

Activity of fly ash as an indicator of their modifying ability

**I Yu Markova, A A Bezrodnykh, A Yu Markov, V V Strokovaya and
M A Stepanenko**

Belgorod State Technological University named after V.G. Shukhov, 46,
Kostyukova str., Belgorod, 308012, Russia

E-mail: nelubova@list.ru

Abstract. The article shows the possibility of using fly ash as an active component of binders of various compositions used in the design of composites for road construction purposes. This study was conducted on the basis of the data on the distribution and concentration of acid-base centers on the surface, sorption capacity, specific surface area, and morphological features of dispersed particles of technogenic raw materials. The study substantiates the feasibility of using ashes as a modifying component of low-calcium composites for inorganic binders (cement) due to the high pozzolanic activity, high-calcium composites for organic binders (bitumen emulsions) due to “inertness” and surface smoothness.

1. Introduction

One of the priority tasks for the development of the transport network of the Russian Federation is to increase the number of roads with improved types of pavement structures, as well as to use the capabilities of local raw materials. The fulfillment of these tasks provides an increase in quality and a reduction in the cost of road construction. In this context, the use of non-deficient substandard raw materials in the form of waste generated in various industries is the most economically feasible [1–5]. Among the entire variety of waste, the most large-capacity waste include fuel ashes of various compositions [1–8]. Numerous Russian and foreign studies have substantiated the effectiveness of using fuel ashes of various compositions as a component of building composites. Due to the specific composition and properties of fly ash (polyminerality, polydispersity at a high specific surface, amorphous), such materials can act not only as a dispersed filler in the preparation of materials based on various types of binders, but also as an active component that ensures a qualitative change in the basic physical and chemical parameters of consolidated systems with their use. However, this requires testing the hypothesis regarding the evaluation of fly ash activity, which determines their effectiveness when used in organic, inorganic, or hybrid (complex) as a modifier.

2. Materials and methods

The materials studied were two types of waste from fuel and energy enterprises. The choice of materials is due to the initial fuel difference and, as a consequence, the formed evils properties. Two types of waste from fuel and energy enterprises that are selected for research:

- high-calcium: ash from Nazarovskaya Thermal Power Station (Krasnoyarsk region) obtained by burning brown coal from the Irsha-Borodinsky deposit;
- low-calcium: ash from Troitsk State District Power Plant (Chelyabinsk Region), obtained by burning coal from the Ekibastuz deposit.



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The chemical composition (Table 1) and mineral composition (Table 2, 3) of fuel ashes were determined using an ARL 9900 WorkStation X-ray fluorescence spectrometer with an integrated diffraction system. A quantitative assessment of the composition of the ashes was carried out using quantitative X-ray diffraction based on the Rietveld method, as well as using reference books and the PDF-2 database of the International Center for Diffraction Data (ICDD).

Table 1. Chemical composition of fly ash

Source of ash	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O	loss on ignition
Nazarovskaya Thermal Power Station	37.80	31.55	8.84	8.99	4.40	6.31	0.76	3.15
Troitsk State District Power Station	0.61	62.53	28.75	4.10	0.21	1.06	1.05	4.95

Table 2. Mineral composition of fly ash (Nazarovskaya Thermal Power Station)

Mineral	Quartz	Anhydrite	Portlandite	CA	CAF	Amorphous phase
Content, %	7.6	7.1	8.5	21.4	4.1	51.3

Table 3. The mineral composition of fly ash (Troitsk State District Power Station)

Mineral	Quartz	Mullite	Magnetite	Amorphous phase
Content. %	9.3	18.7	1.9	70.1

The structural features of fly ash were investigated using a TESCAN MIRA 3 LMU high-resolution scanning electron microscope. The activity of fly ash was evaluated as an integral characteristic. Assessment methods: indicator method (by the number of active centers on the fly ash surface); Zaporozhets method (by absorbed calcium hydroxide from solution).

The distribution and concentration of acid-base centers on the surface of ash particles a spectrophotometric method was used for adsorption of indicators with different pKa values from an aqueous medium. The method is based on the adsorption of monobasic indicators on the surface of solid particles in an aqueous medium. A change in the color of the indicators characterizes the amount of adsorption activity of the material.

The essence of the Zaporozhets method is the evaluation of the studied sample adsorption capacity and consists of the following. During the preparation of the required concentration lime solution distilled water was taken and lump quicklime was added to it and kept in a hermetically sealed container for two weeks. Then 1100 ml of the obtained solution having a concentration of 1.1–1.2 g CaO / L was poured into a cylindrical container. The container was stirred for 10–15 minutes, after which 100 ml of the solution was taken with a pipette and filtered. The required 50 ml of the filtrate was titrated with hydrochloric acid to determine the initial concentration of CaO in the solution.

Then took 10 g of the test material and poured into the remaining 1000 ml of lime solution. The resulting solution was stirred for the required period after which like the previous one a 100 ml sample was taken. The selected sample was filtered into a 250 ml vessel to form a 50 ml filtrate.

The concentration of calcium oxide absorbed by the test material titration with a 0.05 N HCl solution was used. The formula determined the concentration of Cao:

$$C_{CaO} = 758AT/B \quad (2.1)$$

C_{CaO} – CaO concentration, g / l;

A – the amount of HCl spent on titration, ml;

T – the titer of HCl;

B – the amount of solution taken from a cylindrical container, ml.

The amount of CaO absorbed by the lime solution additive was determined by the difference between the initial concentration of CaO and its value at a given time. Based on these data the amount of lime absorbed per gram of the quartz component was calculated.

The active specific surface of the ashes was determined by adsorption of gas (nitrogen) according to the BET method using a Sorbie-M device.

3. Results and discussion

According to the data obtained the studied samples are polyfraction materials with various particle sizes. The size of which varies from a few microns to about 65 microns (Figure 1). Particles with a maximum diameter of up to 75 microns are rare. In this case the bulk of the material is represented by spherical particles 5–15 μm in size. High-calcium ash particles (Figure 2, a) with a diameter of about 15–20 μm have a developed surface due to on the one hand the presence of irregular-shaped fusion products on them and on the other to smaller spherical particles (diameter up to 5 μm). Spherical particles of low-calcium ash with a diameter of up to 15–50 μm (Figure 2, b) have a less developed surface. While smaller anisometric particles are uniformly distributed in the sample volume. Ashes with a smoother surface can cause some liquefaction of the system with their use, i.e. “ball bearing effect” realized. In the case of inorganic binders (in particular cement) it is possible to predict the best “glide” of mineral solid particles on the glassy surface of ash particles. Such a plasticizing effect reduces the water content in the concrete mixture which helps to increase its density and strength. In the case of organic binders (bitumen emulsion, bitumen) this effect ensures the formation of thinner organic films on the surface of solid particles which reduce its consumption without losing the quality of the composite as a whole.

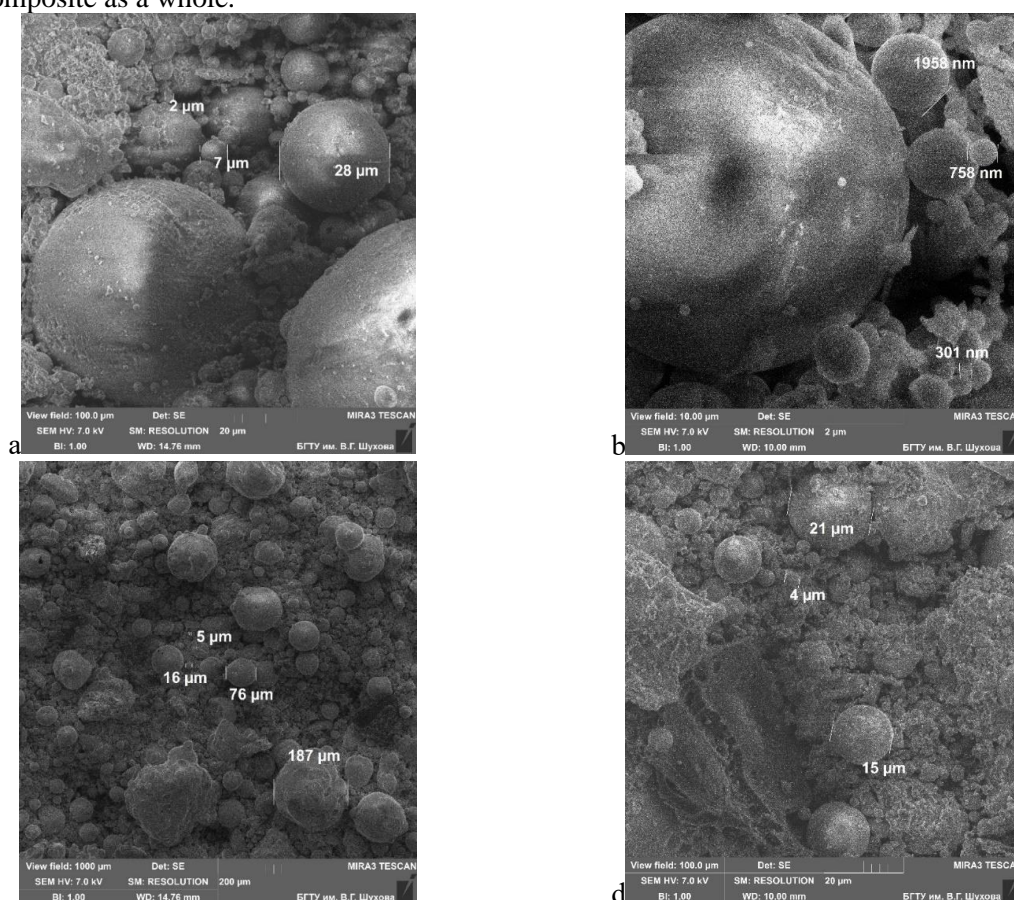


Figure 1. Microstructural features of fly ash: a – Nazarovskaya Thermal Power Station, b – Troitsk State District Power Station

Aluminosilicate polydisperse ash is slightly different in the specific surface area (S_{ss}) (Table 4). For high-calcium ash from Nazarovskaya Thermal Power Station, it is $1600 \text{ m}^2 / \text{kg}$. For low-calcium ash from Troitsk State District Power Station – $3200 \text{ m}^2 / \text{kg}$. There is a discrepancy between the particle size data according to microstructural analysis and the data on the area of the active specific surface. This fact is explained by a large number of anisometric particles of size $<5 \mu\text{m}$ in the composition of low-calcium ash as well as the developed surface of the ash. Which provides a large concentration of adsorbed gas on its surface.

Table 4. Specific surface of fly ash

Ash	$S_{ss}, \text{m}^2 / \text{kg}$
Fly ash from Nazarovskaya Thermal Power Station	1600
Fly ash from Troitsk State District Power Station	3200

According to the data obtained both ashes are bifunctional and heterotypic components characterized by the presence of acids and bases of both types (Table 5, Figure 2). Nevertheless the Trinity fly ash is distinguished by a total of a large number of active centers on its surface. Moreover due to the low content of alkaline elements in the composition of Trinity ash it is characterized by a significantly higher concentration of Bronsted acid centers which are responsible for the formation of stable bonds in the “cement – fly – ash” system as a result of the interaction of the leading cement components with dispersed ash particles.

Table 5. Concentration of active centers on the surface of fly ash ($\times 10^{-3} \text{ mg} \cdot \text{EQ/g}$)

Fly ash	Lewis Foundation -4,4...0	Bronsted acids 0...7	Bronsted Grounds 7...13	Lewis Acids >13	Total
Fly ash from Troitsk State District Power Station	14,3	45,42	70,91	5,05	135,68
Fly ash from Nazarovskaya Thermal Power Station	7,93	4,38	27,86	0	40,17

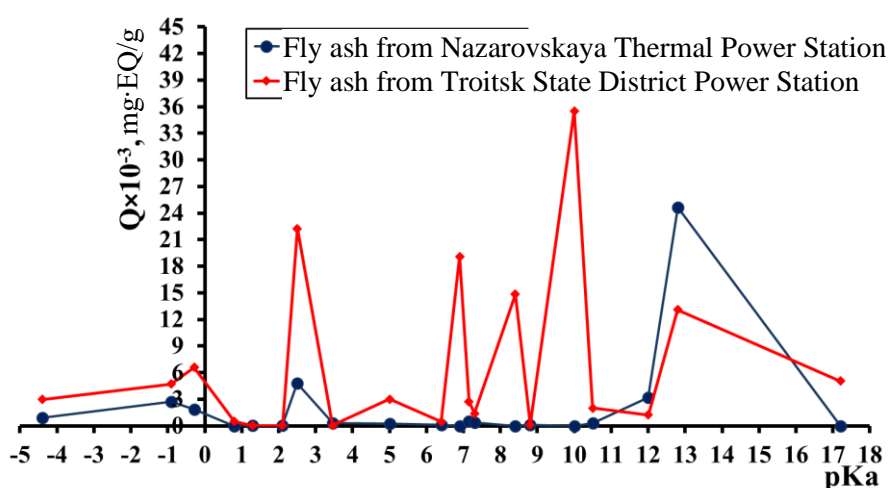


Figure 2. Distribution of acid-base centers on the surface of fly ash: 1 – Nazarovskaya Thermal Power Station; 2 – Troitsk State District Power Station

A high concentration of active centers on the surface of particles of low-calcium fly ash provides the formation of more durable adhesive-cohesive bonds during the structuring and formation of the specified technological physical and mechanical properties of composite materials with their use.

Unlike Troitsk fly ash, the Nazarov fly ash appears to be an almost “inert” component with a significantly lower surface charge (Table 5). The analysis of the Nazarov fly ash shows that the total concentration of active sites of different basicities is almost 3.3 times lower compared to low-calcium

fly ash. Moreover, the maximum content of active centers belongs to the range of Bronsted bases, which is associated with a high content of calcium compounds in the ash. This ratio allows predicting the increase in the adhesive interaction of such ashes in bitumen emulsions due to the heterogeneity of the two contacting surfaces.

Table 6. Sorption capacity of fly ash

Fly ash location	The amount of absorbed CaO, mg / g
Nazarovskaya Thermal Power Station	10
Troitsk State District Power Station	30

The analysis of the sorption capacity of

low- and high-calcium fly ash confirms the data on the concentration of active centers on their surface (Table 6). So, Trinity ash is more active towards free calcium ions in a solution of calcium hydroxide. This feature is associated with a higher content of silicon oxide in the system and, correspondingly, increased content of acidic Bronsted centers. Nazarov ash, characterized by a high content of calcium compounds in its composition, shows a lower sorption capacity. Moreover, in this case, sorption is probably due to the mechanism of ion deposition by chemical affinity.

4. Conclusion

The work shows the activity of fly ash, differing in composition (chemical and mineral), due to the difference in the base burned raw materials. From fuel and energy waste in the form of fly ash, a comprehensive analysis of the composition and acid-base properties of aluminosilicate technogenic raw materials was realized. This analysis allows concluding that all the studied samples have relatively high potential from using them as structuring additives. At the same time, low-calcium ash should be applied as a pozzolanic component in the design of composites based on inorganic hydraulic binders. High-calcium ash has a high potential for use as a hydraulically active component in the design of cementless and organic binders. Besides, due to the high dispersion with a unique polyfraction composition, the use of fly ash in mixtures based on various binders makes it possible to achieve the closest packing of the system, which together provides an increase in the strength of such mixtures compared to traditional mixtures without active components.

5. Acknowledgments

The reported study was funded by RFBR, project number 19-38-90091.

References

- [1] Kozhukhova N I, Teslya A Y, Kozhukhova M I (...) Yermak S N, Ogurtsova Y N 2019 *IOP Conference Series: Materials Science and Engineering* **552(1)** 012035
- [2] Kozhukhova N I, Lebedev M S, Vasilenko M I, Goncharova E N 2018 *Journal of Physics: Conference Series* **1066(1)** 012010
- [3] Kozhukhova N, Zhernovsky I, Voytovich E 2018 *IOP Conference Series: Materials Science and Engineering* **365(3)** 032043
- [4] Kozhukhova N, Kadyshev N, Cherevatova A, Voitovich E, Lushin K 2018 *Advances in Intelligent Systems and Computing* **692** 776–782
- [5] Kozhukhova N I, Zhernovsky I V and Strokova V V 2015 *International Journal of Applied Engineering Research* **10(15)** 35618–35620
- [6] Sobolev K, Flores Vivian I, Saha R, Wasiuddin N M and Saltibus N E 2014 *Fuel* **116** 471–477
- [7] Volodchenko A A, Lesovik V S, Volodchenko A N 2018 *IOP Conference Series: Materials*

- Science and Engineering* **463(3)** 032016
- [8] Lesovik V S, Shukhov V G, Tolstoy A D (...) Novikov K Y, Valerievna S V 2016 *International Journal of Pharmacy and Technology* **8(4)** 24726–24732