

## DEVELOPMENT OF METHODS FOR PREPARING FLY ASH FOR SEPARATION BY ACTIVATION

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### Abstract

**Purpose.** Isolation of the aluminosilicate fraction from fly ash, study of physical and mechanical properties of binders obtained from TPP wastes.

**Methods.** Ash, carbon concentrate (underburn), ash concentrate and products of their treatment with reagents were tested by optical methods. The morphology of the particles of the subjects of inquiry was studied with the scanning electron microscope REM-100. The composition of the ash phases was investigated using the X-ray diffractometer DRON-2.

**Findings.** The technology of sorbents based on coal combustion products through a variety of methods was researched. It is shown that these sorbents are distinctive because their structure has non-localized  $\pi$ -electrons of the graphite-like networks of crystallites of carbon. This circumstance determines not only the uniqueness of electro-physical properties of coal but also adsorption, redox, chemisorption processes on the border of coal-slurry. The listed circumstances allow you to use the original methods of chemical and mechanochemical modification of the surface chemical and coal, due to introducing desired donor and acceptor atoms in carbon frame, which increases the absorption capacity and selectivity carbon sorbents.

**Practical implications.** The article presents the results of receipt of binders based on TPP ash. It has been shown that a component of the fly ash is aluminosilicate spheres that can be used in the production of lightweight concrete. It is proved that the result of mechanochemical activation mixture consisting of alumino-silicates, resulting lightweight concrete has high strength 7-8 MPa, which allows, while maintaining the technical characteristics save from 20 to 30 % of binder. Concrete obtained based on aluminosilicate spheres separated from fly ash may be used to prepare the

outer wall construction, small building blocks, as well as monolithic housing. In comparison with known compositions keramsit compositions comprising TPP waste.

**Keywords:** fly ash, aluminosilicate spheres, mechanical activation, vibro-impact mill

## 1. INTRODUCTION

Solid fuel, which is widely used in the production of electricity, produces a significant amount of ash and slag in the process of combustion.

Given the growing use of solid fuels, in particular low calorific fuel with high ash content, the effective use of TPP ash is in focus. The amount of ash and slag produced by TPPs is 500 thousand tons per 1 million kW of their power. The ash and slag are transported to special waste dumps. An average of 0.3% of the total amount of electricity produced by the TPP is used for the disposal of thermal waste from power plants to the dumps, that is, considerable material resources are spent for that. In addition, waste storage requires the alienation of land that could be otherwise used in agriculture. For example, today's TPP needs 1000 to 2000 hectares of area for its ash-dumps.

The level of ash and slag reuse is about 15% (for comparison: in the USA - 20%, in France - 62%, in Germany - 80%), and they are used as a rule in the production of building materials: as admixture to cement, as components of building concrete and mortar, in road construction, in the manufacture of bricks, and as raw materials for the production of  $Al_2O_3$ ,  $Fe_3O_4$ ,  $TiO_2$ ,  $K_2O$ ,  $Na_2O$ ,  $P_2O_5$ ,  $U_3O_8$ , etc..

Some publications propose methods for the integrated use of TPP ash with the manufacture of conditioned products to be used in various industries as substitutes for natural raw materials.

Studies on the immobilization of heavy metal waste in the mixtures of portland cement and ground fly ash are now of importance. For the research, aqueous solutions containing zinc, cadmium and mercury were used. It was found that the degree of metal immobilization significantly increases in the presence of ash.

So attempts are being made to systematize the TPP ashes according to the specified indicators in order to predict the most rational use of both ash and its individual components obtained by

ash separation in various ways (mechanical, physic-chemical, chemical separation, etc.).

Ash from thermal power plants (TPPs) is produced as a result of coal combustion and is, on the one hand, a source of environmental pollution; but on the other hand, it is a resource of raw materials needed for industry.

In Ukraine, thousands of tons of ash containing a number of useful components have accumulated in the TPP dump. Moreover, more than 10 million tons of fly ash is added to the TPP dumps annually. Despite the relatively high content of phase constituents with high consumer properties in a number of ashes, it is only possible to attribute them to technogenic minerals by convention, since no economically viable methods of extracting the useful components are now available. Therefore, ash from thermal power plants is used to a limited extent.

In Ukraine, up to 75% of all electricity is supplied by thermal power plants that mainly use coal as a fuel; this leads to producing huge quantities of ash and slag waste. Every 10 years (according to statistical data), the amount of ash and slag produced in thermal power plants doubles.

Burned rock and coal waste are useful and widely used mineral raw materials for the production of building materials.

Ash is dust-like residuals formed by burning solid fuels, with particle size of 5 to 100  $\mu\text{m}$ . Ash is classified according to the type of fuel being burned, the way it is prepared and burned, place where ash forms in the boiler, and methods of its disposal.

Fuel combustion is accompanied by the firing of barren rock, which results in the dehydration of clay substances and formation of low-base aluminates and calcium silicates. Depending on the amount of liquid phase in the ash, the content of glass, which usually has a gelenite-melilite composition, may vary widely.

Ash consists of organic and inorganic phases. The inorganic phase, in turn, includes aggregated and non-aggregated glass particles, as well as crystalline matter.

Coal ash may include, by volume, the following components: 1 – 22% unburned fuel particles, i.e., the organic phase; 25 – 85% aggregated vitreous particles; 8 – 57% non-aggregated vitreous particles, and 0.2 – 20% crystalline components [1].

Ash density and volume weight vary depending on the content of unburned fuel particles in it and its granulometric composition. The volume weight of ash is also affected by the fuel combustion temperature, ash humidity and degree of compaction whose values range from 1.75 to 2.4 kg / m<sup>3</sup>, and the volume weight in loose state, which may be 600 to 1300 kg / m<sup>3</sup>. The specific surface area of ash from different TPPs varies and ranges from 1100 to 3000 cm<sup>3</sup> / g and more.

Fuel slags are vitreous grains of irregular shape up to 40 mm in size, and they are the main type of waste in lump coal combustion. In the case of pulverized coal combustion, the slag makes up 10–25% of the mass of the ash formed. Slags form either as a result of sintering of individual particles on the fire grate at a temperature above 1000° C, or as a result of cooling the mineral matter of coal, having been molten at a temperature of above 1300 °C.

## **2. PURPOSE**

Isolation of the aluminosilicate fraction from fly ash, study of physical and mechanical properties of binders obtained from TPP wastes.

## **3. FORMULATING THE PROBLEM**

To obtain a raw material for manufacturing heat-insulating materials, fly ash was subjected to the following operations: preliminary flotation performed to separate the inorganic and organic parts, followed by activation of the inorganic part by two methods, i.e. chemical and mechanochemical activation. The consumer properties of the raw materials were assessed by studying their phase composition, physico-chemical and physico-mechanical properties, and their compliance with the technical specifications for the further processing of the products obtained.

Ash, carbon concentrate (underburn), ash concentrate and products of their treatment with reagents were tested by optical methods. The morphology of the particles of the subjects of inquiry was studied with the scanning electron microscope REM–100. The composition of the ash phases was investigated using the X-ray diffractometer DRON–2.

#### 4. RESULTS OF ANALYSIS

Coal ash is formed from all mineral impurities in the coal bands, rock layers of the roof and soil, which are entrapped in the commercial coal during its mining. The major impurities are clayed minerals and quartz, while carbonates, sulphides, iron oxides and other minerals are present in minor amounts. The phase composition of the ash is mainly determined by clayed minerals, which are transformed into other aluminosilicates (glass phases, possibly mullite, cristobalite) during high-temperature processing in boilers. It should be taken into account that this is a large group of minerals with compositions varying over a wide range [2].

In natural conditions, the group of mixed-layer minerals is the most common. A combination of layers of hydromica, montmorillonites, chlorites and vermiculites is of frequent occurrence. A common feature of all clayed minerals is their aluminosilicate composition.

The challenge is to create a technically rational and cost-effective process for separating the constituent components of TPP ash.

Ash is a complex polymineral system, characterized by varying composition. Depending on its reactivity and mineral composition, the content of components in the waste varies widely. Thus, for example, the carbon content of the waste can vary from 12 to 45% over a period of several hours.

A dispersed analysis of the TPP fly ash suggests a conclusion that it is advisable to separate particles of a narrow class of fineness, within the range of 40 to 150  $\mu\text{m}$ , with an ash content of about 33%.

The product (larger than 40  $\mu\text{m}$  with a yield of 25% of the total ash mass) can be used as a heat-insulating coating in steel casting (instead of ash-graphite mixtures) to produce ingots of killed steel, for example wheel steel.

In addition, the TPP ash may be used to obtain an ash product with an ash content of more than 90% (fineness less than 40  $\mu\text{m}$  with a yield of 75% of the total ash mass) for the production of ceramic and other products.

The former product may be enriched by flotation. As a result, the coal concentrate may contain less than 20% ash with a sulfur content of about 0.4%. The sulfur content exceeds the European

requirements. Such a coal product may be used as a reducing agent in metallurgical processes, agglomeration, etc. The calorific value of the concentrate is about 6,000 kcal / kg (25,000 kJ / kg).

TPP ash with high carbon underburn should be subject to flotation to obtain a carbonaceous fraction (concentrate) and mineral fraction (waste).

The unburned particles of coal can be separated by direct flotation using apolar and heteropolar surfactants at a low pH of the pulp (pH 6 – 8 and pH 3– 6,5 at the first and the second stage, respectively). Several recleanings are needed to obtain products of the specified quality. A method has been developed for ash flotation with the use of MK reagent as a collector in the presence of a depressor. The method ensures obtaining conditioned products without recleaning, with 95-98% carbon yield to the concentrate.

A preliminary hydroclassification of ash into 40  $\mu\text{m}$  class enhances the efficiency of its separation.

The effect of the raw material grinding on the process of ash flotation was studied. Due to the increased contrast range of the phases being separated, a concentrate with a high content of the combustible fraction was obtained with a slight change in the ash content of the waste. The inverse flotation of the TPP ash allows obtaining products with physico-chemical properties that are different from the properties of the products obtained by direct ash flotation. Hence, the carbon-bearing fraction of ash features a high specific surface area, which allows it to be used as an effective sorbent, in contrast to a direct flotation concentrate, which exhibits a slightly less effective specific surface area of the particles due to collector adsorption on their surface. The reverse flotation waste manifests clearly expressed hydrophobic properties due to the collector adsorption on the surface of the particles, which allows using it as a hydrophobic filler of polymer composite materials with no additional surface modification. The essence of this method is the use of a depressor of coal particles (carbon-alkaline reagent) and a MSTM (Soap of crude tallow oil) collector with adjusting the pH of the medium. The method allows the extraction of the ash mineral fraction into the froth, while the flotation tail will be a carbon-containing fraction of ash.

The most important phase components of ash are iron oxides (20%). Iron compounds are part of the spheroidized particles of the glass phase. The magnetic component is black melted balls consisting of magnetite and hematite. The use of dry and wet magnetic separation allows the separation of high-quality magnetite from fly ash. Magnetite, obtained in this way, can be used as a weighting material in heavy medium coal preparation. The nonmagnetic product is used for the manufacture of cement, as a filler for mining workings, etc. Also, dry ash can be separated by electrostatic separation in electrostatic corona drum separators with a sufficiently high carbon extraction into the concentrate.

A complex use of ash components involves extracting rare-earth elements, refractory and non-ferrous metals. The average content of metals in ash is much higher than in sedimentary rocks. Even with minimal content of rare-earth elements in ash, their extraction can be beneficial. Ash and slag waste can be an important raw material for alumina production. For this purpose, several flow processes have been developed, which can be divided into two groups, namely: acid and alkaline methods.

The chemical composition of the mineral matter of the ash enrichment products practically coincides with the chemical composition of the waste, with the exception of the carbon content.

An ash processing technique and a plant operating in conjugation with TPP will allow obtaining products of specified quality irrespective of the conditions of coal combustion at the TPP. This, on the one hand, excludes building new ash dumps at the TPP, and on the other hand, allows the production of sorbents of oil products and heavy metals, heat-insulating coatings for steel casting, low-sulfur reductants, fuels, and raw materials for building materials.

Carbonaceous concentrate is also an effective sorbent of apolar and surface-active substances (surfactants), including petroleum products.

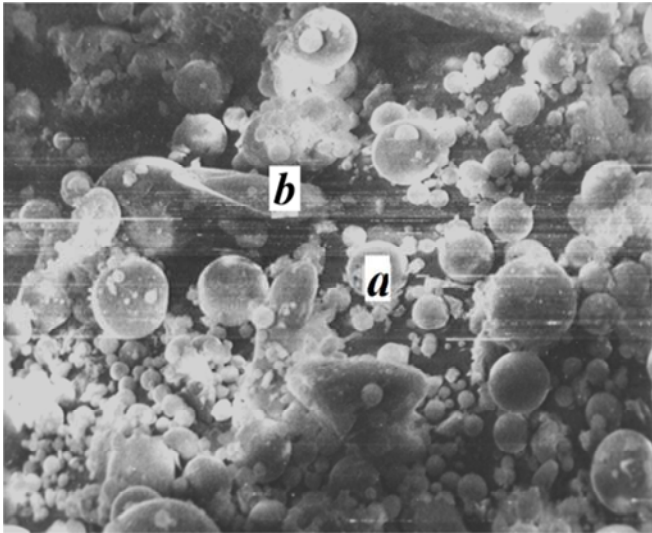
The resulting ash cake (mineral matter of ash) may have an ash content of 90-95%. Decarburized aluminosilicates can find a variety of applications in the production of building materials, composites, in metallurgy and other industries.

The studies confirmed the effectiveness of the use of enriched ash in the preparation of clay-ash claydite and brick, high-quality ash

gravel, contact-condensation mixtures, as well as in the construction of road bases and pavements.

Electron microscopic studies and X-ray diffraction analysis of the morphology of the ash phases and products of its enrichment revealed the features of their surface microstructures. Figure 1 shows the general view of TPP ash particles.

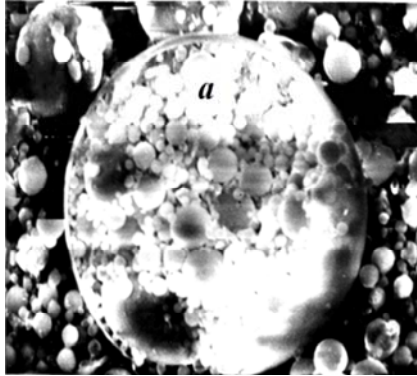
Figure 1 shows that ash consists mainly of two components: alumina-silicate particles of spherical shape and unburned coal particles (carbon underburn).



**Fig. 1.** General view of TPP ash particles (initial), magnification 517x:  
a - spheres; b - coal particles

Silicate particles of irregular shape are few, these are mainly fragments of spherical particles; particles of slag and other minerals occur occasionally. Aluminosilicate particles have different degrees of hollowness: from balls with a thin shell (microspheres), to practically dense particles (with relatively small inclusions of the rock inside). In all cases, their surface is smooth, sometimes characterized by the presence of small protrusions-nipples (Figure 2).



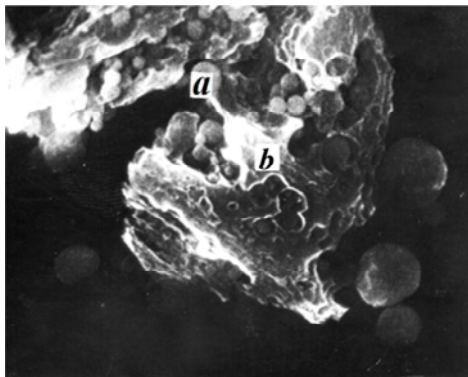


**Fig. 2.** General view of the TPP ash concentrate, magnification 929x:  
a – spheres; b – coal particles

Through-pores occur on the surface, but as a rule, porosity in the form of small bubbles is only observed within the sphere shells. The size of spheres varies in wide limits: from micron fractions, to hundredths of millimeters. Large spheres are single and are formed by smaller microspheres. Spheres with a size of 5 to 20  $\mu\text{m}$  predominate.

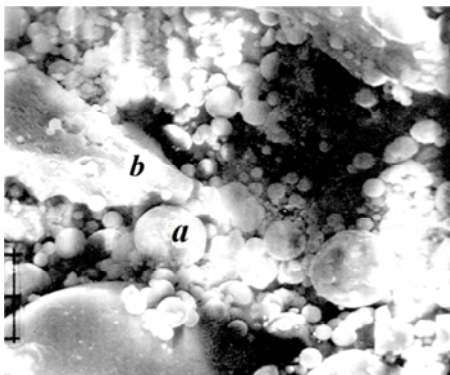
Chemical activation was carried out by treating the ash with NaOH solution.

Figure 3 shows a particle of coal concentrate obtained from TPP ash and treated with a 20% solution of NaOH.



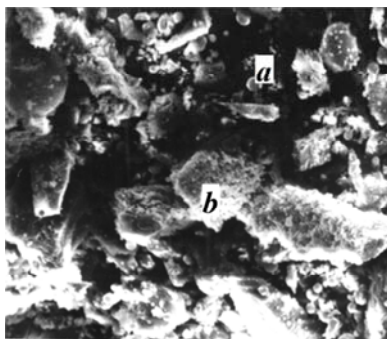
**Fig. 3.** General view of TPP ash particles (after treatment with 20% NaOH), magnification 1305X: a – spheres; b – coal particles

Treating the samples with alkali results in a partial separation of the coal particles and shallowly embedded spheres from the concentrate surface, so that its surface acquires a cellular microstructure. Colonies of spheres located more deeply (in microcracks and microcavities) are not separated by this chemical activation, their separation is possible through mechanical action. After the treatment of the TPP ash concentrate with a 40% solution of NaOH, the sample material predominantly consists of disintegrated spheres (Figure 4).



**Fig. 4.** Ash concentrate after treatment with 40% NaOH, magnification 842x:  
a – spheres; b – coal particles

Figure 5 shows the general view of particles of the TPP carbon concentrate.



**Fig. 5.** General view of the carbon concentrate of TPP ashes, magnification 20x:  
a – spheres; b – coal particles

The spheres are mainly vitreous, colorless of two types: transparent or translucent "white".

Some spheres are located in the depressions of coal particles formed during its uneven burning (gasification), therefore the carbon concentrate consists of a mechanical mixture and technogenic clusters of aluminosilicate spheres and coal particles.

There occur dark opaque spheres, which along with the silicate part contain dendritic magnetite. In addition, the X-ray phase analysis of samples of ash carbon concentrates revealed peaks of quartz, magnetite, hematite and the presence of pyrrhotite and maghemite.

The chemical composition of fly ash from DTEK Pridneprovskaya TES is presented in Table 1.

**Table 1**

**Chemical composition of fly ash**

Product	Content, % on dry substance										
	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	C
Fly-ash	49.7	12.3	2.1	1.3	0.4	12.8	0.5	0.9	3.1	0.6	12.0

Table 1 shows that, after the separation of aluminosilicate spheres (AS) from fly ash, they can be used to produce various grades of concrete [3]. The most common binder used in construction is portland cement. Depending on the purpose, portland cement of M 300, 400, 500 grades is used.

As an alternative raw material, the study used AS that feature latent (hidden) properties; to activate them, it is necessary to carry out special technological operations.

At the first stage, the concrete composition was selected by selecting a rational "cement-to-AS" ratio of their mixture.

The concrete mixtures and cement paste were produced in compliance with DSTU B V.2.7-92-99.

All the compositions feature an increased water consumption, which reduces the strength of the material. This can be explained by the high water demand of the AS, although the water absorption of the concrete remains within the permissible limits.

An analysis of the experimental data leads to a conclusion that compositions 4 – 5 are optimal. These are the compositions with a moderate cement consumption (190–210 kg) and they exhibit the necessary properties (compressive strength, thermal conductivity).

Table 2 shows the compositions of lightweight concrete and their basic physical and mechanical characteristics.

**Table 2**

**Physical and mechanical properties of fly ash-based binders**

Experiment No.	Consumption of materials per 1 m <sup>3</sup>			Main characteristics and properties					
	Cement, kg	Aluminosilicate spheres (AS), kg	Water, l	Density, kg / m <sup>3</sup>	Bending strength, MPa	Compressive strength, MPa	Conductivity coefficient, W / m · °C	Water absorption by volume, %	Frost resistance, cycle
1	300	350	360	750	1.9	7.5	0.16	5	25
2	250	360	360	696	1.7	6.5	0.15	6	25
3	210	380	370	650	1.3	4.8	0.14	6	25
4	190	380	365	620	9.0	4.0	0.14	6	25
5	160	370	330	600	7.0	3.3	0.14	6	25
6	120	390	340	540	6.0	2.6	0.12	7	25
7	100	396	340	530	4.5	1.3	0.12	7	25
8	80	400	360	510	3.5	0.9	0.12	8	25

A feature of the AS use is the creation of a porous (closed) structure throughout the volume of the material. The cement paste envelops the AS in the course of stirring and creates a strong frame after hardening [4]. The experimental results can be explained by the insufficient volume of the cement paste for enveloping the AS and the creation of a strong framework.

It is interesting to note that a decrease in the consumption of cement leads to a significant deterioration of its strength characteristics.

It is known that plasticizers are used to increase the strength of concrete. In this study, the problem was approached by pre-activation of a mixture of cement and AS isolated from fly ash, in a vertical vibratory mill. This approach allows to fully reveal the

hidden properties of some substances and use the potentialities of other substances (binders).

Mechanochemical activation was carried out in a vertical vibratory mill, designed and manufactured at the National Mining University. [5].

Table 3 shows the results of calculating the kinetic curves and internal energy  $U$  consumed in grinding the mixture in a laboratory vertical vibratory mill.

**Table 3**

**Energy characteristics of aluminosilicate grinding process**

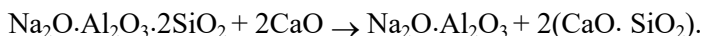
Grinding time, t, s	Internal energy, U, kJ	Specific surface area, S, m <sup>2</sup> / kg	Dispersion constant, k, s <sup>-1</sup>
0	2500.00	165	0.6
1	4210.08	178.7	1.7·10 <sup>-2</sup>
10	5363.14	13431	1.8·10 <sup>-2</sup>
20	6044.00	2665.7	1.9·10 <sup>-2</sup>
30	6031.84	3204.8	2.2·10 <sup>-2</sup>
40	6009.73	3498.4	2.5·10 <sup>-2</sup>
50	5687.38	3797.6	2.9·10 <sup>-2</sup>
60	5658.30	3928.7	3.1·10 <sup>-2</sup>
120	6056.67	3812.9	3.0·10 <sup>-2</sup>
180	6092.47	3851.6	3.1·10 <sup>-2</sup>
240	6082.09	3933.6	3.2·10 <sup>-2</sup>
300	5992.00	4358.1	3.0·10 <sup>-2</sup>

The data in Table 3 demonstrate that grinding predominantly lasts for 40 – 50 minutes, an energetically stable process associated with the formation of activated complexes starts in the 20th minute; the activated complexes should not be confused with aggregates that do not feature the improved energy characteristics.

**Discussion.** A mixture of cement and AS is not individual silicates, but a solid solution. In activating the isolated aluminosilicates in a vertical vibratory mill, the surface is partially blocked by phase contacts and by the formation of micropores inaccessible to water molecules [6]. In this case, the formation of the reinforcing core of the crystallization spatial structure is basically completed. Further grinding results in hardening the condensation-crystallization structure due to the intergrowth of new hydrated

formations and chemical condensation of the surfaces of Si-OH groups with the formation of Si-O-Si bonds; new coagulation contacts appear, which later turn into phase contacts.

Thus, the ability of the components to be set and hardened when mixed with water will depend on the only crystalline component  $\beta$ -2CaO·SiO<sub>2</sub> formed by the reaction:

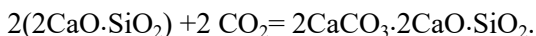


It further interacts with SiO<sub>2</sub> (from AS) by the reaction:



In order to confirm the changes that occur as a result of mixing the concrete components with water, spectroscopic studies were carried out after the vibro-impact processing. The infrared spectra of the activated samples show the main band shift 716, 878 cm<sup>-1</sup>, which intensifies C<sub>3</sub>S. The maximum of the broad vibration band  $\nu_{\text{as}}\text{SiO}_4$  shifts toward larger wave numbers. The spectra of AS being hydrated indicate absorption, which is not characteristic of orthosilicates, in addition to the shift of the stretching band Si=O – vibrations to 1050 cm<sup>-1</sup>. Also, bands of deformation vibrations were detected in the low-frequency region, insignificant absorption was observed in the interval of 600-800 cm<sup>-1</sup>, which indicates the condensation of tetrahedra and formation of layered hydrosilicates.

Absorption in the region 1430 – 1480 cm<sup>-1</sup> is associated with the carbonization of samples, which can occur due to prolonged solidification in the open air. Thus, as a result of the dicalcium silicate interaction with atmospheric carbon dioxide, calcium carbonate crystallizes together with pseudo-wollastonite by the reaction:



Activation of the mixture containing aluminosilicates leads to the formation of particles of irregular shapes. When ground, an AS splits along planes located at an angle of 90°; as a result, its powder consists of block-like particles and fragments. This mineral is characterized by a relatively high Mohs hardness. As the particle sizes are reduced to 5 μm or less, their abrasiveness is reduced due to the reduction of the particle edge sharpness; consequently, the mixture is characterized by a smaller specific surface area due to

enlarged particle sizes and low content of fine fractions. A feature of the aluminosilicate activation in vertical vibratory mills is the production of homogeneous powders with an increased content of fine fractions [4].

The ground samples were also analyzed by X-ray fluorescence spectroscopy to determine the structure changes by a chemical analysis. Fig. 6 shows the obtained X-ray phase spectra.

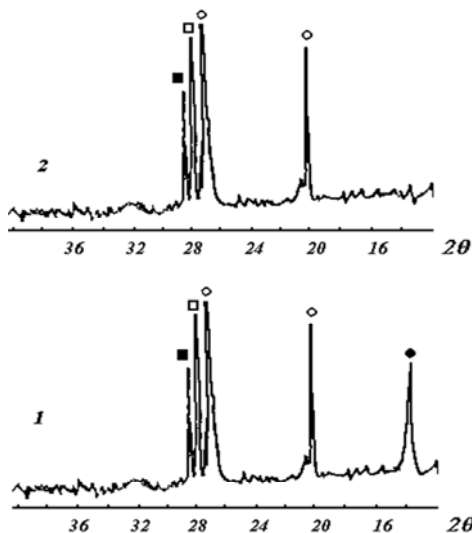


Fig. 6. Diffractograms of vibro-activated (1) and initial (2) ash

It was found that when the mixture is being ground, the structure of the AS changes, since breaking the crystal lattice as a rule destroys the weakest bonds-bridges between sodium, potassium and calcium oxides. Free ions formed on the surface of the particles interact with the environment; thus, in a moist medium they interact with hydrogen ions of water (chemisorption) to form free hydroxyls, which produces an alkaline medium that increases with decreasing the particle sizes.

Products of TPP ash separation may be used in various industries: metallurgy, power engineering, chemical industry, building material production.

In metallurgy, attempts are being made to replace the beneficiated char with the high-temperature char and anthracite in the process of iron ore concentrate agglomeration. Obviously, a high-carbon flotation concentrate can be used to partially replace the beneficiated char.

Table 4 presents the test results for the activated AS samples; the results demonstrate that the mechanochemical treatment enables obtaining high-strength concrete with a strength of 7-8 MPa.

**Table 4**

**Physical and mechanical properties of fly ash-based binders after mechanochemical activation**

Sample	Specific surface, m <sup>2</sup> / g	Density of initial mixture, kg / m <sup>3</sup>	Compressive strength, MPa	Water absorption, %
1	0.18	1700	6.2	2.5
2	0.18	1600	6.8	2.4
3	0.18	1700	7.1	2.2
4	0.18	1700	7.5	2.6

Thus, preliminary mechanoactivation of fly ash-based binders allows to improve the water absorption and enhance their strengths.

In the production of metallized pellets, the fuel additive (beneficiated char) makes up 14% (grain size of <100 microns - 70%, ash content - 18.35%, sulfur content - 0.65%). Thus, without lowering the quality of metallized pellets, the high-temperature char may be replaced by ash flotation concentrate.

As a component of pulverized fuel oil compositions for blast furnace processes, it is possible to use low-ash flotation concentrate. In addition, a method was developed for metal siphoning into a mold, which uses a concentrate with carbon content of 35 - 60% as a heat-insulating coating. It is important that the use of this material allows abandoning graphite for the same purposes.

In the energy sector, the concentrate froth can be used as a fuel admixture to boiler fuel. The use of concentrate can significantly reduce unburned carbon losses when burning the AS grade coal; in addition, the operating parameters of the boiler will not deteriorate under the condition of continuous dispensing of the concentrate.



The method for sorption of heavy metal cations has been developed, which allows capturing them from industrial effluents. In this regard, a concentrate froth of the cleaner flotation is the most effective due to its high carbon content. The cleaner flotation waste with ash content of 40 - 50% may be used as a sorbent of organic acids and various petroleum products. An ash-based sorbent was obtained through changes in the boiler temperatures and coarsening the ground raw materials; it is sufficiently effective for the purification of surfactant-containing sewage.

Waste of TPP ash flotation is more widely used in the production of building materials than the initial ash. This can be explained by the adjustable carbon content and granulometric compositions of the ash mineral fraction.

Flotation waste is beneficially used in the manufacture of various concretes and concrete mixtures in order to save cement without deterioration in the strength characteristics of the concrete. Moreover, they can be used to obtain special concretes, for example, foam concrete, light-weight and cellular concretes. By the addition of ash mineral fraction, the consumption of cement is significantly reduced. In the process of producing asphalt concrete mixtures, it is recommended to use the product of the TPP ash flotation as a mineral powder; the mixture thus obtained is cheaper than that with a limestone mineral powder. It is not inferior in terms of performance and strength parameters. In the manufacture of wall products, a modified ash of low-reactive coal added to clay may serve as raw material. The obtained burned bricks exhibit higher strength characteristics than the material with no modified ash admixtures.

The promising direction of the use of ash wastes is their processing into various fillings for building materials. Lightweight fillers are made by granulation of ash with the subsequent firing of the resulting pellets. Ash, together with loam and waste admixture from a lead mining and processing enterprise, is part of the mixture for agglomerated pyrite. A method for obtaining artificial filler has been proposed, which involves the separation of ash into two classes, with further processing the class that contains about 4.5% of unburned coal residuals.

Methods for the production of sorbents. Carbon sorbents may be obtained by high temperature coal processing and, in particular, by

combustion. The optimum carbon content of the sorbents can be achieved by controlling the coal combustion process or by separating the resulting products. The separation process can occur in air medium (electro- and pneumatic separation) and water medium (flotation, selective flocculation, etc.).

The major parameters that influence the carbon content in the sorbents derived from the coal combustion are the dust dispersity and excess air coefficient. Coarsening the coal grinding and a decrease in the excess air coefficient lead to an increase in the carry-over carbon content. Some methods for obtaining sorbents, which have been developed by our team, are listed below.

The technique refers to the ways of enrichment of dispersed materials having electrical properties. It can be used for enrichment of clayed carbon-containing materials that have undergone heat treatment, for example, ash from thermal power plants.

The technique ensures obtaining a carbon-containing fraction with a carbon content of up to 50% and high-ash waste with ash content of 98%.

The purpose can be reached in the following way: the fuel combustion is performed at a temperature of 900 – 1800°C at a fuel flow rate, the corresponding excess air coefficient of 1-2, and a voltage of 20-30 kV in the first field of high-resistivity electrostatic precipitators, while the ash enrichment occurs directly in the electrostatic precipitator.

Ash component of the ash is captured in the first field of high-resistivity electrostatic precipitators, while carbon-containing particles slip through this area and are caught in the second field, or directly in front of the smoke exhauster. At the same time, the highest possible voltage (close to the breakdown) is being maintained in the second field of the high-resistivity electrostatic precipitators. The temperature of the dust-air mixture is above 100°C.

The variations of the excess air ratio during heat treatment and the voltage on the electrodes forming corona in the process of separation have shown an unexpected result, namely, a product containing up to 78% of carbon is collected in the second field and after the electrostatic precipitators. The separation efficiency is enhanced, firstly, due to the reduction of adhesion properties of the system at a

temperature above the dew point; secondly, as a result of the individual movement of particles in the dust-loaded air stream under the action of the electric field, in contrast to conventional ball electrostatic separation in the electronic drum separator.

When the temperature of the dust-air mixture is below the dew point, the electrical resistance of the system dramatically decreases due to the condensation of water vapor, which leads to a deterioration of the product separation and capture.

The product has beneficial properties and can be used as a substitute for low-sulfur fuel in metallurgical processes, as a heat insulating filler, low-cost sorbent, etc.

The collection electrodes in the first field of the high-resistivity electrostatic precipitator collect a product which is an aluminosilicate fraction with an ash content of up to 98%. The fraction is a dry loose mass, which does not require additional preparation for use in construction, in the preparation of various suspensions, etc.

The separation properties of the high-resistivity electrostatic precipitator with a relatively weak electric field are based on the fact that particles with different resistivity are captured with different efficiency. Fly ash particles about 50  $\mu\text{m}$  in size with a resistivity greater than  $10^2 \text{ ohm}\cdot\text{m}$  are captured effectively, while unburned coal with the particle size of about 120  $\mu\text{m}$  and a resistivity of less than  $10^2 \text{ ohm}\cdot\text{m}$  easily lose the negative charge as they arrive at the collecting electrode. As a consequence, they acquire a positive charge and are repulsed by the collection electrode, re-entrained in the gas stream and carried out of the high-resistivity electrostatic precipitator.

There is an assumption that coal ash particles of an irregular shape may give off their charge, even without touching the electrode, as a result of a corona discharge that occurs between a grounded electrode and negatively charged particles.

In the second field of the high-resistivity electrostatic precipitators operating with relatively high voltage (close to a breakdown), coal particles show less tendency to be repulsed from the collecting electrode due to the electric field strength.

More than 50% of coal particles pass through the second field and settle on the collection electrode of this field. After leaving the high-resistivity electrostatic precipitator, the uncaptured carbon particles

are trapped by well-known methods, e.g. air cyclones, sleeve filters or other devices installed in front of the smoke exhaust.

A decrease in the excess air coefficient, and consequently, in the velocity of the gas stream, is accompanied by underburn in the boiler, which leads to an increase in the amount of carbon-containing particles in the stream. In case of low coal combustion, it is possible to obtain products with the value exceeding the value of unburned coal taking into account the cost of its handling and processing. The carbon content of the enriched product was obtained with an excess air coefficient  $\alpha = 1 - 2$ . At higher values, the effect of enrichment is sharply reduced and heat loss increase. With a reduced excess air coefficient (less than 1.0), the percentage of underburn can exceed 80%, which makes the process economically disadvantageous. In addition, the abrasive wear of metal surfaces rises. When excess air coefficient is raised ( $\alpha = 2$ ), the concentration of carbon in the enriched carbonaceous product decreases dramatically, which is also ineffective. The tables show that the quality of the resulting products is determined by the excess air coefficient and the voltage applied to the electrodes. Voltage below 0.95 of breakdown results in a decrease in carbon content of the enriched product.

The proposed method of electric enrichment of a clayed carbon-containing product will provide the production of desired aluminosilicate and carbon-containing raw materials. The aluminosilicate product may be used as a main component in the manufacture of wall products and in the brick industry, and as an additive to various mixtures. The carbonaceous product may be used as a low-cost sorbent and a substitute for low-sulfur fuel in metallurgical processes, as a heat-insulating additive and for other purposes.

## CONCLUSIONS

The analysis of the obtained results gives grounds for the following conclusions:

1. Concrete obtained on the basis of alumina-silicate spheres isolated from fly ash can be used for the production of lightweight concrete, external wall structures, small building blocks, and also in monolithic housing construction. In comparison with the existing

compositions of expanded clay lightweight concrete, the compositions containing the TPP waste allow to save 20 to 30% of the binder, the performance characteristics being maintained.

2. Preliminary vibro-impact activation allows increasing the reactivity of aluminosilicates due to the formation of new effective bonds, which improves the physico-mechanical properties of binders based on them.

3. The study complies with the high-priority strategic directions in mining industry and is devoted to the development and investigation of multipurpose sorbents to be used in environmentally friendly technologies for mining and processing minerals (coal, ores, ferrous and non-ferrous metals, etc.).

4. It has been discovered that in the case of high-temperature coal processing (within the range of 800-1300 ° C), sorbents of multipurpose use can be obtained.

5. It has been found that the most effective low-cost sorbents may be produced at TPPs with the controlled combustion of coal of certain grades.

6. The mechanism of action of carbon-containing sorbents was studied. It has been found that adsorption of electrolytes occurs due to donor-acceptor interaction, while apolar surface-active substances are adsorbed due to the formation of strong structures.

7. A new mechanism of sorption by certain components of carbon-containing ash (microspheres), which are spherical hollow particles, has been established.

8. Identification of sorbents was carried out; it has been found that the adsorption of organic acids by microspheres obeys the Traube series.

9. Analysis of the microporous structure revealed the presence of micro- and macropores in the sorbents.

10. It has been established that given their adsorption properties, the sorbents under study are amphoteric adsorbents, i.e., they are capable of adsorbing both acids and hydroxides. This implies they can adsorb complex electrolytes, though their anion exchange properties are only expressed in the case of high-temperature processing.

11. The parameters of metal cation adsorption by sorbents of various compositions have been evaluated. The kinetic

characteristics of the isotope exchange of cations in the oxidized coal were determined in the state of the adsorption equilibrium of the coal – solution system.

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