unburned carbon in the coal. The fly ashes in the coarse grain structure are provided with a fine grain structure by grinding and using the fly ashes with such grain structure in concrete improves the mechanical and durability properties. By grinding the coal burned in the thermal power plant, both fine grain structure and spherical shaped grains are formed. Fly ash with finer grain structure has a more glassier structure compared to coarse grain fly ash and performs better in cement and concrete. Today, high performance concretes with fly ash are produced with the effect of ultra-fine fly ash. The fineness is achieved by grinding the fly ash. In the work Felekoğlu et al. [40-43]. In the work [9], attributed the lower blaine values of the ashes in the normal state compared to those of grinded fly ash to the reduction of the hollow carbon grains and spherical but hollow grains with the grinding effect. In the work [44], the grinding process causes the fly ash to lose its rounded shape and increases the density and specific surface area values (Figure 1). The two different types of fly ash used in this study were subjected to different grinding processes to obtain different fineness values. The 28- and 90-day pozzolanic activity index experiments were carried out on the ground (10, 20, 30, 45 and 60 min) and unground ashes. The results obtained showed that the 28-day pozzolanic activity value of the ashes subjected to 20, 30, 45, and 60 minutes of grinding time was higher than the standard value compared to the unground and 10 minutes ground fly ash. In addition, 90-day pozzolanic activity index results for both fly ashes showed that Çayırhan (ÇYH) fly ash was higher than the standard value while Afşin Elbistan (AE) fly ash was lower. The results of this study reveal that the mechanical properties of fly ash produced by coal combustion increase after grinding and thus can be used as a mineral additive. According to the study conducted by TÇMB for Afşin Elbistan fly ash in 2009, it was interpreted that it could not be used as an ash with pozzolanic properties in its ungrinded state, but in 2019, after obtaining different fineness values with the effect of different grinding times, it was qualified that it could be used as a mineral additive in cement [45]. C and F class fly ash were used in the study. Within the scope of the evaluation of the pozzolanic properties of F and C class fly ashes, they have been evaluated from different angles in the literature and contributed to the presentation of this study. However, the distinctive difference or uniqueness of this study from other studies is that 5 different fineness values were obtained when two different fly ash with different finenesses at the beginning were exposed to the same grinding times (10, 20, 30, 45, and 60 min). With the grinding effect, a total of 6 different fineness values were determined with 5 different grinding and 1 original ash. Grinding provided a gradual increase in fineness. The effect of each fineness value on pozzolanic activity was observed. This process was examined for two ashes with different chemical components and the differences between each other were revealed. The results obtained were compared with the appropriate standard and the different effects of the fineness of the two ashes on pozzolanic activity were clearly observed.

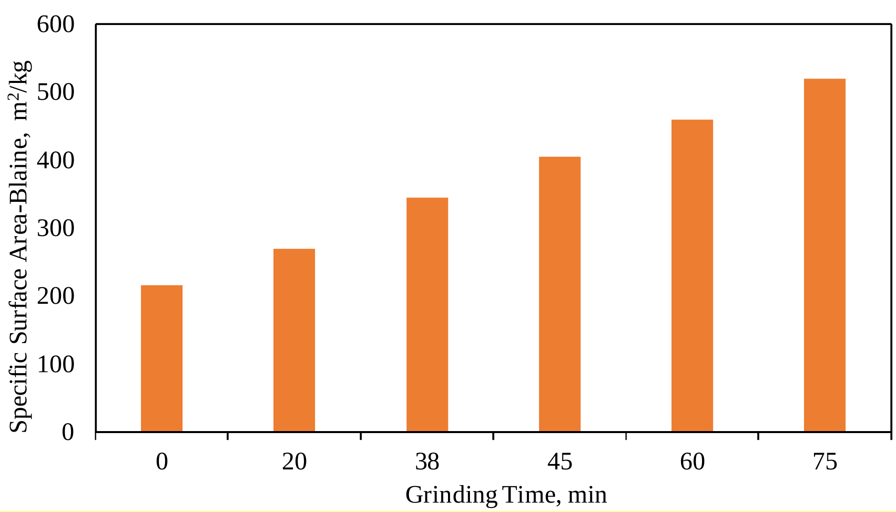

Figure 1. Relationship between specific surface area values and grinding time [46].

2. Materials and Method

One of the fly ashes required for the study is type C and was taken from Afşin Elbistan Thermal Power Plant. The other fly ash was type F and was obtained from Çayırhan Thermal Power Plant. The chemical composition (Table 2) and specific surface areas of the fly ashes were determined by XRF and specific surface area tests performed at the Aşkale Cement Factory Laboratory in Gümüşhane. According to the results of the analysis, fly ashes were analyzed in accordance with the ASTM C 618 standard [46] and the results are compared in Table 2. The 28- and 90-day pozzolanic activity index tests for different grinding times obtained by grinding the fly ashes in the original (0 min-unmilled) and different grinding times in the ball mill were conducted at the Ready Mixed Concrete Association of Turkey.

2.1. Fly ash grinding

The AE and CYH ash used in the study was griended using a ball mill in the laboratory of Karadeniz Technical University, Department of Mining Engineering. The dry and powdered state was taken into consideration in the grinding of fly ashes and the grinding process was carried out in a cylindrical chamber with a device capacity of 6 L The grinding process was prepared as 10 kg in total for each grinding time of fly ash (Table 1).

2.1. Blaine (specific surface area) experiment

This test was carried out in accordance with TS EN 196-6 [47] using an automatic blaine device at the Aşkale Cement Plant in Gümüşhane. The main purpose of this experiment was determined by compressing the cement bed of predetermined size and porosity and monitoring the time it passes through a fixed amount of air. The experiment started with weighing the fly ash and then the sample was placed in the appropriate place in the device. The specific gravity value of the sample was entered into the device and thus the specific surface area value was determined. This was done individually for both the original and the fly ashes milled at different times.

2.2. Pozzolanic activity test in fly ashes

The pozzolanic activity index values of F and C type fly ashes ground at different times after

28 and 90 days of curing period were performed in the laboratory of Turkish Ready Mixed Concrete Association according to TS EN 450-1 standard [48]. For the pozzolanic activity index test stated in the standard, the compressive strength values of mortar samples prepared with 75% cement and 25% fly ash by mass are based on the expression of the ratio (in %) to the mortar sample prepared with cement only. It is calculated as follows: pozzolanic activity index = (A/B) x 100. A represents the average compressive strength values of the mortar samples produced from the pozzolanic materials used for the experiment, while B represents the average compressive strength of the reference sample, i.e. the sample containing only cement. The obtained proportional data were accepted as ≥ 75% and ≥ 85% limits for 28 and 90 days curing times, respectively.

Table 1. Data on ball mill grinding of fly ash.

Ball diameters, cm	Number of balls, Pieces	Rotational speed, rotation/minute	* Amount of grinded material, kg
4	6	66	2
3.5	7		
3	12		
2	50		
1.75	30		

* The amount of fly ash put into the sample chamber at one time

Table 2. Comparison of AE and ÇYH fly ash with XRF results and standards [44]

Oxide compounds, %	Cement I 42.5 R	AE	ÇYH	ASTM C 618 classification		TS EN 450-1 standard, %
				F, %	C, %	
SiO_2	19.48	29.24	49.07			
Al_2O_3	4.36	11.49	12.92			
Fe_2O_3	3.33	6.67	9.35			
S+A+F	-	47.40	71.34	> 70	> 50	> 70
CaO	62.71	37.84	11.25	< 10	> 10	
MgO	0.99	1.86	4.66	< 5	< 5	< 4
Na_2O	0.28	0.38	2.4	< 1.5	< 1.5	< 5
K_2O	1.02	0.69	3.71	_	_	< 5
SO_3	2.43	4.70	1.27	< 5	< 5	< 3
Cr_2O_3	0.006	0.054	0.061			
Mn_2O_3	0.187	0.059	0.133			

3. Results and Discussion

3.1. Determination of specific surface area (Blaine) values of normal fly ashes and fly ashes after grinding

The specific surface area values of the original and post-grinding AE and ÇYH ashes are given in Figure 2. Grinding had an increasing effect on the specific surface areas. This value is a numerical data representing the fineness property of fly ashes. The specific surface area values of AE and ÇYH fly ashes after 10, 20, 30, 45 and 60 minutes of grinding along with the specific surface area values in the original state and the specific surface area value of the cement were determined. The specific surface area values of both fly ashes used in this study before and after grinding were lower than the specific surface area value of cement. According to TS EN 450-1 [48] standard, the minimum fineness value that allows the use of fly ash in concrete is expressed as 3000 cm^2/g. The specific surface area value specified in the standard was compared with the conditions of both fly ashes before and after grinding. According to this comparison, all specific surface area values of AE ash were below the limit value specified in the standard. In the case of ÇYH fly ash, except for the grinding time of 0 and 10 minutes, the grinding times of 20, 30, 45 and 60 minutes were higher than the limit value specified in the standard.

In addition, 28 and 90 days compressive strength values of AE and ÇYH fly ashes and reference specimen are given in Table 3.

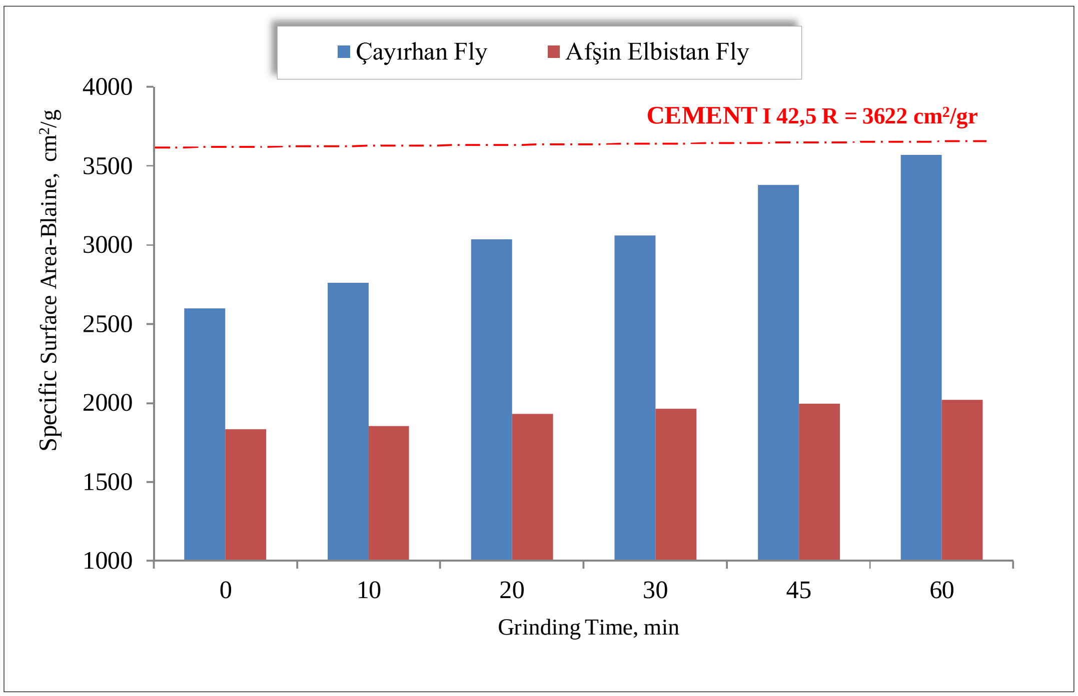

Figure 2. Specific surface area values showing the fineness of two different fly ash after grinding for 0, 10, 20, 30, 45 and 60 minutes.

3.2. Effect of fly ashes thinned by grinding effect on index of pozzolanic activity

In this study, the pozzolanic activity index values of AE and ÇYH fly ashes for both different grinding times and original conditions were obtained from 4 x 4 x 16 cm sized beam specimens produced by using 25% fly ash and

75% reference cement. The strength values of the prepared specimens were expressed as a percentage (%) of the ratio of the compressive strength of the reference specimen prepared using only cement. This value was determined for both 28 and 90 days curing time. The determined experimental values are shown in Figs. 3 and 4. Depending on the grinding, an increase in the 28-day pozzolanic activity index values of the fly ashes was observed. The pozzolanic activity values of AE ash after 0 and 10 minutes of grinding were higher than the same values of ÇYH ash. The specific surface area values of ÇYH ash after 20, 30, 45, and 60 minutes of grinding were higher than the same values of AE ash. Besides, the most striking situation was determined for the grinding time of 20 min and the pozzolanic activity index values were very close to each other.

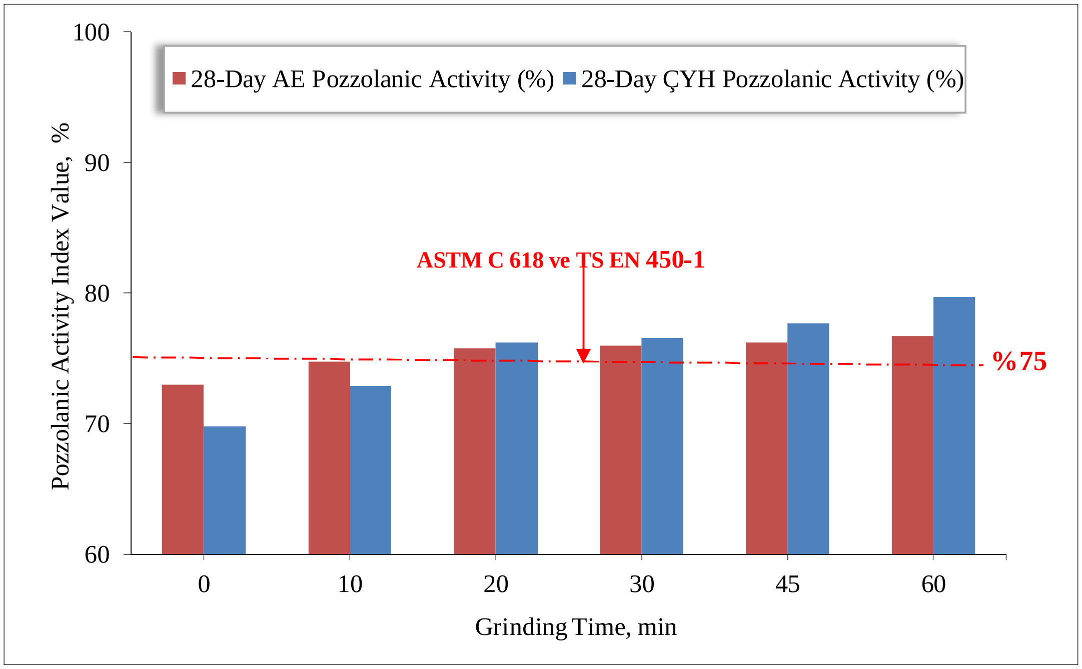

Figure 3. Comparison of the 28-day pozzolanic activity index values specified in the standard for AE and ÇYH fly ash.

The 28-day pozzolanic activity index values specified in TS EN 450-1 and ASTM C 618 standards were compared for the original and all grinding times of AE and ÇYH fly ashes. In these standards, the 28-day pozzolanic activity index value was determined as ≥ 75% and above. For AE and ÇYH fly ash, the values for 20, 30, 45, and 60 min grinding times were higher than the specified limit value, while the values for the original and 10 min grinding times were lower than the specified limit value.

The 90-day pozzolanic activity index values of AE and ÇYH fly ashes increased with increasing grinding time (Figure 4). Figure 4 shows that the 90-day pozzolanic activity index values of ÇYH fly ash were higher than those of AE fly ash.

According to TS EN 450-1 standard, the limit value of 90-day pozzolanic activity index values is required to be ≥ 85% and greater. In the specified standard, the 90-day pozzolanic activity was below the standard value for the original and all grinding times of AE fly ash, while the values for the original and all grinding times of ÇYH fly ash were above the standard value.

Figures showing the change of pozzolanic activity values of AE and ÇYH fly ashes in the original state according to the grinding time in % were created. From these figures, the change in pozzolanic activity index for the 28-day curing period is given in Figure 5 and the change between 90-day values is given in Figure 6.

The data obtained shows that the pozzolanic activity of fly ashes does not depend on a single effect but changes after different effects. The effects that cause the change are the fine grain structure of the fly ash, the change in the curing time of the sample, and the chemical composition of the fly ash, which are also supported by the results obtained. In order for the reaction to start and pozzolanic activity to develop, water and cement must first react. Then CSH and free lime (CH), which gain binding properties, are formed. The released CH structure and the silica (S) from the pozzolan and water react again to form the CSH structure, which gains an extra binding structure.

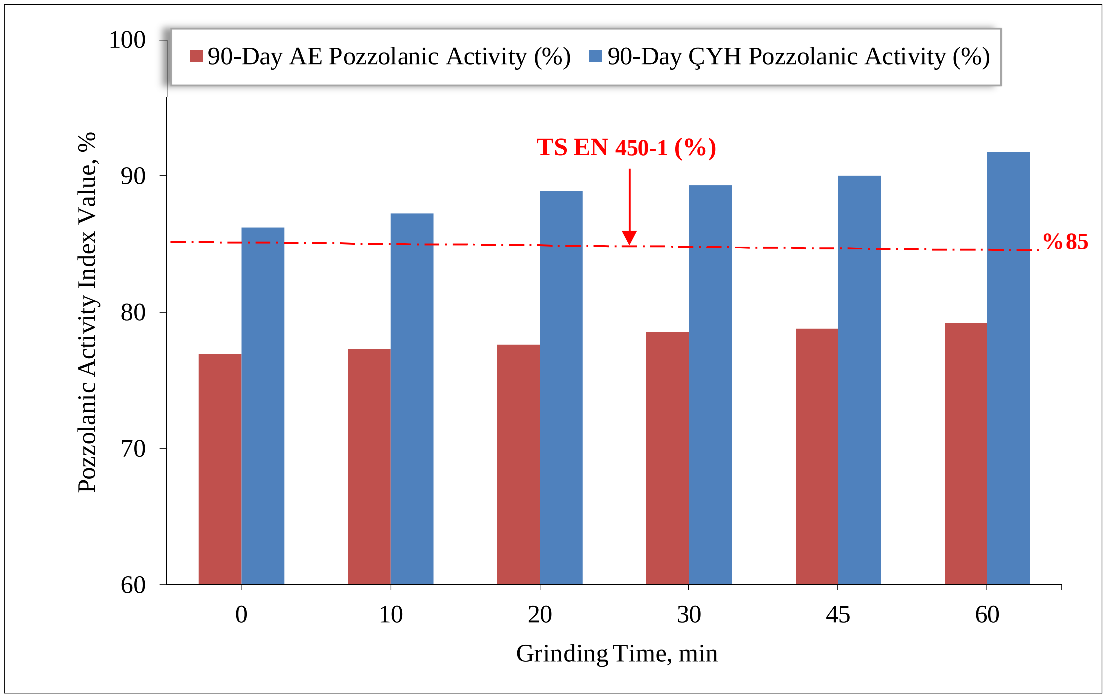

Figure 4. Comparison of 90-day pozzolanic activity index values of AE and ÇYH fly ashes.

Table 3. 28 and 90 days compressive strength values of reference sample and AE and ÇYH fly ash.

Grinding times, dk	28-day compressive strength values, MPa		90-day compressive strength values, MPa		Compressive strength values of reference sample, MPa	
	AE 28	ÇYH 28	AE	ÇYH	28	90
0	40.44	38.67	46.37	51.98	55.4	60.3
10	41.44	40.38	46.62	52.58		
20	41.99	42.22	46.79	53.61		
30	42.11	42.44	47.34	53.85		
45	42.22	43.10	47.52	54.27		
60	42.49	44.20	47.76	55.29		

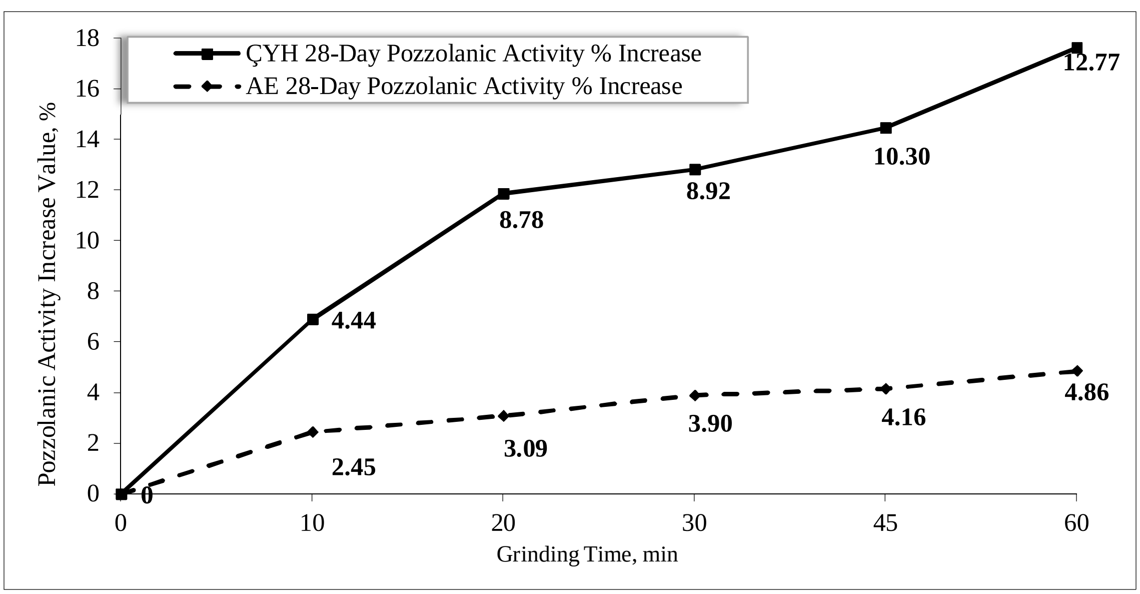

Figure 5. Changes in the 28-day pozzolanic activity index values of AE and ÇYH fly ash belonging to the original fly ash state of the grinding times [45].

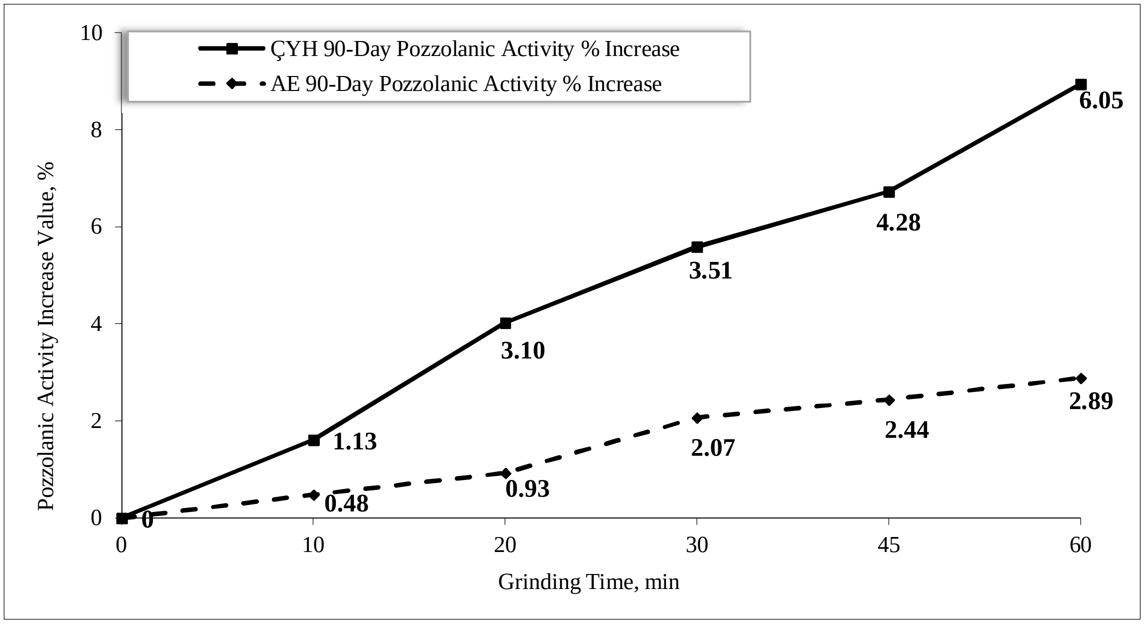

Figure 6. Changes in 90-day pozzolanic activity index values of AE and ÇYH fly ashes belonging to the original fly ash state of the grinding times [45].

The transition time during the release of free lime in the pozzolanic reaction caused the reaction to be slow [47]. Increasing the amount of pozzolan in the reaction caused a slow and long time to obtain strength. The slow but progressive increase in strength over time was reflected in the 28 and 90-day pozzolanic activity index values. Therefore, it was determined that the 90-day pozzolanic activity values were higher than the 28-day values.

There are two different effects of fineness variation on the pozzolanic activity of fly ash. The first of these effects is that bringing the fly ash to a finer grain size by grinding causes the surface area to increase. With the effect of increasing surface area, the pozzolanic reaction starts in the surface area, causing the reaction to accelerate. With the refinement of the grain structure after the second grinding, finer sized fly ashes provide better filling of the intergranular spaces. Filling the gaps better increases the pozzolanic activity [49, 50]. In order to see that fineness is more effective on the pozzolanic properties of fly ash, the Blaine value obtained by grinding should be higher than the Blaine value of the cement. The investigated the pozzolanic property of fly ash, which was ground and made very fine. In the study, they determined the Blaine value of cement as 347 m^2/kg, while they determined the Blaine value of fly ash as a result of grinding as 766.8 m^2/kg. Increasing the fineness value of the fly ash approximately two times the fineness value of the cement in the grinding province improves the pore structure of the fly ash that will interact with the cement, regulates the hydration heat release, facilitates the chemical dissolution of the compounds in the fly ash with the cement and facilitates the chemical composition, as well as increases the pozzolanic properties [51].

Especially the fact that ÇYH fly ash has a finer grain structure after grinding compared to AE fly ash causes ÇYH fly ash to have higher pozzolanic activity index values. The results also showed that the fine grain structure of fly ash plays a more effective role on pozzolanic activity than its chemical composition. This can be seen especially in 28-day pozzolanic activity index values [52]. The low values of 28 and 90-day pozzolanic activity of AE fly ash expressed in the standard showed that the grain fineness had a direct effect. The fact that its grain fineness is thicker than the grain fineness of cement caused the pozzolanic activity values to be low, since it could not fill the voids better [53, 54].

4. Conclusions

In this work, the pozzolanic activity properties of two fly ashes of different origin (F and C type) after grinding for 10, 20, 30, 45, and 60 minutes were investigated. The results obtained from the experimental studies are summarized as follows:

- It was observed that the specific surface area values of both fly ash increased after grinding.
- The specific surface area values of both fly ashes before and after grinding were lower than the specific surface area values of cement.

- It was determined that the specific surface area values of ÇYH fly ash before and after grinding were higher than the specific surface area values of AE fly ash.
- The 28-day pozzolanic activity limit value specified in the standards for the original and all grinding times of AE and ÇYH fly ashes was determined as ≥ 75% and above.
- It was determined that while AE and ÇYH ash values were above the specified limit value for 20, 30, 45, and 60 min grinding times, it was lower than the specified limit value for the original and 10 min grinding times.
- It was established that the highest pozzolanic activity index belongs to ÇYH ash after 20, 30, 45, and 60 minutes of grinding time and AE ash for 0 and 10 minutes of grinding time.
- It was observed that the 90-day pozzolanic activity value of AE fly ash remained below the standard value for the original and all grinding times, while the values of ÇYH fly ash were above the standard value for the original and all grinding times.
- The use of fly ash with two different chemical compositions contributed to the improvement of hydration in cement.
- The pozzolanic properties of the fly ash were determined by mechanical method, and the best-performing fly ash was determined as ÇYH ash.
- It enables the fly ash, which has a fine grain structure by grinding, • The use of fly ash with two different chemical compositions contributed to the improvement of hydration in cement.
- The pozzolanic properties of the fly ash were determined by mechanical method and the best performing fly ash was determined as ÇYH ash.
- It enables the fly ash, which has a fine grain structure grinding, to dissolve easily the compounds such as SiO_2 and Al_2O_3 and to increase the Ca^{2+} absorption capacity from the $Ca(OH)_2$ solution.
- It was determined that the bBaine values of both fly ash increased with the grinding effect, but it was still lower than the cement Blaine value.
- Predicted grinding times were not sufficient to improve the pozzolanic properties of both fly ash.
- Considering the fineness and chemical composition of the pozzolanic feature, the fineness was more effective than the chemical component for this study. This effect was clearly observed, especially in the 90-day ÇYH fly ash, and to increase the Ca^{2+} absorption capacity from the $Ca(OH)_2$ solution.
- It was determined that the blaine values of both fly ash increased with the effect of grinding, but it was still lower than the cement blaine value.
- Predicted grinding times were not sufficient to improve the pozzolanic properties of both fly ash.
- Considering the fineness and chemical composition on the pozzolanic feature, fineness was more effective than the chemical component for this study, and this effect was clearly observed, especially in the 90-day ÇYH fly ash.

This study has shown that the pozzolanic activation of fly ashes in our country, which cannot be used as a by-product in any field due to their low pozzolanic activation value, can be increased with grinding and can be used as pozzolanic material in related fields. In this way, the environment will be protected both by ensuring the disposal of waste materials and by avoiding mining activities for the production of a new material. In order to increase the usability of waste ashes, it is recommended by the authors to eliminate the deficiency in this field by conducting studies with different ashes at different grinding times and temperature conditions.

Acknowledgements

"This study was supported by Gümüşhane University Scientific Research Projects Coordinatorship. Project No: 13.F5118.02.1". "This study was supported by Karadeniz Technical University Scientific Research Projects Coordination Unit. Project number HDP-11361". The authors would like to thank GÜ BAP unit and KTU BAP unit for their contributions to the study.

References

[1]. Scheetz, B.E. and Earle, R. (1998). Utilization of fly ash, Current Opinion in Solid State and Materials Science, Volume 3, Issue 5, 510-520.

[2]. Ahmaruzzaman, M. (2010). A review on the utilization of fly ash, Progress in Energy and Combustion Science. 36 (3): 327-363.

[3]. Payá, J., Monzo, J., Borrachero, M.V., and Peris, E. (1995). Mechanical treatment of fly ashes. part I: physico-chemical characterization of ground fly ashes, Cement and Concrete Research, 25, 7, 1469-1479.

[4]. ASTM C 125-15, (2003). Standard Terminology Relating to Concrete and Concrete Aggregates, Annual Book of ASTM Standarts, Pennsylvania, 3, USA.

[5]. Topçuoğlu, Y.A., Gürocak, Z. (2022). Investigation of pozzolanic properties of acidic and basic tuffs: A case study from Elazığ and Gümüşhane regions, GUJS. 12 (4): 1024-1035

[6]. Ustabaş, İ and Kaya, A. (2018). Comparing the

pozzolanic activity properties of obsidian to those of fly ash and blast furnace slag, Construction and Building Materials, 164, 297-307,

[7]. Golewski, G.L. (2022). The Role of Pozzolanic Activity of Siliceous Fly Ash in the Formation of the Structure of Sustainable Cementitious Composites, Sustain. Chem., 3,520–534.

[8]. Joshi, R.C., (1970). Pozzolanic Activity in Synthetic Fly Ashes: I, Experimantel Production and Characterization, Iowa State University, Ph.D., Engineering, civil, Iowa.

[9]. Lea, F.M. (1940). Investigation on pozzolans. Great Britain Dept. of Scientific and Industrial Building and Research Technical Paper No. 27.

[10]. Wenk, K. (1992). Influence of silica fume and fly ash on hidration, microstructure and strength of cement based mixtures, a thesis submitted to the Faculty of Graduete Studies in Partial Fulfilment of the Requriments for the Degree of Master of Science Department of Civil Engineering Calgary, Alberta, 1-126.

[11]. Payá, J., Monzó J., Borrachero, M., V., Peris, E.M., and González-López, E. (1997). Mechanical treatments of fly ashes. Part III: studies on strength development of ground fly ashes (GFA) Cement mortars, Cement and Concrete Research Volume 27, Issue 9, Pages 1365-1377.

[12]. Payá, J., Monzó J., Borrachero, M., V., Peris-Mora, E., and Amahjour, F. (2000). Mechanical treatment of fly ashes: part IV. Strength development of ground fly ash-cement mortars cured at different temperatures, Cement and Concrete Research Volume 30, Issue 4, Pages 543-551.

[13]. Akkaya, B. and Toroğlu, İ. (2017). Investigation of the Relation Between Fineness of Fly Ash and Its Pozzolanic Activities, Karaelmas Journal of Science and Engineering, 7(2):412-418.

[14]. Abdun Nur, E. A. (1961). Fly ash in concrete: an evaluation. Highway, Research Board Bulletin 284.

[15]. Davis, R.E.A (1949). Review of pozzolanic materials and their use in cement concrete. American Society for Testing Materials Special. Techn. Publ. No. 99: 3-15.

[16] Delbridge, N.G. (1957). Reactivity of various fly ashes with lime. Unpublished M.S. thesis. Ames, Iowa, Library, Iowa State University.

[17]. Davis, R.E. (1950). The uses of pozzolans in cements. American Concrete Institute Journal 46: 377-384.

[18]. Minnick, L.J. (1959). Fundamental characteristics of pulverized coal fly ashes. American Society for Testing Materials Proceedings 59: 1155-1177.

[19]. Minnick, L.J. (1968). Reactions of calcium and magnesium compounds with pulverized coal fly ash. Society of Mining Engineers of AIME Preprint 68-F-70.

[20]. Watt, J.D. and Thorn, D. J. Characteristics of fly ashes. I. (1965). Journal of Applied Chemistry 15: 585-594.

[21]. American Society for Testing Materials. Committee C-9 on concrete and concrete aggregates (1962). Cooperative tests of fly ash as an admixture in portland cement concrete. American Society for Testing Materials Proceedings 62: 314-342.

[22]. Mateos, M. (1963). Stabilization of soils with fly ash alone. Iowa State University Soil Research Laboratory Contribution 63-21.

[23] Fredrick, H.A. (1944). Application of fly ash for lean concrete mixes. American Society for Testing Materials Proceedings 44: 910-820.

[24]. Bascetin, A., Adiguzel, D., Eker, H., Odabas, E., and Tuylu., S., (2021). Effects of puzzolanic materials in surface paste disposal by pilot-scale tests: observation of physical changes. International Journal of Environmental Science and Technology, 18, 949–964.

[25]. Kılınçkale, F.M. (1996). The pozzolanic activity of various pozzolans and the strength of the mortars produced with these pozzolans, IMO Technical Journal, 1217-1229.

[26]. Guerrero, A., HernaÂndez, M.S., and GonÄi, S. (2000). The role of the fly ash pozzolanic activity in simulated sulphate radioactive liquid waste, Waste Management, 20, 51-58,

[27]. Payá, J., Borrachero, M.V., Monzó, J., Peris-Mora, E., and Amahjour, F. (2001). Enhanced conductivity measurement techniques for evaluation of fly ash pozzolanic activity, Cement and Concrete Research, Volume 31, Issue 1, Pages 41-49.

[28]. Osbæck, B. (1985). The influence of air content by assessing the pozzolanic activity of fly ash by strength testing, Cement and Concrete Research, Volume 15, Issue 1, Pages 53-64.

[29]. Payá, J., Monzó J., Borrachero, M., V., Peris-Mora, E., and González-López, E. (1996). Mechanical treatment of fly ashes part II: particle morphologies in ground fly ashes (GFA) and workability of GFA-cement mortars, Cement and Concrete Research, Volume 26, Issue 2, Pages 225-235.

[30]. Başçetin, A., Eker, H., Adıgüzel, D., and Tüylü, S. (2020). Investigation of Pozzolanic Properties of Some Additive Materials in Cemented Paste Backfill. Gumushane University Journal of Science. 10 (2): 415-424.

[31]. Eker, H. and Başcetin, A. (2022 a). The study of strength behaviour of zeolite in cemented paste backfill. Geomechanics and Engineering. 29 (4): 421-434.

[32]. Yazıcı, Ş.and Arel, H.Ş., (2012). Effects of fly ash fineness on the mechanical properties of concrete, Sãdhanã, 37, 389–403

[33]. Tangpagasit, J., Cheerarot, R., Jaturapitakkul, C., and Kiattikomol, K. (2005). Packing effect and pozzolanic reaction of fly ash in mortar, Cement and Concrete

Research, 35, 1145– 1151.

[34]. Tkaczewska, E. and Sitarz, M. (2012). The effect of glass structure on the pozzolanicactivity of siliceous fly ashes, Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B. 54 (2): 89–94.

[35]. Sounthararajan, V.M. and Sivakumar, A. (2012). Experimental studies on the effect of fineness of fly ash particles on the accelerated properties, Journal of Engineering and Applied Sciences (ARPN), 7, 12, 1644-1651.

[36]. Mucsi, G., (2016). Mechanical activation of power station fly ash by grinding – a review, Journal of Silicate Based and Composite Materials, 68, 2, 56-61.

[37]. Abualrous, Y. (2017). Characterization of Indian and Canadian fly ash for use in concrete, a thesis submitted in conformity with the requirements for the Degree of Master of Applied Science Department of Civil Engineering University, Toronto, 1-171.

[38]. Demir, İ., Başpınar, M.S., Görhan, G., and Kahraman, E. (2008). Seyitömer Fly Ash and Afyonkarahisar Region Volcanic Determination of Pozzolanic Characteristics of Tuffs, Electronic Journal of Construction Technologies, 1, 39-46.

[39]. Karim, M. R., Zain, M. F. M., Jamil, M., Lai, F. C., and Islam, M. N. (2011). Strength development of mortar and concrete containing fly ash: a review, International Journal of the Physical Sciences, 6, 17, 4137-4153.

[40]. Kiattikomal, K., Jaturapitakkul, C., Songpiriyakij, S., and Chutubtim, S. (2001). A study of ground coarse fly ashes with different finenesses from various sources as pozzolanic materials, Cement and Concrete Composites, 23, 335-343.

[41]. Bouzoubal, N., Zhang M.H., Bilodeau, A., and Malhotra, V.M. (1997). The effect of grinding on the physical properties of fly ash and a portland cement clinker. Cement and Concrete Research. 27 (12): 1861-1874.

[42]. Dvoøák, K. and Hájková, I., (2015). The Effect of high-speed grinding technology on the properties of fly ash, Materials and Technology, 50, 683-687.

[43]. Felekoğlu, B., Türkel, S., and ve Kalyoncu, H. (2009). Optimization of fineness to maximize the strength activity of high-calcium ground fly ash–portland cement composites, Construction and Building Materials, 23, 2053–2061.

[44]. Hela, R. and ve Orsàkovà, D. (2013). The mechanical activation of fly ash, Procedia Engineering, 65, 87-93.

[45]. Demir Şahin, D. (2019). Effects of Fineness In Fly Ashes on Pozzolanic Activity, Karadeniz Technical University, Graduate School of Natural and Applied Sciences, Department of Mining Engineering, PhD Thesis, Turkey, 124s.

[46]. ASTM C 618-12, (1994). Standart Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, Annual Book of ASTM Standarts, Pennsylvania, 3, USA.

[47]. TS EN 196-6, (2010). Cement test methods - chapter 6: determination of fineness, Turkish Standards Institute, 13, Ankara.

[48]. TS EN 450-1/A1, (2013). Part used in fly ash-concrete: 1 definition, properties and conformity criteria, Turkish Standards Institute, 27, Ankara.

[49]. Gürbüz, E. (2009). Effiency of C Type Fly Ashes, Master Thesis, Istanbul Technical University, Institute of Science and Technology, Istanbul1-97.

[50]. Li, D., Sun, R., Wang, D., Ren, C., and Fang, K. (2021). Study on the pozzolanic activity of ultrafine circulating fluidized-bed fly ash prepared by jet mill, Fuel 291,120220.

[51]. Demir Şahin, D., Çullu, M., and Eker, H. (2020). The effect of different fineness values of Afşin Elbistan fly ash on permeability in concrete. Challenge Journal of Structural Mechanics. 6 (2).

[52]. Eker, H. and Bascetin, A. (2022). Influence of silica fume on mechanical property of cemented paste backfill. Construction and Building Materials, 317,126089.

[53]. Bumrongjaroen, W., S. M., Isabelle, and Pegg, I.L. (2007). Characteritaztion of glassy phase in fly ash from Iowa State University, Technical Report, Vitreous State Laboratory the Catholic University of America, Washington, DC 20064.

[54]. Demir Şahin, D., Işık, E., Işık, I., and Çullu, M., (2021). Artificial neuralnetwork modeling for the effect of fly ash fineness on compressive strength, Arabian Journal of Geosciences, Vol. 14, No. 23, pp. 1–14.

ارزیابی فعالیت پوزولانی دو نوع مختلف خاکستر بادی C و F با فاکتور ظرافت

دمیت دمیر شاهین[1*]، ابراهیم کاووس اوغلو[1] و علی عثمان یلماز[2]

1. گروه فناوری معدن و استخراج مواد معدنی، برنامه فناوری معدن، دانشگاه گوموشانه، مدرسه حرفه‌ای گوموشخانه، گوموشخانه، ترکیه
2. گروه مهندسی معدن، دانشکده مهندسی و علوم طبیعی، دانشگاه گوموشخانه، گوموشخانه، ترکیه
3. گروه مهندسی معدن، دانشگاه فنی کارادنیز، ترابزون، ترکیه

ارسال 2023/03/02، پذیرش 2023/04/11

* نویسنده مسئول مکاتبات: demetsahin@gumushane.edu.tr

چکیده:

امروزه انرژی تولید شده از زغالسنگ در مقایسه با سایر منابع مقرون به صرفه است اما با مشکل ضایعات بسیار جدی مواجه است. با این حال، این ضایعات با استفاده از آنها به عنوان افزودنی‌های معدنی در سیمان ارزیابی می‌شوند که منجر به کاهش هزینه سیمان، صرفه جویی در منابع، تولید سیمان دوستدار محیط زیست، کاهش گاز CO_2 و تولید سیمان با مقاومت بالا می‌شود. در این کار، خواص پوزولانی انواع خاکستر بادی (نوع Afşin Elbistan C و نوع Çayırhan F) مورد بررسی قرار گرفته است. خاکستر بادی استفاده شده در این مطالعه ابتدا تحت فرآیند آسیاب (10، 20، 30، 45 و 60 دقیقه) قرار می‌گیرد و سپس آزمون شاخص فعالیت پوزولانی 28 و 90 روزه خاکستر آسیاب شده و آسیاب نشده انجام می‌شود. نتایج به‌دست‌آمده نشان می‌دهد که در مقایسه با آسیاب نشده و 10 دقیقه ارزش فعالیت پوزولانی 28 روزه خاکسترهای 20، 30، 45 و 60 دقیقه‌ای آسیاب بالاتر از مقدار مشخص‌شده در استاندارد است. خاکستر بادی علاوه بر این، برای همه نمونه‌های خاکستر بادی، نتایج شاخص فعالیت پوزولانی 90 روزه نشان می‌دهد که در حالی که مقدار شاخص فعالیت پوزولانی خاکستر بادی چاییرهان (ÇYH) بالاتر از مقدار استاندارد است، خاکستر بادی افشین البیستان (AE) کمتر است. نسبت به استاندارد نتایج مطالعه حاضر نشان می‌دهد که خواص مکانیکی خاکستر بادی با سوزاندن زغالسنگ پس از فرآیند آسیاب افزایش می‌یابد و بنابراین می‌توان از آن به عنوان یک افزودنی معدنی استفاده کرد. با اثر آسیاب کردن، هر دو خاکستر بادی فعالیت پوزولانی را افزایش می دهند..

کلمات کلیدی: خاکستر بادی، زمان آسیاب، شاخص فعالیت پوزولانی، ظرافت، آسیاب.