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THE ENERGY TECHNOLOGICAL BACKGROUND OF INVOLVING SALTY COALS INTO ENERGY BALANCE OF UKRAINE.

2. NATURAL MINERALS AS CATALYSTS OF THERMOCHEMICAL CONVERSION OF SALTY COALS IN VARIOUS CONDITIONS

Salt coal (SC) of the Northern Donbas in the list of non-project fuels is a perspective source of energy in Ukraine under the conditions of occurrence and reserves. This is due to its relatively high energy (fuel) characteristics and the presence in its composition of the natural catalytic complex - the increased content of salts of alkali and alkaline earth metals and trace elements. These impurities, on the one hand, can lead to some burning problems, but can also have a positive effect when such coal in mixtures with other less reactional fuels is used.

Purpose. Determination of the influence of water-soluble compounds (chlorides and sulphates of sodium, calcium, magnesium, etc.) on the thermolysis (combustion) processes of salt coal of Bohdaniivsk deposit (the Northern Donbas) at different temperatures.

Methodology. Samples of desalted coal were obtained using previously optimized parameters of the process aqueous extraction (time, temperature, and solid to liquid phase ratio). The elemental composition and technical characteristics of coal are determined by appropriate standard methods. The dynamics of gas emission and combustion of coke residues of salty and desalted coal was determined using the "Pyrolysis M" installation. The MX-1215 mass spectrometer was used as a gas analyzer. The kinetic parameters of the process were calculated based on the Arrhenius law.

Findings. The changes in the elemental composition of the organic mass of coal (OMC) occurring during the purification of salty coal by water extraction are determined. Experimental studies have been conducted on the combustion of salty and desalted coal of the Bohdaniivsk deposit in the temperature range of 550–850 °C. It has been determined that native water-soluble minerals of salty coal lead to intensification of ignition processes, accelerated yield of gaseous products (H₂, CO, CO₂) and changes in the gas content ratio. The activation energy of combustion coke residual salty and desalted coal has been determined.

Originality. Some characteristics of combustion of salty and desalted coal are compared. It is shown that aqueous extraction of salty coal leads to improvement of the fuel and energy characteristics. It is established that salts of alkali and alkaline earth metals, which are a part of salty coal, are natural catalysts for the processes of thermolysis and burning of organic mass of coal. It is determined that in the temperature range of 550–850 °C, depending on the fractional composition of the sample, the water-soluble salt complex accelerates the emission (elimination) of hydrogen by 3–4 times, carbon monoxide by 2–3.5 times, carbon dioxide by 2.5 to 3 times.

Practical value. The study shows the prospect of involving salt coal to the fuel base of Ukraine, not only as a separate fuel, while reducing the concentration of harmful impurities (by water extraction), and as a component of blended fuels to increase the reactivity of composite fuel raw materials.

Keywords: *salty coal, native minerals, chlorides, sulfates, water extraction, pyrolysis*

Introduction. Coal with high content of alkali and alkaline earth metals (so-called salty coal (SC)) occupies its definite place among the reserve sources of energy not only in Ukraine but also in many countries of the world (China, USA, Russia, Germany, Australia, etc.) [1]. The deposits of Ukraine's salty coals have shallow layers of deposits and high energy indices of fuel. They are located in the West (Petrykivske and Novomoskovsk deposit) and the North (Starobelsk coal field, Bohdaniivske and Petrivske deposits) of the Donbas, with explored reserves of about 25 billion tons [1].

Compounds of alkaline metals (alkali, salts) are universal catalysts (reagents) in many processes of thermal conversion of

fossil fuels and biomass [2–4], which is established by the research of many domestic and foreign scientific schools. Alkaline compounds accelerate the reaction of gasification, liquefaction, oxidation, thermal degradation of coal in order to obtain hydrogen, affect the caking of coal dust. This applies to the reactive and catalytic action of alkaline compounds, which are artificially introduced in various ways in the reaction environment – mechanical mixing, impregnation, seepage (J.A. Cusumano, R.A. Dalla Betta, R.B. Levy. *Catalysis in Coal Conversion*). The ways of the influence of the artificially introduced alkaline components on the structural parameters of coal of different degrees of metamorphism are considered and generalized, and probable mechanisms of their influence on the reactivity of samples of fuel raw materials are proposed.

One of the mechanisms proposed by Ukrainian scientists (Rudakov E. S.) is the process that leads to the formation of compounds of the inclusion of alkali metals in the organic (polyaromatic) carbon matrix, which causes the growth of the reactivity of the whole system. Another mechanism takes into account the possibility of the reaction of Kanizzaro (the dismutation of two molecules with an aldehyde function) in an alkaline reaction medium, which, with further rise in temperature, results in the decarboxylation of the formed carboxylic acids.

The influence of major mineral components (kaolinite, iron compounds, calcium oxide, etc.) of various types of solid fossil fuels (SFF) on the processes of their thermal conversion has also been extensively studied by leading coal and shale centers (USA, RF, Estonia, Australia, China, Australia). The influence of water-soluble compounds on the conversion of SFF combustible mass was investigated much less due to their relatively low content in the mineral components of typical project fuels. But for the so-called salty coal, the role of alkaline and alkaline earth metals and their salts must be clearly defined.

Literature review. Salty coal (SC) stands out from other fuels not only for the problems of traditional combustion (slagging, corrosion) [4], but also for being an energy raw which contains a natural catalytic complex – alkali and alkaline earth metals salts, iron sulfides and some of catalytically active trace elements in significant amounts. The composition and properties of the mineral part of the Novomoskovsk salty coal are given in the monograph by Shendrik T. G. and Sarancuk V. I. “Salty Coals”, Donetsk, 2003. Studying the structural features and properties of salty coal, it is worth to assume that finely dispersed salts in the organic mass will affect all the processes of thermal conversion of salty coal. This phenomenon must be used to increase the efficiency of salt coals burning.

Previous studies by Shendrik T. G. on the influence of sodium chloride of the salty coal of Novomoskovsk deposit on the process of thermal decomposition (TGA method) showed that the removal of salts by aqueous extraction leads to an increase in the activation energy (from 28–30 to 40–70 kJ/mole) and to the difficulty of destruction of the organic mass of coal (OMC). In other words, the presence of salt facilitates the decomposition of macromolecules OMC in the interval of the main thermal decomposition (MTD), significantly reduces the interval MTD (from 100 to 80–60°), and also leads to an increase in the yield of liquid products in the process of hydrogenation. Similar regularities for the Belarusian shale were established in the works by Gorky Yu. I., Lukyanova Z. K., Martynovich K. B., conducted in the 1980–1990s. At the same time, experiments on the liquefaction of a number of initial samples of Novomoskovsk SC (with different content of Na₂O in ash – from 4 to 11 %) in the atmosphere of hydrogen or in the mixture of CO and H₂ did not show a clear correlation between the content of alkali metals and the degree of conversion of OMC. In this case, special experiments with desalted (washed water) of the SC again revealed a deterioration of the main indicators of the process of liquefaction. Thus, the degree of conversion of OMC fell from 68 to 63 %, the yield of liquid products to the organic mass of paste (OMC) decreased from 77 to 70 % after the removal of water-soluble compounds.

Ambiguous results on the influence of native salts on the course of the pyrolytic processes of salt coals are associated with a certain influence of other indicators of raw materials (petrographic composition, different mineral composition of coal samples). Thus, an influence factor on the yield of liquid products in the process of hydrogenation of salty coal of different layers in the medium of tetralin was the content of liptinitum – a petrographic component, which is formed from spore components of plants – one of the precursors of coal.

From the results of fundamental studies by Kuznetsov B. M., etc. [3] on the influence of anion on the catalytic activity of alkaline salts, it was found that potassium, sodium, and lithium carbonates and sulfates exhibit a greater catalytic

(promoting) effect in thermochemical transformations of coal than chlorides. The ambiguous effect of various cations (K, Zn, Mn) in the composition of their chlorides on the course of thermolysis purified by strong acids of coal (China) was established in [5]. It is stated that the mechanisms of catalysis of the selected chlorides differ, but their understanding is not clear. From the analysis of the results, it can be concluded that chlorides K and Zn behave as typical catalysts (after the thermolysis of the treated coal are remained in the form of chlorides), while Mn chloride is converted to its MnO oxide. This indicates that the manganese cation is also involved in the redox reactions that may precede the thermolysis process.

As for salty coal, it is necessary to highlight the recent work by Chinese scientists, which considered the possibility of using salty coal of Zhundong field as a catalyst for the combustion of oil shale [6]. The catalytic effect of Na, Ca and Na + Ca on the burning characteristics of shale combustion during co-combustion with Zhundong coal was analyzed. The characteristics of the ignition, combustion and complex index of combustion of the oil shale in the mixture were determined.

The study of the influence of native alkaline compounds on the thermolysis processes of non-project fuel is also significant in view of the need to reduce the formation of known pollutants of the atmosphere – nitrogen compounds, which are formed in all thermal reactions of fossil fuels without exception. In [7], the effect of temperature on the yield of gaseous products (composition, volume of output and caloric content) and the characteristics of coke residue during the pyrolysis of subbituminous coal of the Zhundong deposit were evaluated, and in [8] the transformation of nitrogen during steam gasification of lignite was investigated. Chinese scientists, having a large arsenal of modern scientific equipment, have studied the conversion of the nitrogen of the source fuel in the process of steam gasification of lignite (Shengli deposit) with a high content of alkaline compounds, which in terms of salt content is close to our Bohdanivske (0.5–0.7 % of sodium oxide per dry matter). They found that at temperatures of 700–1000 °C, the Na, Ca, Mg compounds catalyze the conversion of fuel nitrogen to ammonia and promote the secondary reactions of nitrogen from coal char and the resulting hydrogen cyanide to be converted to ammonia. They also claim that the presence in the fuel of Na, Ca, Mg leads to the formation in the mass of carbon residue of pyridine compounds and quaternary bases of nitrogen [8].

In our previous studies, it was found that not only chlorides (sodium, calcium, magnesium) but also sodium and calcium sulphates are present in salty coal of deposits of Ukraine, which are clearly identified in the composition of water extracts of SC [9].

That is why **the purpose** of this work was to determine the role of natural water soluble compounds in the processes of thermolysis of the salty coal of Bohdanovske deposit (the Northern Donbas). This coal has a convenient location of deposits, has a different content of sodium chloride (compared to the Novomoskovsk SC) and other composition of water-soluble minerals, while maintaining attractive energy characteristics (Table 1).

Experiment. Investigation of the ignition process. The processes of ignition and combustion of single particles of salty and desalted coal were investigated using an installation developed by the Department of physics of high temperature processes of the Coal Energy Technology Institute of NASU (the optical scheme is shown in Fig. 1)

As a result of experiments, the dependence of the ignition induction time, the ignition temperature, and the combustion of salty and desalted coal particles depending on the surface temperature and the fractional composition of the selected samples were determined (Figs. 2–3). It is shown that the ignition and combustion of single particles of semi-coke of salty coal are faster than those of desalted coal (the time of induction of desalted coal is 200 to 500 seconds longer than in the

Characteristics of salty coal of Bohdanivske and Novomoskovsk deposits

Deposit	Heat of combustion, kcal/kg	Ash A^d , %	Volatiles V^{daf} , %	Na ₂ O in ash, %	Chloride Cl, %	Sulfur S, %
Novomoskovsk	7200–7500	10.1–15.0	44.0–47.3	0.6–1.0	0.6–0.9	2.1
Bohdanivske	7020–7580	12.6–14.6	41.2–42.6	0.5–0.7	0.3–0.6	1.6–2.1

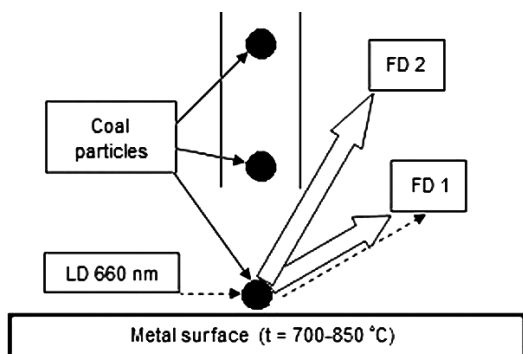


Fig. 1. Optical scheme of installation for the study of the interaction of coal particles with a heated metal surface:

FD1, FD2 – photodiodes; LD 660 nm – a semiconductor laser (radiation wavelength = 660 nm)

case of the initial salt coal). And the average combustion temperature of a single particle of desalted coal is 30–40 °C higher than for salty coal. It is also determined that salty coal in its kinetic parameters of the combustion process is similar to Donetsk gas coal.

Investigation of the change in elemental composition of salt coal in the process of desalination. Another factor that needs attention is the changes in elemental composition (dry ash-free mass) and in the yield of volatiles in the purification of salty coal by water washing. Extraction of salts from coal was

carried out according to the parameters optimized in previous studies [10]: time (5–10 minutes), temperature (20 °C) and the ratio of solid phase to liquid (T : P = 1 : 3), followed by drying the sample to a constant mass.

As a result of desalting (Fig. 4) there was a decrease in the concentration of oxygen (decrease from about 17 to 14 %), a less significant reduction of hydrogen (about 1 %) and nitrogen (by ~ 0.5 %). The loss of sulfur content does not exceed 0.25 %, which is close to the error of the experiment. Ash content was reduced by 0.5–2 %. At the same time, carbon content increased substantially from 74 to 80 % and accordingly the heat of combustion of coal (calculated by Mendeleev’s formula) increases from 27.3 to 28.4 MJ/kg. From these data, it becomes clear that major changes in elemental composition occur within the first 5 minutes of desalting. The loss of oxygen, nitrogen and hydrogen can be explained by extraction during water desalting, the so-called fulvic acids – water-soluble organo-mineral compounds are characterized for low metamorphism coal. The reduction of the total sulfur content may be due to the presence of sulfates in the composition of water-soluble minerals of SC and their removal by aqueous extraction [9].

In comparison with the work [8], we determined only the change in the content of the main macroelements of coal in the process of water extraction of SC. Our data (in the case of nitrogen) reflect the opposite trends for domestic and Chinese fuels. This is due to the different origins of fuels and the other way of extracting alkaline compounds (aqueous [10] and acid extraction [8]).

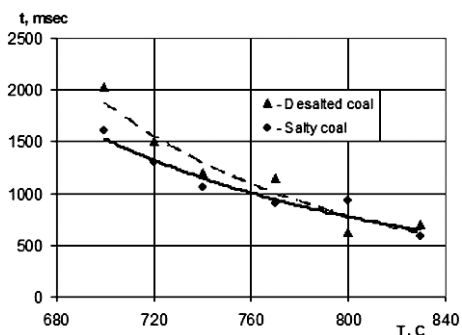


Fig. 2. Time of the inflammation induction (msec) of salty and desalted coal particles with an average diameter of 180 μm, depending on the surface temperature (°C)

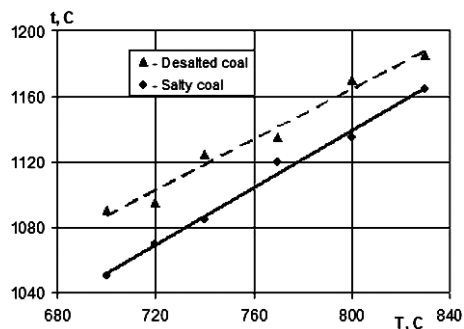


Fig. 3. Average burning temperature (°C) of salty and desalted coal particles with an average diameter of 180 μm depending on the surface temperature (°C)

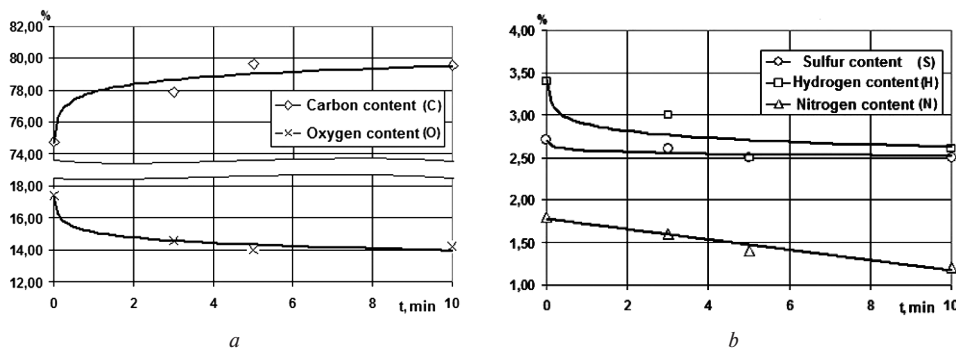


Fig. 4. Macroelements content in organic mass of coal depending on the time of desalination

Determined changes in the elemental composition of the OMC necessitated the determination of changes in one of the main characteristics of the fuel raw – the yield of volatiles – in the purification of salt coal by water washing. The proportion of volatiles in the various fractions of salt and desalted coal of the Bohdanivsk deposit was determined by gravimetric method according to ISO 562 : 2010. For this purpose, the loss of the mass of adsorbed moisture is not counted to volatiles when heated to high temperature, the capillary and adsorbed moisture was removed from the analytical sample (coal particle size less than 0.2 mm) by drying at 105–110 °C to constant weight. The results of volatile measurements for different size fractions are shown in Table 2.

The above results indicate that the leaching of salt coal leads not only to a decrease in the concentration of harmful impurities, but also to a significant decrease in volatiles. In other words, aqueous extraction of salt coal artificially “enhances” the metamorphism stage of the coal. *The results, which allow us to draw such a conclusion, were obtained for the first time.*

Investigation of the dynamics of gas formation during thermolysis of salty and desalted coal. In order to obtain a larger database on the effect of salts on coal thermolysis, further experiments were carried out at the “Pyrolysis M” installation of the Laboratory of fuel problems of energy of Department of coal combustion and gasification of Energy Technologies Institute of NASU. The installation (Fig. 5) is intended for the study of the dynamics of gas release and combustion of coke in thermal contact pyrolysis of coal in a fluidized layer at atmospheric pressure. It also allows determining rate constants of volatile and specific burn rates of carbon.

Samples of coal were introduced into the reactor of “Pyrolysis M” with a pre-heated to the required temperature by a

Table 2

The content of volatiles in the coal of the Bohdanivsk deposit

Fraction, microns	Volatiles, %	
	Salty coal	Desalted coal
50–100	38.0	29.8
100–160	36.5	30.8
160–200	37.6	30.0
Average	37.4	30.2

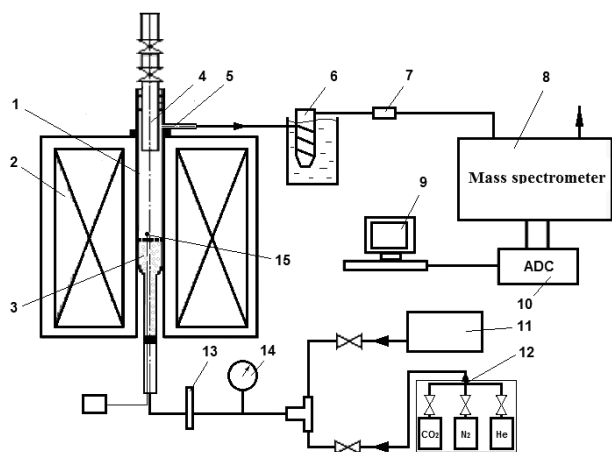


Fig. 5. Scheme of the experimental installation “Pyrolysis M”:

1 – reactor; 2 – heating furnace; 3 – layer of inert material; 4 – sluice chamber; 5 – outlet pipe; 6 – cyclone of cooling of the exhaust gases; 7 – filter; 8 – mass spectrometer; 9 – PC (personal electronic computer); 10 – ADC (analog-digital converter); 11 – compressor; 12 – ramp model gas; 13 – rotameter; 14 – gauge; 15 – thermocouple

fluidized layer of inert material (sand). Initial temperatures of the fluidized layer were 550, 650, 750, 850 °C. Samples introduced into a layer under their own weight through a locking chamber immersed in the working area by 100 mm. Outlet pipe for gaseous products is located directly under the insulated cork. Thus, the flow of coal by weight did not affect the gas output from the reactor. The liquefying and reaction agent (air) was arrived to the reactor from below. Gaseous products of oxidative pyrolysis and combustion from the outlet pipe were fed to a water cooling cyclone, where dust particles and resins were caught. Further through the silicon tube, the products were transported to a mass spectrometer.

During the experiment, there were stages of output and combustion of volatile (stage 1) and combustion coke residue (stage 2). On the dynamic curves of the concentrations of gaseous products (Fig. 6) there are observed sections of the pyrolysis stage lasting from 5 to 20 seconds (depending on the initial temperature). They are characterized by the yields of H₂, CO, CO₂ at close to zero concentration of O₂. The combustion area of the coke residue, characterized by a gradual decrease in the yield of CO₂, an increase in the concentration of O₂ and the absence of other gaseous products.

From the above graphs (Fig. 6) we can see that the yield of gaseous products (H₂, CO, CO₂) during combustion of salty coal is much more intense than during the combustion of desalted coal, both during the characteristic time of the pyrolysis stage and the magnitudes of the yield maxima of H₂, CO, and CO₂.

The calculation of the rate of gas formation (%/sec) was performed for the interval of maximum output (%) of the corresponding gases according to the experimental data (Fig. 6). It was found that the rate of hydrogen (H₂) output during the first 5–15 seconds of the process at a temperature of 750 °C in the case of the original salty coal is 3–4 times higher than for desalted SC (0.54–0.65 against 0.16–0.18 %/sec). For CO, its rate was 2–3 times higher for salty coal compared to desalted coal. A similar phenomenon is observed for CO₂ – for an interval of 20 seconds, the rate of yield of this gas is 2.5–3.0 times higher in the case of SC. Under condition of complete elimination of combustible gases (hydrogen and carbon monoxide) at $\tau \geq 20$ sec stable CO₂ emission or its decrease is observed, which indicates the gradual completion of the burning of carbon from the coke residue. It is also noticeable that the carbon dioxide during the period of combustion stabilization is 1.25–1.5 times higher for the initial salty coal. The H₂/CO ratio for the source of salty coal in the output maxima is from 3.6 to 4, while for the desalted SC – 2.5–3.4.

Thus, it is obvious that salts found in the composition of water-soluble minerals of SC (sodium chloride and sodium and calcium sulphates) give the investigated processes a noticeable catalytic effect, which depends on the process temperature, the weight of the raw material and the size of the fuel particles. However, with a decrease in the sample of the investigated coal to 0.1 g, the error of the experiment naturally increases, and the influence of minerals becomes almost unnoticeable (Fig. 7).

With a significant difference in the absolute values of CO₂ output, there is a slight difference depending on the combustion rate (W_m) of coke residue of salty and desalted coal from the temperature in the range of 550–850 °C (Fig. 8). The specific burn rate and degree of the carbon conversion were calculated based on the CO and CO₂ mass flow rates.

The specific burn rates of carbon char to the current mass W_m , 1/s obtained for different temperatures can be described by the expression [11]

$$W_m = k_{oi} \cdot \exp(-E_a/(R \cdot T)), \quad (1)$$

where k_{oi} is the pre-exponential factor ($k_{oi} = k'_o C_o$), 1/s; E_a is the effective value of the activation energy, J/mol; R is universal gas constant, J/(mol · K); T is temperature, K; C_o is oxygen

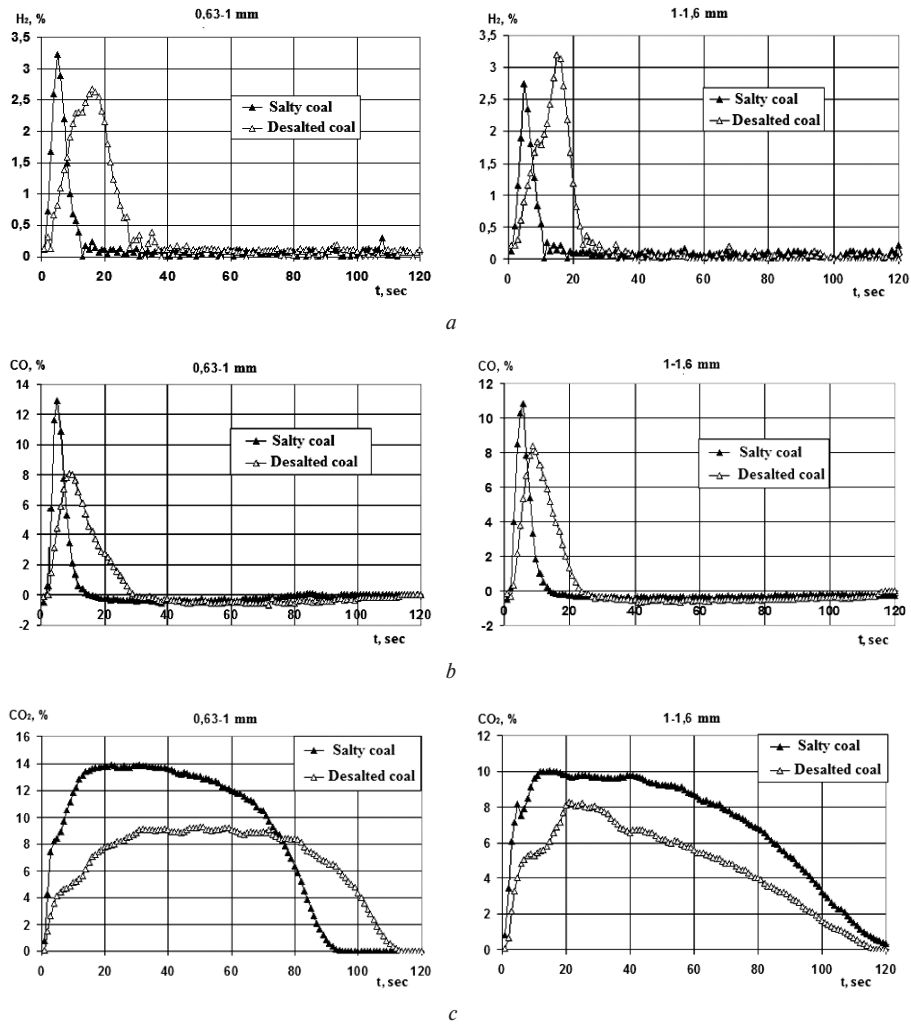


Fig. 6. Yield of gaseous products H₂ (a), CO (b), CO₂ (c) depending on the time of thermolysis and the size of coal (sample weight 0.5 g, temperature 750 °C)

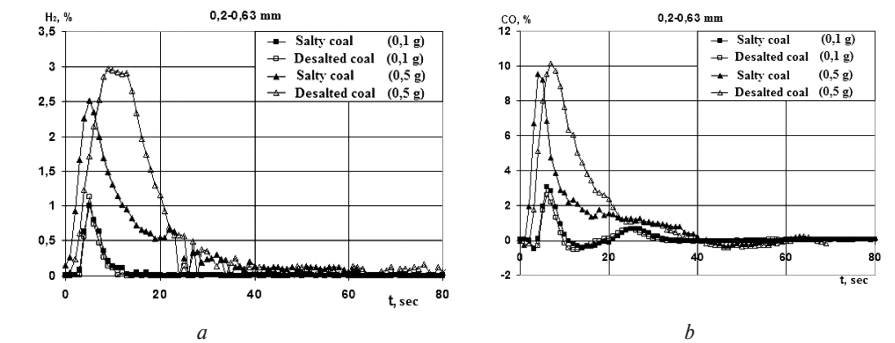


Fig. 7. Yield of gaseous products H₂ (a) and CO (b) depending on the time of thermolysis and the weight of coal samples (temperature 750 °C)

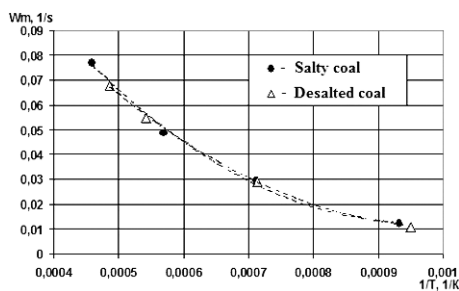


Fig. 8. Carbon char combustion rate of salty and desalted coal depending on the temperature

concentration, kg/m³; β is the stoichiometric coefficient of conversion of oxygen mass reduction into carbon mass reduction ($0.375 \leq \beta \leq 0.75$, for 0.375 – the only product of the reaction $C + O_2$ is CO_2 , for 0.75 – CO); S_{num} – specific particle area, m²/kg; k_o'' is chemical constant of the reaction rate, m/s.

$$k_{oi} = C_o \cdot \beta \cdot S_{num} \cdot k_o'' \quad (2)$$

Substituting (2) into (1) we obtain

$$W_m = C_o \cdot \beta \cdot S_{num} \cdot k_o'' \cdot \exp(-E_a/(R \cdot T)) \quad (3)$$

The values of the activation energy and the chemical constant of the reaction rate can be calculated using the least squares method based on the formula (3) from dependence

Table 3

Kinetic characteristics of the rate of interaction of coke residue salty and desalted coal with oxygen

	k'_o , m ³ /(kg · s)	k''_o , m/s	E_a , kJ/mol
Internally kinetic mode ($\beta = 0.45$)			
Salty coal	2.238	0.481	32.024
Desalted coal	2.179	0.468	32.475

$W_m = f(T)$. For this purpose, the above expression was linearized using the following ratios [11]

$$y = A + B \cdot x,$$

where

$$y = \ln(W_m); \quad x = 1/T; \quad (4)$$

$$A = \ln(\beta \cdot S_{num} \cdot k''_o); \quad B = -E_a/R.$$

From the obtained results (Table 3) we can see the closeness of the values of the activation energy and the chemical constant of the reaction rate of salty and desalted coal by water washing. This indicates that the purification of salt coal by water washing has a much smaller effect on the burning characteristics of the coke residue, namely stage 2 of the process.

Conclusions.

1. The salts of alkali and alkaline earth metals that are part of the native minerals of the investigated salty coal are natural catalysts of the processes of thermolysis and combustion of organic mass of salty coal.

2. The complex of salts present in salty coal accelerates the emission (elimination) of hydrogen by 3–4 times, carbon monoxide – by 2–3.5 times, carbon dioxide – by 2.5 to 3 times in the processes of thermolysis.

3. Considering the presence of a natural catalytic complex in the composition of salty coal, one of the priority areas may be the use of salty coal as a catalytic component in combination with other coal, which does not have an abnormally high content of Na and Cl. This solves 2 problems: 1) the mixture reduces the content of sodium oxide and chlorine to an acceptable value; 2) increases the overall reactivity of the mixed fuel.

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Енерготехнологічне підґрунтя для залучення солоного вугілля до енергобалансу України.

2. Природні мінерали як каталізатори термохімічної конверсії солоного вугілля в різних умовах

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Солоне вугілля (СВ) Північного Донбасу в переліку непроектних палив за умовами залягання й запасами є перспективним джерелом енергії в Україні. Це пов'язано як з його досить високими енергетичними (паливними) характеристиками, так і з наявністю у його складі природного каталітичного комплексу – підвищеного вмісту солей лужних і лужноземельних металів і мікроелементів. Ці домішки, з одного боку, можуть призводити до низки проблем при спалюванні, але й можуть мати позитивний ефект при використанні такого вугілля в сумішах з іншим, менш реакційним, паливом.

Мета. Визначення впливу водорозчинних сполук (хлоридів і сульфатів натрію, кальцію, магнію тощо) на процесі термолізу (горіння) солоного вугілля Богданівського родовища (Північний Донбас) за різних температур.

Методика. Із використанням оптимізованих раніше параметрів процесу водної екстракції СВ (часу, температури та співвідношення твердої та рідкої фази) одержані зразки знесолоного вугілля. Елементний склад і технічні характеристики досліджуваного вугілля визначені за відповідними стандартними методами. Динаміка газовиділення й горіння коксозольного залишку солоного та знесолоного вугілля визначена за допомогою установки „Піроліз М“, в якості газоаналізатора використаний мас-спектрометр MX-1215. Розрахунки кінетичних параметрів процесу виконані на основі закону Арреніуса.

Результати. Визначені зміни елементного складу органічної маси вугілля (ОМВ), що відбуваються при очищенні соленого вугілля водною екстракцією. Проведені експериментальні дослідження зі спалювання соленого та знесоленого вугілля Богданівського родовища в інтервалі температур 550–850 °С. Визначено, що нативні водорозчинні мінерали соленого вугілля призводять до інтенсифікації процесів займання, пришвидшення виходу газоподібних продуктів (H₂, СО, СО₂) і зміни співвідношення вмісту газів. Визначена енергія активації процесу горіння коксового залишку вихідного та знесоленого вугілля.

Наукова новизна. Виконане порівняння деяких характеристик горіння соленого та знесоленого вугілля. Показано, що водна екстракція СВ приводить до покращення паливно-енергетичних характеристик дослідних зразків. Встановлено, що солі лужних і лужноземельних металів, які знаходяться у складі соленого вугілля, є природними каталізаторами процесів термолізу й горіння органічної маси вугілля. Визначено, що в інтервалі температур 550–850 °С, у залежності від фракційного складу досліджуваного зразка вугілля, водорозчинний сольовий комплекс пришвидшує емісію (елімінування) водню у 3–4 рази, монооксиду вуглецю – у 2–3,5 рази, діоксиду вуглецю – у 2,5–3 рази в порівнянні зі знесоленим вугіллям.

Практична значимість. У результаті проведених досліджень показана перспективність залучення соленого вугілля до паливної бази України не тільки як окремого палива, за умови зменшення концентрації шкідливих домішок (шляхом водної екстракції), але й як компонента сумішевих палив для підвищення реакційної здатності композиційної паливної сировини.

Ключові слова: *солоне вугілля, нативні мінерали, хлориди, сульфати, водна екстракція, піроліз*

Энерготехнологическое основание для вовлечения соленого угля в энергодоланс Украины. 2. Природные минералы как катализаторы термохимической конверсии соленого угля в разных условиях

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Соленый уголь (СУ) Северного Донбасса в списке непроектных топлив по условиям залегания и запасам является перспективным источником энергии в Украине. Это связано как с его достаточно высокими энергетическими (топливными) характеристиками, так и с наличием в его составе природного каталитического комплекса – повышенного содержания солей щелочных и щелочно-земельных металлов и микроэлементов. Эти примеси с одной стороны могут приводить к ряду про-

блем при сжигании, однако могут иметь и положительный эффект при использовании такого угля в смеси с другим, менее реакционным, топливом.

Цель. Определение влияния водорастворимых соединений (хлоридов и сульфатов натрия, кальция, магния и т.д.) на процессы термоліза (горения) соленого угля Богдановского месторождения (Северный Донбасс) при различных температурах.

Методика. С использованием оптимизированных ранее параметров процесса водной экстракции СУ (времени, температуры и соотношения твердой и жидкой фазы) получены образцы обессоленного угля. Элементный состав и технические характеристики исследуемого угля определены по соответствующим стандартным методам. Динамика газовой выделенія и горения коксозольного остатка соленого и обессоленного угля определена с помощью установки „Пиролиз М“, в качестве газоанализатора использован масс-спектрометр МХ-1215. Расчеты кинетических параметров процесса выполнены на основе закона Аррениуса.

Результаты. Определены изменения элементного состава органической массы угля (ОМУ), происходящие при очистке соленого угля водной экстракцией. Проведены экспериментальные исследования по сжиганию соленого и обессоленного угля Богдановского месторождения в интервале температур 550–850 °С. Определено, что нативные водорастворимые минералы соленого угля приводят к интенсификации процессов воспламенения, ускорению выхода газообразных продуктов (H₂, СО, СО₂) и изменению соотношения содержания газов. Определена энергия активации процесса горения коксового остатка исходного и обессоленного угля.

Научная новизна. Выполнено сравнение некоторых характеристик горения соленого и обессоленного угля. Показано, что водная экстракция СУ приводит к улучшению энергетических характеристик опытных образцов. Установлено, что соли щелочных и щелочно-земельных металлов, находящихся в составе соленого угля, являются естественными катализаторами процессов термоліза и горения органической массы угля. Определено, что в интервале температур 550–850 °С, в зависимости от фракционного состава исследуемого образца угля, водорастворимый солевой комплекс ускоряет эмиссию (элиминирование) водорода в 3–4 раза, монооксида углерода – в 2–3,5 раза, диоксида углерода – в 2,5–3 раз по сравнению с обессоленным углем.

Практическая значимость. В результате проведенных исследований показана перспективность вовлечения соленого угля в топливную базу Украины не только как отдельного топлива, при условии уменьшения концентрации вредных примесей (путем водной экстракции), но и в качестве компонента смесевых топлив для повышения реакционной способности композиционного топливно-го сырья.

Ключевые слова: *соленый уголь, нативные минералы, хлориды, сульфаты, водная экстракция, пиролиз*

Recommended for publication by I. A. Volchyn, Doctor of Technical Sciences. The manuscript was submitted 05.08.18.