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Saline Coals of the Ukraine

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Abstract—An original concept of salinization of coals at the peat bog generation stage is substantiated on the basis of on new data. The distribution of saline coals within coal and hydrocarbon basins has been revealed to be wider than it was previously assumed. The degree of salt enrichment of organic matter in coal is related to paleogeographic formation conditions of peat bogs that facilitated the penetration of sea waters (under conditions of paralic basins) or NaCl-rich solutions (related to wash-out of halogenic formations) into the coals. The initial salinization degree does not remain constant, because it is intimately related to superimposed processes leading to the desalinization of coals. The desalinization is controlled by the degree of coalification and realized under favorable tectonic and hydrogeological conditions. The paper presents a review of the current state of the elaboration of techniques for saline coal utilization that must meet requirements of economic and multipurpose utilization of raw material and environment protection.

In terms of the principal qualitative parameters and reserves, saline coals represent the most promising and valuable energetic raw material among the so-called low-grade fuels. However, utilization of these coals presents a considerable problem, since high Na and Cl contents in them lead to slagging and corrosion of the heating surface of boiler during their combustion. According to the widely accepted criteria of salinity reviewed in (Ivanova and Krivega, 1985), coals with a Na_2O content of more than 0.5% on a whole coal basis (or more than 2% on a coal ash basis) are referred to as saline varieties. According to later investigations (Kler *et al.*, 1988), coals with the K^+/Na^+ ratio < 1 are assigned to the saline type regardless of the absolute contents of these elements (this is valid for coals with the ash content of no more than 25%).

Saline coalfields are known in many countries of the world, such as Austria, Great Britain, Germany, Poland, Czechia, Russia, the United States, Australia, and others. According to (Zborshchik *et al.*, 1998), their demonstrated reserves in the Ukraine amount to more than 25 Gt. They are mainly concentrated within the western part and, to a lesser degree, northern part of the Donets Basin (hereafter, Donbas), e.g., lignites of the Petrikovka coalfield and high-volatile B bituminous (hvBb) coals of the Novomoskovsk coalfield, Starobel'sk coal-bearing area, and Millerovo coal-bearing district. Coals of the Novomoskovsk field in western Donbas contain nearly 1% Na_2O on a whole coal basis at the ash content of 10%. Coals of northern Donbas are less saline and locally distributed. However, both coals are characterized by very intense slagging. Qualitative characteristics of coals in the western and northern parts of the Donets Basin, Russia, and abroad, are given in (Ivanova and Krivega, 1985).

Further investigations have demonstrated that saline coals are distributed in the Ukraine significantly wider than was previously assumed. The presence of saline coals has been revealed in the Dnepr–Donets Depression (DDD), folded Donbas, Lviv–Volyn Basin (LVB), and Dobrudzha Foredeep (DF). However, the investigations carried out are insufficient for an unambiguous estimation of their real distribution scales.

Despite the domination of the concept of postdiagenetic salinization of coals, the author of their work proposed a concept of their formation at the sedimentary and diagenetic stages. This conclusion is based on results of the study of geological and hydrogeological constraints and regularities in the distribution of saline coals, the facies setting of peat accumulation, and their geochemical and petrographic features (Ivanova, 1983a, Ivanova and Krivega, 1985). The degree of NaCl-enrichment of organic matter is governed by paleogeographic conditions of peat accumulation that regulate the penetration of sea waters (in paralic formations) or NaCl-rich solutions (related to washout of halogenic formations or volcanic activity) into peat deposits. The formation of saline coals at the stage of peat bog generation is confirmed by lithological–geochemical data on coal-hosting rocks in several sections of western Donbas (Radzivill *et al.*, 1990) and X-ray structural data coals from the Novomoskovsk coalfield (Kovalev *et al.*, 1989).

The initial salinization degree does not remain constant and depends on the subsequent superimposed processes (metamorphism, tectonics, and hydrogeologic activity) that result in various degrees of the desalinization of coals. Metamorphism is the major cause of desalinization. It facilitates the carbonization of organic matter and removal of chemical admixtures with pore waters and splitting functional groups. The specific behavior of saline coals during regional metamorphism is determined by the desalinization versus tectonics relationship that control variations in physical and rheologic properties of the coals, formation of their

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porosity and jointing, i.e., conduits for metamorphic products. An important role belongs to the hydrogeological regime that provides the removal of metamorphic products under conditions of open structures or hampers this process under stagnant conditions.

According to proponents of the concept of postdiagenetic coal salinization (Kler *et al.*, 1987; Pozhidaev *et al.*, 1988; and others), the newly formed coals are enriched in NaCl during the percolation of saline solutions in coal beds along cracks. Therefore, only weakly metamorphosed coals (lignites and hvBb coals) with high sorption properties and permeability can be saline. However, this is not consistent with reality: strongly metamorphosed saline coals are encountered in several foreign coalfields reviewed in (Ivanova and Krivega, 1985) and coal-bearing basins of the Ukraine described below.

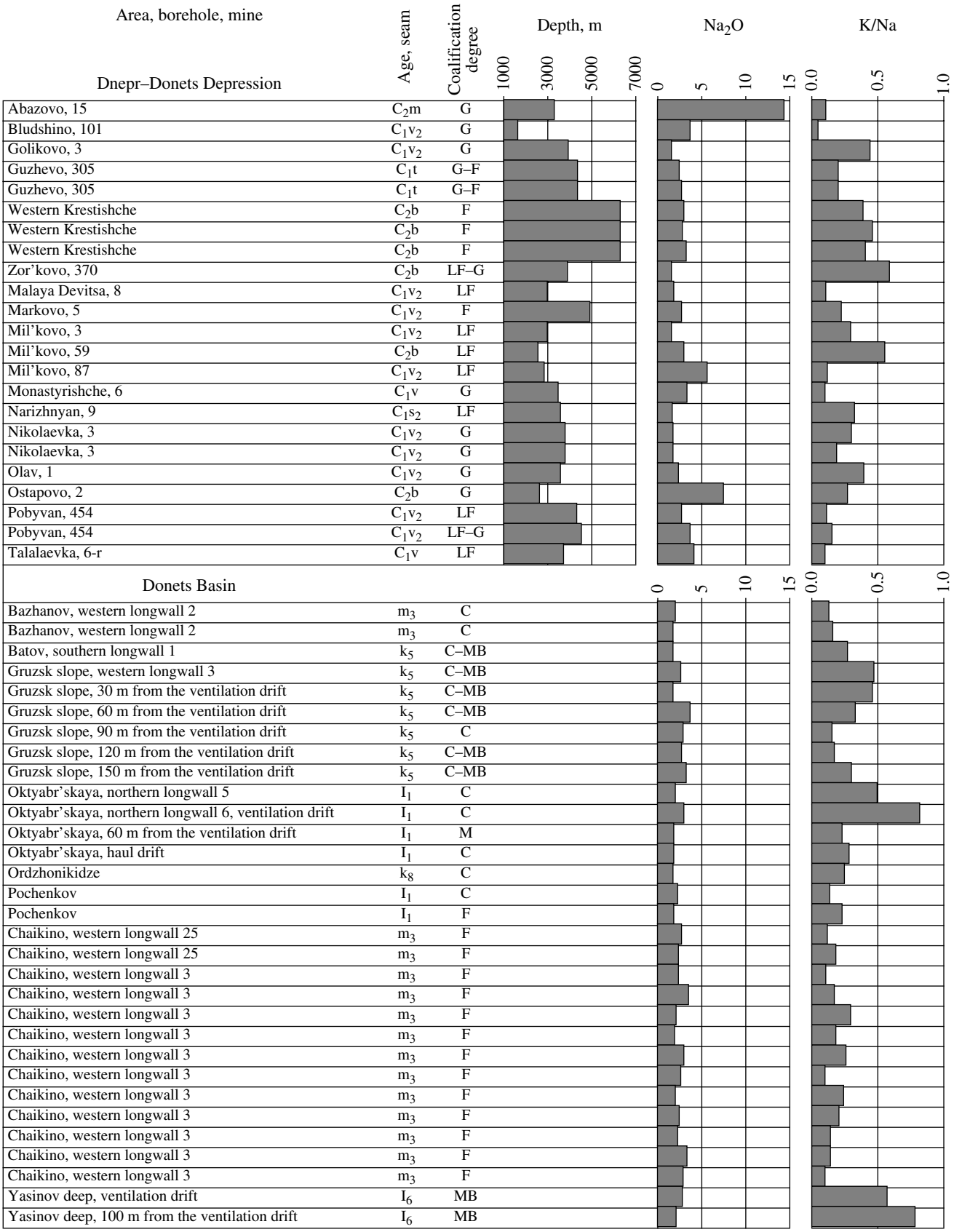
Sea water and NaCl-rich solutions from the washed out Famennian halogenic rocks could serve as the source for peat salinization in the DDD and Donbas. Beginning from the late Bashkirian in the mid-Carboniferous the peat bogs could be salinized by sea water only in the southeastern DDD and Donbas. Salinization in the remaining area was most likely a local process related to washout of salt domes. In the DDD, saline coals have been revealed in Lower and Middle Carboniferous rocks near western Donbas, including the Livny–Mikhailovka area. Based on materials of the Novomoskovsk Geological Exploration Department, the Na_2O content in the ash of these coals is significant and occasionally reaches 12.4–13.5%. As was predicted in our previous works (Ivanova, 1983a; Ivanova and Krivega, 1985), such coals are found not only near walls of the depression (the Golikovo, Markovo, and Narizhnyan structures in the northern segment and the Bludshino, Malaya Devitsa, Monastyrishche, and Ostapovo in the southern segment) but also within the axial zone of the graben (the Abazovo, Guzhevo, Western Krestishche, Mil'kovo, Nikolaevka, Pobyvan, Talalaevka, and other structures). It must be noted that the elevated Na_2O contents are registered not only in the lignites (lig) and high-volatile B bituminous (hvBb) coals, but also in the high-volatile A bituminous (hvAb), medium-volatile bituminous (mvb), and even low-volatile bituminous (lvb) coals (figure). In particular, evidence of salinization ($K^+/Na^+ = 0.34$) was revealed in lvb coals at a depth of 5593 m within the Rudovo structure. This implies that, in spite of the high maturity level achieved, the axial depression lacked active water exchange and other favorable conditions for the removal of metamorphic products.

The geological setting of saline coal formation in western Donbas and constraints of their salinization and desalinization are scrutinized in (Ivanova, 1983a, 1983b; Ivanova and Krivega, 1985). We demonstrated that lignites of the Petrikovka coalfield and hvBb coals of the Novomoskovsk coalfield are characterized by a high content of sodium oxides. Their maximum concentration is observed in coals of the Novomoskovsk coalfield located in the most unfavorable conditions, relative to other districts of western Donbas, in terms of the possibility of organic matter desalinization. In western Donbas, saline coals include not only lignites and lvBb coals (Ivanova and Krivega, 1985) but hvAb coals as well. Within the Pavlograd–Petropavlovka district, the hvAb coals are predominantly nonsaline as a result of the influence of desalinizing factors. At the same time, the hvAb coals locally contain up to 15.3% Na_2O on a coal ash basis with the K^+/Na^+ ratio varying from 0.09 to 1.0 (e.g., the Uspenovka and Vyazovka areas).

Data on the open Donets Basin confirm my opinion that peats could be salinized under certain landscape conditions in the mid-Carboniferous characterized by the accumulation of marine and lagoonal continental sediments over the entire Donets Basin area, resulting in the abundance of saline coals (Ivanova, 1983a; Ivanova and Krivega, 1985). Saline coals could retain their properties to a variable extent in the northeastern and southwestern walls of the basin (northern and western parts of Donbas Basin). In the open Donets Basin, the coals were strongly desalinized as a result of uplifts and metamorphism. Chlorides released during the general uplift of Carboniferous rocks entered the Permian evaporitic basin located within the Bakhmut Depression and eastern DDD. They could also be transported eastward to the present-day North Caspian Basin area. However, despite the high degree of coalification expressed in the development of mvb and lvb coals, some pieces of evidence of primary salinization have remained, such as high Na_2O content in the coal ash and low K^+/Na^+ values. This is illustrated by data on several mines of the open Donets Basin (figure).

Despite a small number of determinations of the alkali content in Lower Carboniferous coals in the western and southwestern parts of the Ukraine, they indicate salinization of hvBb and hvAb coals of the Kovel area and hvAb coals of the Mezhrechensk coalfield in the LVB, where the K^+/Na^+ value varies from 0.33 to 0.91. This value is equal to 0.65 in hvAb coals of the Belolessk Block of the DF. In Jurassic lignite of the Lower Prut Uplift in the DF, which is typically saline terms of all parameters, the Na_2O content (on a coal ash basis) at a depth of 366–378 m amounts to 2.44–6.95% ($K^+/Na^+ = 0.22$–0.90).

Elaboration of the model of saline coal formation and evolution, particularly in paralic basins, is of the general geological significance. From the point of view of sedimentary–diagenetic salinization of coals, one can solve issues of the reconstruction of paleogeographic conditions of peat formation, correlation of geological events, refinement of the history of regional or local geotectonic units, reconstruction of the salt budget of depressions (Ivanova and Krivega, 1985), and so on. In particular, I suggested that formation of the Hercynian Donbas Basin orogen was governed by older tectonic movements, which preceded the accumulation of Lower Permian saliferous sediments or accompanied



Na_2O content in ash (%) and relationship of alkali metals in some samples of saline coals from the Dnepr–Donets Depression and Donets Basin.

this process, rather than the Saalic and Pfalzian phases of orogeny as was supposed by Levenshtein and Popov (*Geologiya...*, 1963), Logvinenko (1956), and others. Based on the study of Permian limestone–dolomite sequences in Donbas, Lapkin (1954) supposed that inversion of the Donets Basin began at the end of Late Carboniferous. Maidanovich (Maidanovich and Radzivill, 1984) and other researchers also followed a similar point of view. Block structures (the Samara Horst, for example) probably formed in the early Serpukhovian rather than prior to the late Serpukhovian, as was supposed by Zaezzhaev (*Geologiya...*, 1963), because the Samara Horst was already manifested in the topography during the formation of coal seam c_1.

Issues of saline coals and the genesis and evolution of coaly matter are intimately related to the task of their utilization. In this respect, occurrence modes and bonds of alkali metals and chlorine with organic matter in the coals are very important. Investigations of saline coals from western Donbas, with contains 0.8–1.2% sodium oxides and 0.6–1.0% Cl on a whole coal basis at the ash content of 4.4–30.1%, demonstrated that the major part of Na (72–90%) is water-soluble. The remaining part enters into the adsorbing complex of the coal as exchange cations (Ivanova, 1996). According to data of some researchers (Kovalev *et al.*, 1989; Simonova and Shendrik, 1995), the main portion of the water-soluble Na enters into the composition of halite, whereas a small portion enters into glauberite. However, despite the water-soluble or exchange cation form of Na, its admixtures have a negative influence on technological properties of the coal as a fuel.

Power industry of the former Soviet Union had no experience of utilization of saline coals. A patent search conducted by the Dnepropetrovsk Division of the Institute of Mineral Resources under the supervision of S.D. Pozhidaev in the 1970s revealed that methods for the enrichment of saline coals have not found. Attempts to utilize saline coals with the application of specially designed boilers in Germany were unsuccessful (Ivanova and Krivega, 1985). Experiments with combustion of saline coals mixed with kaolin in England turned out to be unfeasible. In the United States, saline coals are combusted in special boilers that are cleaned with the use of steam or water blasting. As is known, however, it is often necessary to completely replace pipes of superheaters in the boilers after their slagging. Since combustion of enriched fuel considered a more rational technology, experiments with the enrichment of raw material with the use of ion exchange were carried out in the United States. However, this method also turned out to be unfeasible and did not go beyond the scope of laboratory investigations.

Previously, researchers from the All-Union Research Institute of the Ministry of Energetics (E.P. Dik, supervisor) had investigated saline coals of Donbas. Based on results obtained, they had recommended the creation of new equipment for the Novomoskovsk coalfield and the reconstruction of existing boilers for the combustion of coals from the Bogdanovka coalfield without their purification. However, the task of the creation of new equipment was not solved. Therefore, it was proposed to further investigate corrosion and slagging properties of the Novomoskovsk coals, search for fluxes that would transfer Na into refractory compounds, and study the possibilities of their desalinization.

Study of saline coals to find possible ways of their rational utilization is still in progress. Searches for new technologies are being conducted along two ways (with or without the preliminary processing).

Ya.S. Zholudov (Institute of Problems of Modeling in Energetics) elaborated a method for coal enrichment by the methods of semicoking and gasification that allowed one to obtain a Na-free product or to conserve Na in the solid phase of a stable compound after Cl sublimation into the gas phase.

Several organizations recommended the method of preliminary desalinization of coal with the help of water. The Ukrainian State Institute of Mineral Resources (UkrGIMR) elaborated a desalinization technology based on the use of industrial waters in a closed cycle including distillation of the aqueous phase. Technical solution of the problem of desalinization in the course of hydrotransportation was proposed by the NPO Khaimek in the 1980s. Researchers of Donets State Technical University (DonGTU) elaborated a new technology based on technologies developed in the UkrGIMR and NPO Khaimek (Zborshchik *et al.*, 1998). This refined technology integrates the methods of coal washing and agglomeration. Therefore, the degree of desalinization significantly increases and the agglomerated coal fuel obtained can be used for the production of water–coal, coal–oil, or water–coal–oil fuel mixtures. In this case, the necessity of water separation at the final stage of transportation and canalization of highly mineralized waters is apparently ruled out. The use of highly mineralized waters in the desalinization process and closed enrichment cycle should facilitate the preservation of water resources in Donbas.

Perspective works on the direct utilization of saline coals are also in progress. Investigations of various methods for the production of liquid fuel, which should be 30% cheaper than oil, are of economic interest. Significant advances in the elaboration of optimal technologies have been achieved in the United States where the reorientation from natural oil to coal began as early as the mid-1970s. Ukrainian researchers also give much attention to this problem. Very interesting investigations were conducted at the Institute of Physicoorganic Chemistry and Coal Chemistry (National Academy of Sciences of Ukraine). They demonstrated that saline coals are more amenable to liquefaction than coals desalinized by aqueous extraction and that the product obtained is characterized by a higher content of valuable fractions (Simonova *et al.*, 1991; and others). Works on surficial gasification of saline coals are in

progress (Levchenko and Marudina, 1991; and others). Of great interest are investigations of the influence of sodium salts (including NaCl) on coal gasification in a boiling layer at high pressure during laboratory steam-jet blowing. They demonstrated that NaCl catalyzes gasification and increases the caloricity of gas (Zakhar'yants, 1991). Hence, the natural salinization of coal is not a barrier for its gasification. Conversely, the salinization can be considered a favorable factor increasing the share of combustible components in the gas product.

Saline coals may also be used as a raw material for the production of adsorbents, extraction of rare and trace elements, oil agglomeration, and other purposes (Beletskii *et al.*,1999; Buravtsova *et al.*, 1989; and others).

Of certain interest is the utilization of saline coals by the method applied for combustion of sulfur coals in the United States. The coals are combusted in a device with aerated layer and limestone filler doped with NaCl. We had proposed to elucidate the efficiency of the aforesaid method for the utilization of high-sulfur saline coal or mixture of saline and sulfur coal as early as 1985 (Ivanova and Krivega, 1985).

The relatively shallow occurrence (from 170–200 to 600–640 m) of coal beds within the western and northern parts of the Donets Basin is favors the utilization of saline coal beds for underground gasification. When elaborating the concept of fuel and power industry development in 1992, researchers of the Institute of Problems of Mechanical Engineering offered the Bogdanovka and Petrovka coalfields (northern Donbas) as objects for the underground gasification. However, the large-scale introduction of underground gasification must be preceded by profound investigations of the environmental aspect of this issue.

At the present-day stage of development of society, technologies for the exploitation of saline coals must meet requirements of the feasible utilization of raw materials and environment protection.

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