

**T. G. Shendrik**<sup>1</sup>,  
orcid.org/0000-0001-6629-6471,  
**N. I. Dunayevska**<sup>2</sup>,  
orcid.org/0000-0003-3271-8204,  
**A. I. Fateyev**<sup>2</sup>,  
orcid.org/0000-0003-4129-3703,  
**A. K. Tsaryuk**<sup>3</sup>,  
orcid.org/0000-0002-5762-5584,  
**V. P. Yelahin**<sup>3</sup>,  
orcid.org/0000-0002-4335-5130

1 – L. M. Litvinenko Institute of Physical-Organic Chemistry and Coal Chemistry of the NAS of Ukraine, Kyiv, Ukraine, e-mail: [shendrikte@gmail.com](mailto:shendrikte@gmail.com)

2 – Institute of Thermal Energy Technologies of the NAS of Ukraine, Kyiv, Ukraine

3 – E. O. Paton Electric Welding Institute of the NAS of Ukraine, Kyiv, Ukraine

## PHENOMENA AND MECHANISM OF SLAGGING AND CORROSION IN ENERGY USE OF COAL WITH A HIGH CONTENT OF SALTS

**Purpose.** Determination of the main mechanisms of slagging and corrosion of heating surfaces when using coal or other raw materials with a high content of alkali and alkaline earth metals. Experimental determination of mineral phases of ash residues of burning composite raw materials with the participation of salty coal and the influence of component composition on the formation of refractory compounds.

**Methodology.** Critical analysis and generalization of achievements in the developed theories of slagging and corrosion of surfaces during the combustion of problematic carbon raw materials (salty coal, biomass, some wastes, etc.). Determination of the main approaches to the problem of using coal with a high pollution factor. Selection of objects of experimental study on composite raw materials, including coal of different degrees of metamorphism and salinity. Identification of minerals of ash residues of individual fuels and their blends using X-ray phase analysis (X-ray diffraction). Semi-quantitative phase analysis of diffractograms was performed using MATCH! software.

**Findings.** Modern views on the causes of slagging and corrosion processes during the combustion of fuel with a high salt content are highlighted. It has been determined that the process of intensive slagging is associated with a certain ratio of sodium, calcium and iron compounds. The composition and features of the mineral phases of ash residues of composite fuel with the participation of salty coal are experimentally established. The influence of the content of components on the formation of certain mineral phases of mixed ash was determined.

**Originality.** For the first time, the prospects of using two-component blended fuel with the participation of Ukrainian salty coal have been studied. The analysis of minerals in ash residues of salty coal and its blends was carried out. It has been determined that the main part of Na in ash of salty coal of the Bohdanivske deposit in the Northern Donbas is in the form of sulfates and silicates. For the first time, the composition and ways of formation of new refractory mineral compounds in the ash formed during the combustion of composite fuel from coal of different metamorphism and salinity have been established.

**Practical value.** Based on the analysis of literary sources and conducted studies, the dependence of the ash composition on the minerals of the initial fuel and on the ratio of various components in the blends was determined. The proposed approach has a predictive power, as it allows predicting the formation of the main refractory ash minerals. The expediency and prospects of involving salty coal in the fuel base of Ukraine as a component of blended fuels are shown.

**Keywords:** *salty coal, combustion, slagging, surface corrosion, blends, ash minerals*

**Introduction.** Fossil coal as a component of the world's fuel resources for several decades will still play a significant role in the power engineering both in Ukraine as well as in other countries of the world.

The situation in the power industry of our country is currently characterized by two divergent trends. On the one hand, the role of coal as an energy fuel remains crucial, as far as today more than 30 % [1] of all electricity in the country is produced by thermal generation. According to the New Energy Strategy (NES) of Ukraine, in 2035, Thermal Power plants (TPP) and Combined Heat and Power (CHP) plants will produce about 63 billion kW · h of electricity, and the role of coal heat power engineering in regulating peak loads is and will remain leading. It is also assumed that the share of electric power production by the power units of TPPs and CHP plants in the mentioned period will not be less than 12 % [1].

However, the global trend towards “carbon-free” power engineering requires a blunt refusal from utilization of coal and imposes increasingly rigid environmental requirements for fossil fuels, which will be further combusted in the existing boiler units for electricity and heat production.

As far as in the nearest years complete refusal from coal as a fuel will not happen, and taken into account the present-day

situation around the gas, it is necessary to determine the features of the fuel base of solid-fuel power engineering in Ukraine. That is why it is necessary to include relatively cheap and affordable alternative fuels, as well as to compare the results of studies on the characteristics of domestic raw materials and those of the world's leading countries. In addition, modern approaches to the preparation of raw materials and their environmentally friendly use in our country should be developed (or applied).

In this context, the so-called “salty” coal, the deposits of which are located in the government-controlled territory of Ukraine in Dnipropetrovsk and Luhansk regions, deserves some attention. This off-balance coal with explored reserves of about 10–12 billion tons (estimated reserves amount up to 25 billion tons) is not yet extracted. Coal deposits are characterized by several attractive features: acceptable heat of combustion (about 7,000 kcal/kg per dry ash less mass), small depths (300–600 m), significant stratum depth (sometimes up to 3–5 m) and a moderate ash content (10–15 %). In the grades classification, coal 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 from the gas group (grades G, LG), for combustion of which several modern TPPs are currently adapted [3].

For several decades, the problem of successful utilization of salty coal has been attracting the attention of scientists and

power engineers all over the world, as far as fields of coal with a high content of salts have been explored in many countries like Germany, Poland, the USA, Kazakhstan, RF, the Czech Republic, Great Britain, Australia, China, etc. [2]. Negative world experience in the use of such coal is associated with the fact that aggressive combustion products in salty coal have a strong impact on the state of metal and heating surfaces. Namely, they cause an increased slagging on the intrafuel surfaces and their high-temperature gas corrosion [4, 5].

According to the authors [6], creation of the latest technologies for combustion of salty coal will allow expanding Ukraine's fuel reserves for electricity and heat production by 10 %, as well as reducing the possible shortage of coal of the gas group, especially in the conditions of its current shortage.

**Literature review.** Already since the middle of the last century, it has been known that during a direct utilization of fuel with a high content of salts, energy and environmental indices of a power unit are deteriorated. The rapid sticking of ash deposits, slagging and damage to metal surfaces and heat-insulating carborundum materials of a boiler unit occur as a result of the corrosion activity of volatile products [4, 7].

For efficient use of such raw materials, it is necessary not only to know the detailed composition of fuel minerals, but also to understand the mechanism and all stages of sticking, slagging and corrosion that arise during its combustion. That is why many original and review studies are devoted to complex mechanisms for the formation of slag deposits during utilization of different types of problem raw materials [8–10].

During many year experiments of scientists from the All-Union Thermal Engineering Institute (VTI, Moscow, 1980–90s), on the example of coal from the Novomoskovsk field (Western Donbas, Ukraine), it was established that the highest tendency to slag formation is inherent to that coal, whose composition has a large amount of halite (NaCl). Which, during combustion of coal by first precipitates on cold surfaces in the form of a sticky solid film [11].

The generalization and critical analysis of mechanisms of slagging during combustion of raw materials of different origin with a high content of alkaline and alkali-earth metals were performed in the review [12]. The phenomenon of slag formation was determined as accumulation of molten ash on walls of a furnace unit, a gasifier or a boiler, which is very detrimental, as far as it reduces the rate of heat transfer, the combustion/gasification rate of carbon which did not manage to react, leads to emergency situations, high-temperature corrosion and, in some cases, explosion of superheaters.

In the review, the classification of fuels from the world fields was made according to groups (for coal of a low stage of metamorphism according to the main indices) and in comparison with other types of carbon raw materials (different types of biomass, anthracites). The 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 proposed. An example of the mechanism of slagging is shown in Fig. 1.

The mentioned study (literature review) [12] is distinguished by a broad coverage of world contemporary literature, determination of general factors of fuels which are currently used in the world and are promising in the future because of environmental requirements. This concerns the limited available resources and the need in divergence of a raw material base. Much attention was paid to the study on the viscosity of the molten ash and the impact of the features of mineral components in the fuels.

Despite a rich experimental material gathered by the authors, the main conclusion indicates that we still do not have enough knowledge on the laws of slagging and need new experimental data on different fields of energy coal. In view of these conclusions, the studies on the features of the mineral composition of Ukrainian salty coal and their influence on slagging of heating surfaces and corrosion are quite relevant.

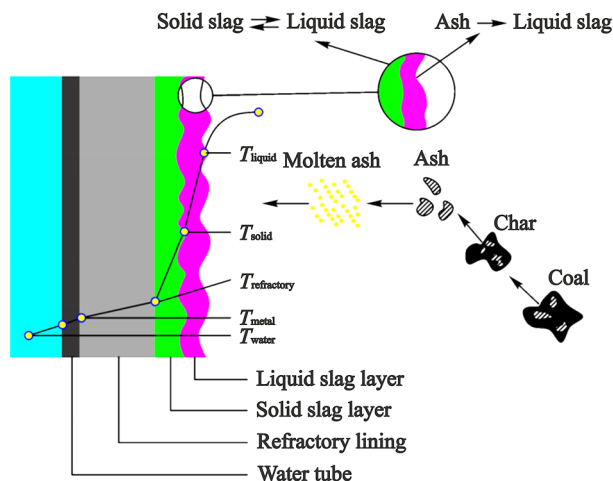


Fig. 1. Formation of slag and deposits inside the gasifier [12]

Domestic research works [13] showed that despite the close index of salinity (elevated ( $\geq 2\%$ ) content of  $\text{Na}_2\text{O}$  in the ash), salty coal significantly differs from each other by natural (native) mineral composition (even within one field). It was found out that halite is not always a prevalent compound among water-soluble components in coal minerals and a significant place belongs to sodium and calcium sulphate, as well as iron salts.

In the case of combustion of such coal, this fact will be essential, since the predicted formation of certain low-melting eutectics of mineral compounds will require special approaches to the preparation and organization of the process.

During the first attempts of combustion of natural salty coal at domestic coal fired TPPs without changing the conditions and power equipment, on heat exchange surfaces a thick layer of sticky and solid deposits was formed, which dramatically deteriorated heat exchange properties of working surfaces, and it was impossible to remove these deposits by conventional methods for cleaning. The same deposits were observed during combustion of solid and liquid fuels with a relatively high content of impurities having low melting and sublimation temperatures (some types of biomass, agro-industrial waste, etc.) [14].

At high temperatures developing in the boiler chamber, alkaline chlorides and some sulfates transfer into vapour phase with the following condensation on the walls of tubes in the region of reduced gas temperatures. On the formed sticky (or liquid) deposits, fly ash is mechanically precipitated. As a result of interaction of these substances with solid ash particles and some components of fuel combustion products ( $\text{SO}_2$ ,  $\text{O}_2$ ), various chemical transformations occur, which lead to sintering and formation of a dense layer of contaminations. In addition, after a short-term operation, under the slag, corrosion damage of the metal occurs [4].

Complex and multi-stage corrosion mechanism during combustion of raw materials with a high content of low-melting salts will be considered in more detail in a separate publication. Here it should be emphasized that the difficulties arising during combustion of ash fuels, are not associated directly with the absolute amount of ash in fuel. Thus, during combustion of fuel oil, in which the amount of mineral impurities does not exceed tenth fractions of one percent, the formation of dense deposits is also possible, which greatly complicates the normal operation of a boiler unit.

In the composition of mineral impurities of problem fuel, as a rule, low-melting substances may be contained [4]. They include alkaline metal oxides –  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  ( $t_m \approx 700^\circ\text{C}$ ), chlorides –  $\text{FeCl}_3$  ( $t_m \approx 670^\circ\text{C}$ ),  $\text{MgCl}_2$  ( $t_m \approx 700^\circ\text{C}$ ),  $\text{CaCl}_2$ ,  $\text{KCl}$  ( $t_m \approx 770^\circ\text{C}$ ),  $\text{NaCl}$  ( $t_m \approx 800^\circ\text{C}$ ) and some sulfates –  $\text{Na}_2\text{SO}_4$  ( $t_m \approx 880^\circ\text{C}$ ),  $\text{K}_2\text{SO}_4$  ( $t_m \approx 1070^\circ\text{C}$ ). Refractory mineral impurities of fuel are calcium sulfate  $\text{CaSO}_4$  ( $t_m \approx 1,400^\circ\text{C}$ ), oxides –  $\text{SiO}_2$  ( $t_m \approx 1,470^\circ\text{C}$ ),  $\text{Fe}_2\text{O}_3$  ( $t_m \approx 1,570^\circ\text{C}$ ),  $\text{Al}_2\text{O}_3$  ( $t_m \approx 2,015^\circ\text{C}$ ),

CaO ( $t_m \approx 2,570^\circ\text{C}$ ), MgO ( $t_m \approx 2,800^\circ\text{C}$ ), silicates – CaSiO<sub>3</sub> ( $t_m \approx 1,540^\circ\text{C}$ ), etc. The characteristic of ash in the boiler chamber depends on the ratio of basic and acidic (according to chemical properties) components included in the melt.

Many modern studies found out that not only salts of alkali metals predetermine slagging of surfaces during combustion of coal and biomass. Calcium and iron compounds play a similar role [15–17].

The authors [18] found a clear correlation between the ratio of sodium and iron content, the sum of silicon and aluminium and the level of slagging and fouling during combustion of high-alkaline coal:

1. For Na, at  $\text{Na}/(\text{Si} + \text{Al}) < 0.05$  – negligible fouling;  
 $\text{Na}/(\text{Si} + \text{Al}) > 0.05$  – significant or severe fouling.
2. For Fe, at  $\text{Fe}/(\text{Si} + \text{Al}) < 0.2$  – negligible slagging;  
 $\text{Fe}/(\text{Si} + \text{Al}) > 0.2$  – increased slagging.

It is noted that is possible to predict the behaviour of fuels regarding the tendency to slagging only if information on the detailed composition of minerals is available and provided, that a preliminary simulation of the properties of molten ash was carried out. A significant contribution to accumulation of experimental data on complications during combustion of coal with a high content of salts was made by the developments of Chinese scientists [15–18, 19]. Visual examples of the formation of ash deposits in the process of operation of boiler units during utilization of high-alkaline coal from Chinese fields are presented in Fig. 2 [18, 19], where the phenomenon of slagging and types of slag formations in various areas of metal surfaces of a boiler unit is shown.

Usually, during combustion of raw materials with a high content of calcium and alkali metals (as an example: Estonian slates, Kansk-Achinsk coal of the Russian Federation [7]) in the conditions of periodic cleaning, on heating surfaces, three-layer ash deposits are formed (according to the works by the Estonian heat engineering school – Epik I. I., etc., 1961). The first layer of ash deposits, which is located directly on the surface of tubes, is strongly associated with the metal. Next, a middle dense layer is located, atop of which a loose layer is formed. During vibration cleaning, blast cleaning and steam blowing, deposits on the surface of tubes and the layer under deposits are not removed, because they have a high strength.

During cleaning of the heating surface, a loose layer, which is located on the middle layer, is almost completely removed. In this case, different layers differ from each other by chemical and mineralogical composition.

Instead, the studies by Finnish scientists [10] show that deposits are formed by multilayer structures with porous inner and dense outer layers. In addition, the outer layer is homogenized. Compaction and chemical homogenization occurred by sintering of a liquid phase and migration of a liquid phase, caused by temperature gradient. It was observed that alkaline chlorides in a gas phase migrate in the direction towards lower temperatures. Compaction of deposits occurs mainly due to sintering of a liquid phase, resulting in the formation of a layer with almost eutectic composition.

Fig. 3 shows phase diagrams for two typical systems that form layered deposits and their image in the scanning electron microscope

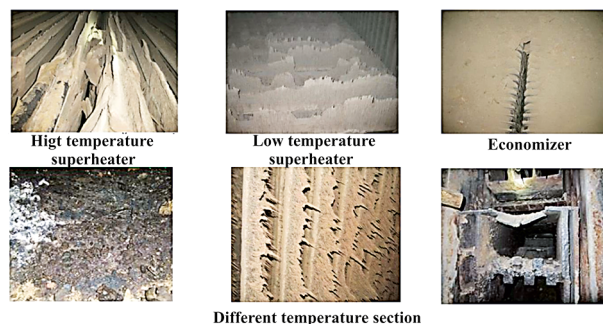


Fig. 2. Examples of strong slagging and fouling of heat exchange surfaces of the boiler [18]

microscope, which reflects the migration of phases in the region of supersolidus. The dashed line shows the initial composition of deposits. The eutectic region (A) is located at subsolidus temperatures (pre-solid), while the regions B and C are at supersolidus temperatures (very solid), which consist of a primary crystallized phase (B) (Na<sub>2</sub>SO<sub>4</sub>) and a liquid phase (C), which follows the line of a liquid state [10].

Modern research methods (X-Ray fluorescence (XRF), X-ray diffraction (XRD), SEM, etc.) revealed that in a high-alkali coal from the Xinjiang field (China) [19], which is very similar to Ukrainian salty coal from the Novomoskovsk field (Na<sub>2</sub>O = 4.0–10 % by weight), (CaO = 20–40 % by weight) in ash deposits rich in iron, prevailed compounds located in the radiation zone are magnetite and wollastonite (CaSiO<sub>3</sub>). They are predetermined by low melting temperatures of Fe/Ca – eutectics. In a convective intersection, the main ways of contamination of water tubes are evaporation of alkali metals, as well as their further condensation with the formation of Na<sub>2</sub>SO<sub>4</sub> and CaSO<sub>4</sub> sulfates. Deposition of ash for this coal, as is shown in [19], has grown rapidly already in the first 1.5 hours. The dominant phases in the growing layer of ash are slags of the composition Na<sub>2</sub>SO<sub>4</sub>, CaSO<sub>4</sub> and Ca–Al–Si – compounds.

The continuous interaction between a liquid phase and re-captured particles leads to the formation of new eutectic compounds containing anhydrite (CaSO<sub>4</sub>), tenardite (Na<sub>2</sub>SO<sub>4</sub>), gehlenite (Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>). In this case, the rate of decrease in the heat transfer at the initial stage of ash precipitation is from –0.26 to –0.28 %/min. The range of temperatures of ash precipitation in the Xinjiang coal varies from 790 to 1,050 °C. It is obvious that these results expand the idea of the main processes of slagging formed earlier (as for example, by Roddatis K. F., Dobrokhotov V. I., and others “Teploenergetika” 1981).

Similar mechanisms of eutectic formation processes with the participation of iron, sodium and calcium compounds are discussed in [20]. It was necessary to determine the reasons of slagging ash coolers of the CFB boiler of Starobeshivska TPP at using anthracite and coal sludge. Several reasons were found, one of which was the excess of Fe/(Si + Al) critical value of this parameter, at which increased slagging already occurs. The cal-

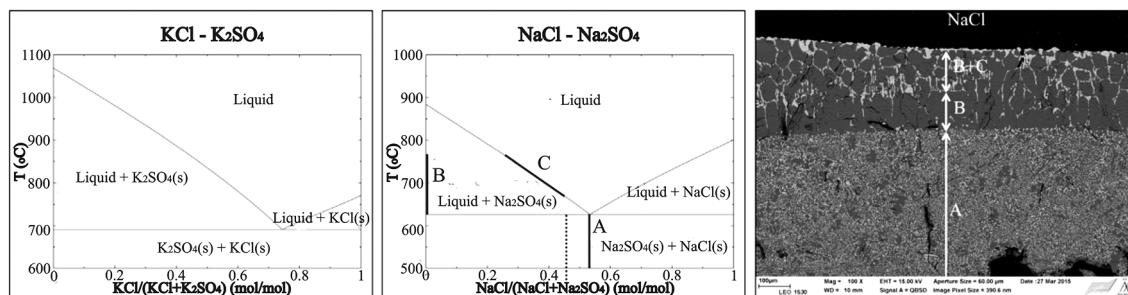


Fig. 3. Phase diagrams of KCl–K<sub>2</sub>SO<sub>4</sub> and NaCl–Na<sub>2</sub>SO<sub>4</sub> systems and their image in the scanning electron microscope (SEM) of reverse scattering [10]

calculation of such a criterion for two samples of coal proved that the value of this ratio of the mentioned elements is 1.8–2 times higher than the critical one (it is 0.02 [19]). X-ray phase analysis of coal showed that its mineral part consists of anhydrite  $\text{CaSO}_4$ , glauberite  $\text{Na}_2\text{Ca}(\text{SO}_4)_2$  and hematite  $\text{Fe}_2\text{O}_3$ , such compounds that readily form Na–Ca–Fe – eutectics and lead to slagging at different stages of boiler operation.

Based on the methods of chemical thermodynamics of multicomponent reacting systems [21], the distribution of the most low-melting components (potassium and sodium) in the combustion products of 15 types of coal was investigated. It was shown that accumulation of potassium and sodium in the products of coal combustion depends on the content and shape of location of these elements in the coal, the total composition of mineral components, ash content, as well as sulphur content in the initial coal. The results of thermodynamic studies are confirmed by the works by Chinese scientists [17], in which during combustion of salty coal, the probable mechanism of precipitation of alkali metals compounds in ash deposits is described (Fig. 4).

Analyzing the proposed mechanism of slagging, it should be noted that it does not take into account some compounds of iron and sulphur, widespread in fuel, as well as ignores the reactions with their participation. As was already shown, they are considered to be involved in the formation of multicomponent slag deposits [16–18, 22]. For example, during utilization of biomass and a blend of coal with biomass, slagging and fouling of heating surfaces tend to increase as a result of a growth in the ratio alkali/acids, alkali metal content and ratio  $\text{Fe}_2\text{O}_3/\text{CaO}$  [23].

A particular interest is paid to corrosion, which occurs in the contact zone of metal and slag deposits. Mostly, their composition is determined by mineral components in fuel, sulphur content and combustion conditions. A high-temperature corrosion of surfaces by compounds of such elements as sulphur, sodium, potassium and vanadium not only deteriorates the ecological indices of the boiler, but also causes destruction of tube walls. The mechanism of corrosion for coal, oil-fired boilers and boilers, where vegetable waste is combusted is similar: iron in a bound state is removed from the upper layer of the tube wall. The differences are predetermined by the content of low-melting components characteristic for each type of fuel. As a result, in different types of boilers chemical reactions with iron are different [24].

In coal boilers, the highest intensity of corrosion is observed in the range of temperatures 580–675 °C, where sulfates of alkali metals  $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4$  in the presence of sulphur compounds, for example,  $\text{SO}_3$ , interact with iron oxide, which covers the tube surface. As a result of reactions, liquid dual sulfates  $\text{Na}_3\text{Fe}(\text{SO}_4)_3$  or  $\text{K}_3\text{Fe}(\text{SO}_4)_3$  are formed, which leads to a gradual destruction of metal surfaces.

Numerous cases and stages of damage to heating surfaces during combustion of salty coal are discussed, where chlorides of alkali metals are considered to be the main cause of corrosion, although the mechanism of corrosion here is somewhat different (see below). Thus, during combustion of British coal

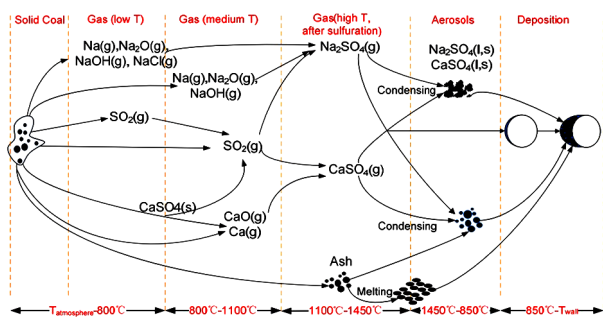


Fig. 4. Possible mechanism of ash deposition during combustion of coal with a high content of sodium and calcium [17]

with the content  $\text{Cl}^d = 0.36\%$ ,  $Q_i^r = 23.3$  MJ/kg, on the boiler of the 500 MW unit, within 20,000 hours, the corrosion rate of the primary stage of the secondary superheater (of austenitic steel) was 0.4 mm/year. According to the data of observations conducted by CEGB (Central Electricity Generating Board, England), corrosion of furnace walls was observed on coal fired boilers of all types, since the content of chlorine in coal in some cases exceeded 0.5 % and in average amounted to 0.25 % [25].

Based on the experience of units operating with the vapour parameters of 10 MPa with a reduced temperature of metal surface being about 370 °C, a linear dependence of corrosion on the content of chlorine in coal was established. In areas with an increased content of hydrogen chloride in flue gases, the corrosion rate of furnace tubes reached several millimetres per year. According to the data published in [9], at the content of chlorine in coal being 0.65 %, the corrosion rate of furnace tubes can reach the value of up to 8.0 mm/year.

In this case, the restoration of one damaged tube of the 500–600 MW unit costs 200 thousand pounds. The rate of corrosion of metal surfaces of the superheater depends on the temperature of gases and tubes. An important role in the corrosion process belongs to such factors as the appearance of zones with a restorative environment and high heat fluxes. In the 500 MW boiler of the Rateliff-on-Sour power plant [9], coal with a high calorific capacity  $Q_i^r = 23.3$  MJ/kg and a relatively low chlorine content of 0.36 % was combusted. At a calculation vapour temperature of 568 °C, the maximum temperature of metal wall reached 650 °C. After 20,000 hours of operation, it became noticeable that the outlet tube (of austenite) corrodes at a rate of 0.4 mm/year, which can lead to an accident already after 30,000 hours at estimated 100,000 hours for design operation of the boiler.

Due to many years of investigations, British scientists obtained integral dependences of corrosion rate of heating surfaces of boilers on the content of chlorine in coal, temperature of metal and gases, as well as the class of used steels [24]. The summarized results (Fig. 5) are of great practical value and are able to predict the course of the corrosion process during utilization of coal with different chlorine content.

From the data in the table (Fig. 5), it follows that at a temperature of gases above 1,000 °C and at a content of chlorine above 0.35 %, even for austenitic steels, corrosion becomes noticeable already at the temperature of walls being  $\geq 540$  °C. In the case of low-alloy ferritic steels, corrosion under similar conditions is noticeable at the content of chlorine being  $\geq 0.15\%$ . Under the conditions of a high temperature of gases and a wall temperature of  $\geq 650$  °C, catastrophic corrosion occurs even at a low chlorine concentration being  $< 0.3\%$ .

Production studies on the combustion of Australian brown coal with a higher chlorine content (this coal is much “saltier” than British) ( $Q_i^r = 10$  MJ/kg,  $\text{Cl}^d = 0.7\%$ ) provided even more specific results. It was found that with an increase in tempera-

Temperature °C	Average wall temperature °C	Low-alloy ferritic steels			High-alloy ferritic steels (up to 12 % Cr)			Austenitic steels (type 347, 321, 316, E1250)		
		more 0,35 % Cl	0,35- 0,15 % Cl	less 0,15 % Cl	more 0,35 % Cl	0,35- 0,15 % Cl	less 0,15 % Cl	more 0,35 % Cl	0,35- 0,15 % Cl	less 0,15 % Cl
975	540									
	580									
	620									
	660									
	700									
1050	540									
	580									
	620									
	660									
	700									
1150	540									
	580									
	620									
	660									
	700									

Fig. 5. Corrosion rate of boiler steels [24]

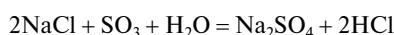
ture of the tube wall ( $t_w$ ) (steel Kh10CrNiNb189) from 550 to 600 °C, the corrosion rate 2.5 times increases at a given temperature of flue gases. However, at  $t_w = 600$  °C, an increase in the temperature of flue gases from 825 to 1,025 °C led to 2.25 times increase in the corrosion rate. Thus, for example, if at  $t_w = 550$  and  $T_f = 825$  °C, the corrosion rate is 0.16 mm/year, then at  $t_w = 600$  and  $T_f = 1,025$  °C, it will be close to 1 mm/year. As the temperature of gases grows, the corrosion rate increases according to the law close to parabolic [26].

As is known, chlorine is present in coal in two main forms: in the form of alkali metal chlorides or in the form of organochlorine compounds, which are destroyed by high-temperature fuel conversion. It is generally considered that the predominant compounds are salts – chlorides [27]. In the process of combustion, the transformation of fuel chlorine into highly-corrosive chlorine-containing components occurs, the main of which, as studies have shown, is hydrogen chloride.

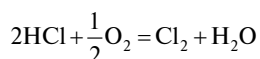
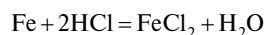
Since the early 70-s, Krause H. H. from the Bettel Institute (USA) has studied the problem of corrosion of heating surfaces in incineration plants. As is known, a significant share of garbage is waste of PVC materials. In [28], he summarized the gathered material. In particular, he proposed a mechanism of corrosion under the influence of chlorine-containing compounds. A visual scheme of the process and probable chemical reactions leading to the formation of chlorides and oxides of iron in the deposits are shown in Fig. 6.

A part of chlorides, such as NaCl, CaCl<sub>2</sub>, evaporates during combustion of raw materials and forms deposits directly from the torch. Corrosion begins in the process of conversion of chlorides in the deposits into sulfates under the influence of SO<sub>2</sub>, SO<sub>3</sub>, oxygen and water vapor.

In this case, near the metal surface hydrogen chloride HCl is formed



Hydrogen chloride can react with metal to form FeCl<sub>2</sub> or oxidize to molecular chlorine



In the article by Krause H. H. [28], it is noted that molecular chlorine unlike hydrogen chloride, was not detected in flue gases, but laboratory studies showed that a small amount of chlorine may be in the form of Cl<sub>2</sub> (obviously, under somewhat different conditions of the gaseous environment). It should be noted that molecular chlorine is much less reactive than hy-

drogen chloride, which reacts rapidly with metals at high temperatures, forming the corresponding chlorides and promoting the formation of oxides.

Based on the abovementioned, it can be concluded that hydrogen chloride has a leading role in a high-temperature corrosion during combustion of salty coal. As a result of sublimation of iron chlorides, on the surface of tubes, a porous oxide film is formed, which no longer has protective properties, which opens an access of new portions of aggressive components of flue gases to the metal.

An analysis of world scientific and practical sources indicates that the mechanisms of slagging and corrosion during the combustion of raw materials with a high salt content are basically clarified. But a general theory that would have predictive power does not yet exist. Each experimental work to determine the characteristics of a particular fuel source adds its contribution to the overall picture of the process and helps to solve practical problems.

**Original studies of the authors.** Taken into account the energy prospects of domestic salty coal, in order to determine the effect of chlorides of alkali and alkaline-earth metals on the formation of ash deposits and signs of corrosion in the processes of a high-temperature conversion, a series of experimental laboratory studies was conducted, involving core samples of coal from the Northern Donbas [29].

Quantitative weight analysis experimentally proved a significant excess in the mass of ash deposits on the metal surface during combustion (ashing) of native (initial) coal unlike during the same process for desalinated coal or some varieties of plant biomass [29].

The propagation of corrosion processes during combustion of salty coal from the Bohdanivske and Starobilske fields of the Northern Donbas was investigated experimentally. Thus, during combustion of the initial salty coal, exfoliated layers on the surface of the metal plate were visually detected, which was in contact with volatile products. Desalinated coal did not occur exfoliated layers during combustion. It turned out that the main compounds of separated exfoliated layers were iron oxides (75–85 % in total). The content of other compounds – iron sulfide (13–25 %) and NaCl (from 0 to 2 %) is associated with quantitative differences in the composition of samples of initial salty coal [29]. Probably, a simple aqueous extraction of salty coal according to the previously developed procedure significantly reduces slagging and corrosion of metal surfaces during combustion of such a coal.

**Purpose.** The goal of the experimental part of the new research is to determine the influence of components ratio on the composition of mineral compounds in ash residues, formed at the combustion of the blends from coals of different metamorphism and salinity.

**Methodology for research.** Considering the high energy (fuel) characteristics and the presence of a natural catalytic complex, one of the promising directions for the use of salted coal is its co-combustion with other coal, which has lower reactivity, a higher ash melting point and does not cause excessive slagging of the heating surfaces.

Two samples of coal with different salt content were selected for the experiment (Table 1). The first sample is salty coal (SC) of the Bohdanivske deposit with a high content of Na<sub>2</sub>O in ash ~7 % and chlorine in coal ~0.8 %. The second sample is lean unsalted coal (LC) (Na<sub>2</sub>O in ash ~0.7 %) from Kuzbass (RF) which is currently burned at TPPs of Ukraine and according to DSTU 4083-2002 is similar to Ukrainian coal of this brand by classification indicators.

Salty coal belongs to bituminous coal, has an average ash content, acceptable heat of combustion ~30.6 MJ/kg and high volatiles (more than 40 %). The main ash-forming components are oxides: silicon (~37 %), aluminium (~8 %), iron (~12 %), calcium (~15 %) and sodium (~6.8 %). Lean coal ash is characterized by a low content of oxides of alkali and alkaline earth metals (in the total amount of 7.3 %) and iron,

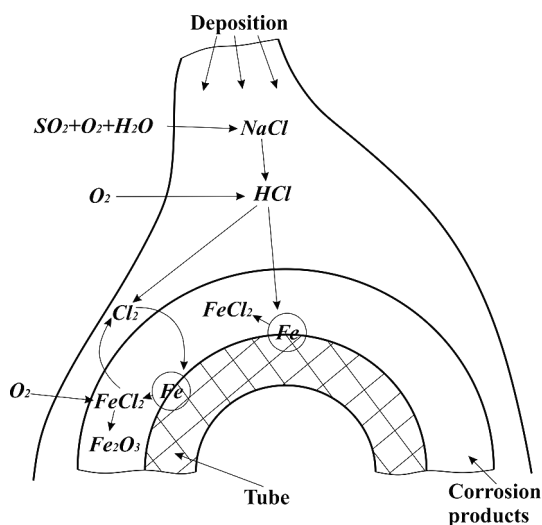


Fig. 6. Schematic representation of successive chemical reactions in chloride corrosion of tubes, according to [28]

Table 1

Characteristics of salty and lean coal

Sample	Coal types	Technical analysis, %			Na <sub>2</sub> O in ash, %	CI, %
		W <sup>a</sup>	V <sup>daf</sup>	A <sup>d</sup>		
Salty Coal	Bituminous coal	12.7	42.8	5.07	6.62–7.22	0.8
Unsalted Coal	Semi-anthracite (lean coal)	1.1	17.9	12.2	0.7	0.04

at the same time high content of aluminium and silicon oxides (26.7 and 54.0 % respectively).

The coal samples were separately crushed to a fraction of 0–0.2 mm. These samples of salty and lean coal separately, as well as their blends weighing 3 g in rectangular vessels were subjected to heat treatment. Heating mode – temperature rise for 1 hour from 20 to 850 °C, then two hours of isothermal holding at 850 °C until complete ashing.

The ash samples were analysed using DRON-4M diffractometer (in the radiation of cobalt or copper anode). The record of powder diffractograms was made in the range of angles  $2\theta$  from 15 to 60° with a step of 0.04°. Determination of inter-layer distances of minerals was made with an accuracy of 0.002 nm. Semi-quantitative phase analysis of diffractograms was performed using MATCH\* software.

**Results.** With the participation of salty coal from the Northern Donbas and lean unsalted coal from Kuzbass (Russia), artificial blends of different component composition (50 : 50, 40 : 60, 60 : 40) were created and combusted in a muffle furnace.

It was found that the mineral composition of ash residues of separately lean and salty bituminous coal has some common features. Namely, oxides of silicon (SiO<sub>2</sub>), oxides of iron (Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>) and aluminosilicate (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>) are determined by clear reflexes in the ashes of both samples, but in different ratios.

Considered separately, in the composition of salty coal ash were found a significant amount of simple oxides, anhydrite (CaSO<sub>4</sub>) and aluminosilicate (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>) and much smaller amount of silicates (CaSiO<sub>3</sub>, Mg<sub>2</sub>SiO<sub>4</sub>) and sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>). Regarding the phases that include Na, two main groups – silicates (Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub>) and sodium aluminate (Na<sub>2</sub>Al<sub>2</sub>O<sub>4</sub>) can be distinguished. Na in a small amount is included in sodium aluminosilicate (NaAlSiO<sub>4</sub>) and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>). A total of 12 main mineral phases have been identified.

The composition of lean coal ash (chosen to create a promising safe fuel) is characterized by traditional silicon and aluminum oxides (reflexes of the latter have the highest intensity), moderate volume of iron oxide (Fe<sub>2</sub>O<sub>3</sub>), simple (Al<sub>2</sub>SiO<sub>5</sub>, MgSiO<sub>3</sub>) and complex silicates (KAl<sub>3</sub>Si<sub>3</sub>O<sub>11</sub>, Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>). A total of 9 main mineral phases have been identified. Sodium compounds under the experimental conditions and recording diffractograms in the ash of lean coal were not detected.

Depending on the ratio of blended fuels in the ash, the appearance of new mineral phases is observed, which are not inherent in the ashes of the initial samples.

For ash residues of blends SC : LC = 50 : 50, it was found that in addition to the main intense reflexes being characteristic of any ash which correspond to the mineral phases belonging to the group of oxides – SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>, simple calcium (CaSiO<sub>3</sub>, Ca<sub>2</sub>SiO<sub>4</sub>) and aluminium (Al<sub>2</sub>SiO<sub>5</sub>) silicates, as well as complex aluminosilicates – KAlSi<sub>3</sub>O<sub>8</sub>, Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> were detected in significant quantities. And sulfates Ca and Mg were detected in a small amount. A feature of the ash from the blends were new mineral phases with the participation of iron – Fe<sub>2</sub>SiO<sub>4</sub>, Ca<sub>3</sub>Fe<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub> have been established. Based on the intensity of characteristic reflexes, in comparison with individual salty coals, in the ash residue of the blend, a much lower volume of silicate (Na<sub>2</sub>SiO<sub>4</sub>) and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) is observed. Instead, reflexes of more complex and refractory minerals (Ta-

ble 2) – nephelines (NaAlSiO<sub>4</sub>, bertollids of type KNa<sub>3</sub>(AlSiO<sub>4</sub>)<sub>4</sub>, K<sub>0.86</sub>Na<sub>0.16</sub>AlSi<sub>2</sub>O<sub>6</sub>) and ultramarines (Na<sub>7</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>S<sub>3</sub>), as well as other new compounds – combeite (NaCaSiO<sub>4</sub>) and sodium aluminates (NaAlO<sub>2</sub> and its dimer Na<sub>2</sub>Al<sub>2</sub>O<sub>4</sub>) were found.

In the blend, where salty coal predominates (SC : LC = 60 : 40), along with a significant amount of minerals Al and Si, quite significant reflexes are noticeable, corresponding to the minerals, which include Fe and Ca – Fe<sub>2</sub>SiO<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, CaFeSiO<sub>4</sub>, CaFe<sub>2</sub>O<sub>4</sub>, CaO, CaSiO<sub>3</sub>, CaSi<sub>2</sub>O<sub>5</sub> (Fig. 7, a, main reflexes – 2.91 Å; 2.75 Å; 2.56 Å; 2.35 Å; 1.71 Å; 1.46 Å).

At the same time, in the blend where lean coal predominates (SC : LC = 40 : 60), the main reflexes correspond to silicates and aluminosilicates – SiO<sub>2</sub>, Al<sub>2</sub>SiO<sub>5</sub> (Fig. 7, b – 3.54 Å 3.4 Å; 2.23 Å; 1.84 Å; 1.5 Å; 1.39 Å), and those reflexes, that determine the compounds Fe and Ca, have a much lower intensity.

In our opinion, it is important to note the results regarding mineral phases of the blended ash to which sodium is included. As compared to the composition of the ash of the initial salty coal, in the ash residue of its blend with lean coal, a significantly lower content of sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) is observed. Instead, more varieties of complex and refractory minerals like nepheline group (NaAlSiO<sub>4</sub>, KNa<sub>3</sub>(AlSiO<sub>4</sub>)<sub>4</sub>), ultramarine (Na<sub>7</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>S<sub>3</sub>), as well as other new complex compounds: combeite (NaCaSiO<sub>4</sub>) and sodium aluminate (NaAlO<sub>2</sub>, Na<sub>2</sub>Al<sub>2</sub>O<sub>4</sub>) are formed. It should be noted that depending on the ratio of salty and lean coal, the composition and structure of formed compounds is changed. Thus, in the blend, where lean coal predominates, in addition to the abovementioned minerals, varieties of nephelines (K<sub>0.86</sub>Na<sub>0.16</sub>AlSi<sub>2</sub>O<sub>6</sub>; (Si<sub>4.1</sub>Al<sub>1.9</sub>)Na<sub>1.86</sub>O<sub>12</sub>; NaAlSi<sub>2</sub>O<sub>6</sub>) were found, whose composition includes a lower percentage of Na than the blend, where salty coal predominates. In the case of higher salt content, the situation is reversed, because in the ash enriched with salty coal, minerals with a higher percentage of Na (compounds Na<sub>2</sub>AlSiO<sub>3</sub> and Na<sub>8</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>SO<sub>4</sub>) were found. Such formations are called bertollids. They represent non-stoichiometric compounds, which exist not in the form of a molecule, but as a phase (i. e. chemically bound huge aggregate of atoms) [30]. As was shown by our experiment, the composition of such a phase depends on the mineral composition of initial components and their ratio. The main factor that determines the formation of these compounds is a sufficient amount of Al and Si in the composition of lean coal.

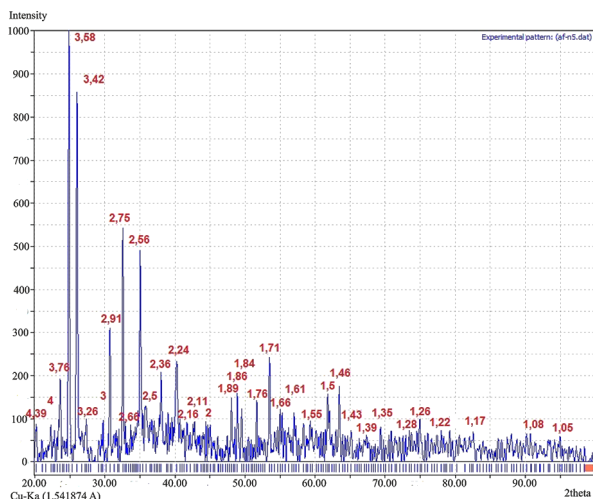
The results of the literature review [31, 32] and our initial studies [29] evidence, that namely aluminium and silicon oxides reveal Na-capturing capability (capable to “capture” alkali metal). In our case, they are supplied namely by a large amount of aluminium oxide and by a sufficient amount of silicon oxide of the initial blend – additionally due to lean coal. A similar mechanism of “absorption”, “capture” can be imagined in the case of alkaline earth metal – calcium and iron. These elements in the blends also form simple and complex silicates CaFeSiO<sub>4</sub>, CaFe<sub>2</sub>O<sub>4</sub>, CaSiO<sub>3</sub>, CaSi<sub>2</sub>O<sub>5</sub>) during ashing.

The results obtained on the formation of nephelines, ultramarines and other complex minerals are confirmed by the stud-

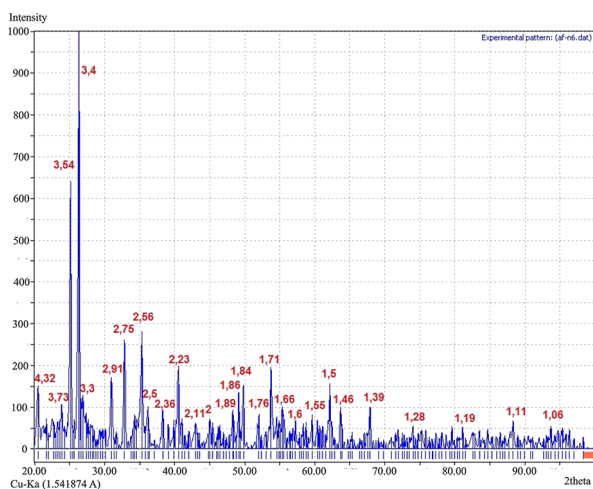
Table 2

Melting point of minerals which contain Na

Mineral	Formula	T <sub>meltr</sub> , °C
Sodium sulphate (Thenardite)	Na <sub>2</sub> SO <sub>4</sub>	883
Sodium silicate	Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> Na <sub>2</sub> SiO <sub>3</sub> , Na <sub>2</sub> SiO <sub>4</sub> , Na <sub>2</sub> Si <sub>4</sub> O <sub>9</sub>	874–1120
Ultramarine	Na <sub>7</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> S <sub>3</sub>	1000–1200
Nepheline	NaAlSiO <sub>4</sub> KNa <sub>3</sub> (AlSiO <sub>4</sub> ) <sub>4</sub>	1526
Sodium aluminate	Na <sub>2</sub> Al <sub>2</sub> O <sub>4</sub> , NaAlO <sub>2</sub>	1650



a



b

Fig. 7. Diffraction patterns of mixtures ash of salty and lean coal: a – blend SC : LC = 40 : 60; b – blend SC : LC = 60 : 40

ies by scientists from other countries. Thus, in [31, 32] the following scheme of formation of similar compounds was described:

1. Nepheline:

- 1)  $2\text{Al}_2\text{SiO}_5 + \text{Na}_2\text{SO}_4 \rightarrow 2\text{NaAlSiO}_4 + \text{Al}_2\text{O}_3 + \text{SO}_3$
- 2)  $\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 2\text{NaAlSiO}_4 + \text{SO}_3$
- 3)  $\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 4\text{SiO}_2 \rightarrow 2\text{NaAlSi}_2\text{O}_6 + \text{SO}_3$
- 4)  $3\text{NaCl} + \text{KCl} + 4\text{SiO}_2 + 2\text{Al}_2\text{O}_3 + 2\text{H}_2\text{O} \rightarrow \text{KNa}_3(\text{AlSiO}_4)_4 + 4\text{HCl}$

2. Ultramarine:

- 1)  $6\text{NaAlSiO}_4 + \text{Na}_2\text{SO}_4 \rightarrow \text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$

3. Sodium aluminate:

- 1)  $\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{Al}_2\text{O}_4$
- 2)  $2\text{NaCl} + \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 2\text{HCl}$
- 3)  $\text{Na}_2\text{SO}_4 + \text{Al}_2\text{O}_3 \rightarrow 2\text{NaAlO}_2 + \text{SO}_3$

Similar reactions can be imagined for other important elements in the slagging process:

- 1)  $2\text{CaSO}_4 + \text{Fe}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 2\text{CaFeSiO}_4 + 2\text{SO}_2$
- 2)  $\text{CaSO}_4 + 2\text{SiO}_2 \rightarrow \text{CaSi}_2\text{O}_3 + \text{SO}_3$
- 3)  $3\text{CaSO}_4 + \text{Al}_2\text{O}_3 + 3\text{SiO}_2 \rightarrow \text{Ca}_3\text{Al}_2(\text{SiO}_4)_3 + 3\text{SO}_3$
- 4)  $3\text{CaO} + \text{Al}_2\text{O}_3 + 3\text{SiO}_2 \rightarrow \text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$

An approximate evaluation of technological and power indices of coal blends (50 : 50) demonstrates that the ash content of fuel will amount to 8–11 % when the content of chlorine in the blend will be up to 0.32 % and sodium oxide in the ash will be less than 1.3 %. The Na/(Si + Al) ratio will not exceed the critical value of 0.05, and the value of Fe/(Si + Al) will be less than the critical 0.2. This content of impurities is acceptable, as

far as it does not interfere with a stable combustion of the blend. The volatile substances will amount to about 28–30 %, indicating a sufficient reactive capacity of the formed composite fuel.

The mentioned experimental data and our previous developments [29, 33] indicate the real ways for utilization of alternative fuels and expanding the fuel base of those countries of the world which have powerful coal deposits with a significant content of alkaline and alkali-earth metals.

**Conclusions.**

1. The review of modern scientific publications shows that despite a “carbon-free” trend in the global power engineering, power engineers and scientists have a stable interest to alternative coal fuels. But such fuels are featured by the mineral composition, which at present prevent their accident-free use. The most intense studies on fuels with a high content of salts are performed in China.

2. For Ukraine, the problem of diversification of the fuel base of the power industry remains relevant, this requires a detailed study on domestic power resources, including salty coal from the Northern Donbas.

3. The results of the experimental determination of peculiarities of minerals composition and their influence on the process of slagging and corrosion for the fields of SC from the Northern Donbas indicate the real ways of expanding the fuel base of both in Ukraine and in those countries of the world which have powerful coal fields with a significant content of alkaline, iron and alkali-earth metals.

4. The next steps are advanced studies on mineral resources of Ukraine in the directions of finding new promising compositions and cheap economically and environmentally acceptable additives in order to eliminate the problems of combustion of raw materials with an increased content of salts.

**References.**

1. *Energy Strategy of Ukraine for the period up to 2035 “Security, Energy Efficiency, Competitiveness”* (n.d.). Retrieved from [https://razumkov.org.ua/uploads/article/2018\\_Energy\\_Strategy\\_2035.pdf](https://razumkov.org.ua/uploads/article/2018_Energy_Strategy_2035.pdf).
2. Ivanova, A. V. (2020). High-chlorine coal as a deferred demand product. *Geological Journal*, 4(373), 34–42. <https://doi.org/10.30836/igs.1025-6814.2020.4.206734>.
3. Chernyavsky, M. V., Provalov, O. Yu., Kosyachkov, O., & Bestseny, I. V. (2021). Scientific bases, experience of production and combustion of coal mixtures at thermal power plants of Ukraine. *Procedia Environmental Science Engineering and Management*, (8), 23–31.
4. Gavrilov, A. F., & Malkin, B. M. (1980). *Pollution and cleaning of heating surfaces of boiler plants*. Moscow: Energiya. Retrieved from <https://de.ua1lib.org/book/2450607/cee44b>.
5. Beletskyy, V.S., Pogidaev, S.D., Kheloufi, A., & Sergeev, P.V. (1998). *Perspectives of development salty coals of Ukraine*. Donetsk: Don. STU. Retrieved from <https://www.donmining.info/2018/11/perspektivy-osvoeniya-solennykh-ugly-ukrainyi.html>.
6. Dunaevska, N.I., Korchevoj, Yu. P., Tuz, V.O., & Neilo, R.V. (2011). Ukraine’s salty coal. State and ways of using. *Energy: economics, technology, ecology*, (1), 16–22.
7. Ots, A.A. (1977). *Processes in steam generators during combustion of shales and Kansk-Achinsk coals*. Moscow: Energiya.
8. Cutler, A. J. B., Halstead, W. D., & Laxtone, I. W. (1971). The Role of Chloride in the Corrosion Caused by Flue Gases and Their Deposits. *Transactions, Series A*, (3), 105–116. <https://doi.org/10.1115/1.3445580>.
9. Lees, D. G., & Whitehead, M. E. (1983). Microanalysis of Scales and deposits Formed on Corroding Furnace Tubes in Coal Fired Boilers. *Corrosion Resistant Materials for Coal Conversion Systems, London – New-York, Conference*, 63–86.
10. Niemi, J., Lindberg, D., Engblom, M., & Hupa, M. (2017). Simultaneous melt and vapor induced ash deposit aging mechanisms – Mathematical model and experimental observations. *Chemical Engineering Science*, (173), 196–207. <https://doi.org/10.1016/j.ces.2017.07.041>.
11. Ershov, Yu. B., Meshcheryakov, V. G., & Enyakin, Yu. P. (1992). Formation of Hydrogen Chloride in Pulverized Coal Flare During Combustion of Coal with High Content of Chlorine. *Thermal Engineering*, 39(7), 61–64.
12. Alam, M. T., Dai, B., Wu, X., Hoadley, A., & Zhang, L. (2020). A critical review of ash slagging mechanisms and viscosity measurement for low-rank coal and bio-slugs. *Frontiers in Energy*, 15, 46–67. <https://doi.org/10.1007/s11708-020-0807-8>.

13. Fateyev, A. I., Shendrik, T. G., Polishchuk, S. S., & Dunayevska, N. I. (2018). The energy technological background of involving salty coals into energy balance of Ukraine. I. Composition of water extracts and the prospects for their utilization. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu*, (6), 40-47. <https://doi.org/10.29202/nvngu/2018/8>.
14. Baxter, L. L. (1993). Ash deposition during biomass and coal combustion: a mechanistic approach. *Biomass and Bioenergy*, 4(2), 85-102. [https://doi.org/10.1016/0961-9534\(93\)90031-X](https://doi.org/10.1016/0961-9534(93)90031-X).
15. Zhang, X., Zhang, H., & Na, Y. (2015). Transformation of Sodium during the Ashing of Zhundong Coal. *Procedia Engineering*, 102, 305-314. <https://doi.org/10.1016/j.proeng.2015.01.147>.
16. Song, G., Qi, X., Yang, S., & Yang, Z. (2018). Investigation of ash deposition and corrosion during circulating fluidized bed combustion of high-sodium, high-chlorine Xinjiang lignite. *Fuel*, 214, 207-214. <https://doi.org/10.1016/j.fuel.2017.11.011>.
17. Wang, X., Xu, Z., Wei, B., Zhang, L., Tan, H., Yang, T., ..., & Duić, N. (2015). The ash deposition mechanism in boilers burning Zhundong coal with high contents of sodium and calcium: A study from ash evaporating to condensing. *Applied Thermal Engineering*, 80, 150-159. <https://doi.org/10.1016/j.applthermaleng.2015.01.051>.
18. Yu, D., Wu, J., Yu, X., Lei, Y., & Xu, M. (2017). On cofiring as a strategy to mitigate ash deposition during combustion of a high-alkali Xinjiang coal. *8th International Conference on Clean Coal Technologies*, Cagliari, Italy, 8-12, May 2017. Retrieved from <https://www.sustainable-carbon.org/workshop/cct-2017>.
19. Wu, X., Zhang, X., Yan, K., Chen, N., Zhang, J., Xu, X., ..., & Zhang, L. (2016). Ash deposition and slagging behavior of Chinese Xinjiang high-alkali coal in 3 MW<sub>th</sub> pilot-scale combustion test. *Fuel*, 181, 1191-1202. <https://doi.org/10.1016/j.fuel.2016.03.069>.
20. Shendrik, T. G., Simonova, V. V., & Dedovets, D. I. (2010). Reasons for furnace ash coolers slagging of CFB boiler Starobashevo HPS at burning anthracite culm and slurry. *Ecology and Industry*, (3), 64-68.
21. Lebedeva, L. N., Kortsenshtein, N. M., & Samuilov, E. V. (2014). Thermodynamic assessment of the possibility of emission of submicron particles in the process of coal combustion. *Thermal Engineering*, (61), 911-916. <https://doi.org/10.1134/S0040601514120052>.
22. Ruan, R., Tan, H., Wang, X., Li, Y., Li, S., Hu, Z., ..., & Yang, T. (2018). Characteristics of fine particulate matter formation during combustion of lignite riched in AAEM (alkali and alkaline earth metals) and sulfur. *Fuel*, 211, 206-213. <https://doi.org/10.1016/j.fuel.2017.08.114>.
23. Wieck-Hansen, K., Overgaard, P., & Larsen, O. H. (2000). Cofiring coal and straw in a 150 MWe power boiler experiences. *Biomass and Bioenergy*, 19(6), 395-409. [https://doi.org/10.1016/S0961-9534\(00\)00051-9](https://doi.org/10.1016/S0961-9534(00)00051-9).
24. Baker, D. W. (1975). The Control of High Temperature Fireside Corrosion. *CEGB report*, 281-302.
25. Weadowcroft, D. B. (1988). An Introduction to Fireside Corrosion Experience in the Central Electricity Generating Board. *Materials and Corrosion*, (39), 45-48. <https://doi.org/10.1002/maco.19880390203>.
26. Brencker, H., & Swoboda, E. (1985). Problem bei der Verfeinerung sairhalltinger Braun kohlen [in German]. *VGB Kraftwerkstechnik*, (5), 487-498.
27. Gluskoter, H. J., & Rees, O. W. (1964). Chlorine in Illinois coal. *Illinois State Geological Survey Circular*, 372. Retrieved from <https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.579.79&rep=rep1&type=pdf>.
28. Krause, H. H. (1986). High Temperature Corrosion Problems in Waste Incineration Systems. *Journal Materials for Energy Systems*, (7), 322-332. <https://doi.org/10.1007/BF02833571>.
29. Shendrik, T., Dunayevska, N., Tsaryuk, A., Yelahn, V., & Fateyev, A. (2020). Experimental development of approaches to reduce the slagging and corrosive activity of salty coal. *Eastern European Magazine of Advanced Technologies*, 6(108), 124-133. <https://doi.org/10.15587/1729-4061.2020.217585>.
30. Zhang, J.-L., & Hong, G.-Y. (2017). Nonstoichiometric Compounds. In R. Xu, & Y. Xu (Eds.). *Modern Inorganic Synthetic Chemistry*, (pp. 329-354). <https://doi.org/10.1016/B978-0-444-63591-4.00013-6>.
31. Wei, B., Wang, X., Tan, H., Zhang, L., Wang, Y., & Wang, Z. (2016). Effect of silicon-aluminum additives on ash fusion and ash mineral conversion of Xinjiang high-sodium coal. *Fuel*, 181, 1224-1229. <https://doi.org/10.1016/j.fuel.2016.02.072>.
32. George, S. M., Haycock, P. W., & Ormerod, R. M. (2018). The Mechanism of Corrosion of Aluminium Zirconium Silicate (AZS) material in the Float Glass Furnace Regenerator. *Journal of The European Ceramic Society*, 38(4), 2202-2209. <https://doi.org/10.1016/j.jeurceramsoc.2017.12.006>.
33. Fateyev, A. I., Krut, O. A., Dunaievskaya, N. I., & Nekhamin, M. M. (2016). *Method of salty coal enrichment*. Ukrainian Patent No. 116778 UA.

## Явища та механізми шлакування й корозії при енергетичному використанні вугілля з високим вмістом солей

Т. Г. Шендрік<sup>1</sup>, Н. І. Дунаєвська<sup>2</sup>, А. І. Фатєєв<sup>2</sup>,  
А. К. Царюк<sup>3</sup>, В. П. Єлагін<sup>3</sup>

1 – Інститут фізико-органічної хімії і вуглехімії імені Л.М. Литвиненка НАН України, м. Київ, Україна, e-mail: [shendrikt@gmail.com](mailto:shendrikt@gmail.com)

2 – Інститут теплоенергетичних технологій НАН України, м. Київ, Україна

3 – Інститут електрозварювання імені Є.О. Патона НАН України, м. Київ, Україна

**Мета.** Визначення основних механізмів шлакування й корозії поверхонь нагріву при використанні паливної сировини з високим вмістом лужних і лужноземельних металів. Експериментальне визначення мінеральних фаз зольних залишків спалювання композиційної сировини за участі солоного вугілля та впливу компонентного складу на утворення тугоплавких сполук.

**Методика.** Критичний аналіз та узагальнення досягнень щодо розроблених теорій шлакування й корозії поверхонь при спалюванні проблемної вуглецевої сировини (солоного вугілля (СВ), біомаси, деяких відходів тощо). Визначення основних підходів до проблеми використання вугілля, що має високий фактор забруднення. Вибір об'єктів експериментального дослідження композиційної сировини, що включає вугілля різного метаморфізму й солоності. Із використанням рентгенофазового аналізу (РФА) ідентифікація мінералів зольних залишків окремих палив та їх сумішей. Напівкількісний фазовий аналіз дифрактограм із використанням програмного забезпечення MATCH.

**Результати.** Висвітлені сучасні погляди на причини шлакування й корозійні процеси при спалюванні палива з високим вмістом солей. Визначено, що процес інтенсивного шлакування пов'язаний з певним співвідношенням сполук натрію, кальцію та заліза. Експериментально встановлено склад і особливості мінеральних фаз зольних залишків композиційного палива за участі солоного вугілля. Визначено вплив вмісту компонентів палива на формування певних мінеральних фаз сумішевої золи.

**Наукова новизна.** Уперше досліджені перспективи використання двокомпонентного сумішевого палива за участі українського солоного вугілля. Виконано аналіз мінералів зольних залишків солоного вугілля та його сумішей. Визначено, що в золі солоного вугілля Богданівського родовища Північного Донбасу основна частина Na перебуває у вигляді сульфатів і силікатів. Уперше встановлено склад і шляхи утворення нових тугоплавких мінеральних сполук у золі, що сформувалася при спалюванні композиційного палива з вугілля різного метаморфізму й солоності.

**Практична значимість.** На підставі аналізу літературних джерел і проведених досліджень визначена залежність складу золи від мінералів вихідного палива та від співвідношення різних компонентів у суміші. Запропонований підхід має прогностичну силу, оскільки дає можливість передбачати формування основних тугоплавких зольних мінералів. Показана доцільність і перспективність залучення солоного вугілля до паливної бази України як компонента сумішевих палив.

**Ключові слова:** солоне вугілля, спалювання, шлакування, корозія поверхонь, суміш, мінерали золи

The manuscript was submitted 03.12.21.