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Hydrothermal Transformations of Organic Matter of Carbon-Rich Domanik Rock in Carbon Dioxide Environment at Different Temperatures

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Abstract—The influence of temperature on the nature of transformation of organic matter (OM) of carbon-rich rocks from Upper Devonian Semilukian–Mendymian (domanik) deposits of the Berezovskaya area of the Romashkino oilfield in hydrothermal processes has been studied. The experiments have been carried out at temperatures of 200, 250, 300, and 350°C in a CO_2 medium in the presence of water in an amount of 30% of rock mass in the reaction system. The yield and changes in the component, structural-group, and hydrocarbon-group composition of extracts obtained from rocks before and after hydrothermal experiments have been evaluated. It has been established that at temperatures of 300 and 350°C, high-molecular-weight components and insoluble kerogen undergo degradation processes, leading to a noticeable increase in the concentration of free hydrocarbons in the rock and their more complete extraction from the rocks. By the nature of molecular-mass distribution of normal and isoprenoid alkanes, the extracts from the rocks are similar to oils of the A^1 and A^2 types (according to the chemical classification by A.A. Petrov) from productive formations of the Devonian and Carboniferous deposits of the Romashkino field. The treatment of the domanik rock at lower temperatures of 200 and 250°C facilitates more intensive recovery of free hydrocarbons from the rock, without significantly affecting the structure of kerogen by destructive processes. The influence of temperature on the phase transformations of asphaltenes and their paramagnetic properties, as well as on the composition of biomarker hydrocarbons associated with the genotype of original OM and lithology and maturity of possible oil producing strata, has been revealed. It has been shown that carbonate–siliceous source rocks of domanik deposits of the Romashkino field can become an additional source of petroleum hydrocarbons in the case of development using hydrothermal technologies.

Keywords: Romashkino oil field, domanik rocks, organic matter, kerogen, hydrocarbons, shale oil, composition, hydrothermal transformations

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The increased interest in high-carbon dense rocks enriched in organic matter (OM) is associated with their reserves and prospects for the production of shale oil from them [1]. Giant accumulations of bituminous rocks in the Bazhenovo Formation in Western Siberia and domanik deposits of the Volga–Ural oil-and-gas province are currently considered an analogue of shale strata in Russia [2–10]. The uniqueness of the presence of hydrocarbon deposits in these rocks is not only that a new previously unknown type of reservoir has been discovered, but also that these are the main oil source strata in the regions of their distribution in which highly depleted hydrocarbon deposits occur at the site of their formation. Domanik deposits of the Ural–Volga region, extending over the entire section from the Middle Frasnian to the Upper Tournaisian stage of the Upper Devonian part of the sedimentary cover, are characterized by the ability to generate liquid and gaseous hydrocarbons (HCs) and accumulate them in the form of unconventional deposits [6, 9]. The reservoirs are characterized by low porosity and very low permeability.

On the territory of Tatarstan, oil deposits in domanik sediments were found within almost all tectonic elements and have an extended reservoir, the boundaries of which are not controlled by structural traps [2, 3, 6, 8–12]. Domanik deposits with high OM content are represented by siliceous–carbonate tiled limestones, dolomites, marls, which are cavernous and fissured to varying degrees, and are source rocks [2]. In this area, domanik deposits are represented by typical domanikites with C_{org} content of 5–20% in the sediments of the Semilukian (domanik), Mendymian and Sargaevian horizons of the Upper