

The problems of reducing the slagging ability and corrosiveness of coal with a high content of low-melting salts (the so-called salty coal (SC) in the processes of its combustion) are considered. Salty coal is considered to be the coal, the ash of which contains $\text{Na}_2\text{O} > 2\%$. The object of study is the salty coal of Donbass and ways of solving the problems of its use. The influence of low-melting salts on the formation of ash deposits and the development of corrosion of the metal surface during the combustion of salty coal from different fields was determined.

A noticeable decrease in the slagging ability and corrosiveness of the test coal was noted during the removal of salts by water extraction. The composition of corrosive compounds (oxides Fe_2O_3 , Fe_3O_4 and iron sulfide FeS) has been determined, formed during the combustion of native coal, and their absence in the case of desalinated coal.

Artificial fuel mixtures produced from more reactive salty and conventional low reactive coal have been studied. To create a mixed fuel, long-flame salty coal (low stage of metamorphism) from the Northern Donbas and unsalty lean coal (high stage of metamorphism) from Kuzbas were used. A significant deviation (to 9 %) was noted for the release of ash during the combustion of mixtures from the additivity, indicating a chemical interaction between the mineral components of the mixture. The formation of new refractory mineral phases of ash (nepheline, ultramarine, combeite) during the combustion of composite fuel from coals of different metamorphism and salinity was established.

The obtained results will be useful in the development of recommendations for the preparation of model fuel mixtures and their accident-free combustion in industrial boiler units. Experimental data on the determination of new mineral compounds in the case of composite fuels can be used to create a general theory of slagging in the combustion of salty coal of different origins

Keywords: salty coal, water-soluble compounds, combustion, slagging, surface corrosion, mixture, ash minerals

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EXPERIMENTAL DEVELOPMENT OF APPROACHES TO REDUCE THE SLAGGING AND CORROSIVE ACTIVITY OF SALTY COAL

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1. Introduction

Fossil coal belongs to a depleted source of energy, and usable deposits around the world are almost depleted. That is the reason why for power production humanity is forced to attract fuel of ever lower quality (carbon-containing wastes, peat, low-quality and low-calorie coal, carbon mixtures of different origins, etc.). However, coal as a component of the fuel base for many years will play a key role in the energy of many countries (China, USA, Poland, Russia, Kazakhstan, Australia, etc.).

The situation in Ukraine's energetics is currently characterized by two divergent trends. On the one hand, the role of coal as an energy fuel remains crucial (similar to the

situation in Poland and China), as far as more than 30 % of all electricity in the country is generated due to thermal coal generation. On the other hand, the global trend of "carbon-free energy" requires a reduction in the share of solid combustible minerals and imposes more strict requirements for the quality of fossil fuels to be used.

The need to preserve and improve the domestic coal power industry in the future is taken into account during the development of the New Energy Strategy (NES) of Ukraine until 2035. Thus, according to the concept of NES, in 2035 TPPs and CHP plants will produce 63 billion kW·h (61 billion kW·h in 2015) of electricity. It is assumed that the share of electricity production by the power units of TPPs and CHP plants will exceed 12 % [1]. It is particularly noted that

the role of coal-steam plants in regulating the schedule of peak power consumption is currently unalterable. Here, peculiarities of the fuel base of coal power engineering should be taken into account and modern approaches to the use and preparation of non-traditional raw materials and their environmentally friendly use should be developed.

In many countries of the world (China, the USA, Poland, the Russian Federation, Kazakhstan, Ukraine, Australia, etc.) powerful deposits of the so-called “salty” coal were found. This coal is distinguished by a high content of alkali metal salts, but at the same time retains attractive thermal technical characteristics [2]. Even in the middle of the last century it was found that the main disadvantage of such coal is an increased rate of slagging and corrosion of heating surfaces due to the effect of a number of aggressive mineral compounds [3]. It is also known that the complex of native (natural) salts and microelements inherent to each field, differs from all the other [3–5] as to their composition. This requires a detailed study of promising fields to determine the conditions of combustion or the choice of other use of energy raw materials. Determining the composition of native compounds of any coal field provides an experimental basis for creating predictive models of behavior of similar coal in the processes of thermal conversion and for the development of acceptable conditions for its use.

Domestic fields of salty coal located in the Western and Northern Donbas are off-balance fuel with explored reserves of about 10–12 billion tons (estimated – up to 25 billion tons). Currently, they are not developed, although coal deposits are characterized by small depths (300–600 m), significant stratum depth (sometimes up to 3–5 m). Coal has an acceptable heat of combustion (about 7000 kcal/kg per dry ashless mass) and a moderate ash content (10–15 %). In the grades classification this fuel is defined as long-flame (*L*), long-flame gas (*LG*) and brown (*B*) [2]. Involvement of salty coal in the country’s fuel balance for electricity and heat production will reduce the possible shortage of coal of the gas group (grades *G*, *LG*), to the combustion of which several existing TPPs are currently adapted [6].

2. Analysis of literature data and problem statement

Coal fields with a high content of salts have been explored in many countries around the world (Germany, Poland, USA, Kazakhstan, Russia, the Czech Republic, Great Britain, Australia, China, etc.) [2, 3].

Negative world experience in the use of such coal is associated with the strong impact of aggressive combustion products on the state of the metal and heating surfaces. During the combustion of such coal an intensive heating by slagging of intrafuel surfaces and their high-temperature gas corrosion occur [3, 5, 7]. Studies of the mechanisms of slagging and corrosion of metal heating surfaces indicate the dependence of these processes on the operating and temperature conditions of combustion and significantly on the composition of the mineral part of the raw materials [3, 4, 8, 9]. The main causes of slagging are considered to be the processes of formation of low-melting eutectics and low viscosity of ash. The review work [3] summarizes modern views on the mechanisms of slagging during the combustion of raw materials with a high content of alkali and alkaline-earth metals. The classification of world coal fields of low stage of metamorphism was carried out by groups according to the

main indicators. The comparison of their features with other types of carbon raw materials (different types of biomass, anthracites) was performed. A phenomenological model of slagging and agglomeration of ash deposits in the process of combustion and gasification of fuels with an increased content of alkaline salts was presented.

Revealed that coal, which contains an increased quantity of halite (NaCl), is the most prone to slag formation [10]. During the combustion of coal, sodium chloride is the first to settle on cold surfaces in the form of an adhesive film [10], which further forms more complex ash formations. These deposits dramatically deteriorate the heat transfer properties of working surfaces and are not removed by conventional methods of cleaning. In general, such deposits are observed during the combustion of solid and liquid fuels with a relatively high content of impurities (in particular, more than 2 % of sodium oxide in the ash), having low melting and sublimation points. On sticky (or liquid) deposits fly ash settles. As a result of the interaction of solid ash particles and some volatile components of fuel combustion products (SO₂, CO₂), chemical transformations occur, which lead to sintering and the formation of a dense layer of contaminants. In addition, after short-term operation of a boiler unit under the slag corrosion damage of metal surfaces occur [11]. It was emphasized that the difficulties arising during combustion of ash fuels, are not directly related to the absolute amount of ash in the fuel. Most likely, the composition of mineral impurities in the fuel may contain a number of low-melting substances [3, 8, 11], such as salts of alkali and alkaline-earth metals: chlorides MgCl₂ ($t_m \approx 700^\circ\text{C}$), CaCl₂, KCl ($t_m \approx 770^\circ\text{C}$), NaCl ($t_m \approx 800^\circ\text{C}$), as well as FeCl₃ ($t_m \approx 670^\circ\text{C}$) and sulphates Na₂SO₄ ($t_m \approx 880^\circ\text{C}$) and K₂SO₄ ($t_m \approx 1070^\circ\text{C}$). Refractory mineral impurities of the fuel are sulfate CaSO₄ ($t_m \approx 1400^\circ\text{C}$), oxides SiO₂ ($t_m \approx 1470^\circ\text{C}$), Fe₂O₃ ($t_m \approx 1570^\circ\text{C}$), Al₂O₃ ($t_m \approx 2015^\circ\text{C}$), CaO ($t_m \approx 2570^\circ\text{C}$) and MgO ($t_m \approx 2800^\circ\text{C}$). The characteristics of the ash in the boiler chamber depend on the ratio of basic and acidic (as to their chemical properties) components included in the melt [3, 11].

Many modern studies also note that not only alkali metal salts affect slagging during the combustion of coal and biomass. Calcium and iron compounds play a significant role [12–14]. Calcium and iron compounds play a significant role [8, 13].

In [14], a clear correlation was found between the ratio of sodium to iron, the sum of silicon and aluminum and the level of slagging during the combustion of high-alkaline coal:

- at the ratio: $\text{Na}/(\text{Si}+\text{Al}) < 0.05$ – slight contamination;
- at $\text{Na}/(\text{Si}+\text{Al}) > 0.05$ – significant or serious contamination;
- at the ratio: $\text{Fe}/(\text{Si}+\text{Al}) < 0.02$ – slight slagging;
- at $\text{Fe}/(\text{Si}+\text{Al}) > 0.02$ – increased slagging.

Modern studies note that it is possible to predict the behavior of fuels in terms of susceptibility to slagging only if the data on the detailed composition of minerals are available and by modeling the properties of a molten ash.

Despite the rich experimental material of works [3, 16], the main conclusion from them states that currently there is insufficient knowledge about the laws of slagging during the combustion of natural fuels. Development of models and theory of slagging require new experimental data on the combustion of problem coal from different fields. Studies [4] have shown that despite a close index of salinity, the content of Na₂O in the ash is increased ($\geq 2\%$), even the composition

of water-soluble minerals from different fields differs significantly. In view of these conclusions, the determination of the mineral composition of the ash of domestic salty coal and its influence on slagging and corrosion of heating surfaces seems quite relevant. It is known that the processes of slagging, ash formation, corrosion during the combustion of even one fuel raw material are very complex, depending on the characteristics of the raw material and still do not have a generalized theoretical basis.

It is especially emphasized that the established dependencies are purely empirical [14] and are valid for specific fields of a common genesis [8, 17]. Whereas with the aim of generalizing and predicting the conditions of accident-free combustion of coal from different fields, having significant differences and features, much more experimental data are required. The process of accumulating new knowledge about the impact of technological procedures, preceding or being used in the process of salty coal combustion is essential to create a common theoretical basis for the rational use of such powerful and backup raw materials for today. A similar approach is applied also to mixed fuels, when the accumulation of the experimental data system will provide the necessary basis for the creation of predictive model fuel systems that will provide an accident-free operation of boilers [14]. The important and unsolved problem is determining the qualitative composition of new mineral phases during the joint combustion of coal of a different degree of salinity and metamorphism.

3. Aim and objectives of the study

The aim of the study is to determine the effect of low-melting native salts on slagging and corrosion properties of coal. This will allow predicting the intensity of slag formation and chemical corrosion of equipment surfaces during a high-temperature combustion of coal with an increased content of low-melting salts. Knowledge of the composition of mineral impurities of fuel raw materials with the participation of salty coal is extremely necessary to determine the conditions for efficient and accident-free operation of boiler units.

To achieve this aim, the following objectives were set:

- to determine the influence of natural water-soluble compounds on the formation of ash deposits and the development of corrosion processes on the surface of metal testers during the combustion of salty coal;
- to establish the mineral composition of ash residues of burnt salty and lean coal and compare it with the mineral composition of the composite fuel ash;
- to assess the promising ways to reduce slagging and corrosion activity of a Ukraine salty coal.

4. Materials and methods of studying mineral composition of salty coal and its influence on the formation of deposits and corrosion

4.1. Procedure for determination of the effect of desalination on slagging and corrosion activity of salty coal during combustion

To evaluate the effect of water-soluble salts on the formation and composition of ash deposits during the thermolysis of salty coal, the experiments on simulating its combustion

were organized. Table 1 shows the characteristics of the studied samples of salty coal from Bogdanovsk and Starobelsk fields. Quantitative characteristics of fuels indicate that the selected coal is low-metamorphosed (volatile yield), typically salty (sodium oxide in ash) with a low ash content and moderate humidity. Only one of the samples has a high sulfur content.

Table 1

Technical characteristics of salty coal samples

Field	Ash content A^d , %	Release of volatiles V^{daf} , %	Humidity W , %	Content of Na_2O in the ash, %	Sulfur, S %
Bogdanovsk field No. 1	11.0	41.0	13.2	3.5	2.7
Bogdanovsk field No. 4	5.5	42.8	12.7	6.9	1.2
Starobelsk field No. 10	11.8	47.4	14.3	3.4	5.4
Starobelsk field No. 12	7.3	43.7	20.3	6.5	2.8

In ceramic vessels (cells) in a thin layer 5 g of a coal sample was loaded, covered with metal plates for accumulation and study of the composition of newly formed structures. On the side of the cells metal rods were placed, preliminary weighed on analytical balances. The samples were combusted in a muffle by heating from room temperature to 850 °C (to remove volatile substances and low-melting salts), keeping the samples at this temperature for 2 h until a complete ashing. After completion of the experiment, the rods were weighed again.

The second stage of the work consisted in determination of the composition of the formations that arised on the metal plates during the combustion of salty and desalinated coal in the muffle. Metal plates were exposed to the action of volatile products of a combusted salty and desalinated coal, which resulted in changes of the color and state of the plate's surface. Exfoliated particles ("scale") were thoroughly separated from the surface of the plates and subjected to study by X-ray diffraction analysis. With the help of X-ray diffraction analysis, the diagnostics of minerals in the ash residues of fuels and their mixtures was performed using DRON-4M diffractometer (in the radiation of cobalt or copper anode). The record of powder diffractograms was made in the range of angles 2θ from 15° to 60° with a step of 0.04°. Determination of interlayer distances of minerals was made with an accuracy of 0.002 nm. Semi-quantitative phase analysis of diffractograms was performed using MATCH* software (released in 2009; version 1.9a; developer Cristal Impact). Determination of mineral phases was performed using MATCH software!

4.2. Procedures of investigations on the formation and determination of the composition of ash residues

For the experiment on joint combustion, the coal samples were separately refined to a fraction of 0–0.2 mm. The samples of salty and lean coal separately, as well as their mixtures weighing 3 g in rectangular vessels were subjected to heat treatment for 3 hours: one hour for heating to 850 °C and two hours for holding at 850 °C until a complete ashing. For the experiments two samples of salty coal of the Bogdanovsk field No. 1 and No. 4 with a medium and high content of Na_2O in the ash (~3.6 % and ~7 %, respectively) and lean non-salty coal were selected. Table 2 shows the characteristics (elemental and technical analysis), and Table 3 shows chemical composition of ash samples of salty and lean coal used in the experiments.

Table 2

Characteristics of salty and lean coal

Field	Elemental composition, %					Technical analysis, %			Na ₂ O in the ash	Cl, %
	C ^{daf}	H ^{daf}	N ^{daf}	S ^{daf}	O ^{daf}	W ^a	V ^{daf}	A ^d		
Bogdanovsk field (SC No. 1)	68.2	5.4	1.3	3.3	21.9	9.6	41.1	10.2	3.9	0.91
Bogdanovsk field (SC No. 4)	70.9	5.2	2.4	1.3	20.5	12.7	42.8	5.07	7.0	0.83
Lean (L)	87.1	4.2	2.3	0.4	6.0	1.1	17.9	12.2	0.7	0.042

Table 3

Chemical composition of salty and lean coal ash

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
Bogdanovsk field	1.85–6.80	0.45–2.52	2.59–24.4	30.36–52.14	0.09–1.20	4.152–0.25	0.20–2.50	4.07–19.2	0.12–0.80	5.89–17.08
Lean	0.7	1.9	26.7	54.0	1.1	1.2	1.9	3.8	1.1	7.5

Salty coal samples are characterized by a moderate ash content (10 % and 5 %) and a significant content of chlorine in the coal (Cl ~1 %). As to the chemical composition of salty coal ashes, a significant content of Na, Ca, Fe and a low content of Mg, K, P can be distinguished in them. It is known that the chemical composition of the ash gives only a general idea of the content of the elements that belong to its composition. But it can not answer in which exactly mineral compounds these elements are present there. The knowledge required to predict the behavior of fuels can be obtained using a physical non-destructive method of X-ray diffraction analysis.

Table 4 shows the composition of the studied mixtures of salty and lean non-salty coal used to establish the phenomenon of additivity (or non-additivity) during the combustion of the composite fuel. As a result, ash residues were obtained, where the samples of salty coal, which had a dark brown color due to a significant concentration of iron, were visually clearly distinguished.

Comparing the results of the experimental determination of the mass of ash mixtures (Table 4) with the results theoretically calculated according to the rule of additivity, it is possible to see that in the experiment the ash residue from the mixtures is formed more than it was theoretically calculated.

Composition of mixtures and comparison of mass of their ash residues

Sample	Ratio	Mass of ash, g (experiment)	Mass of ash, g (theoretically)	Deviations, %
SC No. 1 : LC	50 %:50 %	0,440	0,405	7,955
SC No. 4 : LC	50 %:50 %	0,356	0,350	1,686
SC No. 4 : LC	60 %:40 %	0,331	0,316	4,532
SC No. 4 : LC	40 %:60 %	0,424	0,384	9,434

Therefore, during combustion of mixtures, there is a noticeable, though a low synergistic effect, which directly indicates the chemical interactions during ashing of mixtures and the formation of new compounds. Deviation from additivity for different mixtures amounts from 1.5 to

9 % (rel.). The experimental error for parallel experiments does not exceed 1 % (rel.). The results of weight analysis of ash mixtures provide an additional basis for the study of mineral phases in mixed ashes, the qualitative composition of which was determined by X-ray diffraction analysis using the software MATCH!

5. Results of studies of the effect of water-soluble compounds on slagging and corrosion properties of coal

5. 1. Influence of natural water-soluble compounds on the formation of ash deposits

Fig. 1 shows the results of the experiment on determination of the mass gain of iron rods during the combustion of primary and salty coal washed with water, as well as other kinds of raw materials (for comparison). It is seen that an increase in the mass of a metal rod under the influence of volatile substances from coal samples or from biomass samples depends on the characteristics of raw materials and the presence of water-soluble (volatile) salts. The mass gain of the rod for the desalinated sample is always by 3–5 % lowers unlike for a primary salty coal, and is close to the result of gas coal and straw. During the combustion of pine pellets, the value of gain is significantly lower. As is seen,

Table 4

any fuel provides an effect of “sticking” on the surface of influence of volatile substances, but the greatest effect is observed in the case of salty coal. At the same time, the removal of water-soluble salts according to the method [15] leads to a significant reduction in sticking, even at such a short period of time.

In other words, water extraction of soluble salts, the composition of which for the studied coal was determined in [4], significantly reduces the effect of sticking on metal heating surfaces.

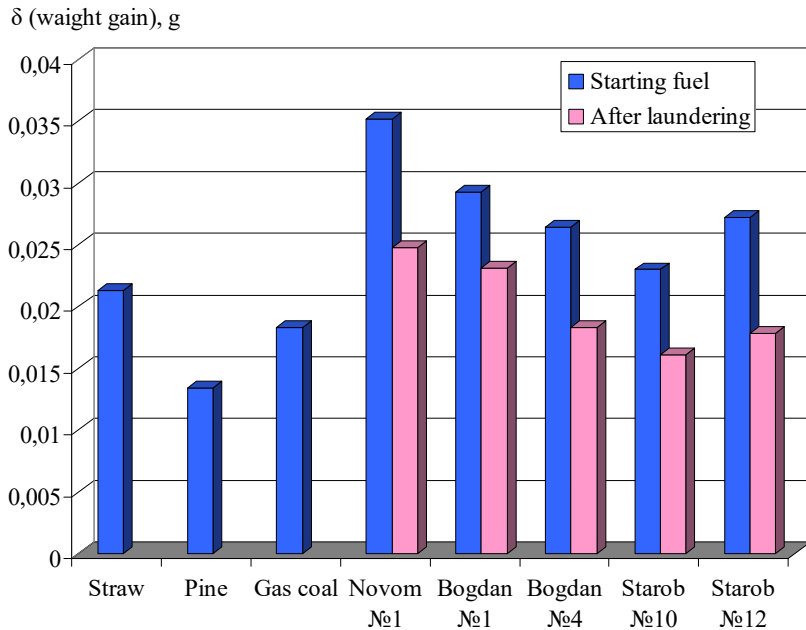


Fig. 1. Mass gain of rods under the action of volatile fuel substances

5. 2. Influence of water-soluble compounds on the development of corrosion processes during the combustion of salty coal

The results of visual inspection of metal plates show a significant difference between the surfaces that were exposed to volatile compounds of salty and desalinated coal (Fig. 2). In all the cases, the zone of influence of such substances is visible, which were formed during the combustion of coal. However, in the case of a primary salty coal, the presence of layers exfoliation and more intense surface color is clearly visible. Therefore, the process of more significant effect and active exfoliation of surface layers for salty coal samples is obvious.

Diffractograms of exfoliations (scale) of three samples of primary coal are shown in Fig. 3. Qualitative and semi-quantitative composition of exfoliated layers of metal is given in Table 5. They contain 4 types of iron compounds, as well as sodium chloride in two samples in small (at the detection limit of the device) quantities. In the case of the least salty coal (Bogdanovsk field No. 1) the presence of sodium chloride in the composition of exfoliated formations was not established.

The main substances of the exfoliated layers are the expected iron oxides (75–85 % in total). The content of iron sulfide (13–25 %) and the presence of NaCl are related to the quantitative technical characteristics of the samples of a primary salty coal. Because of the lack of active exfoliation, it was not possible to collect a sufficient amount of scale from desalinated coal plates.

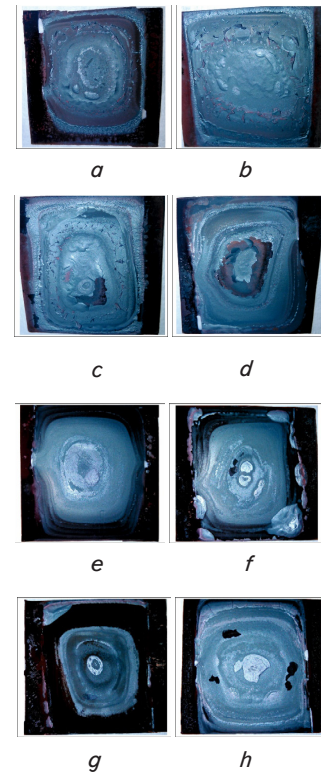


Fig. 2. Appearance of plates after combustion of salty and desalinated coal:

- a – salty coal from Bogdanovsk field No. 1;
- b – salty coal from Bogdanovsk field No. 4;
- c – salty coal from Starobelsk field No. 12;
- d – salty coal from Starobelsk field No. 10;
- e – desalinated coal from Bogdanovsk field No. 1; field No. 4;
- g – desalinated coal from Starobelsk field No. 12;
- h – desalinated coal from Starobelsk field No. 10.

Thus, the removal of water-soluble salts from salty coal leads not only to a decrease in the effect of sticking, but also to a significant reduction (cessation) of corrosion of metal heating surfaces.

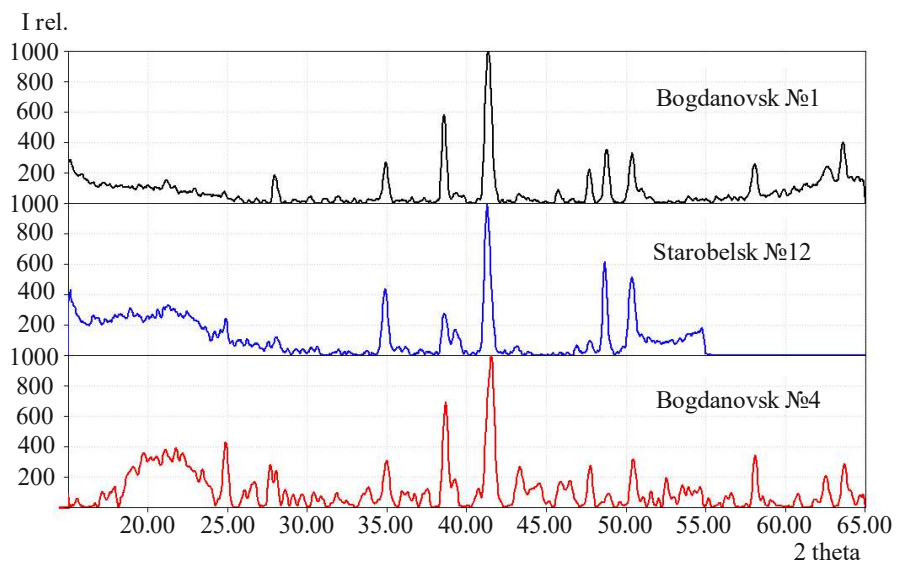


Fig. 3. Diffractograms of scale formed at the interaction of metal with volatiles of salty coal

Table 5

Composition of scale from metal plates, which were in contact with volatile products of SC at 850 °C, 2 h

Sample of SC from fields	Fe ₂ O ₃	Fe ₃ O ₄	FeO	FeS	NaCl
Bogdanovsk field, No. 1	18	34	23	25	0
Bogdanovsk field, No. 4	35	17	30	16	2
Starobelsk field No. 12	44	25	15	13	3

5. 3. Mineral composition of ash of salty and lean coal and ash residues of composite fuel

Fig. 4–6 show diffractograms of ash residues of a primary salty and lean coal, which were combusted separately. Analyzing the diffractogram of salty coal No. 1 (Fig. 4), it is possible to that most of the intense reflexes correspond to the mineral phases, belonging to the oxides, such as SiO₂, Fe₂O₃, Fe₃O₄, CaO and Al₂O₃. A significant quantity of anhydrite CaSO₄ and aluminosilicate Al₂Si₂O₅, silicates CaSiO₃, Mg₂SiO₄ in much smaller quantity and sulfate Fe₂(SO₄)₃ were also revealed. As for the phases, which include Na, two main groups – silicates and sodium aluminate (Na₂SiO₃, Na₂Si₄O₉, Na₂Al₂O₄) can be distinguished. A small quantity of Na is included in sodium aluminosilicate (NaAlSiO₄) and sodium sulfate (Na₂SO₄).

Identification of minerals of ash of salty coal No. 4 (Fig. 5) allowed establishing the following groups of mineral phases, formed in the process of thermolysis. Oxides SiO₂ and Fe₂O₃ have the most intense reflexes. Sulfates anhydrite CaSO₄ and thenarditis Na₂SO₄ have less intense reflexes but their quantity is sufficient. Complex silicates sodium tetrasilicate Na₂Si₄O₉, sodalite Na₆(AlSiO₄)₆ and calcium-magnesium silicate Ca₂Mg(Si₂O₇) correspond to weak reflexes, which indicates their low content.

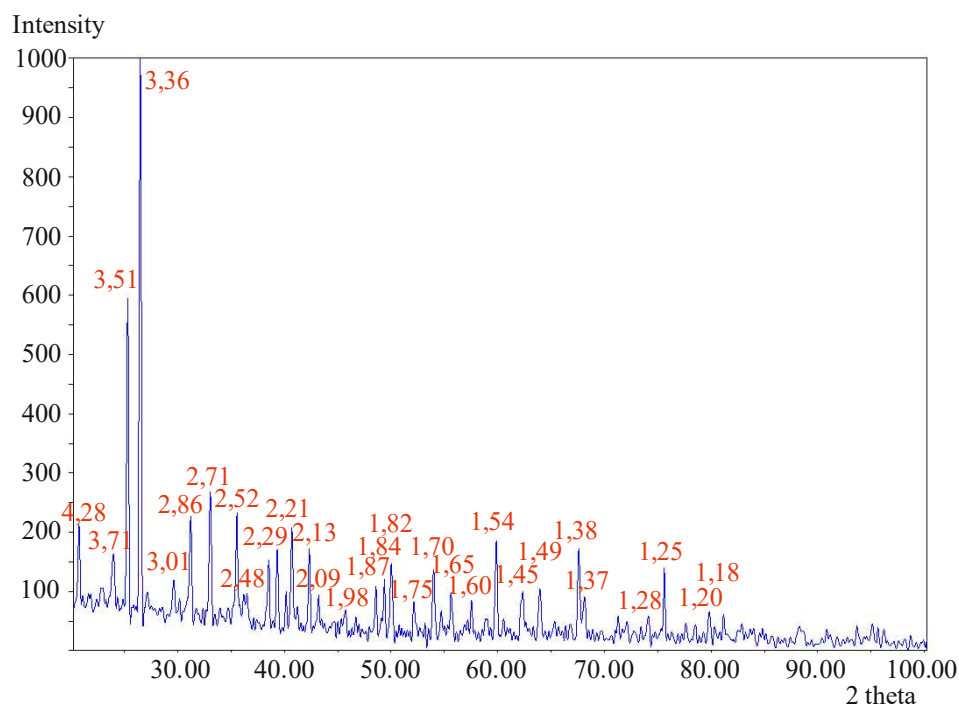


Fig. 4. Diffractogram of ash of salty coal No. 1

The obtained results of X-ray diffraction analysis do not contradict with the data on the chemical composition of salty coal ash and correlate with the literature data of domestic and foreign works [9, 11, 12], devoted to the study of the mineral composition of salty ash residue of coal from Belarus, Russia and China. Comparing the mineral phases of salty coal samples and their melting points (Table 6), it can be noted that the main part of Na of ash compounds is in the form of sulfates (SC No. 4) and silicates (SC No. 1). These substances have relatively low melting points and are the main components that will cause slagging of the studied coal.

Table 6

Characteristics of minerals found in the composition of ash residues of salty coal

Mineral	Formula	T _m , °C
Silicon oxide (quartz)	SiO ₂	1370
Aluminum oxide	Al ₂ O ₃	2044
Iron oxide	Fe ₂ O ₃	1565
Calcium oxide	CaO	2625
Calcium sulfate (anhydrite)	CaSO ₄	1420
Calcium silicate	CaSiO ₃	1544
Calcium orthosilicate	Ca ₂ SiO ₄	2130
Aluminum silicate	Al ₂ SiO ₅	1850
Sodium sulfate (thenardite)	Na ₂ SO ₄	883
Sodium silicates	Na ₂ SiO ₃ , Na ₂ SiO ₄ , Na ₂ Si ₄ O ₉	1088–1120
Sodium aluminates	Na ₂ Al ₂ O ₄ , NaAlO ₂	1650
Nepheline	NaAlSiO ₄	1526

Analysis of the diffractogram of lean coal ash (Fig. 6) allowed identifying such groups of mineral phases which were preserved (such as SiO₂) and formed in the process of ashing: oxides – Al₂O₃ (intense reflexes), and Fe₂O₃, Fe₃O₄ (less intense reflexes). In small quantities such silicates as Al₂SiO₅, MgSiO₃ and complex aluminosilicates as KAl₃Si₃O₁₁, Ca₃Al₂(SiO₄)₃ were identified.

Identification of the obtained results indicates a smaller quantity of components in the composition of lean coal ash, the main compounds of which are simple oxides and complex silicates. Most of these minerals are refractory.

Analysis of diffractograms (Fig. 7) of ash residues of the mixtures (SC:LC=1:1) revealed that most of the intense reflexes correspond to the mineral phases of the oxides group – SiO₂, Fe₂O₃, Fe₃O₄ and Al₂O₃. In significant quantities, anhydrite (CaSO₄), calcium silicate (CaSiO₃) and aluminosilicate (Al₂SiO₅) were identified.

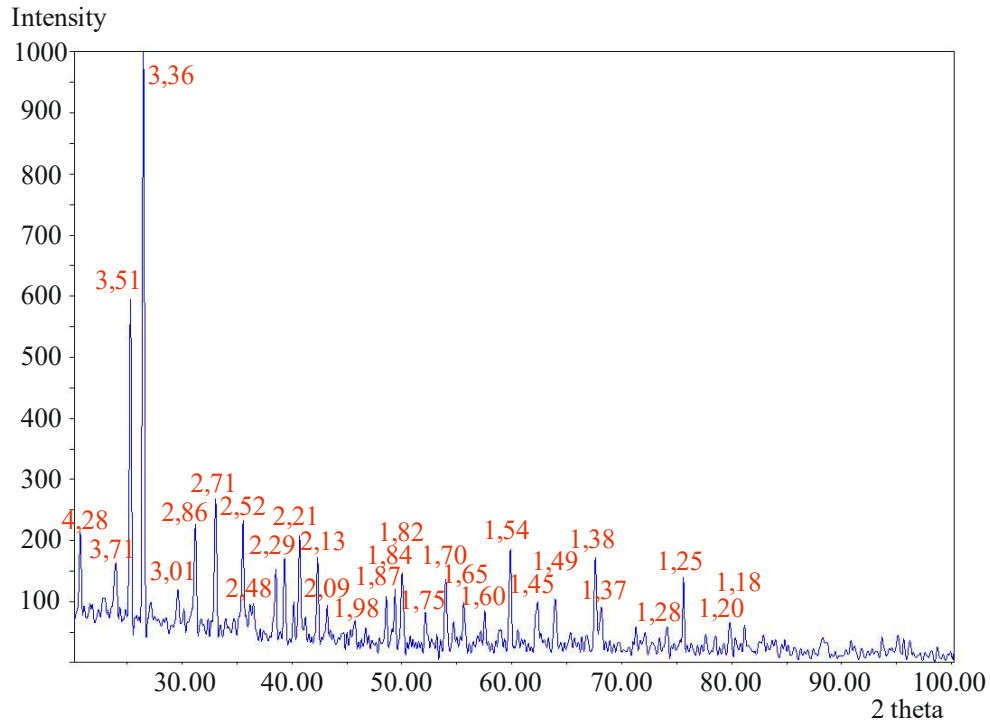


Fig. 5. Diffractogram of ash of salty coal No. 4

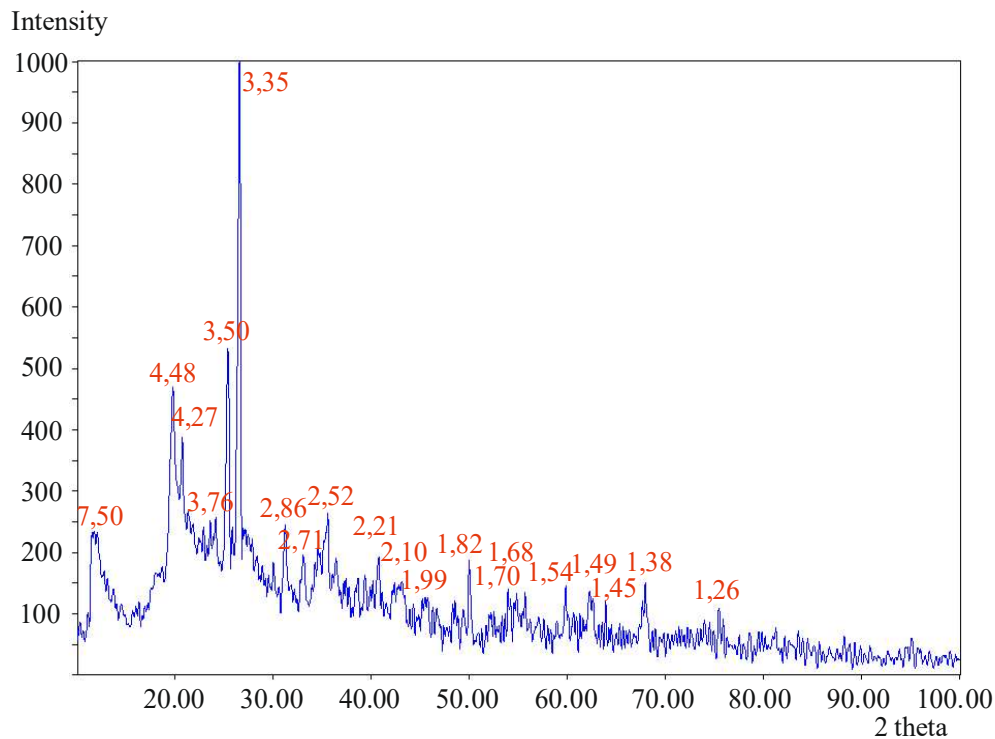
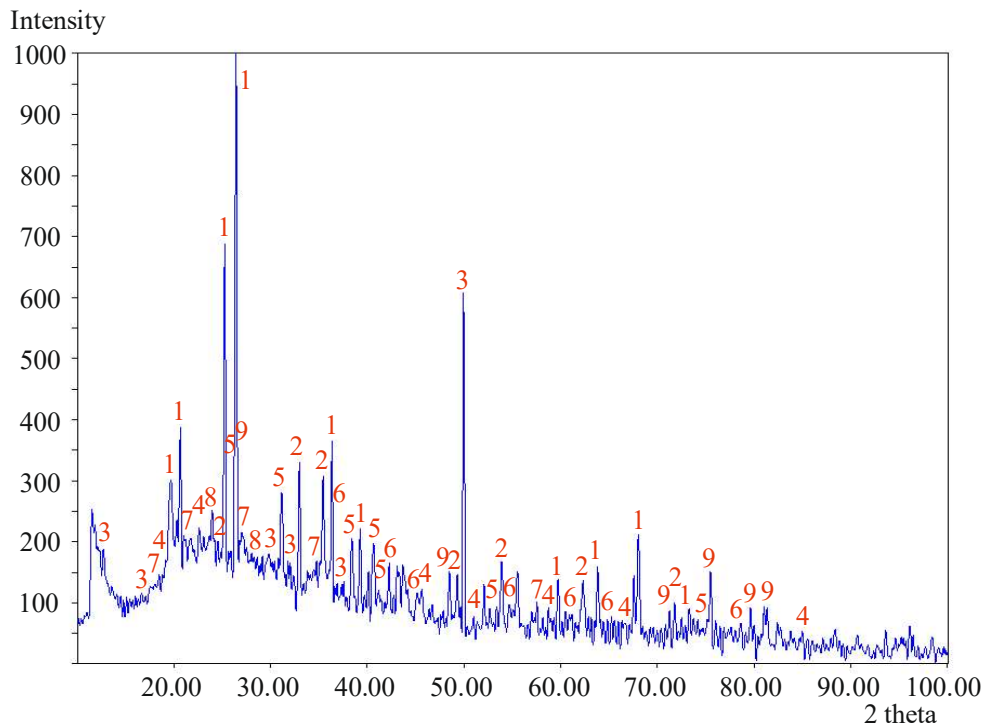


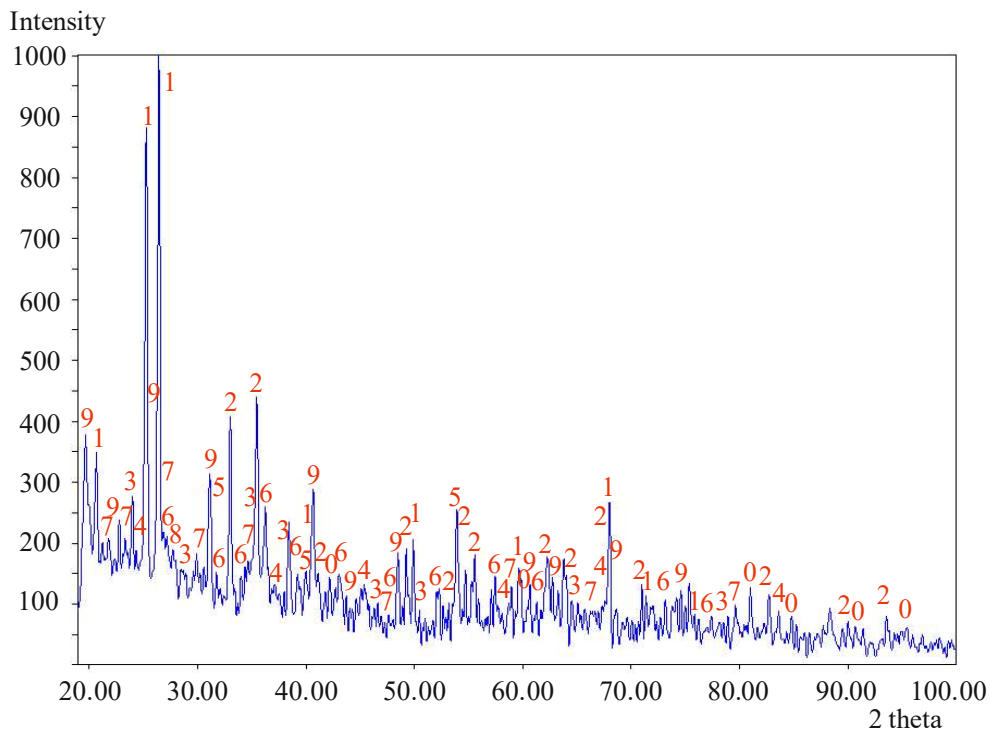
Fig. 6. Diffractograms of lean coal ash

The results on the mineral phases, which include Na, deserve the most attention. As compared with the data of the diffractograms of ash of salty coal, in the ash residue of the mixture a significantly lower content of sodium silicate (Na_2SiO_4) and sodium sulfate (Na_2SO_4) is observed. In-

stead, more complex and first of all refractory minerals are formed: the group of nephelines (NaAlSiO_4 , $\text{KNa}_3(\text{AlSiO}_4)_4$, $\text{K}_{0.86}\text{Na}_{0.16}\text{AlSi}_2\text{O}_6$), ultramarine ($\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$), as well as other new compounds: combeite (NaCaSiO_4) and sodium aluminate (NaAlO_2 , $\text{Na}_2\text{Al}_2\text{O}_4$).



a



b

Fig. 7. Diffractograms of ash: *a* – mixture of SC No. 1: Lean; *b* – mixture of SC No. 4: Lean.
 1 – SiO₂; 2 – Fe₂O₃ and Fe₃O₄; 3 – Na₂SiO₄; 4 – Na₂SO₄; 5 – CaSO₄;
 6 – Ca₂SiO₄; 7 – (Na,K)AlSiO₄;
 8 – Na₇Al₆Si₆O₂₄S₃; 9 – Al₂Si₂O₅; 0 – Na₂CaSiO₄

6. Discussion of the results of the study of the composition and influence of mineral components of coal on the process of formation of refractory components in the mixture ash

In the course of analyzing the obtained results, it is necessary to remind that one of the characteristic features of the combustion of salty coal is the low melting point of its ash, which is predetermined by an elevated content of low-melting salts and the formation of even more low-melting eutectics (LME). Removal of soluble salts from coal applying the method of water, acid and reagent extraction avoids the appearance of LME and, accordingly, the problems of excessive slagging. Significant differences in the mass of deposits observed during the water extraction of salty coal (Fig. 1) indicate that even at a short time of combustion, the difference between the mass of deposits from native and desalinated coal is noticeable – 3–5 % (rel.). As it was established, the error of parallel measurements does not exceed 1.2 %. The method of preliminary preparation of salty coal for combustion is promising in terms of fuel characteristics of raw materials, such as reduction in ash content and content of volatile organic substances, increased calorificity of fuel. The disadvantage is the need for a significant amount of water resources and the problem of using flush water [4].

In addition to preparing coal for combustion applying the method of salt removal, an attractive and rational method is joint combustion of salty coal with other fuel [16], which has excellent characteristics of ash and reactivity. When creating a composite raw material, not only “dilution” occurs, i.e. reducing the content of low-melting salts by adding other fuel to salty coal (coal with a low content of salts of alkali and alkaline earth metals). For the formation of such mineral phases prerequisites are created, that will not complicate the combustion process.

It was found that the content of mixed ash during the combustion of composite fuel is significantly higher than that calculated by the rule of additivity (Table 4). The composition of mineral phases of the ash of the initial components and the ash residue of the mixture of salty and unsalty coal was determined (Table 6, Fig. 5–7). New mineral phases (ultramarine, nepheline, combeite) with the melting point (1500–1600 °C) were found in the ash of the mixture. The obtained results indicate the prospects of using such mixed fuels to provide a stable operation of boiler units.

The totality of the results obtained by us allows proposing at least two methods of reducing the negative phenomena at the energetic use of coal with an increased content of low-melting salts. The first method here is purification of salty coal by a simple water extraction at working concentrating mills, which reduces the slagging ability and corrosion activity of the fuel to a safe level [18].

The second approach is associated with the creation of mixed fuel involving reactive salty and highly metamorphosed non-salty coal. The mixture has more attractive characteristics unlike its separate components. The obtained results from the determination of mineral substances of ash residues of the composite fuel (Fig. 7) indicate the formation of mixtures of more complex (3–4 component) mineral phases with new melting characteristics in the process of ashing. This significantly distinguishes them from the mineral phases of the ash of separate components of the mixtures. At the same time, a simultaneous decrease in the content

of low-melting simple oxides and sulfates (determined because of a decrease in the intensity of the corresponding reflexes on the diffractograms of ash residues) indicates the formation of ash with a high melting point. The results of identification of minerals showed (Fig. 5–7, Table 6) that at a high-temperature ashing (combustion) of the composite fuel, more different transformations of mineral substances occur, during which refractory minerals are created. They include already mentioned minerals of the nepheline group (NaAlSiO_4 , $\text{KNa}_3(\text{AlSiO}_4)_4$, $\text{K}_{0.86}\text{Na}_{0.16}\text{AlSi}_2\text{O}_6$), ultramarine ($\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$) and other new compounds like alkali-alkaline earth metal silicate (NaCaSiO_4) and sodium aluminates (NaAlO_2 , $\text{Na}_2\text{Al}_2\text{O}_4$).

An approximate estimate of the technological and energy indices of the studied coal mixtures (50:50) shows that the ash content of the composite fuel will be 8–11 % when the content of sodium oxide in the ash is lower than 1.3 %. This index does not exceed the standard allowable for stable combustion of the mixture. Here, the release of volatiles will be approximately 28–30 %, which indicates a sufficient level of fuel reactivity. The mineral composition of the mixed ash determined in the work indicates the rationality of using such an approach to the creation of fuel mixtures involving salty coal. The given experimental data also show real ways to expand the fuel base of those countries of the world, that have strong coal deposits with a significant content of alkali and alkaline-earth metals [12, 14, 17].

As far as publications on the similar studies for Ukrainian salty and highly metamorphosed unsalty coal could not have been found, the obtained results can be considered one of the first in this approach on attraction backup fuels to the country's energy balance. An obstacle to the development of similar studies is both the lack of raw materials (only core samples of salty coal were extracted) as well as the presence of only two specialized teams dealing with the problems of conversion of solid fuel into thermal energy or valuable chemicals. The further studies of the processes of combustion of raw materials with the involvement of salty coal can be continued through the organization of the process in the stand units (provided that a significant amount of coal – from hundreds to thousands of kg will be extracted). The accumulation of a significant amount of ash residues (several kilograms) will allow determining the effect of the content of separate components of the ash of the initial coal and other inorganic additives on its melting point and the conditions of the accident-free combustion process.

7. Conclusions

1. On the example of coal from the Northern Donbas, the influence of water-soluble low-melting salts on the formation of deposits and the development of corrosion processes on the surface of metal testers during the combustion of salty coal samples was determined. It was experimentally determined that the mass of ash deposits (3–5 % rel.) on the metal surface during the combustion of desalinated coal significantly decreased as compared to the native sample, which 2.5–4 times exceeds the error of parallel experiments.

During the combustion of salty coal, surface corrosion in the form of exfoliation of metal layers is observed, whereas during the combustion of desalinated coal, this phenomenon did not occur. The main substances of the exfoliated layers are iron oxides (75–85 %) and iron sulfide (13–25 %).

2. It is determined that the main part of Na in the mineral phase of salty coal samples is in the form of sulfates and silicates, having low melting points (800–1100 °C). During the study of a composite fuel ash, consisting of coal of different metamorphic rank (long-flame and lean) and salinity (7 and 0.4 % of Na₂O in the ash, respectively) the formation of complex refractory mineral compounds was established. The mineral phases (such as nepheline, ultramarine, combeite) will prevent an excessive slagging during the combustion of composite raw materials with the involvement of salty coal at the level of 50 %.

3. On the basis of the carried out investigations, two methods of reduction of the problematic phenomena during a power use of coal with an increased content of low-melting salts were offered. The first is the purification of salty coal by simple water extraction in the operating concentrating mills, which reduces the slagging ability and corrosion activity of fuel to a safe level. The second is the use of mixed fuel with the involvement of reactive salty and less reactive unsalty coal, which due to the averaging of the base technical characteristics of fuel and the formation of a refractory mixed ash will provide the stable operation of power equipment.

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