Magnetic sorbents based on Kuzbass long-flame coal

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Abstract. The paper investigates the textural characteristics of carbon sorbents obtained from Kuzbass coal of the LF grade. The sorbents were obtained by activation using ferric chloride, pre-impregnating the coal with an iron III chloride solution at a FeCl3/coal ratio of 1:7 g/g. Powder X-ray diffraction in sorbents proved the presence of the Fe3O4 phase of magnetite. The amount of magnetite in the sorbents varies within 7%. It is shown that sorbents obtained from coal activated with iron chloride have a sufficiently developed porous structure and significant microporosity. The measured values of the specific surface area of sorbents at an activation temperature of 800 °C reach 250 m²/g, and at 700 °C they are an order of magnitude lower. The total pore volume does not exceed 0.1 cm³/g with a micropore fraction of more than 70%.

Introduction
Carbon sorbents are carbon materials, generally characterized by a well-developed porous structure [1]. Sorbents are widely used in various processes, including adsorption, both in gas and liquid phases [2, 3]; as carriers of active phases or bulk catalysts [4] and in electrochemical devices or energy storage devices for use as supercapacitors [5, 6]. There is a renewed interest in research on the synthesis, characterization and use of activated carbons [7]. Activated carbon can be synthesized from any carbon-containing precursor such as coal [1-3, 8], discarded car tires [9], lignin [10], or biomass waste [11], however, raw materials with low inorganic content are most preferred.

Traditional activating agents such as alkali or phosphoric acid are very strong bases and acids. Handling these materials requires stringent safety measures and materials that are more corrosion resistant. In the case of zinc chloride, Zn ions and oxide derivatives are toxic [12] and therefore must be subject to strict disposal regulations. The use of FeCl3 as an activating agent has both environmental and economic advantages over other more traditional chemical activating agents. However, the most interesting feature of activation with iron chloride is that it allows one to obtain magnetic carbon sorbents [13, 14]. The scheme of activation of carbon materials (in our case, it will be applied to coal) with iron chloride was studied in [15-17].

At temperatures from 200 to 350 °C, the hydrated iron chloride salt decomposes into amorphous FeO (OH) through the following reactions [15]:

\[
\begin{align*}
\text{FeCl}_3 \cdot n\text{H}_2\text{O} & \rightarrow \text{FeCl}_3 \cdot (n-1)\text{H}_2\text{O} + \text{H}_2\text{O} \quad (1) \\
\text{FeCl}_3 + 2\text{H}_2\text{O} & \rightarrow \text{FeOCl} \cdot \text{H}_2\text{O} + 2\text{HCl} \quad (2) \\
\text{FeOCl} \cdot \text{H}_2\text{O} & \rightarrow \text{FeO(OH)} + \text{HCl} \quad (3)
\end{align*}
\]
The second stage takes place at temperatures from 350 to 700 °C. As the temperature rises, FeO(OH) first decomposes into Fe₂O₃, which is then reduced by the carbon surface to form Fe₃O₄ in accordance with the following chemical reactions [16]:

\[
\begin{align*}
2\text{FeO(OH)} & \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \quad (4) \\
3\text{Fe}_2\text{O}_3 + \text{C} & \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO} \quad (5)
\end{align*}
\]

The formed iron oxides catalyze the formation of microporosity in the carbon matrix [17]. A further increase in temperature (above 700-800 °C) leads to the fact that particles of iron oxides can be reduced to iron by carbon on the surface of the sorbent by analogy with the blast furnace process of steelmaking:

\[
\begin{align*}
2\text{Fe}_2\text{O}_3 + 3\text{C} & \rightarrow 4\text{Fe} + 3\text{CO}_2 \quad (6) \\
\text{Fe}_3\text{O}_4 + 2\text{C} & \rightarrow 3\text{Fe} + 2\text{CO}_2 \quad (7) \\
\text{Fe}_3\text{O}_4 + 4\text{C} & \rightarrow 3\text{Fe} + 4\text{CO} \quad (8)
\end{align*}
\]

In parallel with the process of reduction of iron chloride with carbon, the processes of destruction of the organic mass of coal with the release of volatile substances, carbon oxides occur; aromatization and cyclization; as well as side reactions of iron chloride with the mineral component of coal.

In the work, the above scheme was used when activating Kuzbass coal in order to obtain carbon sorbents containing magnetic crystals (magnetite) on their surface, and to study the textural characteristics of the obtained magnetic sorbents.

**Experimental**

Magnetic carbon sorbents were obtained using low-ash coal of LF grade mined in the Kuzbass. A coal sample with a particle size of 0.2–0.5 mm was prepared from the commercial grade LF coal by successive grinding and quartering and dried in air. Analytical studies were carried out using ground coal with a particle size of less than 0.2 mm.

Investigations of the characteristics of the original coal were carried out in accordance with the standards ISO 60274, ISO 562–74 (technical analysis) and ISO 625–75 (elemental composition).

The preparation of magnetic sorbents was carried out by the method of activation of coal with iron III chloride. Coal was impregnated with a water-alcohol solution of iron III chloride for 24 hours, and then dried in an oven at 105 ± 3 °C until the residual water and alcohol completely evaporated. A weighed portion of aqueous iron III chloride was chosen so that the final ratio during coal impregnation was 1 g of anhydrous iron III chloride per 7 g of coal (R_{FeCl₃} = 1:7).

Activation of coal with ferric chloride was carried out under isothermal conditions in closed ceramic crucibles at temperatures of 700 °C and 800 °C for 60 minutes. The average heating rate from room temperature to activation temperature was ~ 10 °C/min. The maximum temperature deviation from the preset values did not exceed ± 5 °C. After activation, the sorbents were cooled in an inert atmosphere to room temperature. The resulting sorbents were washed with distilled water and dried in an oven at 105 ± 3 °C until constant weight.

The presence of magnetite in the sorbents was proved by determining the phase composition by powder X-ray diffraction. Diffraction patterns were taken on a Bruker D8 ADVANCE A25 powder X-ray diffractometer (CuKa radiation, Ni filter on secondary radiation) at room temperature using the polycrystal method.

The elemental composition of the sample surface was determined using a JED 2300 energy-dispersive X-ray detector (resolution 133 eV) as part of a JEOL JSM-6390 LA scanning electron microscope. The calculation of the percentage of each element in the analyzed substance was carried out from the obtained X-ray spectra using the Analysis Station software version 3.62.07. by JEOL Engineering using the standard ZAF method.

The study of the porous structure of carbon sorbents was carried out on an ASAP 2020 analyzer by low-temperature nitrogen adsorption. The study included measurement of specific surface area (S_{BET}), total pore volume (V_T), mesopore volume (V_{mc}) and micropore volume (V_{mi}). The measurements of adsorption-desorption isotherms of nitrogen at 77 K were carried out in the range of equilibrium relative pressures of nitrogen vapors from 10^{-3} to 0.995 p/p_0. Before carrying out measurements, the
sorbent samples were evacuated at 200 °C for 720 minutes and a residual pressure of $5 \times 10^{-3}$ mm Hg for complete removal of sorbed impurities from pores.

The Brunauer-Emmett-Teller (BET) model was used to determine the specific surface area of the sorbents. The t-plot method was used to calculate the volume of micropores using the Harkins-Jura equation. Mesopore volume was calculated using the Barrett-Joyner-Halenda (BJH) method. These methods make it possible to calculate the characteristics of the porous structure of carbon sorbents obtained from fossil coals [18]

**Results and discussion**

The characteristics of the LF coal sample correspond to the declared characteristics: analytical moisture $W_a$ 4.6%, ash content $A_d$ 3.4%, volatile matter yield $V_{daf}$ 43.4%. Initial bituminous coal is characterized by low ash and moisture content. The obtained value of the yield of volatile substances is high, which is typical for coals of low stages of metamorphism.

Sorbents at $R_{FeCl_3} = 1:7$ g/g were obtained from the initial bituminous coal upon activation with iron III chloride. The phase composition of the obtained sorbents was determined by powder X-ray diffraction. All diffraction peaks present in the X-ray diffraction patterns were identified using the ICDD and PDF2 powder databases. In the study of the obtained sorbents, wide halos are recorded in the range of angles 10-33 degrees and 40-48 degrees, which are characterized by carbon "graphite-like" turbostratic structures. In the composition of all studied sorbents, a phase of silicon oxide was found as the main ash-forming element of the initial fossil coal. The X-ray diffraction patterns of all studied sorbents show phases of mixed iron oxide Fe$_3$O$_4$ magnetite.

The content of iron (Fe$_3$O$_4$) was determined using an energy-dispersive X-ray detector in a scanning electron microscope. In the obtained sorbents, the iron content is 1.67 atomic% (6.94%) for sorbents activated at 800 °C and 1.85 atomic% (7.48%) for sorbents activated at 700 °C, while in the initial coal its content is less than 0.1 atomic% (less than 0.4%). Since no other iron phases different from the magnetite phase were found by powder X-ray diffraction in the obtained sorbents, all the iron found can be attributed to iron in magnetite (Fe$_3$O$_4$).

| Activation temperature, °C | $S_{BET}$ m$^2$/g $^a$ | $V_\Sigma$ cm$^3$/g $^b$ | $V_{mi}$ cm$^3$/g $^c$ | $V_{me}$ cm$^3$/gd |
|---------------------------|----------------------|-----------------|-----------------|------------------|
| 700                       | 18                   | 0.010           | 0.007           | 0.003            |
| 800                       | 250                  | 0.104           | 0.095           | 0.005            |

$^a$ $S_{BET}$ is specific surface area;  
$^b$ $V_\Sigma$ is total pore volume;  
$^c$ $V_{mi}$ is micropore volume;  
$^d$ $V_{me}$ is mesopores volume.

The investigated characteristics of the pore structure of the obtained sorbents are shown in Table 1. Analysis of the research results shows that the sorbents obtained by the method of activation of grade L coal with iron III chloride at 800 °C have average values of textural characteristics. The specific surface area of the sorbent obtained at 800 °C reaches 250 m$^2$/g, while the specific surface area of the sorbent obtained at 700 °C is an order of magnitude lower and is 18 m$^2$/g. The total pore volume of the obtained sorbents also differs by an order of magnitude, and the proportion of micropores in the sorbents exceeds 70%.

**Conclusion**

As part of the work on the preparation of magnetic sorbents and the study of their properties, carbon sorbents were obtained from Kuzbass LF grade coal by activation with iron III chloride at temperatures of 700 and 800 °C. Powder X-ray diffraction has shown the presence of a mixed iron oxide (magnetite) phase in the structure of the obtained sorbents. It is shown that sorbents obtained
from coal activated with iron chloride have a sufficiently developed porous structure and significant microporosity. The measured values of the specific surfaces of sorbents at an activation temperature of 800 °C reach 250 m²/g, and at 700 °C they are an order of magnitude lower. The total pore volume of sorbents obtained at 800 °C does not exceed 0.1 cm³/g, while the proportion of micropores is more than 70%. The most promising for further use can be sorbents obtained with high-temperature (800 °C) activation with iron chloride, while sorbents obtained at 700 °C, from the point of view of their structure, are not effective sorbents.

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