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Chemical activation as a prospect for the transformation of fossil coal from the Kalewa deposit into active coals

Abstract. For the purpose of evaluation of suitability of the Kalewa fossil coal deposit (Kalewa, Myanmar) for the production of granular active coals, the results of its petrographic analysis in the form of maceral composition and an arbitrary vitrinite reflection index are characterized, indicating the potential possibility of its use for solving this problem, based on the data of thermographic tests performed in a protective atmosphere, the rational limits of the thermal effect on this raw material during pyrolysis are estimated, the rational conditions of this process and the activation of its carbonized residue by water vapor are presented, the low efficiency of steam activation is shown, and the results are presented. The results of the chemical activation of the named fossil coal by alkaline agents in the form of NaOH and KOH, indicating the possibility of obtaining active coals with structural and adsorption properties acceptable for practical use, the conclusion is made that the processes need to be improved.

Key words: fossil coal, petrography, thermography, steam activation, NaOH and KOH, activated carbons, technical indicators.

Introduction

Fossil coals, despite the progressively increasing production of oil, natural and associated petroleum gases, and today continue to be an extremely important type of raw material, widely in demand and used in many countries for energy and other purposes [1; 2]. They are also very important as cheap raw materials for the production of carbon adsorbents, in particular active coals, porous materials with a developed surface, which are used in most areas of the economy and in solving problems of reducing and eliminating pollution of the biosphere by anthropogenic discharges and emissions [3; 4].

The Republic of the Union of Myanmar is a tropical country, the climate and unique natural resources of which potentially provide the possibility of producing these adsorbents with very high-quality and cheap plant raw materials in the form of large-capacity waste from cutting dense wood and various residues of growing and processing food (feed) and technical agricultural crops [5], the effectiveness of the use of which for this purpose is evidenced by numerous publications [6-14]. The fossil coals of domestic deposits located in various territorial areas of Myanmar (16 deposits with total reserves of 258 million tons have been explored in the country) may also be of possible significance in this regard [5]), and among them are those, first of all, the development of which is carried out for the needs of the state in an open way. These include the Kalewa field, which already has a significant impact on the development of the economy, both in individual industries and in the country as a whole.

Along with this, numerous Internet sites and centrally published catalogs, for example [15], they indicate the industrial production of a number of brands of active coals based on some types of fossil coal raw materials. It should be emphasized that Myanmar does not have any production of these adsorbents at all. The only exception is the company "Rectangle Co., Ltd", which produces active coal mainly from bamboo in the amount of 20-30 tons/year for export using Japanese technology at the factory in Zeyawaddi (Taungoo district) [16; 17].

At the same time, the dynamic growth of production in modern Myanmar is associated with an increase of environment protection problems from toxic emissions and discharges of its enterprises, which are practically devoid of deep cleaning due to the significant cost of carbon adsorbents on the world market. These circumstances determine the expediency of research involving the assessment of the possibility and rationality of obtaining active coals based, in particular, on the fossil coal of the Kalewa deposit.

Materials and methods

The above assessment was initially based on the establishment in the laboratory of physical chemistry of coal of the Mining Institute of the National University of Science and Technology MISIS of some petrographic indicators of the fossil coal of the named deposit, indicating the nature of its raw material suitability for the intended purpose, and the data of its thermal analysis performed in a protective atmosphere with programmed uniform heating of the sample to ~900^{o}C using a Q-1200 derivatograph (Paulik and Erdei; Hungary), indicating the appropriate limits of the temperature effect on this raw material (carbon content of about 75 %) during its pyrolysis.

This petrographic analysis included the determination of the maceral composition and an arbitrary vitrinite reflectance index according to standard methods [18; 19] for anschlyph briquettes prepared in accordance with [20].

Studies of the processes of pyrolysis of raw materials using various activation techniques were carried out on laboratory-level installations equipped with steel tubular reactors located in vertical cylindrical electric furnaces and equipped with means for monitoring and controlling the temperature provided in them.

Results and discussion

The results of the evaluation of the petrographic composition and vitrinite reflection index of the samples of the named fossil coal sample resulted in the following values of the volume fractions of the macerals of the groups are in the Table 1.

Table 1 – Petrographic composition and vitrinite reflection index of the samples of the Kalewa fossil coal deposit and long-flame coals (D) from Gramoteinskaya Mining field, Kemerovskaya Oblast (Kuzbass), Russia

Coal	*Vt*, %	*Sv*, %	*I*, %	*L*, %	∑*OK*, %	$R_{o,r}$, %
Kalewa	92.1	2.4	4.1	1.4	6	0.598
D	94	1	5	4.3	5	0.599

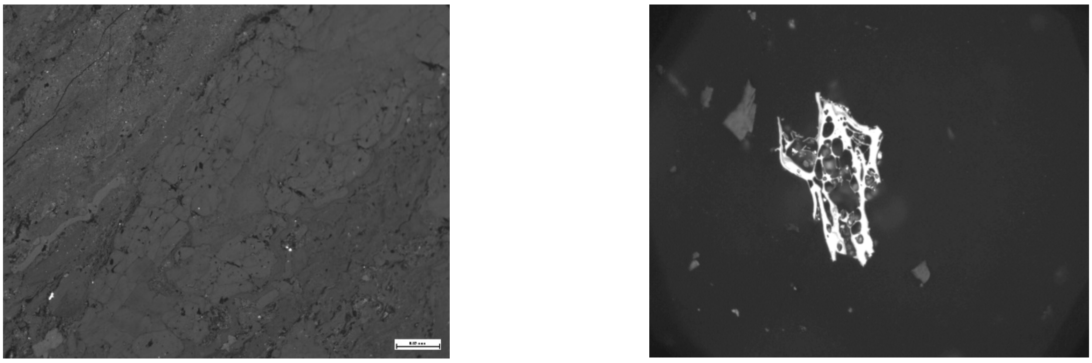
Thus, the value of an arbitrary vitrinite reflection index is ~0.6 %. This indicator for long-flame coals (D) used in Russia on an industrial scale for the production of active coals [15] is in the range from 0.40 to 0.79 % [21].

Micrographs of the samples obtained using the SIAMS-620 petrographic complex are shown in Figure 1. The sample as a whole has the same micro-signs, but there is more telinite (vitrinite that has preserved the cell structure) (a), and inertinite (b) is also represented as small detrital fragments. It also contains pyrite inclusions of 1-10 μm in size.

It should be emphasized that the use of standard petrographic methods for the study of solid fuels allows determining the quality of coal from its oxidized samples, since neither the quantitative petrographic composition nor the signs of metamorphism of micro-components change. Thus, the described experimental data allow us to state a fairly reliable prospect of carrying out research on the use of fossil coal from the Kalewa deposit for the production of active coals.

The process of pyrolysis of the specified raw material in the form of its grains with a fraction of 3-5 mm has been studied in the field of thermal impact parameters based on the data of its thermographic tests [22]. The best results are demonstrated by the target pyrolysis product (carbonizate), obtained at a heating intensity of 10 ^{o}C/ min to 750 ^{o}C, followed by isothermal exposure for 60 minutes. At a yield of 57 %, it is characterized by the following structural and adsorption parameters: total porosity in water V_{Σ} = 0.10 cm^3/g, the volumes of sorbing pores Vs in water vapor, carbon tetrachloride and benzene at 22 ^{o}C 0.16, 0.09 and 0.17 cm^3/g, respectively, the absorption of the dye methylene blue (MB) and iodine (J) from their solutions at the same temperature is 25 mg/g and 150 %.

When studying the appropriate conditions for the activation of this carbonizate by water vapor, it was found that they are provided by a combination of the intensity of the temperature rise of 10 ^{o}C/min, the specific steam consumption of 10 g per 1 g of the resulting adsorbent, the maximum temperature of 850 ^{o}C and the duration of isothermal exposure at it of 30 min. The top row of Table 2 reflects the structural and adsorption properties and the yield with respect to carbonizate of the target product obtained under these conditions.



(a) vitrinite (telinite) (b) inertinite

Figure 1 – Micrographs of the investigated samples

Table 2 – Characteristics of the target products of various activation of the Kalewa fossil coal deposit when the precursor is heated at an intensity of 10 °C/min to 750 °C with an isothermal exposure of 60 min

Activator	Vs, cm^3/g, by steams:			V_Σ, cm^3/g	Absorption		Output, %
	H_2O	CCl_4	C_6H_6		MB,mg/g	J, %	
Vapour H_2O	0.17	0.28	0.29	1.60	278	432	39
NaOH (1:1)	0.28	0.12	0.31	0.27	317	624	52
NaOH (2:1)	0.15	0.13	0.14	0.38	336	288	30
KOH (1:1)	0.25	0.19	0.32	0.75	299	1012	31
KOH (1:1)*	0.39	0.41	0.52	1.16	321	1230	26

Note: * pyrolysis temperature 900 °C

The data of the indicated line of Table 2 underlines far from the best indicators of steam activation coal as an adsorbent. In this regard, the work evaluated the efficiency of chemical activation of the studied fossil coal using relatively cheap sodium hydroxide, which is widely used for this purpose according to the fairly numerous literature data [23; 24].

In accordance with this information, very often, satisfactory results are provided by using a mass ratio of feed: NaOH, which is 1:1. This is what is used in the study of this technology. In this case, the preparation of the raw material composition consisted in careful mechanical mixing of grains of known moisture content of fossil coal of the specified fraction with the product obtained by grinding the flakes of commercial NaOH extracted from the container drum into powder with a particle size of less than 400 microns.

Studies of the pyrolysis of the said composition have established a close to monotonic decrease in the yield of the target product with an increase in the final temperature of the process (in the range of 700-850 °C), other conditions being the same, passing through a maximum at 750 °C of the Vs indices for H_2O and C_6H_6, MG, V_Σ and J of the obtained washed from excess activator and then dried active carbon, and the latter indicator has a maximum at 850 °C.

Depending on the intensity of heating of the raw material composition with NaOH (within the studied range of 5-20 °C/min under other identical conditions), with its increase, the yield of active carbon increases, and all its other estimated indicators have a maximum at a value of the specified intensity of 10 °C/min.

The influence of the duration of the isothermal holding of the product on the effectiveness of the process, while observing the maximum similarity of other conditions for its implementation, is also diverse. Its increase provides relatively small decreases in the yield of active carbon, as well as Vs values for CCl_4, MG and V_Σ vapors, while the Vs values for H_2O and C_6H_6 vapors, as well as J, characterize maxima at 60 min.

The totality of the results of this experimental series allows us to conclude that the rational conditions for the pyrolysis of the raw material composition from fossil coal and NaOH in a mass ratio of 1: 1 are identical (excluding the specific consumption of water vapor) to those of the process of steam activation of the carbonizate obtained by conventional pyrolysis of the considered coal raw material. The adsorption and structural indicators of the target product of the characterized thermal processing of the named raw material composition are presented in the second row in Table 2. The third line of this table characterizes the result of pyrolysis under identical conditions of the raw material composition with the mass ratio of fossil coal: NaOH = 1:2. Comparison of the data of the second and third rows of Table 2 indicates the negative effect of increasing the proportion of NaOH in the raw material composition for pyrolysis.

Along with this, the data in Table 2 indicate that, in principle, the use of NaOH as an alkaline activator makes it possible not only to significantly increase the yield of active carbon in comparison with steam activation, but also to provide a sharp increase in its microporosity with a close to sixfold decrease in the total pore volume index. Such an obvious positive effect of NaOH, which is relatively cheap among alkaline reagents, indicates the expediency of evaluating the use of a similar orientation of KOH as a chemical activator in the technology under consideration, but more often appearing in many studies [23, 25].

The efficiency of using KOH in a raw material composition with fossil coal in the same mass ratio as when using NaOH is illustrated in the fourth row of Table 2. Comparison of the indicators presented in it with similar lines 2 indicates very weak changes in the Vs values for all three vapors, an increase of ~ 2.8 times in the value of the V_Σ index and ~ 1.6 times the absorption of iodine in the case of using KOH with a serious drop in the yield of active coal (from 52 to 31%). With an increase in the limiting temperature of pyrolysis of the raw material composition with KOH up to 900 °C, all the characteristics of the obtained activated carbons, except for the values of their output, significantly increase, which is illustrated by the data of the fifth row of Table 2. The question of the expediency of the practical use of this circumstance requires separate consideration.

Conclusion

Accomplished research determined:

- potential prospect for the transformation of fossil coal from the Kalewa deposit into active coals;
- low efficiency of the use for this purpose of the technology based on the pyrolysis of this raw material and the activation of its remainder with water vapor;
- the prospect of processing fossil coal from the named deposit by chemical activation with alkaline reagents (NaOH, KOH), which, however, requires additional in-depth studies related to the optimization of this technology.

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