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K. UROV and A. SUMBERG

CHARACTERISTICS OF OIL SHALES AND SHALE-LIKE ROCKS OF KNOWN DEPOSITS AND OUTCROPS

MONOGRAPH

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Editor of the Russian publication: Prof. **A. Aarna**,
Member of the Estonian Academy of Sciences, D.Sc. in engineering

Translated by Priit Kogerman, Ph.D.

This booklet has been first published in Russian in 1992. As it become evident, the material presented was of interest for a wide range of researchers working in the field of oil shales and related fossil fuels, but due to language barrier it was not always accessible. Therefore this time we publish the data in English and hope that they will be of use for any who is working or interested in this sphere of science.
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PREFACE

Oil shales are special among organogenous rocks not only in their genesis and composition but also in their role as power and chemical industry raw materials. They differ from humous caustobioliths by higher hydrogen content in their organic matter and consequently by higher yield of liquid organic products (shale oil) from their thermal decomposition. This is why oil shales are regarded as a potential source for producing artificial liquid fuels and raw materials for chemical industry. On the other hand, they are usually rich in mineral matter and for complex utilization of oil shales the problems connected with the utilisation of their mineral components must be solved.

The reserves of oil shales are as of yet insufficiently determined. But even the existing data presented at the 27th International Geological Congress (1984) put them at 11.5×10^{12} tonnes (the potential oil shale resources in the USSR are estimated at 2×10^{12} tonnes) or 550 billion tonnes of shale oil. Oil shale deposits are found on all continents; the reserves are more evenly distributed compared to oil and for many countries, oil shales represent practically the only type of fossil fuels. The actuality of the use of oil shales has always depended on the oil market; as the reserves of the latter are being depleted, the oil shales become more and more important as a source of energy and as alternative source of liquid fuels and chemical raw materials. Some rare and scattered elements are also concentrated in oil shales.

Despite the existence of relatively broad literature on oil shales, the data are dispersed in different sources and are difficult to collect for comparative analysis. The present edition attempts to fill this gap by collecting together the data on oil shales of known deposits and outcrops - the results of technical analysis, data on the composition of the organic and mineral components, the yield and composition of bitumoids and products of thermal decomposition. The data collected in this study may be useful for evaluating the quality of oil shales from specific deposits for use as industrial raw materials, for creating a classification for this class of caustobioliths or for determining, with the help of methods of mathematical statistics, interdependence of different indices that characterize the composition and properties of the oil shales.

INTRODUCTION

Before presenting the data on oil shales, it would be practical to discuss first some terminological questions. It is of course especially important to understand what is the content of the term ‘oil shales’. Already Down and Himus [1] have noted that the term ‘oil shales’ is misleading and proposed to change it to the term ‘kerogenic rocks’. The absence of a precise and generally accepted definition of oil shales has also been observed later [2-5]. Duncan [6] indicated that many deposits that are classified as oil shales are actually not shales, i.e. fine-grained, thin-layered sedimentary rocks. Finding the name ‘oil shales’ misleading, Vassoyevich [7] proposed to discard this failed term as soon as possible and replace it by ‘semicaustoliths’.

At the UN symposium on development and use of oil shale reserves (Tallinn, 1968) Schlatter called the term ‘oil shales’ a misnomer, since these are not shales and they do not contain oil [9]. He noted, however, that this name is firmly in use, it is convenient, short and there is no necessity to change it.

At the present time ‘oil shale’ is still a term that is used quite freely: on the basis of existing definitions it is not possible to decide unequivocally whether a number of organic matter (OM)-containing rocks should be included into the oil shale class or excluded from them.

The diagnostic significance of different properties that are regarded as characteristic for oil shales is now discussed with the aim of finding a more acceptable definition for this class of caustobioliths [10]. For this purpose, oil shales are regarded first as a natural geological object, as a class of rocks that comprise the crust of earth and only then as a potential industrial raw material, i.e. mineral wealth.

As a defining characteristic of oil shales, almost all authors mention their capacity of generating significant quantities of liquid organic products (shale oil) upon their thermal decomposition [1-3, 5, 6, 9-29], although this property is rarely characterized quantitatively [3, 16, 21, 24, 25]. The following characteristics are also considered diagnostic (in the order of frequency that they are mentioned in the literature): high mineral content [1, 2, 4, 6, 8, 11, 15, 19-21, 23, 25, 26, 29, 30-35], insolubility of the major fraction of its OM in organic solvents [1-3, 5, 6, 11-16, 18-20, 26, 29, 35, 36], shale-like, thin-layered structure [2, 11, 13, 14, 16-21, 25, 37, 38], sapropelic origin [4, 8, 9, 13, 14, 16, 20, 22, 23, 25, 32, 39-42], specific elemental composition and especially enrichment in hydrogen (3, 16, 19, 20, 23, 27, 32, 40], the capacity of dry shale to ignite from a match [13, 14, 25, 32, 37, 38] (or a lighter [43]), relatively low degree of catagenetic transformation of their OM [9, 28, 35, 41, 44, 45] and autochthonousness [6].

The colour of the shale and composition of its mineral part are frequently mentioned in the descriptions but these cannot serve as defining features since colour of oil shales may vary from light gray, almost white (Novodmitrovo shale, the Ukraine) and dark yellow (kukersite) to dark brown, almost black (Scottish shale) and the mineral matrix may be with aluminosilicate, carbonate or silicate material prevailing.

Even though the capacity of oil shales to ignite and burn (or smoulder) with production of a strong odour is convenient to use for analysis under field conditions, this property should still be considered only a suggestive indicator since it is characteristic of all sediments that contain sufficient amounts of moderately transformed OM such as coals, rocks impregnated with oil, etc.

If one considers shaliness [13, 14, 16, 21, 37, 38] as defined in [23], this property is not observed in many caustobioliths that by a number of other significant features can be grouped with oil shales. The thin-layered structure, that is sometimes mentioned [2, 11, 17-20, 25], is characteristic for a number of rocks that have nothing in common with oil shales apart from this feature. Consequently, the diagnostic value of the above-mentioned features is not significant. It is inevitable to accept the fact that neither are all oil shales shales nor do all of them burn.

The *in situ* formation of the OM as a defining property of oil shales should be regarded with reservation since kukersite, for example, has allochthonic origin according to some authors [46] and it cannot at all be excluded that some others are not similar. From the geological viewpoint it is quite possible that the formation of allochthonic shales could take place not only *via* transport by water essentially simultaneously with its formation as it possibly happened during the formation of kukersite, but also as a result of a later alluvial deposition of the OM into the preformed deposits of shale.

On the other hand, the insignificant solubility of the OM of oil shales in low-boiling organic solvents (benzene, chloroform, etc.) appears to be an important distinguishing property as it allows to differentiate typical (pyro-bituminous) oil shales from the rocks impregnated with organic compounds that are essentially soluble (natural asphalts, oil-sands, etc.).

It is the quantitative aspect that needs clarification here. Taking into account that in most rocks that are classified as oil shales, the yield of the bitumoid does not exceed 20 % of OM (and is usually significantly less than that), this amount can be accepted as an approximate upper limit. In addition to that the OM of oil shales, and not the OM of little transformed combustible rocks of the humous type, is characterized by low solubility in aqueous solutions of alkali (i.e. insignificant content of so-called humic acids).

The rest of the proposed characteristic features have to be examined in more detail.

High mineral content is, according to most authors, characteristic for oil shales; the opinions on the actual quantity of mineral substances, however, differ quite significantly. Thus, the lower limit for OM content has been proposed to be (%): traces [1, 19] (the upper limit of mineral content is not defined in [11, 15, 30] either), 5 [28], more than 5 (4 % shale oil in the rock) [6], 10 [4, 21, 23, 35], 10-15 [8, 25], 15 [5, 32, 47], 20 [33, 34, 48].

The situation is no better with the upper limit of OM content that has been proposed to be (%): 30 [23], 35 [47], 40 [4, 19, 32], 50 [33-35], more than 50 [1], 55 [21], appr. 60 (more than 30 [30] or 33 % [11, 15] of mineral material), 75 [31], 60-80 [25]. It has also been permitted not to establish any limits at all for the OM content in oil shale [9].

This position was earlier advocated by Dobryanski who argued that œclassification of kerogen-containing rocks according to the property of kerogen amount per unit weight of the rock is not possible: it will always reflect either economic considerations or the situation of the technical culture, i.e., features that are not absoluteB [16, p. 224]. In fact, OM content is first of all an industrial indicator (a simplified evaluation of fuels according to [49]) that cannot therefore serve as basis for a genetic classification.

In conclusion, it is hardly possible to reach universal agreement to the question of œobligatoryB mineral content in oil shale by means of averaging the proposed numerical limits. If one establishes concrete limits for mineral content, some anomalously enriched or, on the contrary, containing less of OM layers of genetically and lithologically relatively uniform deposits should be excluded from this class of caustobioliths which seems to be artificial and unreasonable. For example, some parts of layers B and E of kukersite contain more than 65 % OM, whereas shale of layer IIa from the Lyuban deposit (Byelorussia), the kerogen of which is essentially identical to that of the neighbouring layers, contains less than 10 % OM.

While supporting the notion that oil shales represent an intermediate between dispersed OM and highly concentrated forms of fossil OM, we are still convinced that it is not appropriate to assign rigid numeric limits for the mineral content of oil shales. Neither researchers nor industrial workers will exclude from their sphere of interest specific types of rocks with dispersed OM, oil shales or sapropelitic coals, for the sole reason that the OM content of these samples falls into œthe forbidden zoneB for a given type of sedimentary rocks.

But this is not the main reason. For almost everybody working in the oil shale field, these caustobioliths are specific not so much in the quantity of their OM but rather in its composition. This aspect is characterized by several interdependent properties of shales such as significant yield of oil from its OM by semicoking, low level of its catagenetic transformation and enrichment in hydrogen.

High yield of semicoking oil from OM (even though usually without quantitative estimate) is recognized by the vast majority of investigators as one of the main distinctive features of oil shales. For shales of known deposits this value ranges from 20-70 %. Yield of oil from OM that is lower than 20 % is characteristic of combustible rocks of the humous type; from the OM of some brown coals, 20-25 % of oil is formed by semicoking. Apparently one can accept 20 % of oil from OM as an approximate minimal value for oil shales.

Apart from being an important industrial characteristic, the high yield of semicoking oil from OM is also an external reflection of the chemical composition and structure of the OM, of its specific internal peculiarities that are determined by the composition of the starting material and processes of its transformation. Therefore, this property is also a genetical characteristic of fossilized OM and can be regarded as an important diagnostic feature.

It is often indicated that the kerogen of oil shales has sapropelic origins. However, if ‘sapropelic’ is defined as organic material that has been formed under reducing, anaerobic conditions (according to the apparent contents of the term), a number of oil shales cannot be grouped with sapropelites (e.g. the Jurassic shales of Volga Basin and kukersite that were formed in the sea basin with normal oxygen levels, menilitic shales of the Carpathian region, the OM of which accumulated under semi-oxidative conditions).

Vassoyevich and co-authors note that the term ‘sapropelic’ has lost its meaning and recommend to base the classification on the predominant types of molecular structures, in this case aliphatic and nonaromatic cyclic; i.e., on specific chemical indicators. Unfortunately, the methods of quantitative determination of these structural elements in the OM have not been developed sufficiently; however, there is some evidence that the content of these groups in the OM correlates quite well with the yield of oil on semicoking [51, 52].

From these considerations it follows that before the term ‘sapropelic’ itself has been better specified, it is not appropriate to use it as a determining feature of oil shales. However, it is difficult to disagree with Kotlukov who wrote “carbonaceous argillites (shales) and liptobioliths of high mineral content should not be classified as true oil shales” [20]. In all cases, the main part of the kerogen of shales is a product of transformation of the OM synthesized by the aquatic organisms (aquagenic OM); this feature not only distinguishes it from the OM of humites that originate form the terrigenic OM, but in our opinion also basically determines the unique properties of the OM of oil shales. However, terrigenic OM is often present in oil shales as an additive; according to Dobryanski [16] the content of humous material in the OM of true oil shales should not exceed 25 %.

The peculiarities of the chemical composition of aquagenic OM are retained until a certain stage of catagenesis. The capacity of kerogen to produce significant quantities of liquid organic products under thermal decomposition is realized in mesocatagenesis under natural conditions and as a result, the OM of the shales loses one of its main differentiating features. (According to Gubkin, the oil shales are rocks that have not developed to the stage of production of petroleum [44].) During the late stages of catagenesis, the initial chemical differences in the organic starting materials are lost to a considerable degree [33]. The degree of catagenetic transformation of fossil coals has always been taken into account as a classifying parameter (such as the index of refraction of vitrinite, yield of volatiles, etc.).

It is practical to take this parameter into account in an analogous manner for oil shales as well, and to limit the range of use of the term ‘oil shales’ to the rocks that contain aquagenic OM the degree of transformation of which does not exceed early mesocatagenetic, i.e., that have not yet reached the phase of intensive generation of liquid hydrocarbons. With this definition, a group of œformerB oil shales can be distinguished that to a significant extent have utilized their oil-producing potential. For example, shungites and other graphitoid shales belong to this group; the majority of investigators do not consider these to be oil shales.

It is quite apparent that the origin of the OM is reflected in its elemental composition. Because of the high hydrogen content in the starting, predominantly fatty material, the hydrogen content in the OM of oil shales is in the range of 7-10 % [20] and the atomic ratio of H/C is 1.2-2.0. According to Dobryanski [16], the atomic ratio of H/C of 1.4-1.5 is more typical for kerogens; Kein [27] proposes the ratio of 1.2-1.6. Karavayev [40] used this indicator as a classifying parameter and demonstrated that its value falls into the interval of 1.25-1.95 in all sapropelites and that the majority has H/C ratios of 1.5 or higher.

Thus, besides the yield of semicoking oil, the elemental composition of OM also represents an acceptable diagnostic indicator of oil shales. It must be noted that the yield of oil calculated for the OM correlates with the hydrogen content in the kerogen [53]; this is additional evidence justifying the use of high oil yield as a distinctive characteristic of oil shales.

Proceeding from the indices that the majority of specialists consider characteristic of oil shales and analyzing the diagnostic significance of each of these, this type of caustobioliths can be defined in a general manner as following: œOil shale is a sedimentary rock containing organic matter of predominantly aquagenic origin, the degree of transformation of which does not exceed early mesocatagenetic, that has low solubility in low-boiling organic solvents but generates significant quantities of liquid organic products on thermal decompositionB.

By defining oil shales as rocks containing OM that originates predominantly from aqueous organisms and has low degree of transformation (up to the long flame stage) in conjunction with low solubility and high yield of semicoking oil permits with sufficient certainty to differentiate oil shales and other combustible rocks[*].

The above-mentioned definition is based on the properties of OM of oil shales as their more specific part. Oil shales are usually also characterized by their fine- or small-grained structure, the presence of some argillaceous material and other features which are, however, characteristic of not only shales and are therefore not diagnostic.

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[*] Since the definition of the term 4oil shale’ is at the present time still under discussion, this book also contains data on some caustobioliths that according to the above-mentioned definition do not belong to oil shales by all their properties. However, from the actual data that characterize these combustible rocks, it is always possible to make a decision that corresponds to ones opinion.

When defining oil shales as an industrial raw material, it is necessary to introduce numerical indicators of quality that correspond to their manner of utilization, that change concurrently with technical progress but that are also dependent on the presence of resources of other raw materials. For example, if oil shales are used as fuel, their quality is determined foremost by their heat of combustion (at the present time not less than 1000-1500 kcal/kg or 4.2-6.3 MJ/kg); if used as raw materials for production of artificial liquid fuel - by the yield of semicoking oil (presently the minimum is 5-10 % of shale); as raw materials for the production of building materials, agrochemical products, etc. - by the requirements of the respective industries. These and similar characteristics of oil shales allow the estimation of their reserves for specific areas of utilization but cannot replace the general definition.

When defining the oil shales through the properties of their OM, it would seem to be appropriate to start from the term ‘kerogen’. However, defining this type of caustobioliths as ‘kerogenic (kerogen-containing) rocks’ [1, 9, 54] is not sufficient, not as much because a number of authors define kerogen-containing rocks as the poorer varieties of oil shales (up to 10 % [47] or 15 % [5] OM), but rather because the term ‘kerogen’ itself is poorly defined and ambiguous. The vast majority of investigators working in the field of oil shales define kerogen as the lump OM of shales; however, for a number of scientists studying primarily dispersed OM, kerogen represents the nonsoluble in organic solvents part of fossil OM of any genetic type. Consequently, the use of this definition, that is attractive because of its brevity and closeness to traditional for mined rocks, in this particular case apparently leads to different interpretations of the contents of the term ‘oil shales’.

To characterize the OM in shale we have used the content of so-called conditional organic mass [100 - A^d - $(CO_2)^d_M$] since the determination of the actual OM content in shales is difficult, especially because of the necessity of taking into account the water in crystal hydrates. For utilization of the general but also approximate formula of Krim [55] not sufficient data are available in most cases. Actually, for some oil shales (kukersite [56], Dictyonema shale of Estonia [57], Pripyat shale of Byelorussia [58], etc.) more accurate formulas for calculating the OM content have been developed; however, in the interests of comparability of the data, the content of conditional organic mass is presented for these as well. Since this indicator corresponds only approximately to the actual OM content, it is inevitable that some of the other indicators (that are determined by recalculation of the results of analysis per OM, such as elemental composition of OM, yield of semicoking products per OM, and others) are also approximate.

The part of the OM of shale that is soluble in low-boiling organic solvents is called bitumoid. This term was proposed by Vassoyevich in 1958 [59] and is preferred to the alternative ‘bitumen’ since it is unambiguous.

The designation of analytical indicators takes into account the corresponding standards wherever possible.