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The Influence of Treatment of Apolar Collectors on the Performance of Carbon Extraction from Ash of Coal Power Plants

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The influence of ultrasonic treatment of flotation reagents on the yield of carbon concentrate and its carbon content, and the duration of flotation, was studied. It has been established that the effect of ultrasound on flotation reagents leads to almost complete dispersion and a 3-fold reduction in the consumption of collectors. It is shown that with an increase in the time of ultrasonic treatment of collectors, the volume fraction of collector droplets with a size of less than 1000 nm increases. In addition to reducing collector consumption, the yield of carbon concentrate increases by 20-30 %. The carbon content in the concentrate increases to 72-78 %. The resulting carbon concentrate corresponds to high-grade hard coals in terms of calorific value and can be used as fuel in power plants using solid fuels. Carbon-free ash contains less than 4% unburned carbon and can be used in the construction industry.

1. Introduction

Ash formed as a result of coal combustion at thermal power plants (22-24 million t/y) is a source of both valuable components during its complex processing and a serious environmental threat when stored in ash dumps. At a number of thermal power plants, the settling ponds are overflowing and new storage facilities need to be laid, which entails high financial costs. The current critical situation with the accumulation of ash forces us to look for methods of its disposal. It is reported about the use of ash for laying mountain voids, in the construction of highways (Putilin and Tsvetkov, 2003). As a rule, the ash is not subjected to physical or chemical treatment. On the one hand, the use of ash from coal-fired power plants in road construction makes great practical sense, but at the same time, the implementation of this practice is relevant within 100 km from the power plant. Therefore, for the complete utilization of ash from landfills, technologies for complex ash processing are needed to obtain products with high added value. Depending on the chemical and phase composition of the ash, it can be used to obtain: carbon concentrate, alumina and belite sludge (Delitsyn et al., 2023), magnetite concentrates, and an aluminosilicate product (Delitsyn et al., 2022) used in the production of building materials. The ash of hard and brown coals differs in the content of the main components and, accordingly, require different approaches to its processing. Aluminosilicate ash is heterogeneous in its phase composition and mainly contains carbon (underburned coal), magnetite, hematite, wustite, mullite, quartz. The ash of brown coals from thermal power plants in the Kansk-Achinsk basin mainly contains various phases of calcium compounds (Table 1). A special problem of complex ash processing is the extraction from carbon (underburning). The high carbon content in fly ash (6-20 %) due to its hydrophilicity prevents its full use in the construction industry: the production of cement, concrete, bricks, porous foamed materials, etc. Since wet ash removal is used in most coal-fired power plants, the flotation method is of practical interest for extracting carbon in the form of concentrate. The gravitational method of extracting unburned carbon from fly ash is also described in the literature. Zhang at al. (2020) investigated the removal of unburned carbon from fly ash using enhanced gravity separation under different operation parameters such as rotational angular velocity and backwash water pressure, and the decarbonisation

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performance was compared with the froth flotation. The decarbonisation results of enhanced gravity separation was slightly lower than froth flotation. The traditional collector of unburned carbon flotation is kerosene. However, the search for more effective carbon flotation reagents is continuously underway.

Table 1: Phase composition of fly ash of brown Kansk - Achinsk coals

Minerals (phases)	Power plants			
	Nazarovskaya	Berezovskaya	Krasnoyarskaya	Kanskaya
$Ca(OH)_2$	-	+	-	-
$Ca_3Si_2O_7$	-	+	-	-
$CaSO_4$	-	+	-	-
CaO	+	+	+	-
$CaCO_3$	-	+	-	+
β-2CaO•SiO_2	+	+	+	+
3CaO•Al_2O_3	+	+	-	-
CaO•Al_2O_3	+	+	+	+
Quartz	+	+	+	+
MgO	-	+	+	+
Fe_3O_4	+	+	+	+
Fe_2O_3	+	-	-	-

Synergistic collection of unburned carbon particles using the mixture of Triton X-100 and kerosene was studied by Zheng et al. (2021). Compounding Triton X-100 with kerosene as a mixture collector to separate unburned carbon from fly ash using flotation obtained better performance than sole kerosene as collector. Because the polar groups of Triton X-100 adsorbed on the oxygen-containing functional groups of unburned carbon through hydrogen bonding and increased the hydrophobicity of the unburned carbon surface. Hydrophobic-hydrophilic separation was proposed by Zheng et al. (2023) based on the adsorption mechanism. The developed method takes into account the concentration of oxygen-containing groups on the carbon surface before and after the treatment with the flotation agents. The surface interaction between the carbon particles and the flotation agents were also discussed by Ma et al (2023). However, the application of flotation agents can be ineffective, thus the activation techniques are required. Recently, the use of ultrasound has been of great interest for the intensification of various chemical transformations of coals and for the production of valuable carbon chemical products. Mao et al. (2019) found that the mechanical effects produced by ultrasonic cavitation remove the clay and oxide layer from the coal surface to restore the hydrophobic surface of coal particles, resulting in an increase in flotation selectivity. Chen et al. (2021) observed an interesting effect in the flotation of coal sludge using ultrasonic pulp treatment. It was found that the maximum flotation metallurgical responses were obtained under the highest examined USW frequency (600 kHz). However, the flotation outcomes by a low USW frequency (50 kHz) were even lower than the conventional flotation tests. Observation and theoretical calculation results revealed these results were originated from the influence of frequency on the carrier bubble formation and the action of the secondary acoustic force during USW-assisted flotation. These outcomes demonstrated that frequency is a key factor determining the success of attractive mineralization for fine particle flotation. The ultrasonic pre-treatment was found to minimize the ash material concentration on the surface and in the pores of the carbon concentrate (Xue et al., 2023). Although the ultrasonic treatment showing high efficiency in ash processing, further studies are required to determine the effects of the pre-treatment conditions. Moreover, the ash from different coal types and the different coal plants can sufficiently vary in term of composition and properties, thus, the data collection is of great interest to develop the effective technology for the utilization of ash and slag from coal plants. The purpose of this work was to study the effect of ultrasonic processing of collectors on the ash flotation indicators of the Kashirskaya coal-fired power plant using the coals of the Kuznetsk basin.

2. Experimental Methods and Materials

The initial material (ash of the Kashirskaya coal-fired power plant) was averaged by the ring and cone method, moored with subsequent classification (< 200 μm) on a laboratory sieving U1-ERL-10. The ring and cone method is used for the sample reducing (Raval et al., 2018) and involves pouring the sample so that it takes on a conical shape (Zhang and Guo, 2018). Experimental studies on the extraction of unburned carbon from ash were carried out in a flotation machine 237 FL-A, TU 24-8-1090-77 with a chamber volume of 1.7 L. Ash loading was 0.25 kg, the duration of the main flotation was 5-10 min. Petrochemical products were used as collectors:

- vacuum gasoil grade B type 2, TU 38.1011304-2004, Gazpromneft-Moscow Oil Refinery Plant

• kerosene TU 0251-015-57859009-2015 (Nizhny Novgorod Chemical Industry),

as foamers:

• flotation agent-oxal T-66 TU 20.14.60-029-05766801-2016. PJSC (Nizhnekamskneftekhim);

Foam flotation product (carbon-containing concentrate) and the flotation tails were filtered on a nut filter and dried to a constant weight at a temperature of 105 °C. Ultrasonic processing of the collector was carried out using an immersion ultrasonic emitter (frequency - 25 kHz, power – 100 W). The duration of ultrasonic treatment of collectors was 2-4 min. The volume fraction and the size of the emulsion droplets were determined by the method of dynamic light scattering on the ZetaSizer Nano ZS (Malvern) analyzer. The unburned carbon content in ash and its flotation products was determined as the weight loss of a sample of a sample calcined in an air atmosphere in a muffle furnace PM-14M1P-1250T at a temperature of 1000 °C, τ = 1 h, in porcelain cuvettes. The concentration of major oxides and some trace elements in the samples was determined by X-ray spectral fluorescence analysis (XRF) on a sequential vacuum spectrometer (with wavelength dispersion), the Axios mAX model according to the NSAM VIMS 439-PC 2010 technique, which provides results of the III category of accuracy of quantitative analysis according to the OST of the Russian Federation '41-08-205-04' Specific heat of combustion was determined in a calorimeter IKA C 6000 equipped with a standard oxygen bomb. Electron microscopic examination of ash particles, underburning and flotation tailings was carried out using a Phenon Pro X electronic scanning microscope.

3. Experimental Results and Analysis.

The main components contained in the test ash are silicon oxides, aluminum oxides, unburned carbon and iron oxides (Table 2).

Table 2: Chemical composition of ash.

Main components, wt. %										
TiO_2	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	C	P_2O_5
0.75	48.69	21.5	7.44	2.12	1.32	0.13	0.65	1.84	14.8	0.76

Electron microscopic examination of the underburning particles showed that their surface is characterized mainly by increased porosity (Figure 1), depending on the conditions of its combustion in the boiler furnace.

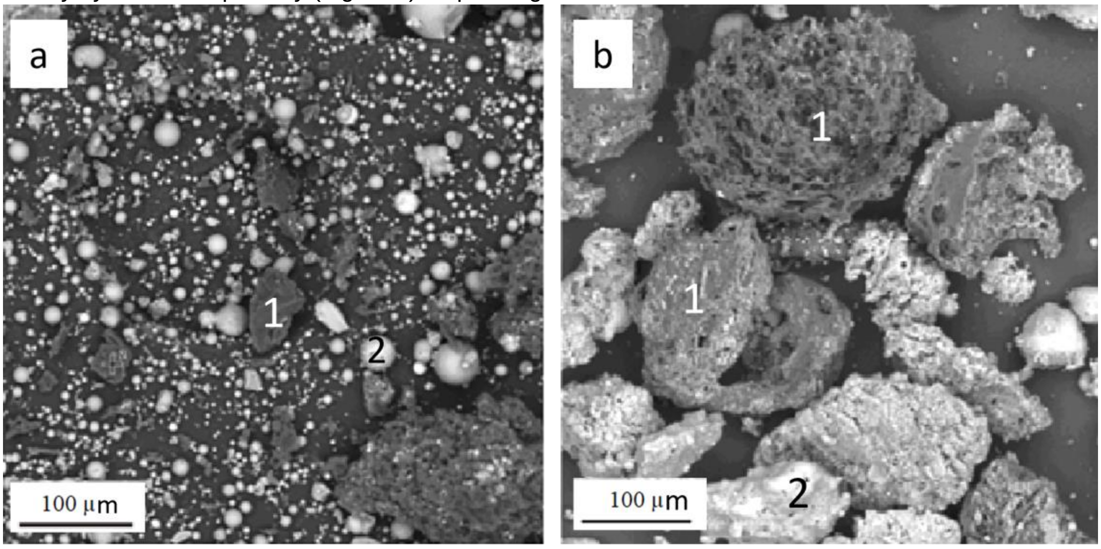

Figure 1: a – ash before carbon flotation, b – carbon concentrate with pores, 1- carbon particles, 2- silicate particles.

Unburned carbon is a mesh frame (Figure 2) which is probably formed by the volumetric diffusion of gas during combustion. It also follows from the experimental data that the unburned coal particle was in the combustion zone for a short period of time or in a temperature zone of less than 1500-1600 °C, as evidenced by the presence of individual non-spherical quartz microparticles (white inclusions) on the carbon skeleton frame. The carbon concentrate obtained as a result of ash flotation is a powdered black material with a carbon content of more than 60 % (Table 3). This surface configuration confirms the need for the use of an apolar reagent during flotation, which, due to surface tension forces, passes inside the structure of the underburning particle, but does not ensure its sufficiently strong fixation on the air bubble. The positive aspect of such a particle structure can only be called the effect of wetting hysteresis due to the sharp edges of the particle surface, which increases the efficiency of extracting particles into the foam layer under turbulent flotation conditions. In this regard, it can be assumed that reducing the size of collector droplets due to dispersion will lead to their penetration into small pores of carbon particles, which will have a positive effect on the results of flotation. One of the most effective methods of dispersing organic liquids in water is ultrasonic exposure. To increase the dispersion of collectors in water, the method of ultrasonic dispersion was applied.

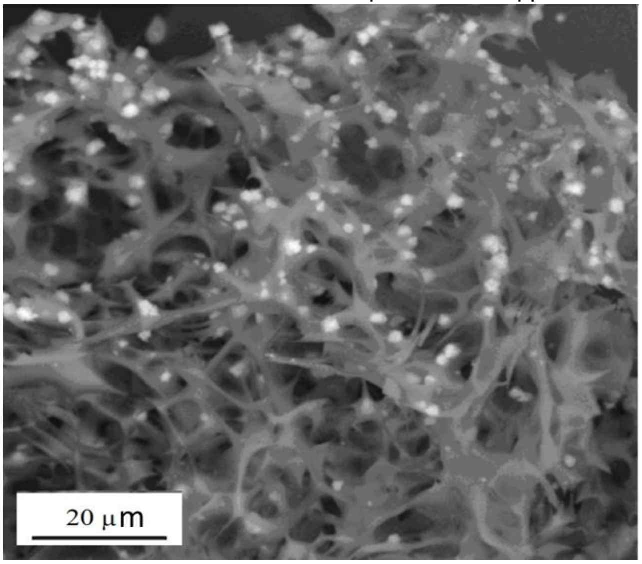

Figure 2: Carbon mesh of unburned carbon and light quartz inclusions.

Table 3: Average composition of flotation carbon concentrate (collector consumption 4 kg/t, foamer consumption 0.4 kg/t).

Main components, wt. %										
TiO_2	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	C	P_2O_5
0.40	21.80	9.50	3.19	1.11	0.68	0.12	0.30	0.80	61.8	0.30

Due to the oscillatory movements of particles of a heterogeneous system, finely dispersed emulsions of the collector in water are formed under the influence of sound waves. The duration of ultrasonic treatment of the collector (Figure 4) leads to an increase in the volume fraction of collector droplets smaller than 1500 nm.

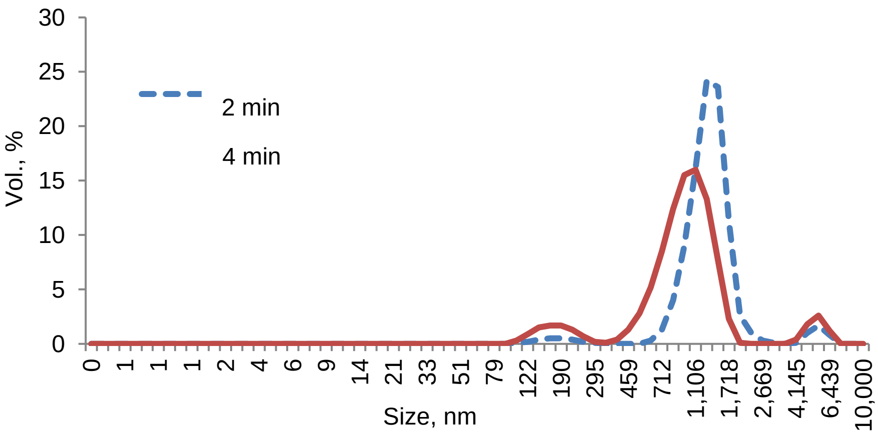

Figure 3: The dependence of the volume fraction and the size of the collector droplets on the time of ultrasonic treatment.

However, ultrasonic treatment of the collector for more than 4 min does not lead to an improvement in flotation performance. Ultrasonic dispersion of the collector made it possible to reduce its consumption from 4 kg/t to 2 kg/t and improve the quality of the carbon concentrate (Table 4).

Table 4: Average composition of flotation carbon concentrate (collector consumption 2 kg/t, foamer consumption 0.4 kg/t).

Main components, wt. %										
TiO_2	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	C	P_2O_5
0.30	16.10	6.90	2.31	0.79	0.51	0.09	0.21	0.59	72.00	0.20

A consequence of the physico-chemical transformations of coal into ash is a change in the negative value of the zeta-potential of ash particles from the values for coal particles -(15-20) mV in a neutral environment to a value of the order of -43 mV. Such a change may be due to the increased content of aluminosilicate components in the ash, which generally emphasizes the decrease in the flotation ability of ash during the extraction of underburning by apolar reagents. For aluminosilicate flotation tailings, the negative value of the zeta-potential increases to -49 mV. The content of unburned carbon in the flotation tailings (aluminosilicate product) was 2-4% by weight (Table 5), which meets the requirements of the construction industry. Unlike carbon concentrate particles, the specific surface area of which is 7.8 m^2/g, the specific surface area of the aluminosilicate product particles is much smaller (3.5 m^2/g) and does not have such a developed porosity. Such changes in the structure of the flotation tailings can be addressed to the enhancement of the carbon removal from the aluminosilicate concentrate. The crystallin residue is characterized by the lower concentration of an amorphous inclusions with high porosity that results in a decrease in the specific surface area.

Table 5: The average composition of the aluminosilicate flotation product (collector consumption 2 kg/t, foamer consumption 0.4 kg/t).

Main components, wt. %										
TiO_2	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	C	P_2O_5
0.80	55.60	23.90	8.30	2.40	1.50	0.10	0.70	2.00	2.40	0.80

The structure of the aluminosilicate product is represented by a glass phase, in some parts of which crystal formations of quartz are visible (Figure 4).

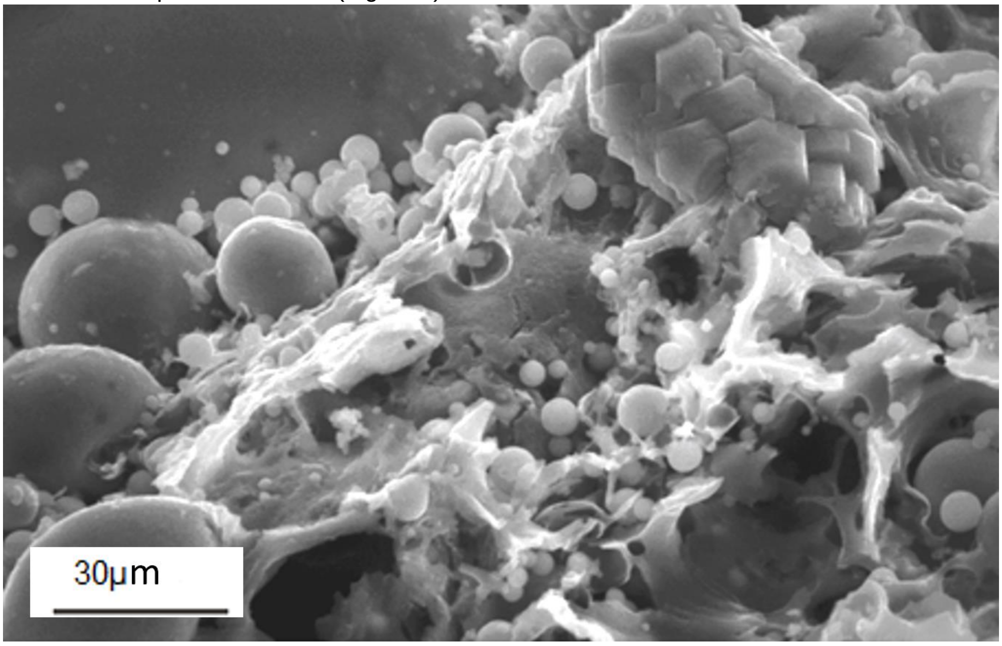

Figure 4: Structure of the aluminosilicate product.

It is worth noting that the ratios between the main SiO_2/Al_2O_3 components in both ash and flotation products are almost ‘identical’.

4. Conclusions

It has been established by electron microscopy that the surface of unburned carbon particles is characterized mainly by increased porosity. Due to the poor solubility of nonpolar organic collectors in water, formed by mechanical mixing of the collector with water, it is difficult for large droplets of the collector to penetrate into the small pores of unburned carbon. It is shown that the use of ultrasonic processing of the collector allows it to be dispersed to droplet sizes less than 1500 nm. Due to this phenomenon, small droplets more easily penetrate the pores of unburned carbon, which leads to a two-fold reduction in collector consumption, and an increase in the yield and quality of carbon concentrate. The resulting aluminosilicate product (flotation tailings) contains less than 4% unburned carbon and can be used in the construction industry. Ultrasonic processing of collectors is a promising method for the preparation of flotation reagents.

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