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M. Yu. NAZARENKO [1], Associate Professor, Candidate of Engineering Sciences, nazarenko_myu@pers.spmi.ru
V. A. RUDKO [1], Chief Operating Officer, Candidate of Engineering Sciences
S. N. SALTYKOVA [1], Associate Professor, Candidate of Engineering Sciences

[1] Saint-Petersburg Mining University, Saint-Petersburg, Russia.

WORLD RESERVES OF OIL SHALES: REVIEW

Currently, the search is underway for new promising carbonaceous materials that can partially or completely replace high-quality coking coals in a number of metallurgical and coke-chemical processes, for example, in reduction or agglomeration. In addition, effective and economical ways of using local low-grade hydrocarbon raw materials, including oil shales, are being developed, which is an urgent area of research in many countries. The world's reserves of oil shales are huge, and the potential for their use has not yet been fully explored. This work is devoted to the analysis of the properties and composition of oil shales at the largest deposits in the world. The theoretical studies described in this work allow identifying possible potential ways of processing oil shales to obtain valuable products for the metallurgical and coke chemical industries, based on the knowledge of the chemical composition and properties of this raw material.

Keywords: *oil shale, low-grade carbon raw materials, oil shale coke, shale oil, deposit, integrated processing, rational use of natural resources*
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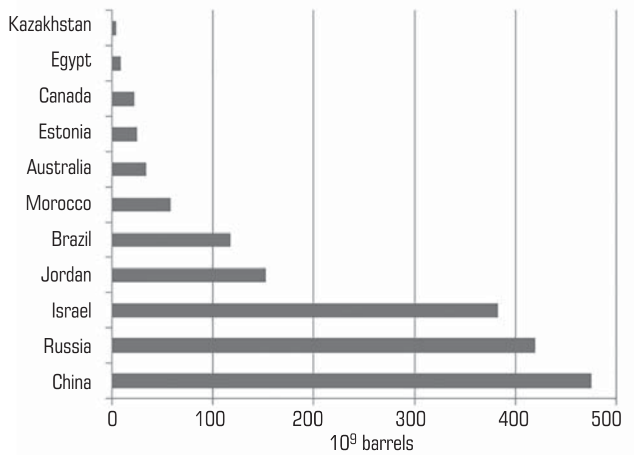
Introduction

Currently, the search is under way for new promising carbonaceous materials capable to replace, partly or entirely, high-grade coking coals in some processes in metallurgy and coke chemistry, for instance, in reduction or agglomeration. Furthermore, in view of depletion of oil and natural gas reserves which take the first place in the world's fuel and energy supply and consumption, many economies suggest utilizing all available and potential sources of carbons and hydrocarbons, including low-grade resources [1–3]. One of such promising low-grade carbon raw materials can be oil shale [1, 4].

Oil shale is a solid mineral product with large content of mineral admixtures and organic mass (kerogen) [5, 6]. The global reserves of oil shales are huge (more than 600 proven fields) and total (5860–12160) $\cdot 10^9$ barrels in shale oil equivalent (CIS countries — 3500, USA — 2000–8000, Europe — 50–100, China — 30–170, etc.) [7]. A top country with the largest oil shale reserves (in shale oil equivalent) is the USA (2000–8000$\cdot 10^9$ barrels). The international distribution of the rest of the oil shale reserves is described in the **Figure** [8, 9].

It is rather difficult to give a precise estimate of oil shale reserves in a country as oil shales from different fields differ in chemical composition, content of organic matter and in technologies of extraction. One of the benefits of oil shales is their occurrence mostly in the easily accessible places with well-developed transport systems, which facilitates the search, exploration and extraction of this low-grade raw material [12, 13]. High ash content of oil shale reduces greatly its calorific value and makes its long-distance transport economically inefficient [14, 15]. One of the promising methods of oil shale processing is in-situ thermal treatment and production of a liquid product — shale oil and coke oven gas. Considering the increased demand for liquid oil products and simultaneous depletion of oil reserves, huge oil shale reserves can be assumed as an inexhaustible source of carbons and hydrocarbons in the short term [16]. This trend, though promising, is unable to solve all problems connected with oil shale processing. Expansion of application range of such low-grade local raw material as oil shale by means of using it in metallurgy and coke chemistry can increase its application efficiency, promote energy policy diversification and add up total energy resources of a country [17, 18]. Evidently, improvement and development of the existing and new technologies used in thermal processing of oil shales for manufacturing products usable in different economic sectors (energy, metallurgy, coke chemistry, etc.) requires a comprehensive and integrated analysis of this low-grade raw material [10, 19].

Based on the afore-said, **the aim of this study** was to examine the theoretical research on the global reserves of oil shales. To that effect, the following objectives were set and met: comparative analysis of physicochemical properties of oil shales at different fields; determination of potential ways of processing oil shales to use the products in metallurgy and coke chemistry with regard to the known chemical composition and properties of the raw material.



Top countries – holders of largest oil shale reserves in shale oil equivalent, Mt [10, 11]

Characteristic of oil shales from different fields

Each oil shale field features unique conditions of formation and origin of the organic and inorganic matter, which has a great influence on the properties and composition of oil shales. Many oil shale fields need additional exploration and analysis of properties and composition of oil shales, and numerous studies into properties and composition of this raw materials in different countries point at the relevance of the problem. Below in this article, a brief characteristic of properties and composition of oil shales is given in terms of some large fields, and the comparison of these characteristics is carried out.

The authors of [20] analyzed the use prospects of oil shales from fields in Kazakhstan. Spotlight was on the fields characterized in **Table 1**.

The mineral component of oil shales from these fields mostly represents the following oxides: SiO_2, Fe_2O_3, CaO, MgO and Al_2O_3. Alongside with these oxides, there are Mn, Ni, Pb, Cu and other elements. Based on the analysis of properties and compositions of oil shales from the listed fields of Kazakhstan, the authors of this article arrive to a conclusion on essentiality of using these oil shales in the chemical and petrochemical industries.

The studies [9, 21] inform on the oil shale reserves in the Republic of Uzbekistan, which total 47.0 Bt. The Uzbekistan oil shales contain (56.0–70.0) mass% of carbon, (5.0–10.0) mass% of hydrogen, (0.2–20.0) mass% of nitrogen, (23.0–40.0) mass% of oxygen and (0.2–11.0) mass% of sulfur. The calorific value is low, in a range of 8 to 12 MJ/kg. For this reason, processing of these oil shales is attractive only in terms of the inorganic matter which contains many valuable components, for example, U, Mo, Au, W, Ag, Re, Cd, Se, Cu, Ni and Pb, including rare earth and platinum group metals.

The study [22] describes the oil shale fields in Bulgaria (**Table 2**).

The authors emphasize that Borov dol's oil shales contain less organic matter (19.9%) as compared with the fields of Krasava (28.5%), Mandra (27.7%) and Pirin (34.5%). Finally, the authors tell on the promising nature of using oil shales in power generation in Bulgaria.

The co-authors of [24] from Morocco point at the usability of oil shales in manufacture of both organic products, such as resins, carbon adsorbents or carbon fiber, and inorganic materials, for instance, cement, calcium, alumina, zeolite etc. The authors arrive to a conclusion that Tarfaya oil shales, Morocco, is a suitable feedstock to manufacture adsorbents for removal of organic matter and metals from wastewater.

The main reserves of oil shales of Turkey are described in [25, 26]. Oil shales are the critical potential energy source in the country, and are the second largest energy source after lignite. The main fields of oil shales in Turkey occur in the region of central and western Anatolia; the fields of the largest volume, highest quality and best mineability of oil shale reserves are: Miocene Beypazarı in Ankara — 330 Mt; Seyitömer in Kütahya — 120 Mt; Himmetoğlu in Bolu — 660 Mt; Paleocene–Eocene Hatildağ in Bolu — 360 Mt. The calorific value of oil shales from these fields ranges from 773.86 to 847.9 kcal/kg.

Jordan by recent estimates holds 50 Bt of proven oil shale reserves (24 fields) which are assumed as a promising alternative energy source in the country [27], as the fields lie nearby potential consumers, which heightens interest in studying properties of this raw material and its processing methods. **Table 3** offers a short characteristic of oil shale properties from the Al-Lajjun and El-Lajjun fields [27].

One of the largest holder of oil shale reserves in the world is China [28]. Oil shale reserves in China locate in 50 basins in 20 provinces and autonomous regions of the country. China possesses 978 Mt of proven oil shale reserves. The properties of China's oil shales are described in terms of the fields of Huadian and Luozigou (**Table 4**).

Another country having large oil shale reserves is Estonia: the use of this raw material in the energy sector of the country reaches 90.0%. Oil shales in Estonia contain 77.00 mass% of carbon, 9.70 mass% of hydrogen, 0.40 mass% of nitrogen, 10.60 mass% of oxygen and 1.60 mass% of sulfur (**Table 5**).

The largest oil shale province Green River occurs in the USA and includes three oil shale fields: the Piceance Basin in the northwest of Colorado, the Uinta Basin in the northeast of Utah and the Greater Green River Basin holding the potential oil shale reserves of 4.285 trillion barrels in shale oil equivalent [29]. The carbon content of the organic matter in these oil shales is 80.50 mass%, hydrogen content is 10.30 mass%, nitrogen content is 2.40 mass%, oxygen content is 5.80 mass% and sulfur content is 1.00 mass%.

Russia possesses huge resources of such low-grade raw material as oil shales at the estimated level of 700288.85 Mt [30]. For example, the Baltic Basin within the boundaries of the Leningrad, Pskov and Novgorod Regions includes the Leningrad, Veimarn and Chudovo–Babino fields. The properties and composition of the Leningrad field oil shales are described in [31, 32] (**Table 6**). The content of carbon in the oil shales from the listed field ranges as 76.50–77.50 mass%, hydrogen — as 9.40–9.90 mass%, nitrogen — as 0.20–0.50 mass%, oxygen — as 9.50–12.00 mass% and sulfur — as 1.20–2.00 mass%.

Table 1. Characteristic of oil shales from fields in Kazakhstan

Field	Moisture content, mass%	Ash content, mass%	Calorific value, kcal/kg	Sulfur content, mass%
Kendyrlyk	4.0	71.0	1430.0	1.0
Kushmurun	7.0	58.0	1852.0	2.6

Table 2. Characteristic of oil shale fields in Bulgaria

Field	Moisture content, mass%	Ash content, mass%	Calorific value, MJ/kg	Sulfur content, mass%
Krasava	1.4	55.9	10.4	1.72
Borov dol	3.0	73.3	15.08	2.6
Mandra	0.8	58.7	8.8	2.6
Pirin	2.8	60.9	16.0	2.2

Table 3. Characteristic of oil shales in Jordan

Field	Moisture content, mass%	Volatile yield, mass%	Ash content, mass%	Sulfur content, mass%	Calorific value, kcal/kg
Al-Lajjun	2.43	–	–	3.10	1590.00
El-Lajjun	1.82	13.70	63.27	8.20	1792.00

Table 4. Characteristic of oil shales in China

Field	Moisture content, mass%	Ash content, mass%	Volatile yield, mass%	Calorific value, kcal/kg
Huadian	7.51	50.28	39.44	11 539.14
Luozigou	2.58	72.24	20.44	5226.48

Table 5. Characteristic of oil shales in Estonia (average values) [23]

Field	Moisture content, mass%	Ash content, mass%	Volatile yield, mass%	Calorific value, kcal/kg
Estonia	6.0–10.0	45.0–50.0	38.2–42.5	8.0–12.0

Table 6. Characteristic of oil shales from the Leningrad field

Field	Moisture content, mass%	Ash content, mass%	Volatile yield, mass%	Sulfur content, mass%
Leningrad	2.30	50.80	40.50	1.80

Regarding mineral composition, Leningrad oil shales contain, mass%: alumosilicates and quartz — 58, calcium and magnesium carbonates — 34, sulfates — 4, pyrite — 3, phosphates — 1.

Conclusions

Large-scale development of the oil shale industry in many ways depends on the level of study of oil shale properties and composition, as well as on the comprehensiveness of the approach to this low-grade solid mineral raw material. Systematization of the accumulated knowledge and new research findings can allow promising ways of improving technologies of extraction and processing of oil shales.

For finding a smart and efficient way of using oil shales from a specific field, it is necessary to have data on the three basic characteristics of the raw material: ash content, inorganic composition and calorific value. Depending on a field of oil shales, their ash content ranges from 42.5% (Ermelo field, South Africa) to 82.3% (Turov, Lyuban, Pripyat field, Belarus). The calorific value of oil shales from different fields can vary in a wide range, from 3.9 MJ/kg (Wurtemberg, Germany) to 21.2 MJ/kg (Yarega field, Timan–Pechora Basin, Russia). Aside from that, it is required to take into account the needs of the economy of a specific country: whether it needs a wide range of chemical products, or it has to produce fuel and power only using available raw material.

After a detailed analysis of oil shales, a usage trend is selected for oil shales from a specific field, based on the organic or inorganic matter of the raw material, or both. Such usage trends may be: mining and combustion as boiler fuel; mining and use as a feedstock for manufacturing cement with by-production of energy; mining and conversion to a more valuable energy (resin, fuel), chemical (benzol, toluol, etc.) or coke-chemical (coke, semi-coke) feedstock; mining and processing of oil shales as inorganic raw materials with manufacture of sorbents, fluxing additions, catalytic agents, fertilizer and high-value micro components. For example, oil shales in such countries as the USA, Australia, England, Kazakhstan and Estonia contain much carbon (to 80.00 mass%) and hydrogen (to 11.00 mass%) in their organic matter, which implies expediency of their processing with a view to producing both power and different fuels and chemical agents. High calorific values of oil shales in Bulgaria and Ethiopia (to 15 MJ/kg) suggest combustion of the raw material for producing electric power. Most oil shale reserves in such countries as Russia, China, Uzbekistan, Azerbaijan, Turkey, Serbia and Morocco need integrated processing to enable manufacture of high-value products both from the organic and inorganic matter of this mineral raw material.

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