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THERMAL ANALYSIS OF PRODUCTS OBTAINED BY BENEFICIATION OF DICTYONEMA OIL SHALE WITH THULE LIQUID

Introduction

It is very difficult to obtain organic matter concentrates from most of oil shales by common methods of beneficiation. It concerns dictyonema oil shale (DOS) as well. In the hydrocycling and flotation processes concentrates with 57.8 to 59.5 per cent of organic matter (Toolse deposit) [1, 2] and 62.2 per cent of organic matter (Maardu deposit) [1] were obtained. Flotoconcentrate from Toolse deposit (further: base concentrate) was in its turn enriched with Thule liquid (K_2HgI_4) which gave very rich concentrates, up to 93.4 per cent of organic matter content.

The aim of this study was to characterize concentrates obtained by Thule liquid beneficiation (thermal and ultimate analysis) and elucidate whether the fractionation of DOS organic matter takes place by stepwise beneficiation with Thule liquid, or not.

Base Concentrate

Base concentrate was obtained from Toolse DOS deposit with high pyrite content (10.1 per cent). Flow sheet for beneficiation of Toolse DOS to obtain base concentrate was published earlier [2]. It must be stressed that the pyrite content in the intermediate concentrate of hydrocycling overflow was only 1.0 per cent, but that of jarosite — 8.0 per cent. The latter is a most characteristic compound arised from pyrite in the course of natural weathering of DOS.

The content of pyrite in base concentrate is 1.6 per cent while that of jarosite is 6.7 per cent (!). Also quartz (11.8), hydromica (12.6), feldspar (9.5) and probably some colloidal oxides of ferrum are present in the concentrate [1]. 57 per cent of organic matter of DOS reached the base concentrate, 28 per cent — the pyrite concentrate and only 15 per cent remained in the mineral residue (Table 1).

Table 1. **Distribution of Organic Matter between Base Concentrate and Other Products of Beneficiation of Dictyonema Oil Shale, %**

Fraction	Yield, [3]	Organic matter content, [1]	Separation of organic matter into fraction
Dictyonema oil shale (feed)	100.0	14.5	100
Base concentrate	15.5	57.8	57
Mineral residue	57.0	4.2	15
Pure pyrite	2.1	-	-
Pyrite concentrate	14.0	31.4	28
Pyrite flotation tails	11.4	-	-

At first concentrate of the highest organic matter content was separated with Thule liquid diluted with water then concentrates with lesser organic matter content were obtained by stepwise raising of the density of the solution.

Concentrates

To remove residue of flotoreagents and Thule liquid, concentrates were washed with water and solvents at room temperature. Organic matter content in washed concentrates was 59.8 to 93.4 per cent (Table 2). Heating loss of sulphur-rich (7.3 per cent) beneficiation residue was 13.5 per cent. Decrease in organic matter content of concentrates correlates with decrease in carbon and hydrogen content in organic matter and also values of atomic ratio H/C. At the same time oxygen content and values of O/C and N/C were increased. Total sulphur content in concentrates, determined by method [4], ranges from 1.8 to 3.5 per cent.

Table 2. **Chemical Composition of Products of Beneficiation, %**

Concent-rate	W^a	Organic matter content $(100—A^d)^*$	S^d	Elemental composition, *daf*				Atomic ratio		
				C	H	N	O_{diff}	H/C	O/C	N/C
I	3.2	93.4	1.8	74.6	7.3	0.8	17.3	1.17	0.17	0.009
II	3.8	83.5	3.4	72.5	6.7	1.5	19.3	1.11	0.20	0.017
III	5.1	78.4	3.3	69.0	6.0	2.2	22.8	1.04	0.25	0.027
IV	4.3	61.9	3.5	67.7	5.6	2.0	24.7	1.00	0.27	0.025
V	4.4	59.8	1.6	65.1	5.3	1.9	27.7	0.98	0.32	0.025
Residue	1.1	13.5	7.3	...	...	...	...	...	...	...

*Organic matter content, by thermal analysis data, 90.4, 82.2, 78.4, 59.4, 59.8 and 10.7 %, respectively.

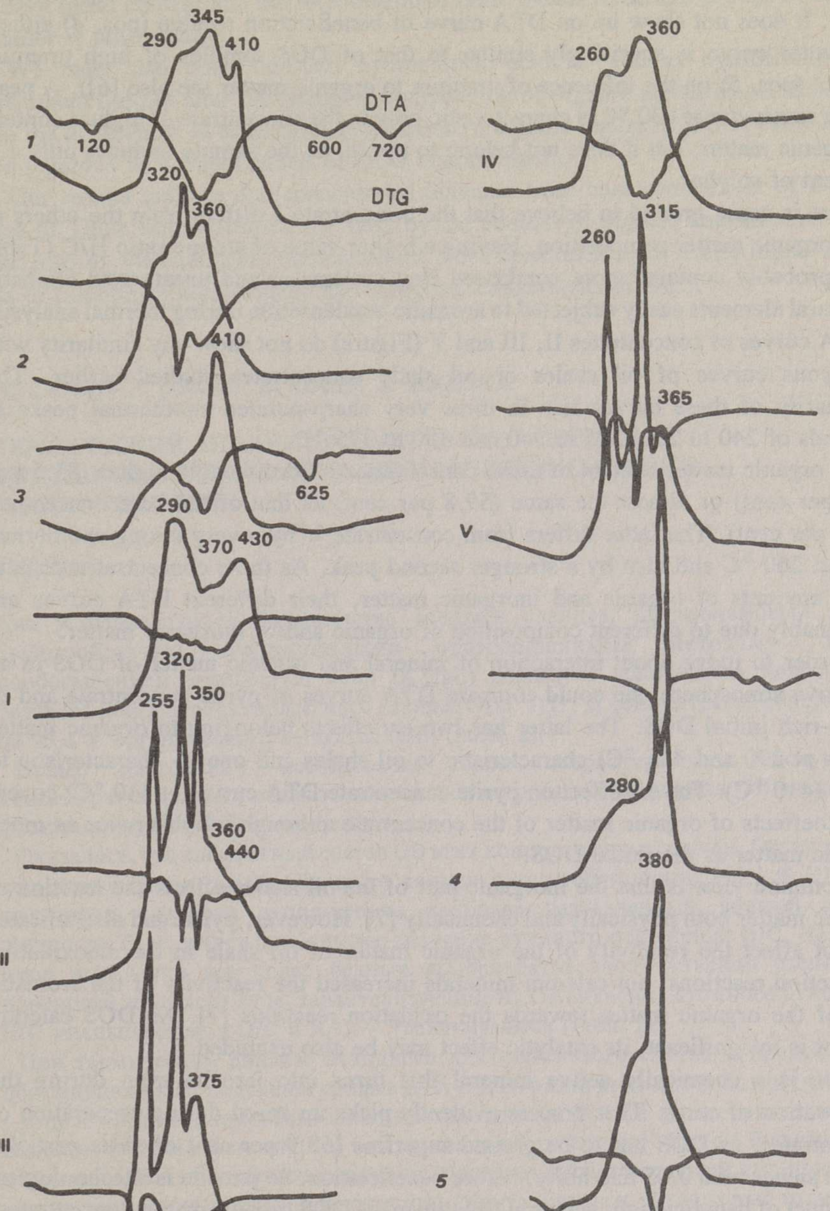
Thermal Analysis

The thermooxidative destruction of DOS samples and beneficiation fractions with varying organic matter content was carried out on an OD-102 Q-1000 derivatograph (TG=50 mg, sensitivity: DTA 250 μV, DTG 500 μV) in air stream (100 ml/min). Organic matter content of samples was approximately 13 mg. DTA and DTG curves with varying morphology were obtained (Figure).

Discussion

Three steps in the exothermal period were observed on DTA curves of DOS from Toolse deposit. The first two of them with maxima at 290 and 345 °C (Figure, position *1*) are characteristic to most oil shales including DOS from Maardu deposit (290 and 370 °C [5, 6]). The third step with a maximum at 410 °C indicates a high pyrite content in DOS from Toolse deposit, not characteristic to Maardu deposit.

Maximum at 410 °C is also characteristic to pyrite concentrate (Figure, pos. *2*), but it is lacking on DTA curves of base concentrate (pos. *2*) as well as of all



DTA and DTG curves of dictyonema oil shale from Toolse deposit: *1* - initial oil shale, *2* - base concentrate, *3* - pyrite concentrate, *4* - mineral residue, *5* - dictyonema oil shale with uranium content of 450 g/t (450 ppm), I—V - concentrates of stepwise beneficiation with Thule liquid (see Table 2) concentrates of low sulphur content obtained by the use of Thule liquid (positions I to V). It does not show up on DTA curve of beneficiation residue (pos. *4*) either. The latter curve is suprisingly similar to that of DOS samples of high uranium content (pos. *5*; on the influence of uranium to organic matter see also [6]). A peak with a maximum at 430 °C is characteristic only to the concentrate of highest content of organic matter, but it does not belong to pyrite, as the sample includes only 1.8 per cent of sulphur.

There is some ground to believe that the concentrate I differs from the others in their organic matter composition. Having a higher value of atomic ratio H/C (Table 2) it probably contains more condensed ring systems or/and unsaturated aliphatic structural elements easily subjected to aromatic condensation during thermal analysis.

DTA curves of concentrates II, III and V (Figure) do not show any similarity with analogous curves of oil shales or oil shale concentrates studied earlier. The peculiarity of these curves lies in three very sharp-pointed exothermal peaks at intervals of 240 to 260, 315 to 340 and 350 to 375 °C.

The organic matter content of those concentrates is considerably higher (83.5 and 78.4 per cent) or almost the same (59.8 per cent) as that of the base concentrate (57.8 per cent). The latter differs from concentrate V by a very strong exothermal peak at 260 °C and also by a stronger second peak. As these concentrates contain equal amounts of organic and inorganic matter, their different DTA curves are presumably due to different composition of organic and/or inorganic matter.

In order to judge about interaction of mineral and organic matter of DOS in an oxidative atmosphere one could compare DTA curves of pyrite concentrate and of pyrite-rich initial DOS. The latter has two exoeffects belonging to organic matter (peaks at 290 and 345 °C) characteristic to oil shales and one — characteristic to pyrite (410 °C). The exoeffect on pyrite concentrate DTA curve (at 410 °C) covers the exoeffects of organic matter of the concentrate although it holds twice as much organic matter as the initial DOS.

A common view is that the inorganic part of the oil shales affects the reaction of organic matter both physically and chemically [7]. However, pyrite and also silicates did not affect the reactivity of the organic matter of oil shale in thermooxidative destruction reactions, but calcium minerals increased the reactivity of the aromatic part of the organic matter towards the oxidation reactions [7]. As DOS calcium content is insignificant, its catalytic effect may be also excluded.

Pyrite is a chemically active mineral that turns into jarosite even during the preservation of cores. That process evidently picks up speed during preparation of concentrates, as DOS has to be ground superfine (68.9 per cent of shale particles passed sieves with 0.05 mm holes) before beneficiation. So jarosite is a technological byproduct of beneficiation, a natural constituent of DOS organic matter concentrates.

The exceptionally high thermal activity of the three DOS organic matter concentrates cannot be due to Thule liquid or flotoreagents as the samples analyzed were previously washed with water and solvents. We must mention that identical sharp-peaked DTA curves arised from unwashed samples as well.

To solve the origin of sharp-peaked DTA curves, concentrates were treated with 10 per cent hydrochloric acid. After the treatment sharp peaks on DTA curves almost disappeared. So those exoeffects were related to the inorganic ingredients insoluble in water and solvents, but mostly soluble in hydrochloric acid. Although jarosite is also soluble in hydrochloric acid while pyrite is insoluble, the sharp exothermal peaks do not belong to jarosite as jarosite has no noticeable exoeffects during thermal analysis at all.

There remains the possibility that the thermal activity of the concentrates originated from some colloidal ferrum hydroxides or from some heavy metal compounds. The heavy metal content and the relationship of these metals to certain groups of organic matter is under study.

We must also point out that hydrochloric acid as well as hydrofluoric acid treatment did not alter the chemical composition of organic matter of oil shales [7]. So the differences in elemental composition of organic matter of DOS (Table 2) may be regarded as a fractionation of DOS organic matter.

Our results indicate that concentrates obtained from base concentrate of DOS by use of Thule liquid differed not only by the content of organic and mineral matter but also by the chemical composition of those constituents. So Thule liquid enables us to fractionate both organic and inorganic constituents of DOS.

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ТЕРМИЧЕСКИЙ АНАЛИЗ ПРОДУКТОВ ОБОГАЩЕНИЯ ДИКТИОНЕМОВОГО СЛАНЦА МЕСТОРОЖДЕНИЯ ТООЛСЕ ЖИДКОСТЬЮ ТУЛЕ

Резюме

Как и подавляющее большинство горючих сланцев, диктионемовый сланец труднообогатим традиционными промышленными методами. Только дообогащением жидкостью Туле (K_2HgI_4) оказалось возможным получить из базового концентрата тоолсеского сланца (табл. 1) [1, 2] концентраты, содержащие до 93,4 % органического вещества (ОВ) (табл. 2).

Целью настоящего исследования было охарактеризовать полученные концентраты, а также выявить, имела ли место дифференциация ОВ сланца при фракционирующем дообогащении.

Оказалось, что элементный состав ОВ этих концентратов различен. Органическое вещество первого, самого богатого концентрата дообогащения (93,4 % ОВ), при получении которого использовали наиболее разбавленный водный раствор жидкости Туле, имеет наибольшее значение атомного отношения H/C. Далее, по мере выделения все более бедных концентратов соответственно увеличению плотности жидкости Туле, характеризующие их ОВ значения атомного отношения H/C уменьшаются, а O/C и N/C — увеличиваются (табл. 2).

При термическом анализе исходного диктионемового сланца и продуктов его обогащения были получены кривые ДТА и ДТГ различной морфологии (рисунок).

В целом, диктионемовый сланец месторождения Тоолсе характеризуется более высоким содержанием пирита, чем сланец месторождения Маарду. В связи с этим на кривых ДТА тоолсеского сланца проявляется дополнительный пик при 410 °С — пик термоокислительной деструкции пирита (рисунок, *1*), который отсутствует на кривых ДТА маардуского сланца [5, 6]. Из остальных проб аналогичный пик дал только пиритный концентрат (рисунок, *3*).

В отличие от всех изученных нами горючих сланцев и концентратов их ОВ, кривые ДТА концентратов дообогащения II, III и V отличаются наличием острых экзотермических эффектов в температурных интервалах 240—260, 315—340 и 350—375 °С. Представленные на рисунке кривые получены при анализе концентратов, промытых водой и растворителями с целью удаления как солей жидкости Туле, так и флотореагентов, используемых при получении базового концентрата. Промывка не влияла на морфологию кривых ДТА; и только после обработки концентратов 10 %-ным водным раствором HCl острые экзотермические эффекты практически исчезали. Отсюда следует, что эти эффекты были связаны

с неорганическими водонерастворимыми соединениями. Пирит к таковым не относится. Исключить можно и кислоторастворимый ярозит — типичный продукт выветривания пирита в случае диктионемового сланца, так как, разлагаясь, он дает только эндоэффекты. По всей вероятности, острые экзоэффекты обусловлены некоторыми соединениями железа или тяжелых металлов.

Таким образом, при фракционирующем дообогащении диктионемового сланца жидкостью Туле получаются концентраты, которые различаются наличием или отсутствием термоактивных (т.е. таких, которые активны сами или катализируют термоокислительное разложение ОВ) водонерастворимых кислоторастворимых неорганических соединений. ОВ концентратов дообогащения различается как элементным составом, так и показателями термического анализа.

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