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# Specific Heat Capacities as Key Factors for the Calcination of Carbonaceous Materials

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## Abstract

The development of new and improvement of existing technologies for the calcination of carbonaceous materials requires their specific heat capacities, which are key factors of the process. Analytical temperature dependences of specific heat capacities of carbonaceous materials were established in the study, considering material transformations and determination errors when they are heated to a temperature of 1800°C and then cooled to a temperature of 20°C. The minimum necessary temperatures of the calcination process and their duration are also determined, which are guaranteed to ensure the required quality of the products in conditions of dispersion of the properties of the raw materials. The new dependencies facilitate for more reliable mathematical modeling of the calcination process of carbonaceous materials by taking into account material transformations and the direction of temperature change and will ensure a more rational development of calcination furnaces and the process. Additionally, the determined theoretical minimum possible specific energy consumption allows for estimating the energy efficiency of the calcination process.

***Keywords****: Carbonaceous materials; Specific heat capacity; Calcination; Electrocalciner, Thermoanthracite; Calcined petroleum coke.*

## 1. Introduction

Carbonaceous materials such as anthracite, petroleum coke, and pitch coke are thermally treated and widely used in the production of iron, steel, aluminum, and ferroalloys. The process of heat treatment at temperatures up to 1800°C without air access is called calcination. This process allows for significantly improve quality of carbonaceous materials, namely, to reduce electrical resistance, remove moisture and volatile substances, reduce sulfur content, increase true density [1-3].

Calcined anthracite, also called thermoanthracite, is widely used in the production of electrode mass, electrodes, cathodes, and lining blocks, as pulverized coal fuel in the blast furnace, basic oxygen furnaces, and electric steel production. The global annual production of calcined anthracite is about 10 million tons. Approximately 75% of calcined anthracite is produced in electric furnaces of direct heating – electrocalciners, which are high-temperature furnaces and at the same time more economically profitable. The other 25% is produced in gas furnaces, generally rotary drum furnaces [4]. It should be noted that only 2% of the total world production of anthracite is processed into calcined anthracite.

Calcined petroleum coke is used mostly in the production of graphite electrodes for electric furnaces and anodes for aluminum electrolyzers. The global annual production of calcined petroleum coke is about 30 million tons. Calcined petroleum coke is produced entirely in gas furnaces. Rotary drum furnaces produce 85% of the volume, the rest is equally divided between rotary hearth and shaft furnaces. Approximately 30% of the total world production of petroleum coke is calcined [5].

Pitch coke is also can be calcinated. Although the amount of its production is about one million tons annually [6]. The qualities and production technology of calcinated pitch coke are similar to petroleum coke [7]. Therefore, it is not considered in this work.

Existing furnaces for the calcination of carbonaceous materials have significant disadvantages: low efficiency, low productivity, and significant heterogeneity of the processed material properties. The development of calcination technologies is currently aimed at both the modernization of remaining furnaces [8] and the creation of fundamentally new furnaces and even complexes [9-10].

A special feature of calcination furnaces is the difficulty of direct measurements of the environment parameters inside the furnaces. Therefore, one of the few tools for investigating the calcination process is mathematical modelling, usually implemented in computer programs using the finite element method, for example, COMSOL or ANSYS. The key factors affecting the reliability of the obtained results are the thermophysical properties of the processed materials, which are input data for modelling. One of these properties is specific heat capacity. It affects both the calcination process and determines the required specific consumption of thermal or electrical energy. The specific heat capacity is of particular importance in the numerical investigation of the operation of hybrid calcination furnaces, in which regeneration of the physical heat of carbon material is used [9,11].

A separate issue related to the specific heat capacity is the minimum required temperature of carbonaceous materials calcination that ensures their required final quality. Determining this temperature will avoid overspending on thermal or electrical energy during calcination, which is currently a typical phenomenon in existing calcination furnaces, primarily electric ones.

Analytical expressions for specific heat capacities and the determination of the minimum required calcination temperature allow the establishment of a certain theoretical minimum possible limit of specific energy consumption for the process.

Over the past 30 years, a significant number of articles have been published on numerical investigations of the calcination process of carbonaceous materials in rotary drum furnaces [12-20], shaft furnaces [21-22], and electrocalciners [23-33]. The analysis of these works showed that a significant number of them [13-14, 16-17, 20-23, 27-29,30,33] do not provide any data on expressions or even values of specific heat capacity, which were used for simulation. In publications [12,15,32] constant values of specific heat capacity were used. In the works [21-22, 24-26, 31], the dependences of the specific heat capacity were used for already calcined materials [21-22,31], or graphite [24-26].

The general shortcoming of all the cited works is that the models do not consider the change in the mass of the carbonaceous materials during calcination, which significantly affects the modelling results, as it can reach 20% of the initial mass only due to the loss of moisture and volatiles release. Additionally, the abovementioned works do not consider the error in determining the specific heat capacity. Practically, the uncertainty of input data in the model is not taken into account in any way, which is a disadvantage.

The reliability of the modelling results in the cited works is affected by the unaccounted factor that the specific heat capacity of anthracite and petroleum coke during heating or cooling is not the same, as it is determined during heating by endothermic and exothermic transformation processes in the carbonaceous materials. The difference between these heat capacities, both in terms of the nature of the change and numerical indicators, is quite significant and should be considered.

Thus, reliable input data for mathematical modelling of the calcination process of carbonaceous materials regarding their specific heat capacity cannot be obtained from the previously published articles.

In order to obtain information that can be used for modelling, an analysis of publications on the study of specific heat capacities of carbonaceous materials was performed. Publications on this issue over the past 50 years were analysed [34-47].

A significant part of the publications [34, 36-37, 39-47] is devoted to the experimental determination of both the effective specific heat capacity of carbonaceous materials during heating and the actual specific heat capacity of the already processed material. Some articles [35,38] consider theoretical approaches to determining specific heat capacities. Especially, there are data on anthracite and petroleum coke. A significant amount of experimental data is summarized in the form of formulas.

The analysis of the publications indicated that the experimental data were obtained only up to 1300°C, and in some cases excluding the change in the mass of the investigated material during heating. The obtained theoretical dependences [35,38] differ significantly from the experimental results. Formulas obtained on an experimental basis have significant differences in quantitative values, in particular for the organic part without volatile components, moisture, and ash, this spread is about 30 wt.% from the middle of the range. There are also significant differences in the dependences on the yield of volatiles and on temperature.

A common feature of the publications is the absence of error values of the obtained experimental data, which is a significant shortcoming. Some works provide data on method errors, which do not specify the criteria by which they are determined. Additionally, based on [48], a reasonable conclusion can be made that the relative error in measuring the specific heat capacity of carbonaceous materials is about 2% according to the 1-sigma criterion.

The specific heat capacity is mainly influenced by the origin and structure of the carbonaceous raw material, which affects the quality of its organic part and its feature. In the context of the influence of the change in the mass of carbonaceous materials during heating on their specific heat capacity, it is important to study the pyrolysis process, especially the yield of volatile substances.

Over the past 50 years, a significant number of results have been published on the study of the pyrolysis process of coal and petroleum coke. The analysis of the publications [49-51] showed that the nature of the release of volatile substances from anthracite and petroleum coke depends to a large extent on their initial content. Also, the value of the yield of volatiles affects the distribution of their chemical composition. Thus, the nature of the release of volatile substances is specific for each sample of anthracite or petroleum coke. This statement is also correct and has important relevance to other solid fossil fuels and biofuels [52-54] and processes in which the fuels are utilized [55-58].

The next, quite difficult issue is the determination of the technologically minimum necessary temperature of anthracite and petroleum coke calcination, which will ensure the required quality of the processed material with minimal energy consumption.

Calcined anthracite can have both metallurgical and electrode quality. The latter has special requirements for the specific electrical resistance of thermoanthracite. Therefore, the required calcination temperatures differ significantly. Calcined petroleum coke is mainly used for electrode production, but due to its much lower specific resistance, its calcination does not require very high temperatures and does not differ from production for metallurgical purposes. Thus, depending on the purpose of the processed carbonaceous materials, there is a certain set of requirements for their quality.

It was experimentally established [59] that at the maximum temperature of 1150°C thermoanthracite from all places of origin fully meets the requirements of metallurgical quality. Therefore, the issue of requirements for it within the framework of this work cannot be considered, but the specified temperature can be used for the calculations.

The requirements for thermoanthracite of electrode quality are presented in the standard [60], distributed in the current and former Commonwealth of Independent States (CIS) countries. According to the standard, there are two varieties of electrode thermoanthracite, the first and higher. Each manufacturer, usually, has its own set of requirements and standards. The problem of comparing the requirements of the standard of the CIS countries and the standards of other manufacturers is quite complex and is considered in this work.

Regarding the requirements for calcinated petroleum coke, there is no single universal quality standard [61]. Each manufacturer has its own set of requirements and standards. However, a key requirement is a certain level of the specific resistance of calcined petroleum coke that was implemented based on research and production practice [61-62].

The specific resistance is the key quality parameter of carbonaceous materials, and it is measured in powder form and under standardized conditions. There are two main standards for this measurement: standard 4668 [63], which is used almost unchanged until present-day in the CIS countries, and ISO 10143 [64], which is used in European Union and other countries. In some cases, certain manufacturers use their specific resistance measurement methods.

Over the past 60 years, a significant number of works have been published on the experimental study of specific resistance for calcinated carbonaceous materials [2,62,65-74]. It was established that the specific resistance depends on both the maximum temperature of calcination and the duration of its action. Based on the experimental data, approximating dependencies for specific resistance were obtained. The analysis of the experimental data showed that the specific resistance of both thermoanthracite and calcined petroleum coke have significant quantitative differences and are individual.

In addition, in all the works cited above, the results do not indicate the measurement errors of the specific resistance, which is a significant shortcoming. The error of the specific resistance measurement according to the above standards can be estimated by [75] and is ± 20 μΩ·m conforming to the 1-sigma criterion.

The following general conclusions can be done based on the literature analysis:

1) reliable data on specific heat capacities of carbonaceous materials cannot be obtained from publications devoted to mathematical modeling of the calcination process;
2) publications on the experimental or analytical determination of specific heat capacities do not contain information in an explicit form that can be directly used for modeling;
3) there is no unified quality standard for calcined carbonaceous materials;
4) the available data on the temperature and duration of the calcination process of carbonaceous materials do not allow one to immediately and unambiguously choose any of them as the reference parameters of the first approximation when developing new calcination technologies, even in conditions of certainty of the quality standard;
5) experimental data show that the specific heat capacities, composition, and character of the volatiles released during pyrolysis, as well as the specific resistance, are individual indicators for each material and must be determined experimentally for each specific case.

## 2. The unresolved aspects of the problem

The most reliable and precise way to eliminate shortcomings is the experimental determination of specific heat capacities, the composition, and character of the volatiles released during pyrolysis, and the specific resistance of carbonaceous materials. However, this requires clearness, both for the raw material and the quality standards of the calcined material. Unfortunately, this cannot be achieved in terms of first approximation development. It is expedient to use this way during a deeper stage of development.

In the context of the development of calcination technologies of carbonaceous materials, the unresolved issues are:

1) lack of reliable dependences of specific heat capacities for carbonaceous materials, both for heating and cooling conditions, taking into account material transformations during the calcination process; in addition, the lack of error values does not allow modeling in conditions of uncertainty of the initial data;
2) the uncertainty of the correlation of various quality standards of calcined carbonaceous materials (except thermoanthracite of metallurgical quality), which does not allow the development of calcination technologies of the first approximation, since it is not clear for which standard to choose project parameters;
3) lack of values of the guaranteed minimum necessary temperature of the calcination process and the duration of its action, which ensure the required quality of the product (except thermoanthracite of metallurgical quality), under conditions of uncertainty and dispersion of the properties of raw materials of different origins that make it impossible to develop a first approximation.

The main aim of this study is the determination of the initial data for the development of new technologies for carbonaceous materials calcination. Specifically, the determination of analytical dependences for specific heat capacities during heating and cooling, taking into account material transformations and errors, as well as the guaranteed minimum required temperature of the calcination process and its action.

Achieving the main aim is possible after determining the differences and possibilities of replaceability between the requirements for the quality of calcined carbon materials in different countries. This will make it possible to develop a technology suitable for wide use and to proceed to the determination of the guaranteed minimum required temperature and the duration of its action.

Achieving the main aim will allow determining the theoretical minimum possible specific energy consumption for obtaining calcined carbonaceous materials of the required quality.

## 3. Materials and methods

### 3.1. Method for determining specific heat capacities

The method is based on the data obtained experimentally up to a temperature of 1300°C for the cases of heating and cooling, i.e. effective and actual heat capacity. The processing of these data determines the dependence for dry anthracite or petroleum coke of a certain averaged composition in terms of volatile matter and ash. For the temperature range from 1300 to 1800°C, a dependence is chosen that monotonically increases to the values of the specific heat capacity of graphite at the temperatures of the start of graphitization, when the difference in properties between graphite and the processed materials is leveled.

According to the available experimental data for anthracite and petroleum coke of average composition, the amount of volatiles and the character of their release during pyrolysis is determined. The function of residual volatile substances $M_v(T)$ is determined by a one-component scheme individually for anthracite and petroleum coke. It is also used to determine the change in the total mass of the processed material. The heat capacity of carbonaceous materials is considered the sum of the heat capacities of the carbon component, volatiles, ash, and moisture, attributed to the mass portion of each component.

During heating the carbon component *O* and ash *A* are constant values in absolute terms. The dependence of the specific heat capacity of ash on the temperature $C_p^a(T)$ is selected according to the data of the Kirov model [35] obtained experimentally. The maximum ash value based on a dry state for anthracite is 5 wt.%, and for petroleum coke is 1 wt.%.

The moisture *W* is taken into account as constant when the heating temperature increases from 20 ℃ to 100 ℃, and after 100 ℃ it is considered that the moisture is completely removed. At the same time, the specific thermal effect of moisture evaporation *L* is considered due to uniform distribution in the temperature range of 20-100°C. The specific heat capacity of water $C_p^w$ is constant and is selected according to the reference books. The moisture *W* as a received mass for anthracite, usually, is up to 6 wt.% and for petroleum coke up to 12 wt.%. The specific heat capacity of water is determined by Eq. 1:

$$C^w = C_p^w + \frac{L}{80}. \qquad (1)$$

The total specific heat capacity of volatiles is defined as the sum of the specific heat capacities $C_p^i$ of each of the i^th components, attributed to their volume portions $\phi_i$ in percent according to Eq. 2:

$$C_p^v = \sum \frac{\phi_i \cdot \mu_i}{\sum \phi_i \cdot \mu_i} \cdot C_p^i \ , \qquad (2)$$

where $\mu_i$ is the molar mass of the i^th component.

The specific heat capacities of the i^th components are constant according to the average values in the temperature range of 20-700°C and are determined as stated in the reference books. Volatile *V* yields are considered to be in the range of 2 to 8 wt.% dry ash-free state for anthracite and 8 to 12 wt.% for petroleum coke, which are typical values for these feedstocks. Volume portions of i^th components in pyrolysis products are determined separately for anthracite and petroleum coke based on available publications.

The selected dependences of effective specific $C_p^n(T)$ and actual specific $C_p^o(T)$ heat capacities are mathematically processed to obtain analytical dependences of specific heat capacities for other cases of ash, volatile matter, and moisture values.

The effective specific heat capacity of dry ash carbon material without volatile substances $C_{pv}^{n}(T)$ is determined by Eq. 3:

$$C_{pv}^{n}(T)=\frac{C_{p}^{n}(T)-(1-A_{av})\cdot V_{av}\cdot M_{v}(T)\cdot C_{p}^{v}}{1-(1-A_{av})\cdot V_{av}\cdot M_{v}(T)}, \qquad (3)$$

where $A_{av}$ is the average value of ash based on the dry state in units; $V_{av}$ – the average value of volatile matter based on dry ash-free state in units.

The effective specific heat capacity of dry ash-free carbon material $C_{po}^{n}(T)$ is determined by Eq. 4:

$$C_{po}^{n}(T)=\frac{C_{pv}^{n}(T)-A_{av}\cdot C_{p}^{a}(T)}{(1-A_{av})}. \qquad (4)$$

The effective specific heat capacity for the jth case of a random value of ash and volatile matter in dry carbon material $C_{pj}^{n}(T)$ is determined by Eq. 5:

$$C_{pj}^{n}(T)=\frac{\begin{matrix}(1-A_{j}-(1-A_{j})\cdot V_{j})\cdot C_{po}^{n}(T)+\\ +(1-A_{j})\cdot V_{j}\cdot M_{v}(T)\cdot C_{p}^{v}+A_{j}\cdot C_{p}^{a}(T)\end{matrix}}{1-(1-A_{j})\cdot V_{j}\cdot(1-M_{v}(T))}. \qquad (5)$$

The effective specific heat capacity for the jth case of a random value of ash, volatile matter, and moisture in the carbon material $C_{pwj}^{n}(T)$ is determined by Eq. 6:

$$C_{pwj}^{n}(T)=\begin{cases}\dfrac{\begin{matrix}W_{j}\cdot C^{w}+(1-W_{j})\cdot(1-(1-A_{j})\cdot\\ \cdot V_{j}\cdot(1-M_{v}(T)))\cdot C_{pj}^{n}(T)\end{matrix}}{1-(1-W_{j})\cdot(1-A_{j})\cdot V_{j}\cdot(1-M_{v}(T))}\\ C_{pj}^{n}(T) \quad T>373\ {}^{\circ}K\end{cases} \qquad (6)$$

For modelling, a conventionally calculated effective specific heat capacity is used, which takes into account changes in the mass of the carbonaceous material during heating. It is recognized as the product of the value of the current effective specific heat capacity and the ratio of the current mass to the final mass without moisture and volatiles.

The conventionally calculated effective specific heat capacity for the nominal case of the averaged ash value and volatile matter in dry carbonaceous material is determined by Eq. 7:

$$C_{p}^{ur}(T)=\frac{1-(1-A_{av})\cdot V_{av}\cdot(1-M_{v}(T))}{1-(1-A_{av})\cdot V_{av}}\cdot C_{p}^{n}(T) \qquad (7)$$

The conventionally calculated effective specific heat capacity for the nominal case of the average ash value, volatile matter and moisture content in the carbonaceous material is determined by Eq. 8:

$$C_{pw}^{ur}(T)=\begin{cases}\dfrac{\begin{matrix}(1-W_{av})\cdot\\ \cdot\left(1-(1-A_{av})\cdot V_{av}\cdot(1-M_{v}(T))\right)\cdot\\ \cdot C_{p}^{n}(T)+W_{av}\cdot C^{w}\end{matrix}}{(1-W_{av})\cdot(1-(1-A_{av})\cdot V_{av})}\\ C_{p}^{ur}(T) \quad T>373\ {}^{\circ}K\end{cases} \qquad (8)$$

where $W_{av}$ is the average moisture content as a received state in units.

The conventionally calculated effective specific heat capacity for the jth case of a random value of ash and volatile matter in dry carbonaceous material $C_{pi}^{ur}(T)$ is determined by Eq. 9:

$$C_{pj}^{ur}(T)=\frac{1-(1-A_{j})\cdot V_{j}\cdot(1-M_{v}(T))}{1-(1-A_{j})\cdot V_{j}}\cdot C_{pj}^{n}(T), \quad (9) \qquad (9)$$

The conventionally calculated effective specific heat capacity for the case of a random value of ash, volatile matter, and moisture content in the carbonaceous material is determined by Eq. 10:

$$C_{pwj}^{ur}(T)=\begin{cases}\dfrac{\begin{matrix}(1-W_{j})\cdot\\ \cdot\left(1-(1-A_{j})\cdot V_{j}\cdot(1-M_{v}(T))\right)\cdot\\ \cdot C_{pj}^{n}(T)+W_{j}\cdot C^{w}\end{matrix}}{(1-W_{j})\cdot(1-(1-A_{j})\cdot V_{j})}\\ C_{pj}^{ur}(T) \quad T>373\ {}^{\circ}K\end{cases} \qquad (10)$$

The actual specific heat capacity of dry ash-free carbonaceous material $C_{po}^{o}(T)$ is determined by Eq. 11:

$$C_{po}^{o}(T)=\frac{C_{p}^{o}(T)-A_{av}\cdot C_{p}^{a}(T)}{(1-A_{av})} \qquad (11)$$

The actual specific heat capacity of the carbonaceous material for the jth case of a random value of ash is determined by Eq. 12:

$$C_{pj}^{o}(T) = \left(1 - A_j\right) \cdot C_{po}^{o}(T) + A_j \cdot C_{p}^{a}(T)\,. \qquad (12)$$

Limiting specific heat capacities, which take into account the uncertainty of experimental data, are determined by adding to a certain specific heat capacity and subtracting from it a relative error of 6% according to the 3-sigma criterion, which guarantees the determination of the limits of its possible values.

The lower limit specific heat capacity for the $j^{th}$ case of specific heat capacity is determined by Eq. 13:

$$\overleftarrow{C}_j(T) = 0{,}94 \cdot C_j(T)\,. \qquad (13)$$

The upper limit specific heat capacity for the $j^{th}$ case of specific heat capacity is determined by Eq. 14:

$$\vec{C}_j(T) = 1{,}06 \cdot C_j(T)\,. \qquad (14)$$

The method of determining the guaranteed minimum necessary temperatures of the calcination process and duration of process.

The guaranteed minimum necessary temperature of the calcination process and the duration of its action are determined firstly for the electrode thermoanthracite according to the standard [60] for the first and higher grades. Experimental data on the specific resistance of thermoanthracites produced from raw materials of various origins are considered. At the same time, the duration of the temperature effect is determined by such a time value, after which, during further holding at this temperature, the specific resistance of thermoanthracite practically does not decrease. Considering this time, the calcination temperature is determined, at which the vast majority of the investigated thermoanthracites will have a specific resistance not greater than the requirements according to the standard.

In the lack of reliable data on the quality standards of thermoanthracite electrodes outside the CIS countries, it is not possible to directly compare them with the requirements [60]. Therefore, a comparison of the temperature-time modes of operation of furnaces is used with the specified guaranteed minimum necessary temperatures that meet the requirements [60]. If the value of the temperature in the first case is less than in the second case for the same value of the duration of its action, it can be stated that the requirements of the standard in the specific resistance part also satisfy the requirements outside the CIS countries, and the value of the temperature and duration of its action can be taken as a basis in the first approximation when developing an anthracite calcination technology.

The guaranteed minimum necessary temperature of petroleum coke calcination and the duration of its effect are initially determined based on experimental data and requirements for the needed specific resistance values for the conditions of the CIS countries. At the same time, the duration of the temperature effect is determined by such a time value, after which, during further holding at this temperature, the specific resistance of petroleum cokes practically does not decrease. Considering this time, the calcination temperature is determined, at which the vast majority of the analyzed petroleum cokes have specific resistance not greater than the requirements of the standard. Then the values of temperature and the duration of its action are compared with the temperature-time modes of operation of the most common furnaces outside the CIS countries. The temperature value is chosen, which is the maximum of those considered for the same value of the duration of action. The value of the temperature and the duration of its action is chosen in the first approximation as model parameters in the development of the petroleum coke calcination technology.

### 3.2. The method of determining the theoretical minimum possible specific energy consumption of the calcination process

The theoretical minimum possible specific energy consumption for the calcination process of carbonaceous materials are determined by integrating the dependences of conventionally calculated effective specific heat capacities in the temperature range from 20 ℃ to the guaranteed minimum required temperatures.

Energy consumption for the nominal, better, and worst cases, taking into account the composition of materials and uncertainty limits, are of practical importance.

The amount of thermal energy released during the cooling of the processed materials from the guaranteed minimum necessary temperatures to a temperature of 20 ℃ for the nominal, better and worst cases is determined individually, considering the composition of the materials and uncertainty limits.

## 4. Results and discussion

### 4.1. Specific heat capacities

The dependences of the effective specific $C_p^n(T)$ and the actual specific $C_p^o(T)$ of the heat capacities, which are chosen as a basis, are determined separately for dry anthracite and petroleum coke at the average values of ash and volatile matter. For anthracite, the average index of ash is $A_{av}^A$ = 2.5% on a dry state, the volatile matter is $V_{av}^A$ = 5% on a dry ash-free state. For petroleum coke, the average ash index is $A_{av}^{PC}$ = 0.5%, the volatile matter is $V_{av}^{PC}$ = 10%, respectively.

Dependencies of the effective specific heat capacity $C_p^{hA}(T)$ for the case of heating anthracite and $C_p^{hPC}(T)$ for the case of heating petroleum coke, as well as dependencies for the actual specific heat capacity $C_p^{cTA}(T)$ for the case of cooling thermoanthracite and $C_p^{cPC}(T)$ for the case of cooling of calcined petroleum coke, are determined in the form of a cubic spline according to Eq. 15:

$$C_p(T) = A + B \cdot T + C \cdot T^2 + D \cdot T^3 \,, \qquad (15)$$

where $C_p(T)$ is the specific heat capacity function; *A*, *B*, *C*, *D* are coefficients; *T* is the absolute temperature, K.

The values of the coefficients for Eq. 15 are shown in Table 1, and the graphs of the obtained dependencies are shown in Fig. 1.

The volatile residue function is determined by Eq. 16:

$$M_v(T) = e^{-k\cdot e^{\left(\frac{-E\cdot\mu_{av}}{R\cdot T}\right)}} \,, \qquad (16)$$

where *k* is the pre-exponential factor, 1/s; *E* is the activation energy, J/mol; $\mu_{av}$= 0.047 kg/mol is the weighted average molar mass of volatiles; *R* = 8.31 J/K·mol is the universal gas constant; *T* is the absolute temperature, K.

Table 1. Coefficients in the formula for specific heat capacities selected as a basis.

| T, K | | A | B | C | D |
|---|---|---|---|---|---|
| $C_p^{hA}(T)$ anthracite heating, curve A | | | | | |
| 293 | 473 | $6,034499\cdot10^{2}$ | $1,784795$ | $-4,611884\cdot10^{-4}$ | $5, 246739\cdot10^{-7}$ |
| 473 | 673 | $8,106458\cdot10^{2}$ | $4,706568\cdot10^{-1}$ | $2,317117\cdot10^{-3}$ | $-1,433258\cdot10^{-6}$ |
| 673 | 773 | $-1,035602\cdot10^{2}$ | $4,545869$ | $-3,738176\cdot10^{-3}$ | $1,565896\cdot10^{-6}$ |
| 773 | 823 | $3,171631\cdot10^{4}$ | $-1,189465\cdot10^{2}$ | $1,560191\cdot10^{-1}$ | $-6,732469\cdot10^{-5}$ |
| 823 | 873 | $-1,746267\cdot10^{4}$ | $6,032076\cdot10^{1}$ | $-6,180261\cdot10^{-2}$ | $2,089795\cdot10^{-5}$ |
| 873 | 893 | $8,425624\cdot10^{4}$ | $-2,892287\cdot10^{2}$ | $3,385977\cdot10^{-1}$ | $-1,319849\cdot10^{-4}$ |
| 893 | 943 | $-8,737346\cdot10^{3}$ | $2,317967\cdot10^{1}$ | $-1,124371\cdot10^{-2}$ | $-1,398378\cdot10^{-6}$ |
| 943 | 993 | $-4,897921\cdot10^{4}$ | $1,512025\cdot10^{2}$ | $-1,47005\cdot10^{-1}$ | $4,659077\cdot10^{-5}$ |
| 993 | 1063 | $-4,654161\cdot10^{4}$ | $1,438382\cdot10^{2}$ | $-1,395887\cdot10^{-1}$ | $4,410125\cdot10^{-5}$ |
| 1063 | 1093 | $-7,826662\cdot10^{4}$ | $2,333725\cdot10^{2}$ | $-2,238167\cdot10^{-1}$ | $7,051329\cdot10^{-5}$ |
| 1093 | 1163 | $6,709748\cdot10^{4}$ | $-1,656139\cdot10^{2}$ | $1,412212\cdot10^{-1}$ | $-4,081272\cdot10^{-5}$ |
| 1163 | 1273 | $-7,455985\cdot10^{4}$ | $1,997961\cdot10^{2}$ | $-1,729749\cdot10^{-1}$ | $4,924063\cdot10^{-5}$ |
| 1273 | 1393 | $1,12794\cdot10^{5}$ | $-2,41729\cdot10^{2}$ | $1,738634\cdot10^{-1}$ | $-4,157851\cdot10^{-5}$ |
| 1393 | 1473 | $-1,666464\cdot10^{3}$ | $4,775948$ | $-3,096337\cdot10^{-3}$ | $7,664887\cdot10^{-7}$ |
| 1473 | 1573 | $-8,026809\cdot10^{3}$ | $1,77298\cdot10^{1}$ | $-1,189053\cdot10^{-2}$ | $2,756577\cdot10^{-6}$ |
| 1573 | 1673 | $1,139103\cdot10^{3}$ | $2,487265\cdot10^{-1}$ | $-7,773283\cdot10^{-4}$ | $4,015846\cdot10^{-7}$ |
| 1673 | 2073 | $7,851336\cdot10^{3}$ | $-1,178755\cdot10^{1}$ | $6,417101\cdot10^{-3}$ | $-1,031854\cdot10^{-6}$ |

| T, K | | A | B | C | D |
|---|---|---|---|---|---|
| $C_p^{cA}(T)$ cooling of thermoanthracite, curve TA | | | | | |
| 293 | 463 | $4,84082\cdot 10^{2}$ | 1,265532 | $7,883075\cdot 10^{-4}$ | $-8,968231\cdot 10^{-7}$ |
| 463 | 573 | $4,344733\cdot 10^{2}$ | 1,586971 | $9,405473\cdot 10^{-5}$ | $-3,970011\cdot 10^{-7}$ |
| 573 | 743 | $5,369821\cdot 10^{2}$ | 1,050275 | $1,030695\cdot 10^{-3}$ | $-9,418767\cdot 10^{-7}$ |
| 743 | 853 | -6,955396 | 3,246524 | $-1,925223\cdot 10^{-3}$ | $3,842425\cdot 10^{-7}$ |
| 853 | 973 | $1,142115\cdot 10^{3}$ | $-7,947559\cdot 10^{-1}$ | $2,812502\cdot 10^{-3}$ | $-1,467154\cdot 10^{-6}$ |
| 973 | 1123 | $-1,948251\cdot 10^{3}$ | 8,733611 | $-6,980269\cdot 10^{-3}$ | $1,887682\cdot 10^{-6}$ |
| 1123 | 1273 | $-1,079602\cdot 10^{3}$ | 6,413089 | $-4,913909\cdot 10^{-3}$ | $1,274337\cdot 10^{-6}$ |
| 1273 | 1500 | $1,499444\cdot 10^{3}$ | $3,352076\cdot 10^{-1}$ | $-1,394546\cdot 10^{-4}$ | $2,415315\cdot 10^{-8}$ |
| 1500 | 1800 | $1,730251\cdot 10^{3}$ | $-1,264061\cdot 10^{-1}$ | $1,682877\cdot 10^{-4}$ | $-4,423405\cdot 10^{-8}$ |
| 1800 | 2073 | $9,697144\cdot 10^{2}$ | 1,141155 | $-5,359132\cdot 10^{-4}$ | $8,617354\cdot 10^{-8}$ |
| $C_p^{hPC}(T)$ petroleum coke heating, curve PC | | | | | |
| 293 | 553 | $5,885532\cdot 10^{2}$ | 1,794666 | $1,912577\cdot 10^{-4}$ | $-2,335259\cdot 10^{-7}$ |
| 553 | 773 | $-1,885093\cdot 10^{3}$ | $1,521408\cdot 10^{1}$ | $-2,407532\cdot 10^{-2}$ | $1,439371\cdot 10^{-5}$ |
| 773 | 823 | $-2,834608\cdot 10^{4}$ | $1,179087\cdot 10^{2}$ | $-1,569273\cdot 10^{-1}$ | $7,168222\cdot 10^{-5}$ |
| 823 | 873 | $7,101281\cdot 10^{4}$ | $-2,442743\cdot 10^{2}$ | $2,831492\cdot 10^{-1}$ | $-1,065586\cdot 10^{-4}$ |
| 873 | 903 | $1,620713\cdot 10^{6}$ | $-5,569706\cdot 10^{3}$ | 6,383301 | $-2,435749\cdot 10^{-3}$ |
| 903 | 923 | $-2,317441\cdot 10^{6}$ | $7,513864\cdot 10^{3}$ | -8,105704 | $2,91272\cdot 10^{-3}$ |
| 923 | 973 | $4,284147\cdot 10^{5}$ | $-1,410911\cdot 10^{3}$ | 1,563609 | $-5,792673\cdot 10^{-4}$ |
| 973 | 1023 | $-7,238605\cdot 10^{5}$ | $2,141838\cdot 10^{3}$ | -2,087727 | $6,716186\cdot 10^{-4}$ |
| 1023 | 1073 | $-1,825693\cdot 10^{6}$ | $5,373019\cdot 10^{3}$ | -5,246261 | 1,700792 |
| 1073 | 1098 | $-9,571401\cdot 10^{4}$ | $5,361718\cdot 10^{2}$ | $-7,384817\cdot 10^{-1}$ | $3,00426\cdot 10^{-4}$ |
| 1098 | 1123 | $5,318064\cdot 10^{6}$ | $-1,425557\cdot 10^{4}$ | $1,273305\cdot 10^{1}$ | $-3,789292\cdot 10^{-3}$ |
| 1123 | 1173 | $-2,02801\cdot 10^{5}$ | $4,929549\cdot 10^{2}$ | $-4,000977\cdot 10^{-1}$ | $1,08941\cdot 10^{-4}$ |
| 1173 | 1323 | $-8,382506\cdot 10^{4}$ | $1,886686\cdot 10^{2}$ | $-1,406891\cdot 10^{-1}$ | $3,522444\cdot 10^{-5}$ |
| 1323 | 1573 | $-4,203191\cdot 10^{3}$ | 8,120173 | $-4,220146\cdot 10^{-3}$ | $8,407219\cdot 10^{-7}$ |
| 1573 | 2073 | $-1,586901\cdot 10^{3}$ | 3,130425 | $-1,048025\cdot 10^{-3}$ | $1,685198\cdot 10^{-7}$ |
| $C_p^{cPC}(T)$ cooling of calcined petroleum coke, curve CPC | | | | | |
| 293 | 473 | $3,672368\cdot 10^{2}$ | 1,512214 | $1,692078\cdot 10^{-4}$ | $-1,925004\cdot 10^{-7}$ |
| 473 | 673 | $4,0584\cdot 10^{2}$ | 1,267374 | $6,868402\cdot 10^{-4}$ | $-5,572871\cdot 10^{-7}$ |
| 673 | 873 | $9,748726\cdot 10^{2}$ | -1,269174 | $4,455858\cdot 10^{-3}$ | $-2,424062\cdot 10^{-6}$ |
| 873 | 1073 | $-1,638309\cdot 10^{3}$ | 7,710832 | $-5,830518\cdot 10^{-3}$ | $1,503535\cdot 10^{-6}$ |
| 1073 | 1273 | $-1,52266\cdot 10^{3}$ | 7,387488 | $-5,529173\cdot 10^{-3}$ | $1,409921\cdot 10^{-6}$ |
| 1273 | 2073 | $1,261546\cdot 10^{3}$ | $8,261219\cdot 10^{-1}$ | $-3,749179\cdot 10^{-4}$ | $6,028589\cdot 10^{-8}$ |

The values of pre-exponential coefficients and activation energy in Eq. 16 according to [51] are presented in Table 2.

Table 2. Values of pre-exponential coefficients and activation energy as a function of volatile matter.

| Carbonaceous material | k , 1/s | E , J/mol |
|---|---|---|
| Anthracite | 121 | 813 000 |
| Petroleum coke | 213 | 872 000 |

The dependence of the rate of volatiles release from carbonaceous materials during heating is determined by Eq. 17:

$$v(T) = -\frac{dM_v(T)}{dT}. \qquad (17)$$

Curves of the rate of volatiles release from anthracite (curve A) and petroleum coke (curve PC) during heating are shown in Figure 2.

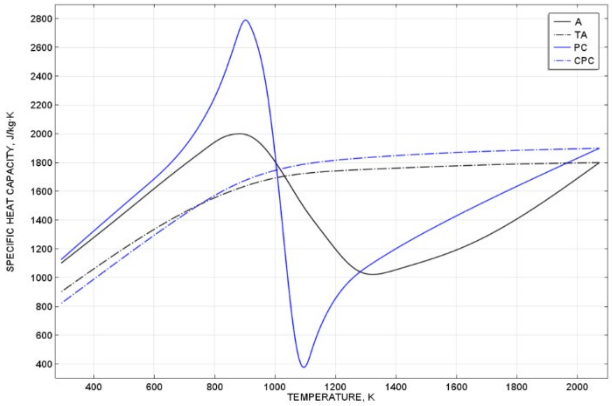


Fig. 1. Graphs of specific heat capacities selected as a basis.

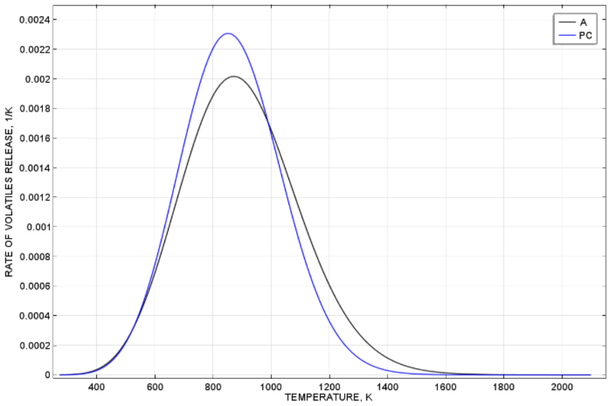


Fig. 2. Graphs of the rate of volatiles release during heating.

The dependence of the specific heat capacity of ash on temperature, which is the same for both anthracite and petroleum coke, is determined according to the Kirov model [35] by Eq. 18:

$$C_p^a(T) = 594 + 0{,}586 \cdot T\,, \qquad (18)$$

where $T$ is the absolute temperature, K.

The numerical value of the specific heat capacity of water, determined by Eq. 1, is: $C^w = 32\,406\ J/(kg \cdot K)$.

To calculate the total specific heat capacity of volatile matter of anthracite and petroleum coke according to Eq. 2, the initial data [2,50,67] listed in Table 3 are used.

Table 3.Properties of volatile components.

| *i*-component | $\phi_i$ , % | | $\mu_i$ , kg/mol | $C_p^i$ , J/kg·K |
|---|---|---|---|---|
| | Anthracite | Petroleum coke | | |
| $H_2$ | 80 | 12 | 0,002 | 14 200 |
| $CH_4$ | 5 | 77 | 0,016 | 3 467 |
| CO | 8 | 6 | 0,028 | 1 137 |
| $CO_2$ | 4 | 5 | 0,044 | 1 000 |
| $H_2S$ | 3 | – | 0,034 | 1 176 |

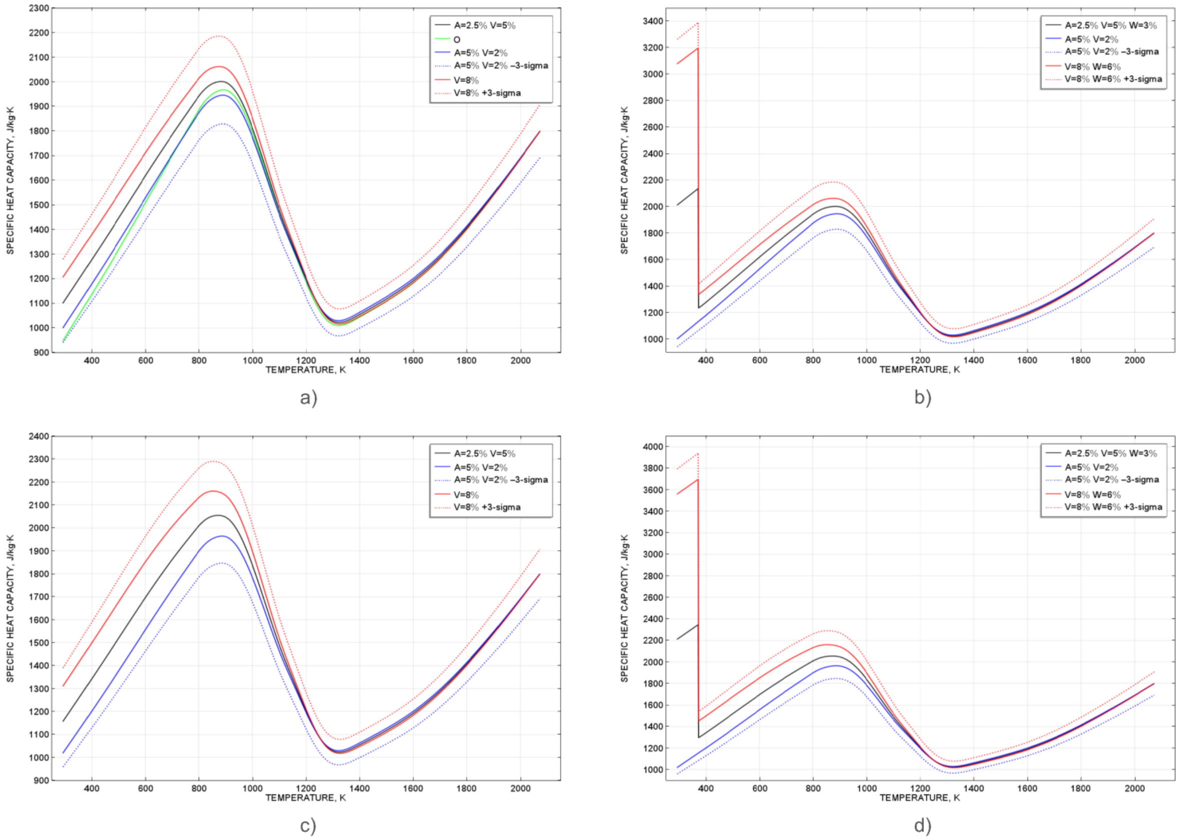
The values of the total specific heat of volatile matter of anthracite and petroleum coke, calculated according to Eq. 2, are provided in Table 4.

Table 4. The value of the total specific heat of volatiles.

| Carbonaceous material | Anthracite | Petroleum coke |
|---|---|---|
| $C_p^v$ , J/kg·K | 4 178 | 3 055 |

The obtained results of the dependence of specific heat capacities are shown graphically in Figures 3-5. The results obtained using the developed model of the specific heat capacity of carbonaceous materials should be compared with the results previously obtained by other researchers.

The model values of effective specific heat capacities for the organic part of dry anthracite at a temperature of 293 K without volatiles and with volatiles were compared with the results of other publications for coals of the same state and under the same conditions [34-35, 38-39, 42,45]. The model values are consistent with previously obtained data, and their significant deviation can be explained by different degrees of metamorphism and different origin of the studied coals.



a)

b)

c)

d)

Fig. 3. Effective specific heat capacities of anthracite during heating:
a) dry state; b) wet state; c) conventionally calculated on dry state; d) conventionally calculated on wet state

The values of the effective specific heats of dry petroleum cokes, obtained according to the developed model and data [40] of the seven samples study from different origins, for which confidence intervals are determined at a confidence probability of 0.997, were compared. It was established that the model values are consistent with the data of the previous research.

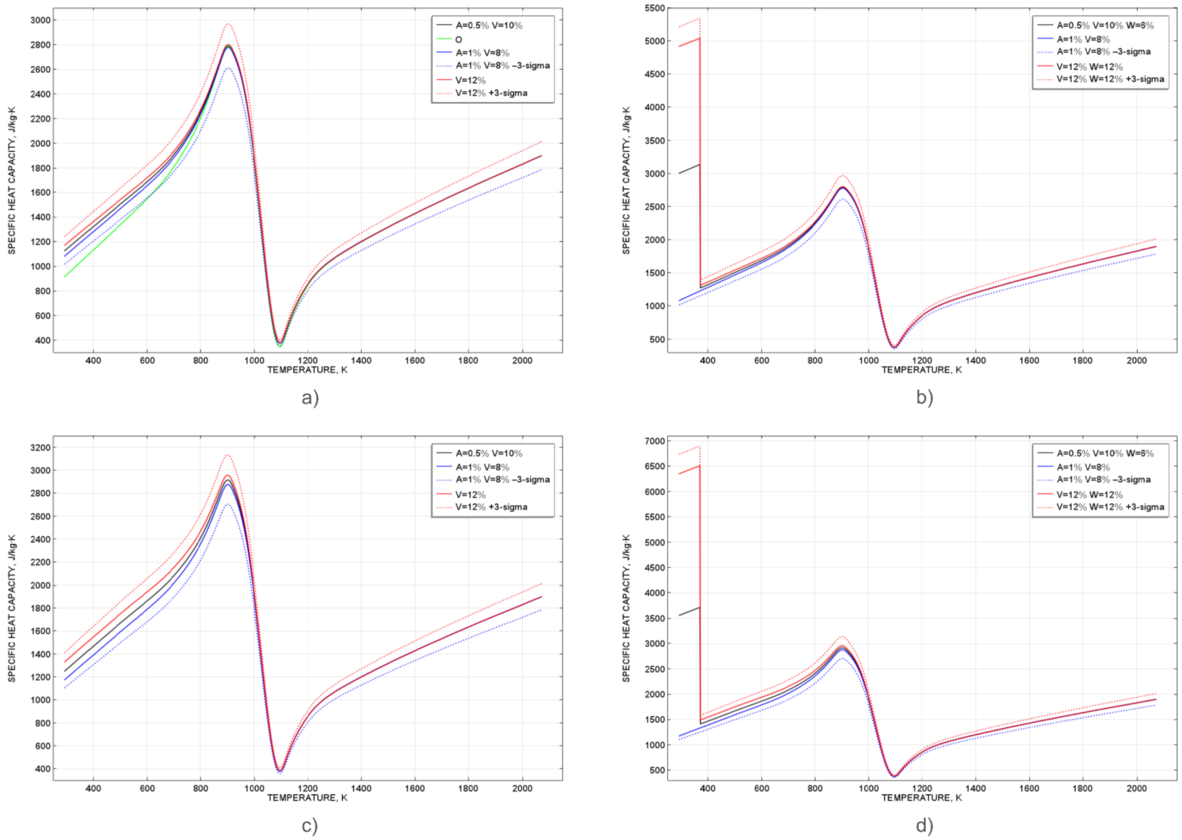
Thus, the developed model does not contradict previous results of specific heat capacities of carbonaceous materials. The guaranteed minimum necessary temperatures of the calcination process and the duration of their action.

The known experimental data on the specific resistance of calcined anthracites [15, 67-70, 73, 74] and petroleum cokes [62], determined according to the standard [63], were analyzed and summarized. They are presented in Figure 6.

The considered anthracites originate from the Donetsk and Horliv coal basins and the Nazarailok deposit, and the petroleum cokes are from Caspian oil. These carbonaceous materials are constantly used in CIS countries.

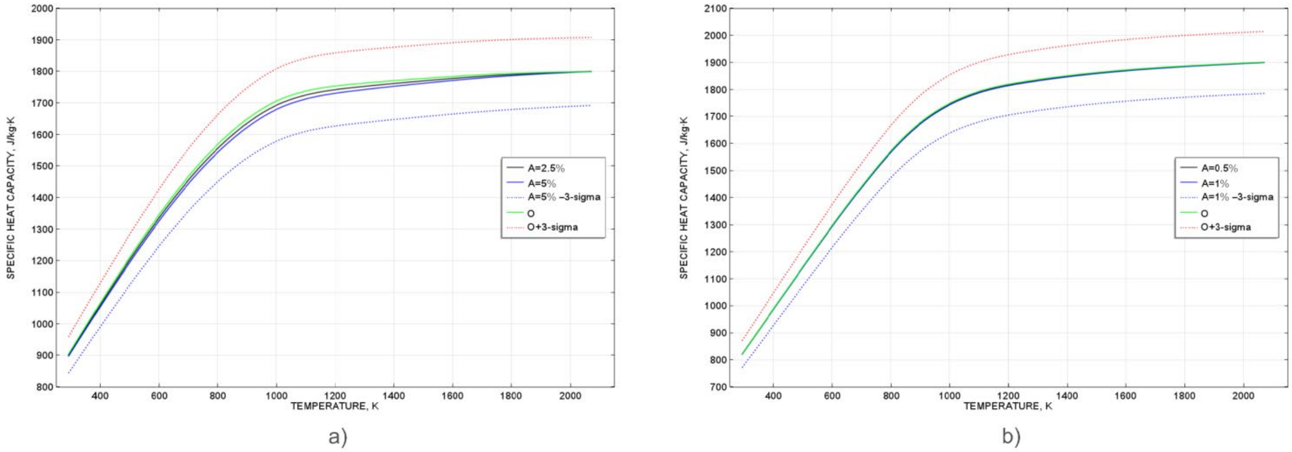
According to publications [15,62,67], holding for more than 1 hour at the maximum temperature, both for anthracite and for petroleum coke, does not lead to a significant decrease in their specific resistance corresponding to [63]. That is, the value of the holding time of 1 hour can be taken as a basis in the first approximation when determining the minimum required calcination temperatures.

The electrode thermoanthracite should have a specific resistance of no more than 1000 μΩ·m for the first grade of quality, and no more than 970 μΩ·m for the highest grade according to [60]. The specific resistance of calcined petroleum coke should not exceed 600 μΩ·m [62].



a) b) c) d)

Fig. 4. Effective specific heat capacities of petroleum coke during heating:
a) dry state; b) wet state; c) conventionally calculated on dry state; d) conventionally calculated on wet state



a) b)

Fig. 5. Actual specific heat capacities during cooling; a) thermoanthracite; b) calcined petroleum coke

There is a significant spread of specific resistance values for the considered calcined anthracites and petroleum cokes. This can be explained by the different electrical properties of raw materials from different mining sites. The vast majority of calcined anthracites at a temperature of 1500 ℃, and in the absence of holding, have a specific resistance of 1000 μΩ·m or less. At a temperature of 1600 ℃, without holding, the specific resistance is no more than 970 μΩ·m. The vast majority of calcined petroleum cokes at a temperature of 1200°C and in the absence of holding for it have a specific resistance of 600 μΩ·m or less.

During an isothermal holding for 1 hour, the specific resistance of the vast majority of considered calcined anthracites does not exceed 1000 µΩ·m even at a temperature of 1400 ℃, and 970 µΩ·m at 1500°C. For the vast majority of considered calcined petroleum cokes, for the same duration of holding, the specific resistance reaches a value of no higher than 600 µΩ·m at a temperature of 1150°C.

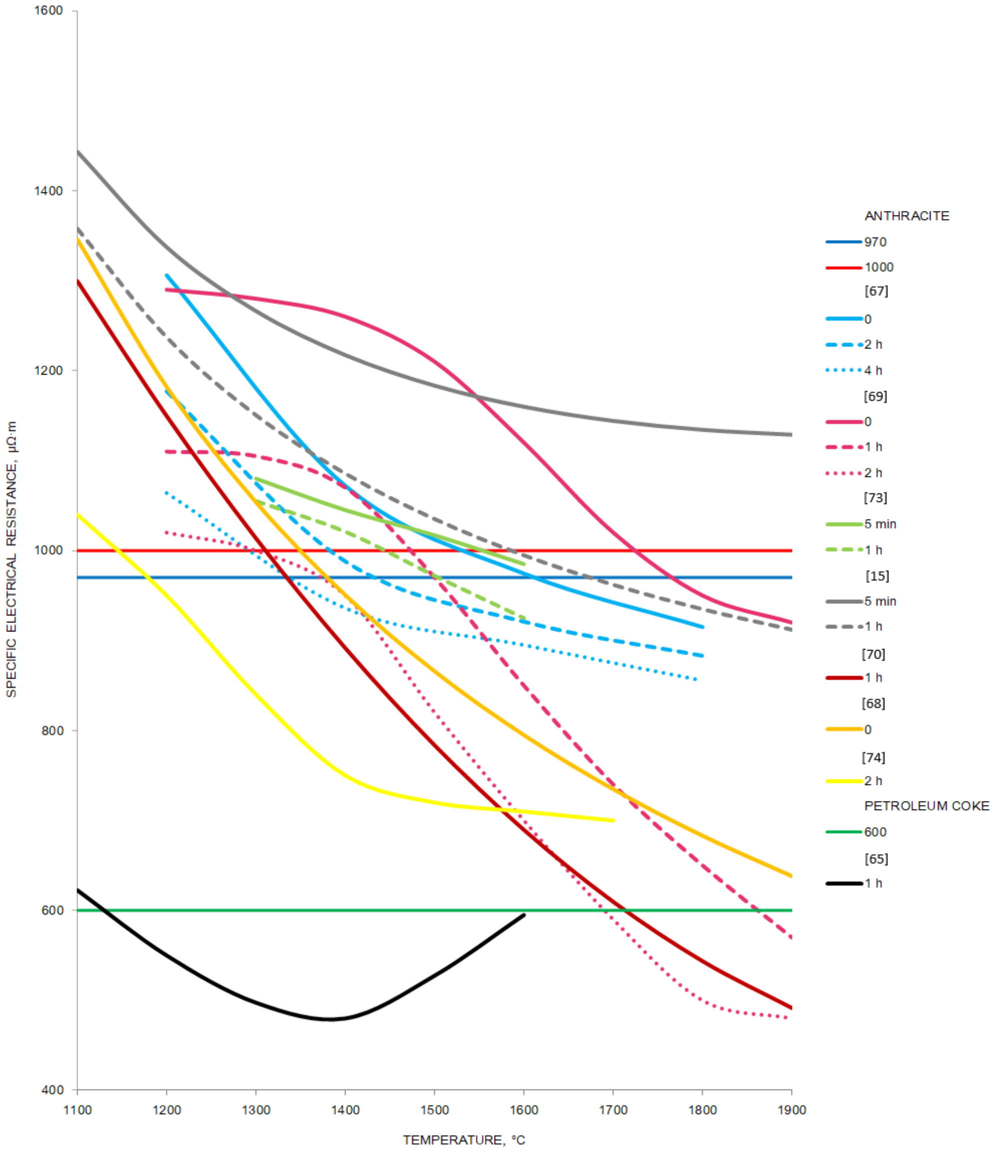


Fig. 6. Summarized experimental data of specific resistance of calcined anthracites and petroleum cokes

According to [23], the minimum temperature in the main calcination zone of electrocalciners of the ELKEM type (the most widespread outside the CIS countries) is no more than 1400°C, with a duration of stay at this temperature of several hours. So, this temperature-time mode of anthracite calcination allows the production of electrode thermoanthracite of the first grade corresponding to the specific resistance criterion [60]. Thus, in a first approximation, it can be assumed that the requirements of the quality standard for electrode thermoanthracite, which is adopted in the CIS countries, also meet the requirements for electrode thermoanthracite in other countries of the world.

During the petroleum cokes calcination, the maximum temperature of the working process in a rotary drum, rotary hearth, and shaft furnaces outside the CIS countries is 1300 ℃ for a duration of several hours [4,13-14,21]. This temperature is taken as a basis in the first approximation, as it is higher than the temperature previously determined by experimental data for specific resistance of calcined petroleum cokes produced in the CIS countries.

Consequently, the guaranteed minimum required calcination temperatures are chosen as a first approximation as follows:

- metallurgical thermoanthracite – 1150°C;
- electrode thermoanthracite of the first grade – 1400 °C;
- electrode thermoanthracite of the highest grade – 1500 °C;
- calcinated petroleum coke – 1300 °C.

Theoretical minimum possible specific energy consumption of the calcination process. The values of the specific energy consumption required for heating anthracite and petroleum coke during calcination, as well as the amount of heat energy released during their cooling, are indicated in Table 5.

Table 5. Specific energy characteristics of the calcination process of carbonaceous materials.

| Share, wt. % | | | Relative error ± | Specific energy | |
|---|---|---|---|---|---|
| Ash | Volatile matter | Moisture | | J/kg | kWh/t |
| Metallurgical thermoanthracite, heating | | | | | |
| 2,5 | 5 | – | – | 1 748 095 | 485,58 |
| 5 | 2 | – | – | 1 657 827 | 460,51 |
| 5 | 2 | – | –3-sigma | 1 558 357 | 432,88 |
| – | 8 | – | – | 1 849 066 | 513,63 |
| – | 8 | – | +3-sigma | 1 960 010 | 544,45 |
| 2,5 | 5 | 3 | – | 1 832 568 | 509,05 |
| – | 8 | 6 | – | 2 029 342 | 563,71 |
| – | 8 | 6 | +3-sigma | 2 152 724 | 597,98 |
| Metallurgical thermoanthracite, cooling | | | | | |
| 2,5 | – | – | – | 1 696 926 | 471,37 |
| 5 | – | – | – | 1 685 194 | 468,11 |
| 5 | – | – | –3-sigma | 1 584 082 | 440,02 |
| – | – | – | – | 1 708 658 | 474,63 |
| – | – | – | +3-sigma | 1 811 178 | 503,11 |
| Electrode thermoanthracite of the first grade, heating | | | | | |
| 2,5 | 5 | – | – | 2 036 954 | 565,82 |
| 5 | 2 | – | – | 1 948 905 | 541,36 |
| 5 | 2 | – | –3-sigma | 1 831 970 | 508,88 |
| – | 8 | – | – | 2 135 815 | 593,28 |
| – | 8 | – | +3-sigma | 2 263 964 | 628,88 |
| 2,5 | 5 | 3 | – | 2 121 700 | 589,36 |
| – | 8 | 6 | – | 2 316 630 | 643,51 |
| – | 8 | 6 | +3-sigma | 2 457 254 | 682,57 |
| Electrode thermoanthracite of the first grade, cooling | | | | | |
| 2,5 | – | – | – | 2 140 315 | 594,53 |
| 5 | – | – | – | 2 126 837 | 590,79 |
| 5 | – | – | –3-sigma | 1 999 227 | 555,34 |
| – | – | – | – | 2 153 794 | 598,28 |
| – | – | – | +3-sigma | 2 283 022 | 634,17 |
| Electrode thermoanthracite of the highest grade, heating | | | | | |
| 2,5 | 5 | – | – | 2 168 503 | 602,36 |
| 5 | 2 | – | – | 2 081 218 | 578,12 |
| 5 | 2 | – | –3-sigma | 1 956 345 | 543,43 |
| – | 8 | – | – | 2 266 629 | 629,62 |
| – | 8 | – | +3-sigma | 2 402 626 | 667,40 |
| 2,5 | 5 | 3 | – | 2 252 747 | 625,76 |
| – | 8 | 6 | – | 2 446 419 | 679,56 |
| – | 8 | 6 | +3-sigma | 2 594 821 | 720,78 |

| Share, wt. % | | | Relative error ± | Specific energy | |
|---|---|---|---|---|---|
| Ash | Volatile matter | Moisture | | J/kg | kWh/t |
| Electrode thermoanthracite of the highest grade, cooling | | | | | |
| 2,5 | – | – | – | 2 318 891 | 644,14 |
| 5 | – | – | – | 2 304 946 | 640,24 |
| 5 | – | – | −3-sigma | 2 166 649 | 601,85 |
| – | – | – | – | 2 332 836 | 648,01 |
| – | – | – | +3-sigma | 2 472 807 | 686,89 |
| Calcined petroleum coke, heating | | | | | |
| 0,5 | 10 | – | – | 2 018 785 | 560,77 |
| 1 | 8 | – | – | 1 974 945 | 548,60 |
| 1 | 8 | – | −3-sigma | 1 856 448 | 515,68 |
| – | 12 | – | – | 2 067 079 | 574,19 |
| – | 12 | – | +3-sigma | 2 191 104 | 608,64 |
| 0,5 | 10 | 6 | – | 2 205 160 | 612,54 |
| – | 12 | 12 | – | 2 470 914 | 686,37 |
| – | 12 | 12 | +3-sigma | 2 619 169 | 727,55 |
| Calcined petroleum coke, cooling | | | | | |
| 0,5 | – | – | – | 1 991 675 | 553,24 |
| 1 | – | – | – | 1 989 004 | 552,50 |
| 1 | – | – | −3-sigma | 1 869 664 | 519,35 |
| – | – | – | – | 1 994 346 | 553,99 |
| – | – | – | +3-sigma | 2 114 007 | 587,22 |

Based on the obtained data, the theoretical minimum possible specific energy consumption of the calcination process, taking into account the error of determination according to the 3-sigma criterion, are in kilowatt-hours per ton of the product:

- metallurgical thermoanthracite – $461_{-28}$;
- electrode thermoanthracite of the first grade – $541_{-32}$;
- electrode thermoanthracite of the highest grade – $578_{-35}$;
- calcined petroleum coke – $549_{-33}$.

## 5. Conclusions

Analytical temperature dependences of the specific heat capacities of anthracite and petroleum coke were obtained experimentally and analytically for the cases of their heating and subsequent cooling in the temperature range of 20-1800°C, taking into account material transformations and determination errors.

It has been established that the quality requirements for thermoanthracites and calcined petroleum cokes, both in the CIS countries and outside them, are practically identical. It was established that the duration of the maximum calcination temperature of more than 1 hour does not lead to a significant decrease in the specific resistance of carbonaceous materials.

The guaranteed minimum necessary temperatures of the calcination process of carbonaceous materials were determined: metallurgical thermoanthracite – 1150°C; electrode thermoanthracite of the first grade – 1400°C; electrode thermoanthracite of the highest grade – 1500°C; calcined petroleum coke – 1300°C.

The theoretical minimum possible specific energy consumption of the calcination process of carbonaceous materials were determined (without taking into account the error of definition): metallurgical thermoanthracite – 461 kW/hr; electrode thermoanthracite of the first grade – 541 kW/hr; electrode thermoanthracite of the highest grade – 578 kW/hr; calcined petroleum coke – 549 kW/hr.

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