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TECHNOLOGIES AND PROCESSING OF OIL SHALE DEPOSITS OF UZBEKISTAN

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Abstract
The object of the study is oil shale and host rocks of the Sangruntau deposit and oil shale of the Baysun deposit. During the work, thermal decomposition of the sample material was carried out using a two-stage scheme on geological samples collected from the experimental block of the Sangruntau deposit. At the first stage, pyrolysis (burning without oxygen access) was carried out, and at the second stage, oxidative burning. Based on the results of thermal analysis, the yield of liquid and gas phases of pyrolysis, semi-coke and semi-coke ash from oil shale, overlying and underlying rocks was determined. It is shown that the main criterion for determining the boundaries of the shale formation is the yield of shale oil, and not the color of the rock. A pattern of increasing concentrations of many metals (vanadium, molybdenum, REE) with an increase in the yield of shale resin for rubidium and cesium is the opposite. The 20 most promising elements for extraction have been identified.

Keywords: Flammable shale , bituminized marls , thermal decomposition , liquid phase pyrolysis , metals , shale oil , UTT -3000.

Introduction
In the medium term, oil shale could become an important mineral resource for a number of industries in Uzbekistan.
Oil shale is a multi-component raw material consisting of both organic matter (kerogen) and an inorganic part, represented mainly by silicate minerals and sulfides.
A distinctive feature of domestic oil shale is its high metal content. At the same time, metals are part of sulphide and non-metallic minerals, and also form complex compounds with organic molecules. Shales of almost all deposits in Uzbekistan are classified as shales with a high sulfur content - up to 6.0%. Sulfur in reduced form is divided into "mountain" sulfur (sulphide minerals) and "organic" sulfur. In the form of sulfates (oxidized sulfur) is 20-40% of its total sulfur content. Shales of the Sangruntau and Baysun deposits differ sharply in their physical and chemical properties. Sangruntau shales contain a significant (40% and higher) amount of clay minerals, which leads to their easy erosion by water - "hydrophilicity". On the contrary, the Baysun shales have a pronounced hydrophobicity, are not washed away by water and when in contact with water only the uppermost layer of shale particles is wetted. The spectrum of metals in the shales of both deposits is almost the same, their content in the Baysun shales is 1.5-2 times higher. The spectrum of metals itself is very wide and includes molybdenum,

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vanadium, nickel, uranium, rare earths (more than 60 valuable elements in total). The content of individual metals (vanadium, molybdenum) is quite significant 0.5-2.0 kg/t, the content of others (nickel, copper, rare earths, uranium) is within tens and hundreds of grams per ton. The content of phosphorus, aluminum and iron reaches tens of kilograms per ton. [1]
Thermal decomposition of shale in conditions without oxygen access results in three products: liquid phase of pyrolysis, gas phase and semi-coke (solid product). In turn, the liquid phase of pyrolysis can be divided into shale resin (oil, petroleum) and pyrogenetic solution, which also contains hydrocarbons in the form of an aqueous suspension, phenols, nitrogen compounds, etc. Shale oil contains saturated and unsaturated hydrocarbons with different boiling points, a large set of aromatic compounds, including sulfur-containing ones, heavy hydrocarbons. In its composition, shale oil differs from oil produced in the Republic, primarily in its activity, i.e. easy oxidation and tendency to enter into chemical reactions between the various compounds included in their composition.
All the above-mentioned features of Uzbekistan shale classify them as multi-component refractory raw materials, requiring the development of special technological schemes for their processing. At the same time, any technology proposed for processing must ensure the extraction of both hydrocarbon raw materials and metals from the source material.
In this work, comparative studies on the composition of oil shales and host rocks of the Sangruntau shales, and the Sangruntau and Baysun shales themselves, are carried out. A large volume of research was carried out on geological samples collected from the experimental block of the Sangruntau deposit.

LITERATURE REVIEW AND METHODS

Abroad, mainly in the USA, intensive research is being conducted to create processes and units for the thermal decomposition of oil shale. At present, the following can be considered promising processes and units that have passed industrial tests and are ready for implementation:
1) the Unocal unit at Parachute Creek (the only operating shale processing unit). The design capacity for resin is 1,600 m3 / day;
2) the Tosko-2 process, in which fine-grained shale (up to 12 mm) is heated by a circulating solid heat carrier – ceramic balls. The advantages of the Tosko-2 process are: high resin yield (100% of the laboratory yield), small volume of steam-gas mixture, the possibility of processing fines and ordinary shale, low resin solidification temperature, which will allow its transportation through pipelines to the processing site. The process was tested on a plant with a capacity of 900 tons/day;
3) the Paraho process. A design has been developed for a plant with a resin capacity of 318-795 m3 / day. The cost of building the plant should be between 150 and 250 million dollars.
In Brazil, the Petrobras company developed the Petrosix process.
The scheme of processing shale by this method has common features with the "Parajo" process. Experimental work was carried out on a plant with a shale capacity of 2200 tons/day. This plant

is designed to obtain from the shale of the Irati deposit about 160 m3 / day of resin, 36500 m3 / day of gas and 19 tons of sulfur.

The Lurgi and Ruhrgas companies have developed the universal Lurgi-Ruhrgas process for processing coals, oil shale, oil sands and liquid hydrocarbons. The applicability of the process for processing oil shale was demonstrated at a pilot plant with a capacity of 16 tons per day. The yield of products during the processing of Colorado shale was in % (based on shale with a resin yield of 125 l/t and a humidity of 0.5%): heavy resin - 3.06, medium - 8.68, gasoline - 1.33, gas - 2.66. The disadvantage of the method is the high content of mechanical impurities in the resin (up to 40% in heavy resin). Almost only one process is being developed for producing gas from shale - hydrogasification. These studies are being conducted by the Institute of Gas Technology (IGT) in the USA. Shale pyrolysis is carried out in a hydrogen atmosphere under pressure. The advantage of the method is the possibility of processing both rich and relatively poor shales, the possibility of obtaining both gas and medium distillates as the target product, a high degree of conversion of organic carbon into target products (for Colorado shales 95%, for eastern shales 70-85%, which is 2-3 times higher than with conventional dry distillation).

The conducted analysis of foreign studies shows that the proposed use of oil shale is primarily focused on the production of shale resin as a substitute for oil in the production of motor and boiler fuels. In addition to resin, high-calorific gas is obtained, which can be used for household purposes and chemical syntheses.

The U.S. Department of Energy believes that research and development in the field of oil shale is sufficient and that fuels from oil shale will remain uneconomical in the near future. All research in this area for several years will be theoretical and conducted in laboratories. Large-scale use of oil shale is delayed by economic considerations and depends mainly on the situation in the oil market. [2]

DISCUSSION

Preparation of samples for research. To study the enrichment, 6 technological samples from oil shale deposits were presented: two samples from the Sangruntau deposit (actually oil shale GS, containing marl VM), one from the Baysun deposit (actually oil shale TP-1) and three samples composed of individual rock samples (ferruginous clay, gray clay, light yellow clay) taken from pits at the Sangruntau deposit . [3]

To determine the nature of the distribution of components in the sample, a study of the material composition of the sample was conducted. When preparing the material for testing according to the scheme, samples were selected for spectral, chemical, gravitational and granulometric analysis. Specific gravity of samples: VM - 2.047 g / cm ^{3} , GS - 2.14 g / cm ^{3} , TP-1 - 1, 9097 g / cm $^{3.}$.

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Spectral, mass spectrometric, and chemical analyses of average samples were performed in the chemical laboratories of the State Enterprise "Central Laboratory".

Table 1 Results of full semi-quantitative spectral analysis (g/t) of samples from the Sangruntau and Baysun deposits

Elements	Field		
	Sangruntau		Baysun
	Oil shale (OS)	Containing marl (CM)	Oil shale (TP-1)
Si	> 30000	>30000	>30000
Al	>30000	>30000	>30000
Ca	>30000	20000	>30000
Na	>10000	9000	5000
K	8000	8000	-
Fe	>30000	>30000	10000
Mg	>30000	>30000	20000
P	5000	2000	1000
Ba	300	200	600
Sr	200	100	100
Mn	600	500	400
V	500	200	400
You	3000	3000	2000
Cr	200	100	80

Table 2 Metal content (g/t) in samples collected at the Sangruntau and Baysun deposits. Analyses were performed by mass spectrometry

Elements	Field		
	Sangruntau		Baysun
	GS	VM	TP-1
1	2	3	4
Li	63	46	29
Be	2.5	2.9	1.7
Na	8500	6600	1900
Mg	19000	17000	9200
Al	77000	92000	39000
P	3300	2000	5500
K	16000	19000	10000
Sc	16	20	8.4
You	3600	3900	1400
V	470	360	1600

Cr	230	250	120
Mn	190	200	600
Fe	36000	42000	37000
Co	10	11	26
Ni	100	78	500
Sr	200	180	860
1	**2**	**3**	**4**
Mo	80	17	1100
Ag	0.17	0.14	0.46
Cd	4.9	1.6	25
Sn	3.6	4.4	2.7
Sb	7.6	5.3	22
Te	0.29	0.32	0.66
Ta	1.5	2	0.80
Cs	9.1	12	5.1
Ba	390	280	780
La	28	29	28
Ce	46	48	34
N.d.	22	22	16
Hf	2.6	3.0	1.8
W	6.3	1,1	1.5
Tl	0.26	0.11	1,1
Pb	18	18	22
Bi	0.61	0.65	0.37
Th	12	15	6.3

It follows from the data provided that the conducted studies show that during thermal decomposition of the material of oil shale, selected in the experimental block of the Sangruntau occurrence, a stable yield of shale resin (analogous to crude oil) is observed, as a rule, at a level higher than 5% of the original (the exceptions are wells 3/8 and 4/1, where the resin yield is 3.9% and 4.8%, respectively). The average indicator for 32 wells is 6.4%, with a total yield of the gas phase, consisting of pyrolysis gases and "furnace" gases from the combustion of semi-coke, 14.6%, and semi-coke ash - 76.4%.

The conducted studies on the metal content of Sangruntau shales clearly indicate that the problem of reliable determination of the content of most metals in the original shales is one of the main ones. There is a significant spread in the results depending on the analysis methods used and, especially, the methods of preliminary preparation (decomposition) of the sample. The same picture is observed when comparing the analysis results obtained in Uzbekistan, Japan and Russia. This problem is largely due to the variety of forms of compounds in which metals are found [4]. Metals in shales are present in sulfides, phosphates, oxides, organometallic complexes, in the form of isomorphically substituted impurities and other forms. The high content of individual metals is confirmed by the results obtained in other countries, which should be considered as an independent examination. Separately, it is necessary to consider the data on the content of gold, silver, platinum and palladium in the original samples. In general, the results show a very low content of these metals in the studied samples.

CONCLUSION

The main result of the works carried out in this section of the topic is the confirmation of the high content of many metals in both the Sangruntau shales and the Baysun shales [5-6]. The ecologically acceptable yield of shale resin (petroleum oil) from samples of actual combustible shale of more than 5% of the weight of the processed material has been confirmed (for the Baysun shales it is 1.5-2 times higher). The relatively "young" (50-55 million years) age of the Sangruntau shales (the Estonian shales are 500 million years old) leads to the fact that during their thermal decomposition in the liquid phase of pyrolysis, a significant content of unsaturated organic molecules is detected, which leads to a high reactive (chemical) activity of the entire distillate as a whole, which can be classified as "young" oil. Addition of 20-30% shale resin to such oils leads to a significant increase in the total yield of light (gasoline, kerosene, diesel) fractions. An important technological factor in the processing of shale resin itself is the low yield of oil sludge (non-distilled residue) during its distillation of only 1-3% of the original weight of the resin.

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