Research article

Technologies of coatings employment for coals oxidation resistance improvement

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Abstract: The paper is dedicated to studying of the efficiency of application of the dust control agents not only for their original aims, but also for increasing of oxidation resistance of the solid fossil fuels. The complex investigation included: studying of coals quality alteration after treatment by the selected solution, scanning electron microscopy for investigation of their surface topology changes and, finally, ozonating treatment at low ozone concentrations with kinetic modeling for evaluation of oxidation resistivity. As it was expected, application of the selected solution allows no quality loss for coals. Scanning electron microscopy allowed to visualize the mechanism of working of the dust control agent. It revealed that the studied solution forms a thin smooth film around coal particles. This film tightly binds all the fine particles that were already formed and stored at the coal surface. Also, the solution tends to cover the surface thus decreasing the accessibility of the surface to active oxygen. The latter was proved by treated and untreated coals ozonating processing at low concentrations of ozone. The applied kinetic model allowed evaluation of the total coals activity to ozone decomposition. It was found that the treated coals have twice as low total activity to ozone decomposition as compared with the untreated ones. The latter parameter is closely related to coals oxidation resistivity (the lower the coals activity, the higher the coals oxidation resistivity). Therefore, it was finally concluded that application of the studied dust control agent allows for significant increase of sought-for quality indicator.

Keywords: coal; coal dust suppressant; coating; oxidation resistance; quality; ozone; kinetic modeling

1. Introduction

Modern mining led to intensification of the processes of solid mineral fuel extraction and processing. Unfortunately, this relates to quite substantial environment contamination, including the atmospheric air dust pollution. The latter, especially when exceeding the maximal allowable concentration, is one of the main challenges to be solved for coal underground and opencast mines. High dust emission in the working zone serve as a negative effect at safety of mining, and also causes serious occupational diseases. Under these circumstances, dust control measures are one of the most important challenge of the national economy. Therefore, it is urgently required to develop a series of actions aimed at providing of the allowable workplace sanitary-hygienic exposure limits and environment protection from noxious effects of coal dust under the conditions of positive and/or negative temperatures.

In the view of above, the modern investigations are concentrated at development of means and measured for decreasing of fine coal dust concentrations that has already been formed. Such techniques are using the systems for air purification (see, e.g., [1–3]) or working zones wetting by water [4] and steam [5]. To this end, the various researches are being done aimed at studying of coal fine dust particles wettability by water [6–8]. It should be pointed out that treatment by water and steam is one of the most widespread means of dust control. On the other hand, this approach gives only a short-time action, and in the cases of its lack of efficiency in terms of atmospheric air dust concentration decrease it is recommended to additionally apply the special chemical agents. Their application method is based on preparation of the solution with the specified concentration of the chosen chemical reactant and further wetting of the dust-forming coal surface at storage, loading/unloading and handling. Analysis of such additives and chemical agents towards their effects at increase of dust consolidation activity is nowadays being performed by many researchers. In [9] it was shown that after addition of chemical reactants for dust control, the size of the droplets grew drastically, and the efficiency of dust removal significantly increased in comparison to pure water. In another analogous work [10] the interrelation between the concentration of magnetized solution of surface-active agent (SAA) and surface tension was studied. This investigation led to a conclusion that the surface tension of such solution is decreasing with SAA concentration growth. Also, authors of [10] gave recommendations on rational concentration of SAA for dust controlling aims. In article [11] a new type of chemical agents was proposed based on two-phase solution of sodium dodecyl sulfate (SDS) with polyethylene oxide (g-PEO). This agent allowed to remove the aerosol dust with high efficiency and without substantial altering of coal products quality. Analogous works were performed by authors of [12–14], where different reagents were used as dust control agents, including magnetic particles. An important issue of such investigations is also related to control of stability and performance of such agents under different external conditions, such as high or very low (sub-zero) temperatures and transitions of the latter through zero [15].

A number of studies were dedicated to creation and choosing of chemical inhibitors aimed not only at dust control, but also at deceleration of coal oxidation processes. For example, in work [16] authors investigated the effects of chemical agent additive at the parameters characterizing the oxidation resistivity of coals such as crossing point temperature, alteration of active functional groups, etc. Other studies are aimed at construction of new types of additives and their optimization for deceleration of the coals oxidation and self-heating rates for control of coals spontaneous

combustion in mines [17]. An efficient solution for coals spontaneous combustion control during mining was proposed by authors of [18].

On the other hand, only a few studies exist on dust control during transport and storage of coals. What is more important, the most of the currently used dust control agents are not biodegradable. Authors of [8] developed an environmentally friendly dust-separating cementing solution with high adhesion capacity. This allows to use it during transportation, packing and storage of coals.

Currently, more and more manufacturers and scientists offer their products—specialized agents for dust control and internal structure binding in various industry sectors, for different materials [19], including coals. Using of chemically active reactants became one of the most perspective directions within the area of dust control.

The aim of this work is to evaluate the efficiency of application of the aforementioned products not only for dust control aims, but also for increasing of oxidation resistance of the solid mineral fuels. In the current article authors analyzed the effects of coals treatment by the specialized solution "AMS-1000" [20] on their quality indices and those related to tendency to oxidation, and also alteration of surface structure.

2. Materials and methods

2.1. Characteristics of the selected coals

In this work, two lignite coals were used for the tests. These coals differ by their origin: Coal #1 from Kansko-Achinsky basin, coal #2—Moscow basin. The coals samples were grinded to the particle sizes of <3 mm and <0.2 mm. Before all the experiments, grinded coals were stored in air-tight containers in order to prevent their oxidation. This is especially important for storage of lignites as they are well known to be prone to rapid oxidation [21].

The following quality indices were found using the standard techniques: Vitrinite reflectance index $R_{o,r}$, (ISO 7404-5:2009), coals total moisture W^r (ASTM D3302/D3302M–17), analytical moisture W^a (ISO 11722:2013, ISO 5068-2:2007), ash contents A^d (on dry basis) (ISO 1171:2010), Sulphur S^d (on dry basis) (ISO 19579:2006) and gross calorific value Q_s^{daf} (on dry, ash-free basis) (ISO 1928:2009). The determined quality indices for the selected coals are listed in Table 1.

Table 1. Coals quality indices.

Coal #	$R_{o,r}$, %	Q_S^{daf}, kcal/kg	W^r, %	W^a, %	A^d, %	S^d, %
1	0.33	7013	31.0	6.53	11.56	0.48
2	0.32	6257	31.1	4.42	44.08	3.15

It could be seen that coal #2 (in comparison with coal #1) is characterized by lower calorific value and analytical moisture, and sufficiently higher ash and Sulphur contents.

2.2. Coals treatment by the dust control agent

Effects of dust control agent on coals dust suppression and their quality indices alteration were studied in laboratory environment. The aforementioned agent was developed for dust control at

long-term and short-term coal piles by forming a semi-stationary film around them. This provides a durable waterproof coating, decrease of wind weathering and protection from atmospheric-induced oxidation. For this work, solution "AMS-1000" [17] was used. It is a polymer emulsion based on acrylic copolymer of milky white color with density greater than the density of water.

Preparation of the solutions is based on their diluting with water up to the necessary concentration. Utilization of it is based on simple irrigation of the coals surface prone to dust formation. In this work, the solution was prepared as 1 part of the agent with 5 parts of water. These shares may be corrected in accordance with the specific conditions of using. Water for dissolving should answer the following requirements:
- Pure fresh technical water;
- Absence of solid inclusions;
- Any water hardness;
- Size of solid particles in water not more than 0.15 mm.

After diluting the solution with water, a foam layer is formed on the surface. Before use, in accordance with the Producer's instructions on solution preparation, it must be allowed to stand for 30 minutes, during this period of time the foam falls off. Then the solution is poured into the sprayer.

In order to perform the treatment by the prepared additive based on "AMS-1000" agent, 20 g of each coal samples were selected (grinded to the particles size 1–3 mm). Next, the samples were distributed on a baking sheet, treated by the sprayer with a diluted solution (5 ml of solution per 20 g of one sample) and kept in air for 3–5 hours. Samples grinded to the particles size <0.20 mm were treated in the same way. The latter were used further for studying of coals oxidation activity (resistivity) and proximate analysis.

2.3. Scanning electron microscopy

In order to determine the possible mechanism of the solution action, a complex of studies was carried out to determine changes in the structure of the surface of the coal after processing.

The initial and processed samples were analyzed for their microstructure and texture using the field emission scanning electron microscope JSM-6700F (Jeol). For the experiment, samples of coal grinded to the size of 1–3 mm were used. With the help of double-sided conductive tape, several particles of coal of each sample were placed on an object table, which was then fixed on the sample holder, and placed in the working chamber, where the analysis took place.

2.4. Determination of coals oxidation resistivity by ozonating

In order to determine the possible mechanism of action of the solution, a complex of studies was carried out to determine the change in the chemical and sorption activity of the coal after treatment. To this end, the initial and processed coals were studied for determination of their oxidation resistivity at interaction with ozone.

Ozonating of coals was performed using an experimental assembly consisting of two devices: ozone generator GS-024-1M and chemiluminescent gas sensor 3.02P-A (JSC "Optek") [22] (see Figure 1). Coal sample of <0.2 mm size was brought to air-dry condition. Further, one gram of this sample was placed to the special reactor which was hermetically connected with ozone generator and gas sensor. Ozone-air gas mixture was supplied from underneath of the coal sample, the outlet ozone

concentration was measured by gas sensor at the coal sample outlet (from above) [23,24]. The reactor diameter was 2.5 cm, the coal sample height was 0.2 cm, linear gas flow velocity was 2.5 cm/s. Prior to ozonating, the coal sample was treated by the so-called "zero-gas" (air with zero ozone concentration) for one hour. A study of the ozone sorption by each coal sample under study was carried out at a constant inlet ozone concentration of 300 µg/m^3.
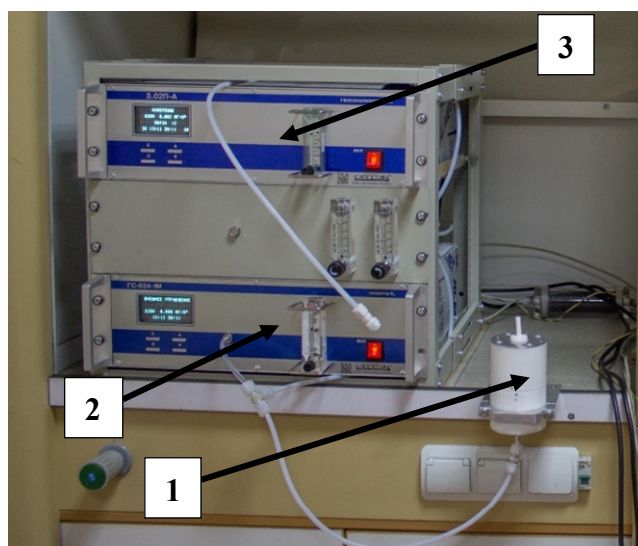
Figure 1. Experimental assembly for coals ozonating: 1—reactor; 2—ozone generator GS-024-1M; 3—chemiluminescent gas sensor 3.02P-A.

Oxidation resistivity of coals with respect to ozone was evaluated with help of kinetic modeling fully described in [23]. The basis of the model is the assumption that there exist zones at the coals surface (active sites) that are able to decompose ozone at interaction. During these processes, the active sites are being "switched off" (decomposed or changed), therefore, the coals activity to ozone is changing with time. This is directly related to oxidation of coal matter at the surface. In order to determine the coals activity to ozone within the framework of the proposed kinetic model, one needs to solve the following problem (1)–(3).

Under the assumptions presented in [23], the equation of convective transport with chemical reaction (reaction between coal and ozone) has the form (1):

$$u\frac{\partial c}{\partial z} = -\left(k_1(z,t) + k_2(z,t)\right)c(z,t), \tag{1}$$

where c is the ozone concentration, u linear gas flow, k_i are the constants of quasi-homogenous reaction (they determine the coals activity to ozone), t—time, z—linear coordinate varying along the filter (coal sample) height ($0 \leq z \leq L$), L is the filter height (in our case $L = 0.2$ cm).

It should be mentioned that in this model we consider the heterogeneity of active sites distribution at coals surface. Two types of active sites were allocated differing by their rate of deactivation with time. The first type is characterized by relatively high deactivation rate, whereas the rate of the second type is significantly less.

Initial activity of coal to decompose ozone for each of the active sites types could be found by solving the following Eq 2 under the assumption that the activity decreases proportionally to the ozone decomposition rate.

$$\frac{\partial k_i(z,t)}{\partial t} = -a_i k_i(z,t) c(z,t), \quad i = 1, 2, \tag{2}$$

where a_i are related to the deactivation rate of active sites of types 1 and 2, respectively.

Solution of Eq 1–Eq 2 is found with help of initial and boundary conditions (3).

$$c(0,t) = c_0, c(z,0) = 0, k_i(z,0) = k_{i0}, i = 1, 2, \tag{3}$$

where c_0 is the inlet concentration of ozone (300 µg/m^3), k_{i0} initial values of quasi-homogenous reaction constants (initial activity of sites of types 1 and 2).

In order to determine the integral activity of each coal sample, one may use the value given by relation (4).

$$K_L(t) = \frac{1}{u} \int_0^L \left(k_1(z',t) + k_2(z',t) \right) dz'. \tag{4}$$

On the basis of equality (4), it is possible to find a dimensionless parameter characterizing the initial integral activity of the coal sample to ozone $K_L(0)$.

The full description and derivation of the aforementioned model could be found in article [23]. The procedures of finding the sought-for parameters characterizing coals oxidation resistivity are also shown in the aforementioned paper.

3. Results and discussion

Analysis of the main quality indices of the treated coals revealed that moisture contents (both analytical and total) were not altered by the used agent. For example, treated coal #1 had W^r of 31.7%, whereas the initial one—31.0% (see Table 1). Analytical moisture W^a also has not changed significantly (6.46% for treated samples and 6.53 for untreated ones). Similar observations were found for coal #2. All the above mentioned allows to conclude that coals treatment by "AMS-1000" dust control agent does not lead to alteration of their quality, including calorific value (i.e. heat production capacity).

Results on microstructure and texture of the samples are shown in Figure 2. It could be seen that the treated samples obtained a thin film of their surface. The fine particles were mostly bound by the solution in comparison with the untreated samples. The surface of the latter is characterized by a large amount of fine coal particles of micron sized and a system of developed microfractures. Therefore, it may be concluded that the experimental investigations on the dust control additive action is shown in formation of a smooth thin film at the surface leading to agglomeration of fine dust particles.
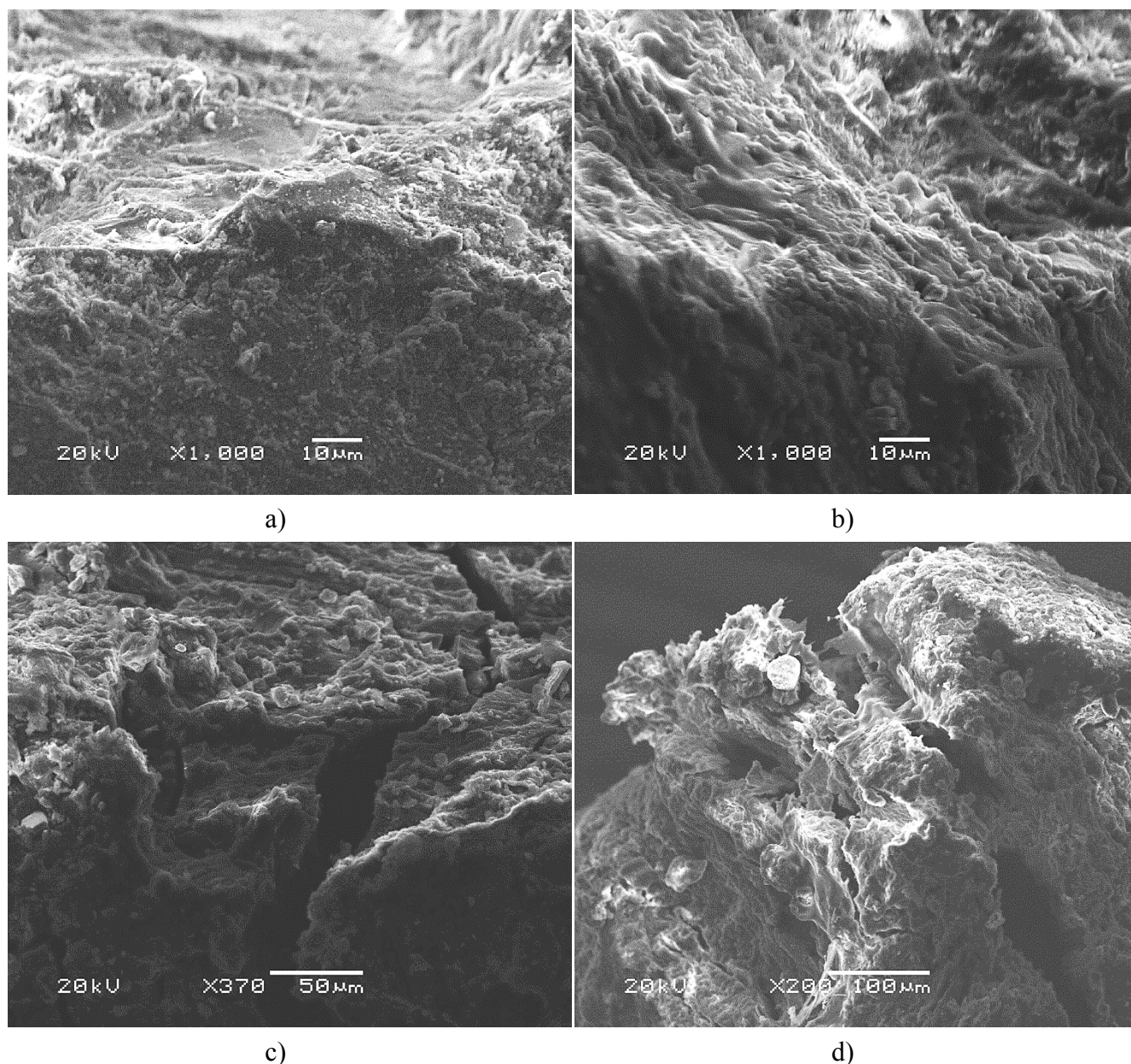
Figure 2. Microphotographs of coals particles surfaces: a) coal #1, initial; b) coal #1, treated; c) coal #2, initial; d) coal #2, treated.

Figures 3 and 4 demonstrate dependencies of outlet ozone concentrations for untreated and treated coals with time. It could be seen that for both coals #1 and 2 after treatment, their activity to ozone decomposition changes drastically. This could be observed in Figure 4, where outlet ozone concentrations at the initial times (5 hours after ozone was switched on) became non-zero and started growing rather linearly (with different rate for different coals). The shapes of the ozone outlet concentration curves also changed as compared to the ones of the untreated coals (see Figures 3 and 4).
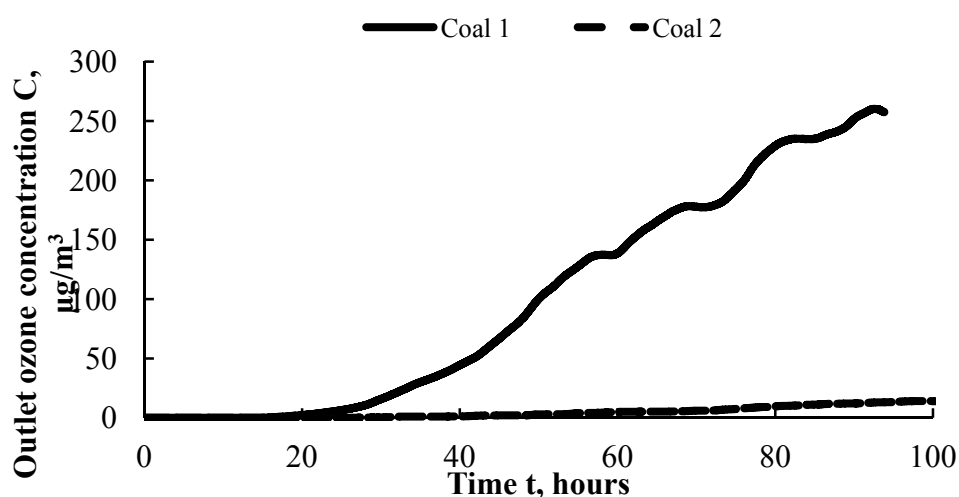
Figure 3. Graphs of ozone outlet concentrations obtained during ozonating of initial (untreated) coals #1 and 2.
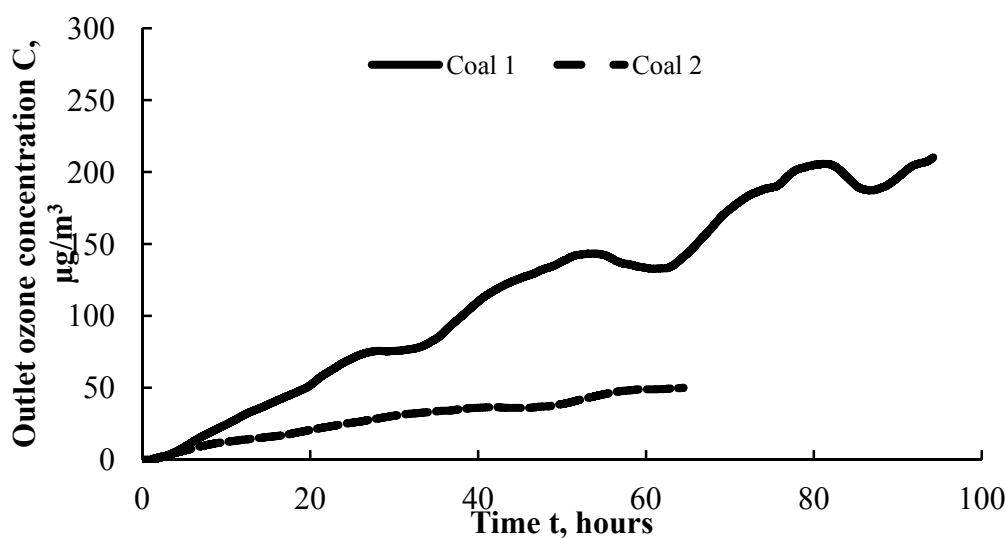
Figure 4. Graphs of ozone outlet concentrations obtained during ozonating of coals #1 and 2 after treatment by the dust control agent.

The aforementioned data allowed evaluation of coals activity to ozone on the basis of the previously described kinetic model [23]. In accordance with this model, the main kinetic parameters characterizing coals oxidation resistivity, were chosen as follows: integral activity to ozone decomposition $K_L(0)$, parameter related to the number of active sites with high rate of deactivation k_{10} and their deactivation rate a_1. The lower the values of $K_L(0)$, k_{10} and a_1, the higher the coals oxidation resistivity.

Table 2 demonstrates the results of the calculations of the aforementioned parameters as for initial coals, as for the ones after treatment by the dust-control agent.

Table 2. Kinetic parameters of coals activity to ozone.

Coal #	Treatment	k_{10}, 1/min	k_{20}, 1/min	$a_1 \cdot 10^{-6}$, m^3*μg^{-1}*min^{-1}	$a_2 \cdot 10^{-6}$, m^3*μg^{-1}*min^{-1}	$K_L(0)$
1	initial	5050	205	8	0.50	7.0
	treated	2050	475	7	0.50	3.4
2	initial	4500	2205	21.8	0.20	8.9
	treated	2050	1305	17	0.0002	4.5

Comparison of the values of integral activity to ozone $K_L(0)$, parameter related to the total number of active sites with high rate of deactivation k_{10} and their deactivation rate a_1 for the initial and treated coals allowed to come to the following conclusions. All the considered coals sufficiently lose their activity to ozone after treatment with "AMS 1000" solution. This could be observed by the significant decrease of $K_L(0)$ and k_{10} values. At the same time, deactivation rate a_1 remains almost the same. From the combination of changes of the kinetic parameters characterizing the oxidation resistance of coals, it can be concluded that the treatment by "AMS 1000" solution significantly increases this characteristic for both considered samples.

4. Conclusions

In this article, two lignites were studied in terms of their oxidation resistivity. This was done in order to investigate the efficiency of dust control agent "AMS-1000" for not only the decreasing of fine dust formation but also for increasing of coals oxidation resistivity. The research revealed the following.

First, as it was expected, application of such solution allows no quality loss for coals. This was established by proximate analysis of treated and untreated lignites.

Scanning electron microscopy allowed to visualize the mechanism of working of the dust control agent. It revealed that the studied solution forms a thin smooth film around the coal particles. This film tightly binds all the fine particles that were already formed and stored at the coal surface. Moreover, the solution tends to cover the surface thus decreasing the accessibility of the surface to active oxygen.

The latter was proved by treated and untreated coals ozonating processing at low concentrations of ozone. The applied kinetic model allowed to evaluate the total coals activity to ozone decomposition. It was found that the treated coals have twice as low total activity to ozone decomposition as compared with the untreated ones. As this parameter is closely related to coals oxidation resistivity (the lower the coals activity, the higher the coals oxidation resistivity), it was finally concluded that application of such an efficient dust control agent as the one studied in this article, allows for significant increase of sought-for quality indicator.

Conflict of interest

Authors declare no conflict of interest.

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