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R. VESKI, H. TAAL, S. SIDOROVA, L. POBUL

OXIDATIVE AND THERMOOXIDATIVE DESTRUCTION OF KHODZHAIPAK BLACK SHALES OF UZBEKISTAN

Р. ВЕСКИ, Х. ТААЛЬ, С. СИДОРОВА, Л. ПОБУЛЬ

ОКИСЛИТЕЛЬНАЯ И ТЕРМООКИСЛИТЕЛЬНАЯ ДЕСТРУКЦИЯ ЧЕРНЫХ СЛАНЦЕВ ХОДЖАИПАКСКОЙ СВИТЫ УЗБЕКИСТАНА

The present work is a continuation of investigation into Upper-Jurassic black shales whose samples have been taken from the Khodzhaipak formation (southwestern Uzbekistan) by the Geological Production Association 'Uzbekneftegazgeologiya'. These shales have been first referred to in [1]. In this paper, the thermooxidative and oxidative destruction of Khodzhaipak black shales has been presented. Up to that time, the above destruction methods were used to investigate the region's oil shales only [2—4]. The respective researches have been reviewed in [3].

Thermooxidative destruction

Borehole samples from three deposits (Table 1) were subjected to thermooxidative destruction using an OD-102 Q-1000 derivatograph in air stream (conditions see in [3]), treated first with HCl and then with organic solvents to remove bitumoids A and C [1]. The former give DTA curves with three exothermal effects with maxima in the range of 335—340, 410—435 and 450—470 °C, differing from each other mainly in the capacity of the middle exothermal effect. The latter differs from the former in the absence of the middle exoeffect on the DTA curve (Fig. 1, 173* and 116*).

On the DTA curves for some of the HCl-treated black shale samples the endothermal effects of carbonates decomposition were observed (715—760 °C). After treatment of samples with 10 % HCl according to Stadnikov, they completely disappeared (173**). At the same time, the

Table 1. **Geological characteristics of black shales [1]**
Таблица 1. **Геологическая характеристика черных сланцев [1]**

Borehole No.	Sample No.	Sampling depth, m	Field determination
2	182	2715.0	Calcareous carbonaceous shale of argillite dimensions
2	179	2739.0	The same
6-p	177	2786,0	,, ,,
6-p	170	2795.5	Carbonaceous calcareous shale of argillite dimensions
2-p	173	3123.0	Carbonaceous shale of aleurite dimensions
2-p	116	3125.5	The same

* Boreholes: 2 — Baishirin, 6-p — Markovskaya, and 2-p — Kapali.

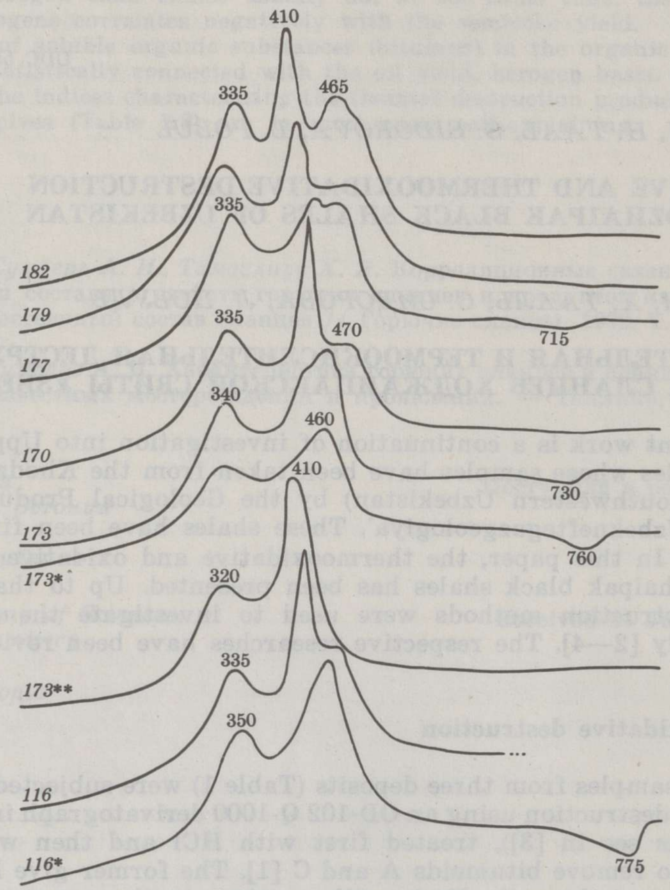

Fig. 1. **DTA-curves of HCl-treated (without an asterisk) and debitumized (with an asterisk*) Khodzhaipak black shale samples as well of those treated additionally according to Stadnikov (**) (numbers of samples see in Table 1)**

Рис. 1. **Кривые ДТА проб черных сланцев Ходжаипакской свиты, обработанныех HCl, затем дебитумоидированных (обозначены звездочкой *) и дополнительно обработанных по Стадникову (обозначены двумя звездочками**) (номера проб см. в. табл. 1)**

Table 2. **Mass losses by derivatograpic analysis of black shales (designation as in Fig. 1)**

Таблица 2. **Потеря массы при дериватографическом анализе черных сланцев (обозначения см. в подписи к рис. 1)**

Sample No.	Exothermal period			Endothermal period
	Total, mg	1st effect, %	Remaining effects, %	$(CO_2)^d_M$, %
182	11.9	17	83	0
179	9.9	18.	82	0
177	10.0	29	71	4.0
170	9.8	21	79	1.8
173	14.0	224	76	10.6
173*	8.2	20	80	13.1
173**	12.3	19	81	0
116	9.8	20	80	not determ.
116*	5.7	18	82	9.5

maxima of exoeffects were formed at lower temperatures, i. e. the morphology of an exothermal part of the DTA curves of black shales depends on the presence of both bitumoids and carbonates.

Mass losses during the formation of the first exoeffect of the black shale samples investigated ranges from 17 to 29 % (Table 2) and it is insignificantly lower for the debituminized samples (173* and 116*). Judging by the difference in the total mass loss for samples 173 and 116 prior to and after extraction, viz. 14.0 as against 9.8 and 8.2 as against 5.7 %, respectively, high amounts of bitumoids are removed by extraction of Khodzhaipak black shales. The data obtained indicate that the exothermal effects observed only by thermal oxidation of HCl-treated black shale samples not subjected to extraction belongs to bitumoids. After removing the latter, the exothermal effects are formed only on account of the kerogen and pyrite of black shales.

Oxidative destruction

The oxidative destruction of debituminized black shale samples 173 and 116 was carried out by $KMnO_4$ in alkali medium at 60 °C for 1 h, at room temperature and at 95 °C (oxidation and analysis conditions see in [3]). In the products of oxidative destruction carried out at room temperature and 60 °C, aliphatic mono- (C_6—C_{21}, C_8 at most) and dicarboxylic acids (C_4—C_{18}, C_4 at most) were identified in low amounts. The benzenecarboxylic acids (BCA) obtained at 60 °C and at room temperature are practically similar in composition, differing in this respect from the acids formed under hard oxidation conditions at 95 °C. At the same time low-basicity BCA are more abundant than the high-basicity ones. For the formation of the latter hard oxidation conditions are required.

Discussion

Although samples 116 and 173 were taken almost at the same depth (borehole 2-p, Kapali deposit), they differ considerably in mineral composition, as well as in the yield of bitumoid A [1]. The difference in BCA composition of the products of destruction taking place at 95 °C is less significant (Fig. 2). Unlike low-deposited Dzham oil shale [4], both the above shales are characterized by the predominance of benzenepentacarboxylic and mellitic acids among those formed.

The presence of high-basicity BCA in the oxidative destruction products of Suzak oil shales is attributed to the diagenetic aromatization of the starting sapropelic material in H_2S medium [3]. The same applies to the sulphurous black shales investigated. As to the starting biomaterial, it is known that in the Callovian-Oxfordian almost on the entire territory of the Afghan-Tayik depression marine, mainly carbonate sediments [5] rich in sapropelic organic matter were formed [6]. The oil-generating Khodzhaipak formation is in many respects similar to the Bazhenov formation of West Siberia more thoroughly studied so far [7].

Judging by the depth of occurrence (Table 1) and recent as well as paleotemperatures of the region [8], the kerogen of Khodzhaipak black shales belongs to lithogenesis stage MK_1—MK_2, that may be indicative of the generation of maximum amounts of oil hydrocarbons from sapropelic organic matter. It has shown earlier that by apocatagenesis-initial metagenesis, the BCA composition from sapropelic black shales [9] differs considerably from that of studied black shales, i. e. only mellopha-

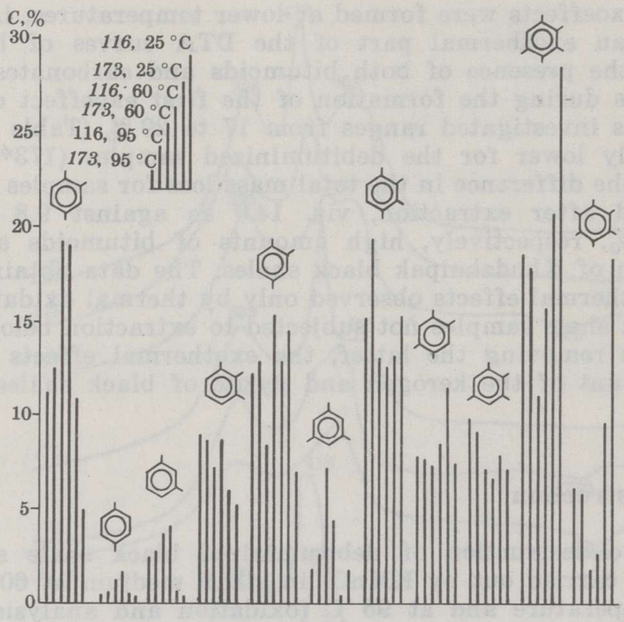

Fig. 2. The relative component composition of benzenecarboxylic acids formed by oxidative destruction of debituminized Khodzhaipak black shales

Рис. 2. Относительный компонентный состав бензолкарбоновых кислот, образовавшихся при окислительной деструкции $KMnO_4$ дебитумоидированных черных сланцев Ходжаипакской свиты

nic, benzenecarboxylic and mellitic acids are present, while the predominance of the latter is noticeable.

The main exoeffect of thermooxidation for highly metamorphosed black shale is observed (a maximum at 565—615 °C [9]) at higher temperatures than for Khodzhaipak black shales (Fig. 1). If the pyrite content of highly metamorphosed black shales is high, then the exothermal effect of pyrite (a maximum at about 450 °C) appears separately from the peaks of kerogen thermooxidation. As the pyrite and kerogen contents of Khodzhaipak black shales are almost similar [1], the second exothermal effect of debituminized samples with a maximum at 410—460 °C may be definitely considered the result of a joint thermooxidative destruction of kerogen and pyrite.

The influence of pyrite should not be neglected also by formation of the first exothermal effect observed in model experiments with the mixtures of brown coal and pyrite [10]. A comparison of DTA curves showed that the maxima of exothermal effects (at 255—300 and 325—380 °C [3, 4]) for Suzak oil shales are in the region of lower temperatures than for Khodzhaipak black shales (at 320—340 and 410—460 °C) that is indicative of the higher degree of catagenetic transformation of deep-deposited black shales.

Conclusions

1. The composition of the benzenecarboxylic acids formed by oxidation, as well as the morphology of DTA curves of thermooxidative destruction of debituminized Khodzhaipak black shales allows establish-

ment of the higher degree of catagenetic transformation as compared with Suzak oil shales of Uzbekistan.

2. The possibility of determining the presence and an approximate content of bitumoids in Khodzhaipak black shales has been established.

РЕЗЮМЕ

Представлены сведения о термоокислительной (дериватограф ОД-102 Q-1000 в токе воздуха) и окислительной деструкции ($KMnO_4$ в щелочной среде, в течение часа при 60 °C и исчерпывающе при 95 °C) черных сланцев Ходжаипакской свиты, характеристика которых приведена в табл. 1. Морфология кривых ДТА термоокисления (рис. 1) и данные о потере массы во время термоокисления (табл. 2), а также состав образовавшихся бензолкарбоновых кислот (рис. 2) дебитумоидированных ходжаипакских черных сланцев позволяют установить их большую катагенетическую превращенность по сравнению с сузакскими горючими сланцами Узбекистана. Установлено, что дериватографический анализ дает возможность определить наличие и примерное содержание битумоидов в изученных черных сланцах.

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Estonian Academy of Sciences,
Institute of Chemistry
Tallinn,
Republic of Estonia

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Институт химии
Академии наук Эстонии
г. Таллинн,
Эстонская Республика