

## Extraction of Carbon-Containing Concentrate from Fly Ash and Its Application

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The results of tests of various types of flotation machines for carbon concentrate extraction showed that the jet flotation machine, due to more intensive mixing and dispersion of air, provides better fixation of carbon particles on air bubbles, which improves the quality of the carbon concentrate (LOI increases from 49 to 65 %). It has been established that more than 90 % of the mineral component of the carbon concentrate (predominantly SiO<sub>2</sub>) can be effectively removed by converting it into water-soluble (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>. This is achieved either by interaction with ammonium hydrofluoride in an aqueous medium, or by sintering at 320–360 °C followed by sublimation of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>. It has been shown that desilicization occurs not only from the surface of carbon particles but also from internal cavities and lacunae (providing the volume of mesopores), which leads to both an increase (from 9.5 to 15.1 m<sup>2</sup>/g) in the total specific surface area S<sub>BET</sub> and a redistribution of pores.

### 1. Introduction

In the modern world, one of the key indicators of enterprise efficiency is the minimization of harmful and persistent production waste. From this point of view, the coal power industry of Russia, which annually generates over 20 Mt of ash and slag waste with a utilization level of less than 10 %, does not meet the efficiency criteria. The disposal of coal-fired power plant fly ash in open waste dumps not only occupies large land areas but also causes environmental issues, such as dust emissions and the leaching of toxic trace elements into groundwater, adversely affecting ecosystems both locally and in remote areas (Kozhukhova et al., 2018). Nearly all coal-fired power plants utilize hydraulic systems as the primary method for ash and slag removal. However, this hydraulic ash handling and disposal system creates a range of complex engineering challenges. Ash slurry ponds, in particular, have a high risk of failure. At the same time, the ash and slag waste sent to these disposal sites holds significant potential as a raw material for producing high-value industrial products (Gollakota et al., 2019). Since coal-fired power plants in Russia burn coal from various basins, the chemical composition of their ash varies significantly (Table 1). As a result, each ash disposal site typically requires a tailored processing approach. In addition to differences in chemical composition, there are also substantial variations in the phase-mineralogical composition of the ash, which significantly affects carbon recovery by flotation methods. The construction industry is objectively the largest consumer of ash, where its mineral component can serve as a partial substitute for cement in the production of concrete and building materials to enhance their performance characteristics (strength, corrosion resistance, durability). Given the chemical composition of ash, the primary focus is on recovering unburned carbon, which negatively affects the quality of concrete. The extracted carbon concentrate (CC) from ash can be further utilized as a solid fuel, an adsorbent, a filler, and more (Wang et al., 2005). Carbon concentrate can be obtained from ash via wet processing (froth flotation) or dry techniques (triboelectrostatic separation, sieving). During triboelectrostatic ash enrichment, ash particles suspended in the air stream are subjected to intensive tribo-charging, after which the particles are separated in a quasi-uniform electrostatic field according to the charges obtained (Li et al., 2019).

Table 1: Average composition of ash from the main coal basins of the Russian Federation (Delitsyn et al., 2025)

Main components, wt. %										
Basin	LOI	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	SO <sub>3</sub>	K <sub>2</sub> O	Others
1	7.4	40.0	16.0	22.0	5.6	1.8	0.5	5.0	1.5	0.2
2	12.8	52.1	21	5.2	3.8	2	0.4	1.6	0.7	0.4
3	1.4	31.4	13.2	8.9	36.3	6.2	0.7	-	1.0	0.9
4	5.8	57.6	28.4	4.8	0.95	0.48	0.52	0.11	0.27	1.07
5	8.2	45.0	24.4	9.2	3.2	2.8	0.8	4.8	1.2	0.7

Coal ash from basins: 1 - Donetsk, 2 - Kuznetsk, 3 - Kansk-Achinsk, 4 - Ekibastuz, 5 - Ural

As a rule, unburned carbon particles acquire a positive surface charge, while aluminosilicate particles acquire a negative one (Figure 1).

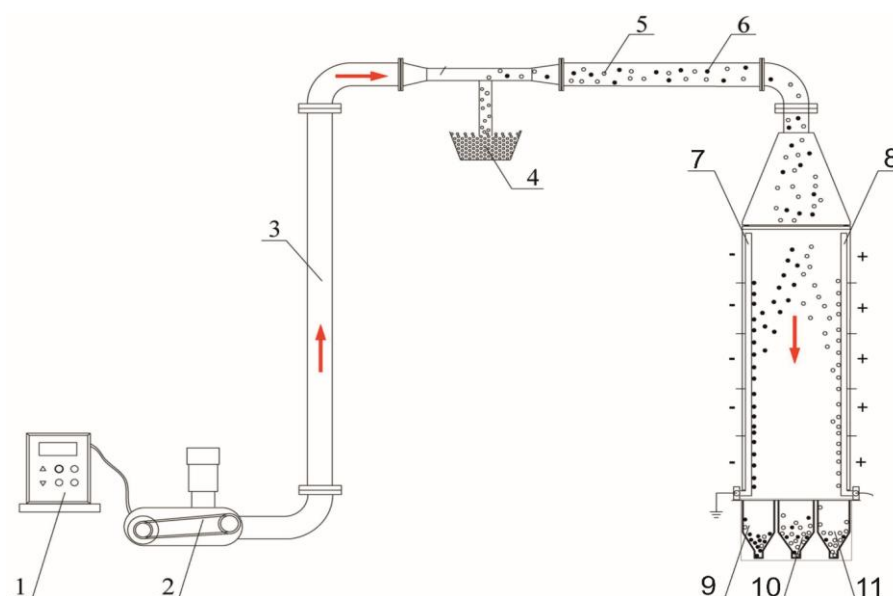


Figure 1: Triboelectric ash separation scheme (Li et al., 2019): 1-frequency converter, 2- air pump, 3- air duct, 4- ash, 5- aluminosilicate particles, 6- carbon particles, 7.8 – multicharged plates, 9-carbon-enriched concentrate, 10-ash, 11- tails

Despite the relatively simple hardware setup of triboelectrostatic separation, a key drawback of this method is its insufficiently effective ash separation. The yield of the carbon concentrate averages only about 30 %, with unburned carbon content reaching up to 50 % (Zhou et al., 2024). Moreover, prolonged exposure of ash to atmospheric moisture significantly reduces the efficiency of carbon-ash separation due to poor redistribution of surface charge between particles during charging (Cangialosi et al., 2009). Since most coal-fired power plants in Russia use wet ash disposal systems, froth flotation is the most effective method for recovering unburned carbon (UC). The principle of froth flotation relies on the separation of hydrophobic and hydrophilic ash particles through the addition of reagents such as collectors (e.g., kerosene, gas oils with a wide boiling range) and frothers (e.g., pine oil, T-66, butanol distillation residues, and others). The recovery of UC is significantly influenced by several factors, including the nature of flotation reagents (Zheng et al., 2022), flotation machine design (Samygin et al., 2016), pulp pH, and pulp density. To enhance flotation performance, researchers aim to hydrophobize the surface of carbonaceous ash particles by optimizing collector selection and promoting air bubble attachment. The fundamental mechanism of unburned carbon flotation is clearly illustrated in Ma et al. (2024) (Figure 2). Thus, the extraction of unburned carbon from ash must be considered from different perspectives. Firstly, the carbon concentrate extracted from the ash has a high calorific value (21-24 MJ/kg) and can be used as an additive to coal during combustion in power plants, increasing the energy efficiency of the process (Wang et al., 2005). Secondly, after steam activation, it can be used as a sorbent (Izquierdo et al., 2008).

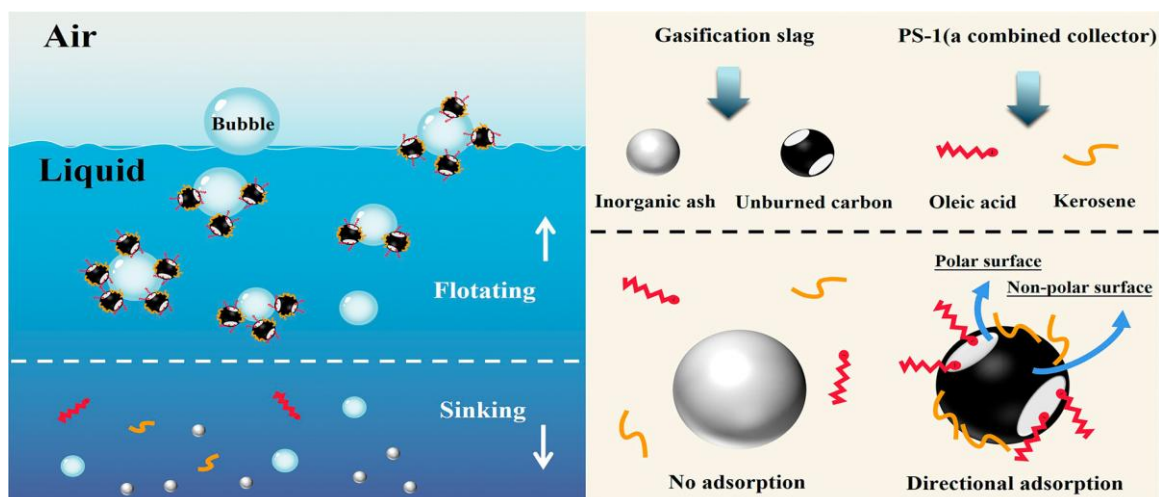


Figure 2: Illustration of the mechanism of unburned carbon flotation (Ma et al., 2024)

On the other hand, the extraction of carbon from ash is absolutely necessary to obtain a high-quality aluminosilicate product used in the production of concrete products. The specific surface area and, accordingly, the sorption activity of a carbon concentrate depend on its ash content, which usually varies between 45-30 %. Research on the use of unburned carbon from fly ash as a sorbent has been conducted for a long time. For instance, Rubel et al. (2005) studied the adsorption of  $\text{NO}_x$  on activated carbons derived from fly ash and found that carbon fractions from a gasifier adsorbed 30 % less  $\text{NO}_x$  compared to commercial activated carbon. Serre et al. (2000) investigated the potential of unburned carbon for mercury capture at waste incineration plants. The results showed that such carbon could only adsorb a negligible amount of mercury. In addition to flue gas purification from  $\text{NO}_x$ ,  $\text{SO}_x$ , and mercury, fly ash is also effective in removing organic compounds and heavy metals (Lin et al., 2001). Numerous studies have demonstrated that the adsorption process on unburned carbon follows a pore diffusion mechanism similar to that of conventional adsorbents. However, traditional steam activation can only partially open the pore volume of the carbon material, as some silicate particles embedded in the carbon matrix are chemically inert to steam. Therefore, the aim of this study was to develop a method for desilicification of a carbon concentrate (obtained by flotation of coal-fired power plant fly ash) to produce a de-ashed carbon with an increased specific surface area.

## 2. Experimental Methods and Materials

The initial material (ash from the Kashirskaya coal-fired power plant) was homogenized using the ring and cone method, thoroughly mixed, and then classified ( $< 250 \mu\text{m}$ ) using a U1-ERL-10 laboratory sieve shaker. 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 liters, and on a jet flotation machine with a Jameson cell SF C150/1 with a chamber volume of 80 L. Ash loading was 0.25 kg and 15 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); as chemical reagents were used:  $\text{NH}_4\text{OH}$  (analytical grade, 25 %, JSC Novomoskovsk Azot);  $\text{NaOH}$  (analytical grade, JSC Kaustik);  $\text{NH}_4\text{F}\cdot\text{HF}$  (pure, LLC Chemical Plant of Fluorosalts). The foam flotation product (carbon-containing concentrate) and the flotation tailings were filtered using a nutsch filter and dried to constant weight at  $105 \text{ }^\circ\text{C}$ . Desilicification of carbon-containing concentrate was carried out in various ways: 1) the carbon concentrate was mixed with ammonium hydrofluoride and ground with a pestle in a corundum cup until a homogeneous mixture was obtained. Ammonium hydrofluoride was taken in excess (10–12 % of the stoichiometric amount). Subsequently, the resulting batch was loaded into a corundum crucible, which was then placed in a vertical electric furnace and heated to the target temperature range of  $320\text{--}360 \text{ }^\circ\text{C}$ . A reflux condenser was installed in the upper part of the furnace to trap sublimates. 2) The carbon concentrate was leached with a 20 %  $\text{NaOH}$  solution or an  $\text{NH}_4\text{F}\cdot\text{HF}$  solution in a fluoroplastic beaker in a water bath at a temperature of  $90\text{--}95 \text{ }^\circ\text{C}$  and constant stirring with a magnetic stirrer for 180–300 min. The enriched concentrate was washed with distilled water to a neutral pH and dried in a drying cabinet at a temperature of  $120 \text{ }^\circ\text{C}$ . Textural characteristics of the samples were determined by low-temperature

nitrogen adsorption using a BELSORP Mini-X analyzer (MicrotracBEL, Japan). Prior to analysis, the samples were pre-treated by degassing under vacuum (2–4 Pa) at 350 °C for 12 h in a BELPREP-vac III system (MicrotracBEL, Japan). Nitrogen adsorption was performed at 77 K. The total specific surface area and total pore volume were calculated using the Brunauer–Emmett–Teller (BET) method at a relative partial pressure ( $P/P_0$ ) of 0.2. Mesopore size distribution, mesopore surface area, and mesopore volume were derived from the desorption branch using the Barrett–Joyner–Halenda (BJH) method. Micropore size distribution was analyzed from the adsorption branch using the MP method, while the external surface area was determined via the t-plot method (based on the adsorption curve). The discussion of the adsorption isotherms of the tested samples is based on the official IUPAC classification proposed by Brunauer et al. (1940).

### 3. Experimental Results and Analysis

When obtaining carbon concentrate using various ash flotation methods (jet flotation, chamber flotation), the best process performance is achieved with jet flotation using the Jameson Cell (Table 2), since the goal of flotation is to produce both an aluminosilicate product with low carbon content for use in the construction industry and a carbon concentrate whose value for energy applications increases with higher carbon content. The key difference from tank flotation lies in the fact that in jet flotation, the slurry and air are mixed in the downcomer pipes. As a result, the probability of particle-bubble contact reaches nearly 100 %. Since coal-fired power plant ash particles primarily consist of fractions smaller than 50  $\mu\text{m}$ , the fine-dispersed nature of the bubbles (0.3 to 0.5 mm in diameter) enhances their ability to carry fine mineral particles, enabling the production of higher-quality concentrates. The yield of carbon concentrate in jet flotation is lower, while its quality is higher, due to the froth being washed with water at the top of the column. As a result, carbon particles agglomerated with large mineral inclusions are washed back into the pulp.

Table 2: Comparison of chamber and jet flotation performance

Flotation indicators	Type of flotation			
	Chamber flotation		Jet flotation	
	Carbon concentrate	Tails	Carbon concentrate	Tails
Yield, wt. %	29.32	70.68	21.74	78.3
LOI, wt. %	49.53	4.4	65.77	4.14

The unburned carbon forms a mesh-like framework (Figure 3). Individual non-spherical silicate microparticles (white inclusions) fused with the carbon skeleton framework are practically impossible to separate by froth flotation. Therefore, the LOI (Loss on Ignition) of the floated carbon concentrate rarely exceeds 70 %. One of the effective methods for silicate rock decomposition is based on the fluoroammonium technology (Medkov et al., 2011), where ammonium bifluoride ( $\text{NH}_4\text{F}\cdot\text{HF}$ ) is used as the main reagent. Silica removal from ash is also possible through leaching with a NaOH solution (Delitsyn et al., 2022). The mechanism of interaction of silicon oxide with ammonium bifluoride can be represented as follows:



The ammonium hexafluorosilicate formed as a result of reaction Eq(1) sublimates upon heating, removing silicon oxide from the system in the case of a homogeneous reaction or dissolving it if the reaction is carried out in the presence of water. The advantage of using ammonium fluoride as a reagent for silicon removal is the possibility of its recovery into the cycle through ammonia hydrolysis Eq(2), Eq(3). As a result of hydrolysis, amorphous silica precipitates.



The degree of silicon removal from the averaged carbon concentrate (a mixture of carbon concentrates from jet and chamber flotation,  $S_{\text{BET}} = 9.53 \text{ m}^2/\text{g}$ , LOI = 60 %) depends on the type of desilication reagent and the reaction medium (homogeneous or heterogeneous) (Table 3). Repeated treatment of CC2 with ammonium hydrofluoride in an aqueous medium made it possible to obtain CC3, the mineral component of which was only 3.6 % (Table 4), and the specific surface area of  $S_{\text{BET}}$  increased by almost 60 % compared to the initial carbon concentrate and amounted to 15.1  $\text{m}^2/\text{g}$ .

Table 3: LOI of the concentrate after silicon removal

Reagents			LOI, % of desilicized carbon concentrate (CC2)
CC1	NH <sub>4</sub> F·HF	H <sub>2</sub> O	82.9
CC1	NH <sub>4</sub> F·HF	-	84.4
CC1	NaOH	H <sub>2</sub> O	64.1

CC1, - initial, CC2, - desilicated carbon concentrate

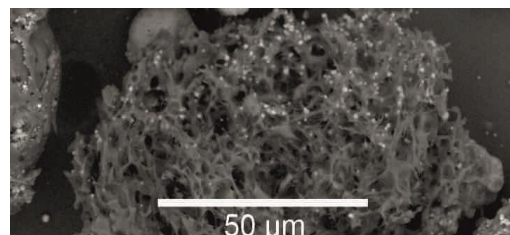


Figure 3: Carbon mesh and silicate particles

Both samples, CC1 and CC3, have a mesoporous structure; however, it is much more pronounced in CC1. Its isotherm is classified as type II, indicating strong interaction between the adsorbate (the substance that concentrates at the interface) and the adsorbent (the material on whose surface adsorption occurs). The presence of a distinct H4-type hysteresis loop (Figure 4) indicates the existence of mesopores with an average diameter of 12.9 nm, which, in combination with micropores, form a complex structure typical of zeolites.

Table 4: Composition of the carbon concentrate in its initial state (CC1) and after desilicization (CC2, CC3)

Main components, wt. %									
Concentrate	LOI	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	SO <sub>3</sub>	K <sub>2</sub> O
CC1	60.0	26.6	9.1	2.7	0.9	0.4	0.2	-	0.1
CC2	82.9	5.5	7.2	3.1	0.6	0.6	0.1	-	-
CC3	96.4	0.4	1.8	1.3	0.1	-	-	-	-

At the same time, the proportion of micropores in this sample is extremely small. The isotherm of sample CC3, obtained from CC1 via desilication, is also a Type II isotherm.

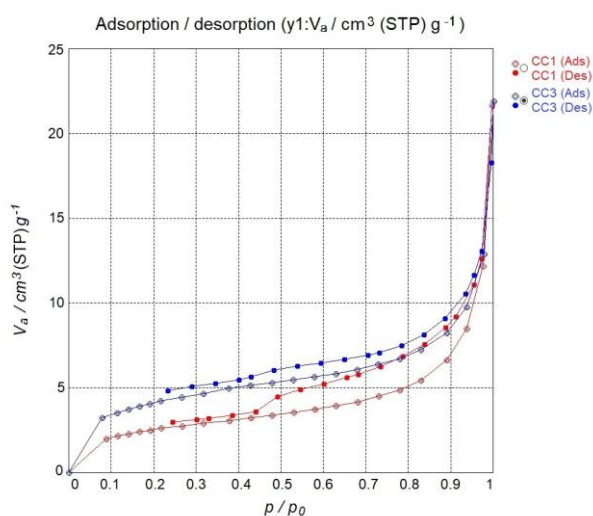


Figure 4: Ads./Des. isotherms of CC1 and CC3

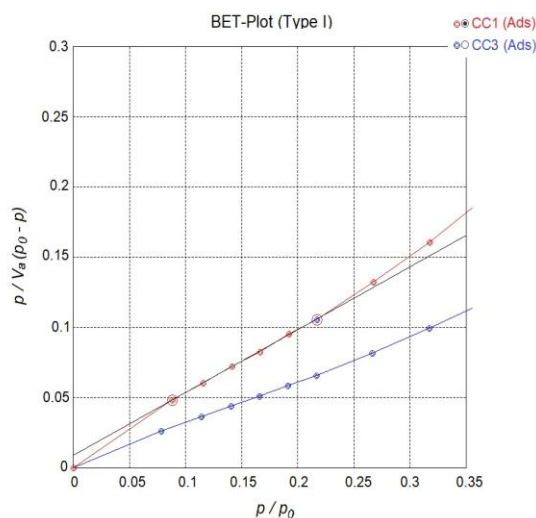


Figure 5: BET graphs of CC1 and CC3

However, unlike CC1, it exhibits a well-defined H3-type hysteresis loop, indicating the predominance of slit-shaped mesopores with an average diameter of 14.7 nm. Additionally, the formation of micropores can be observed, albeit in small quantities. The change in the hysteresis loop shape and the 'appearance' (or more precisely, 'manifestation') of micropores in the CC3 structure may indicate that the process of obtaining 'CC3' from 'CC1' leads to the removal of aluminosilicate not only from the surface but also from the internal cavities and lacunae that provide the mesopore volume. This results in both an increase in the total specific surface area (Figure 5) and a redistribution of pores. In the work of Izquierdo et al. (2008), it was shown that thermal activation of carbon concentrate leads to a significant increase in its  $S_{BET}$  (from 2 to 117 m<sup>2</sup>/g). Obviously, thermal

activation of the desilicized carbon obtained in this study will also significantly increase its  $S_{\text{BET}}$ , greatly improving its sorption properties.

#### 4. Conclusions

The carbon concentrate obtained from coal power plant ash via froth flotation is a high-calorific product with a specific combustion heat of 21–24 MJ/kg. The mineral component of the carbon concentrate is inert to alkali but reacts actively with ammonium bifluoride. When the concentrate is treated twice with  $\text{NH}_4\text{F}\cdot\text{HF}$  in an aqueous medium, 91 % of its mineral content is removed. After desilication, the carbon concentrate is dominated by slit-shaped mesopores with an average diameter of 14.7 nm. Additionally, a small number of micropores appear. The total specific surface area increases by 60 %. It is evident that after thermal activation, due to the removal of flotation reagents blocking pore entrances for gas adsorption, the specific surface area will increase significantly. Further research on the development of a line of low-cost adsorbents with tunable properties based on ash will not only reduce environmental impact but also enable their use in wastewater treatment, volatile organic compound capture, and catalytic applications

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