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INVESTIGATION OF MINERAL MATTER OF THE MONGOLIAN KHOOT OIL SHALE

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The mineral matter of Khoot oil shale was investigated by petrography, FT-IR, SEM, XRD, chemical, atomic absorption methods and emission spectral analysis. Khoot oil shale contains 25 % organic matter and belongs to the aluminosilicate-carbonate type of oil shales with 51 % clay-minerals and 10 % calcite and dolomite. It contains also some rare elements such as yttrium, scandium and beryllium. SEM photography shows that Khoot oil shale is of pleated-sheet and schistose external structure and blasto-aleuropelitic internal texture.

Introduction

The world's increasing reliance on liquid fuels combined with its decreasing oil reserves has provided the impetus for research into alternative fuel sources such as oil shale. Oil shales consist of organic matter distributed in an inorganic matrix [1]. For oil shale rational, complex and wasteless utilization, detailed investigations of its chemical composition are needed. The amount of organic matter and the composition of the mineral part influence the quality of oil shale and determine its usability as raw material for power and particularly for chemical industry [2].

Kerogen types and kinetics of its decomposition and conversion into organic products have been studied rather extensively by many researchers, using various oil shales [3–12], whereas less attention has been paid to the investigation of oil shale mineral composition. Mineral matter accounts for 60–80 % of oil shale, so tremendous amounts of solid waste are discarded after oil shale pyrolysis or burning. These waste occupy land and pollute the environment [13]. Earlier studies in the field of oil shale mineral matter were carried out by Pets and other researchers [1, 13–16]. Mostly they report about the effect of minerals on retorting and the content of trace elements measured by neutron activation analysis. A detailed study of oil shale mineral matter is important for both its complex utilization and theoretical

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knowledge. The main characteristics of the Mongolian oil shale are described in [17–18]. These papers include also the conditions of its pyrolysis and thermal degradation, and the kinetic parameters determined.

In this study, chemical composition of the mineral matter of Khoot oil shale has been determined by using petrography, FT-IR, SEM, XRD, chemical, atomic absorption methods and emission spectral analysis.

Experimental

The Mongolian Khoot oil shale samples were ground for ten minutes in a vibration mill (VM-4, Czechoslovakia) and sieved to –150 mesh (ASTM).

Table 1 gives the main characteristics of the oil shale samples taken from the Khoot deposit.

Table 1. **Proximate and Ultimate Analysis Data of Khoot Oil Shale**

Indices	Khoot oil shale
Moisture W^a, %	5.70
Ash A^d, %	61.80
Organic matter, %	27.50
$(CO_2)^d_M$, %	10.65
S_{total}, %	0.32
High calorific value Q^d, kcal/kg	2070

The samples for taking the FT-IR spectra were prepared by mixing oil shale of known weight with dry KBr. Spectra were recorded between 4000 and 400 cm^{-1} using a Bruker model Vakuum-FT-IR-Spectrometer IFS. The densities of the oil shale samples were determined using a Micromeritics AccuPys 1330 instrument.

Petrographic analysis was carried out using ground oil shale. Oil shale morphologic analysis was carried out on a CamScan 3 scanning electron microscope on samples coated with Au. The X-ray diffractograms (XRD) of oil shale were obtained on a Siemens D-5000 diffractometer using the CuK_α radiation and those of oil shale ash on a *D*/max 2200 diffractometer with CuK_α radiation, Rigaku, Japan. Chemical composition of oil shale ash was determined by chemical and atomic absorption methods, and trace elements by emission spectral analysis using spectrometer (DFS-8, Russia).

Results and Discussion

The IR spectrum (Fig. 1) shows peaks at 3434 cm^{-1} for hydroxyl groups, at 2930, 2850 and 1380 cm^{-1} for CH_2 and CH_3 aliphatic groups, at 1710 cm^{-1} for carboxyl and carbonyl groups, at 1630 cm^{-1} for aromatic C=C bonds, at 1430 and 870 cm^{-1} for CO_3^- or carbonate, at 1030, 530 and 470 cm^{-1} for Si–O–Mineral bonds of clay minerals and quartz, at 800 and 776 cm^{-1} for Si–O bonds, at 710 cm^{-1} for aromatic C–H, and at 427 cm^{-1} for Me–OH bonds [19].

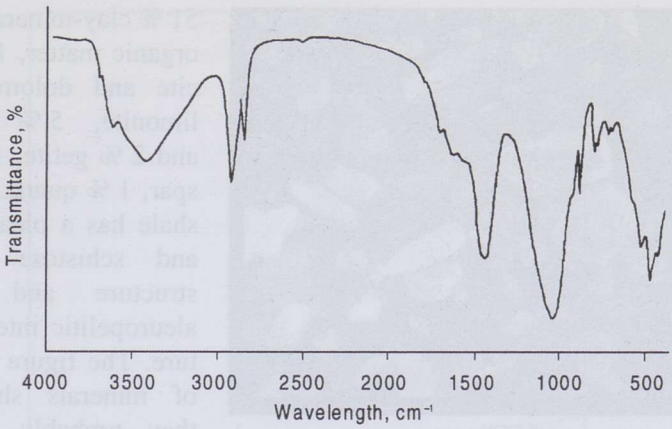

Fig. 1. IR spectrum of oil shale sample

The optical density of spectrum was calculated using IR spectra as shown in Table 2.

Table 2 shows that oil shale consists mainly of clay minerals, carbonate and organic matter which has dominantly aliphatic and naphthene-type structure. The peaks at 400–500 cm^{-1} are indicative of organo-mineral structure of Khoot oil shale. The relative intensities were calculated on the basis of optical density and compared with similar results from other investigations [20].

Table 3 shows that the index Si–O–Mineral/CH_3 for the Khoot oil shale sample is higher than that for Estonian shale. It seems that the content of minerals exceeds that of organic matter.

Table 2. **Characteristics of IR Spectrum**

Wave length, cm^{-1}	Khoot oil shale
Optical density A 10^2 cm^2/g	
3424	2.15
2924	2.50
2852	1.65
1704	0.96
1631	1.53
1434	4.60
1384	2.12
1032	8.50
526	2.2
471	3.4
Optical density B 10^4 cm^2/g	
874	2.43
800	1.9
714	0.53

Table 3. **Relative Intensities of the Oil Shale Spectra**

Relative intensities	Oil shale		
	Khoot (Mongolia)	Turov (Russia)	Estonian
D_{3400}/D_{1440}	0.86	1.2	0.4
D_{1440}/D_{2930}	1.84	1.1	2.2
D_{1040}/D_{2930}	3.4	8.0	1.1
D_{1040}/D_{1440}	1.85	5.7	0.8
D_{1440}/D_{800}	2.42	2.1	32.0

The index OH...O/CH_3 for the Khoot sample is also high and shows that its organic matter is mainly connected with active groups of clay minerals.

The density of Khoot oil shale is 1.9353 g/cm^3.

Petrographic analysis showed that Khoot oil shale consists of approximately

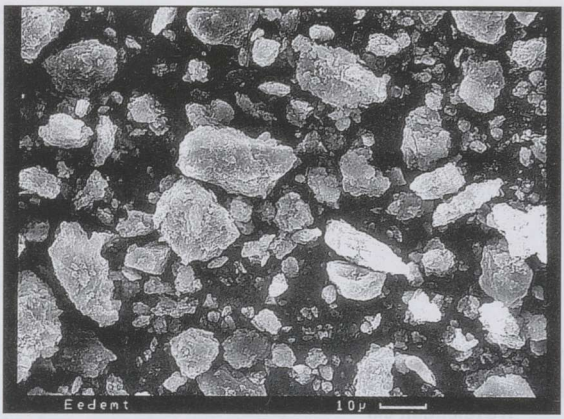

Fig. 2. SEM photograph of Khoot oil shale

51 % clay-minerals, 25 % organic matter, 10 % calcite and dolomite, 5 % limonite, 5 % epidote, and 2 % getite, 1 % feldspar, 1 % quartz. This oil shale has a pleated-sheet and schistose external structure and blasto-aleuropelitic internal texture. The figure and type of minerals show that they probably originate from the plagioclase.

The SEM photograph (Fig. 2) illustrates oil shale morphology, and Khoot oil shale XRD spectrum is shown in Fig. 3.

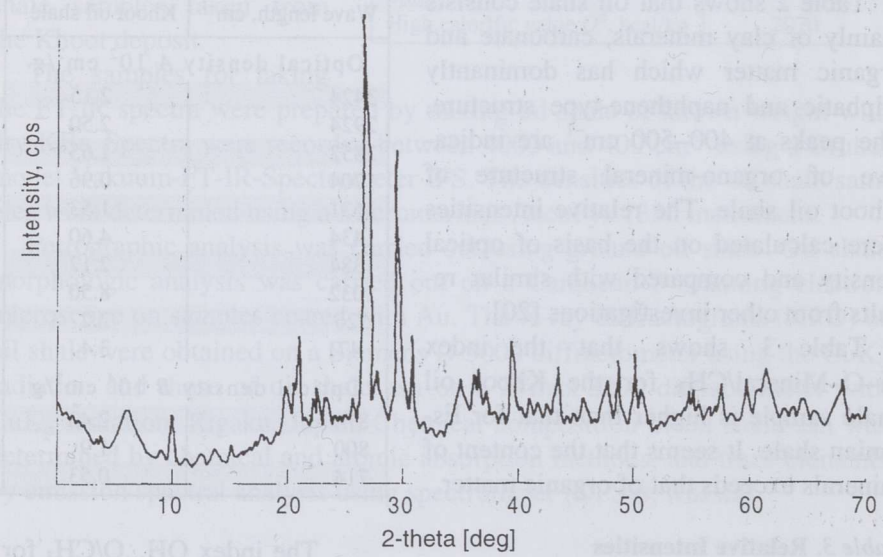

Fig. 3. X-ray diffraction patterns for Khoot oil shale

The spectrum shows the presence of calcite (d = 3.03, 2.08, 1.87 Å, e.g.), dolomite (d = 2.89, 1.78, 2.19 Å), quartz (d = 3.34, 1.81, 1.54, 1.37, 2.45, 2.12 Å), illite (d = 2.57, 1.49 Å), smectite (d = 1.495, 4.45 Å), getite (d = 2.45 Å), halloysite, feldspar (3.21, 3.18, 3.95 Å) and hydromica (d=2.54, 4.41, 1.48 Å). The distinctive feature of the Khoot oil shale is that its mineral matter contains no kaolinite and the content of quartz is low in comparison with Stuart and other oil shales [5].

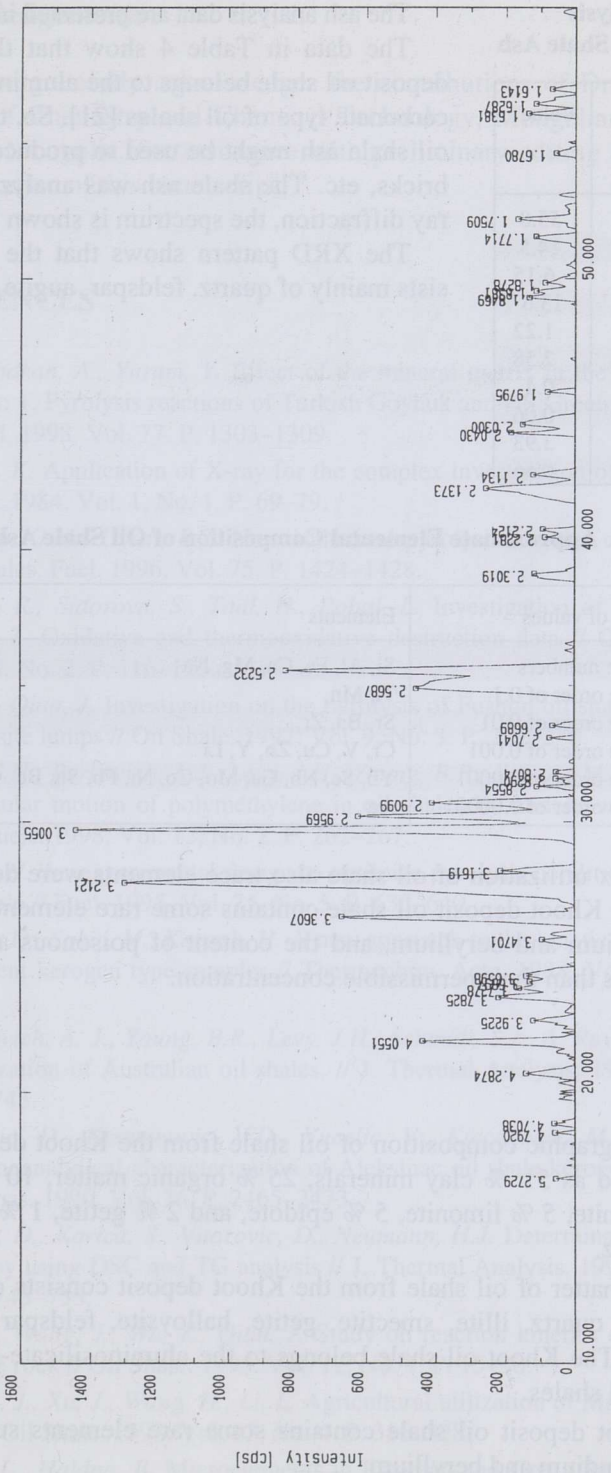

Fig. 4. X-ray diffraction pattern for ash of Khoot oil shale

Table 4. **Analysis of Khoot Oil Shale Ash**

Ash composition, wt %	Value
SiO_2	55.8
Al_2O_3	14.5
Fe_2O_3	6.15
CaO	13.6
Na_2O	1.22
K_2O	2.58
CO_2	0.4
P_2O_5	0.06
MgO	3.93
TiO_2	0.56

The ash analysis data are presented in Table 4.

The data in Table 4 show that the Khoot deposit oil shale belongs to the aluminosilicate-carbonate type of oil shales [21]. So, the Khoot oil shale ash might be used to produce cement, bricks, etc. The shale ash was analyzed by X-ray diffraction, the spectrum is shown in Fig. 4.

The XRD pattern shows that the ash consists mainly of quartz, feldspar, augite, etc.

Table 5. **Approximate Elemental Composition of Oil Shale Ash**

Order of values	Elements
Whole numbers	Si, Al, Fe, Ca, Mg, Na
Of the order of 0.1	Ti, Mn,
Of the order of 0.01	Sr, Ba, Zr,
Of the order of 0.001	Cr, V, Cu, Zn, Y, Li
Of the order of 0.0001	Yb, Sc, Nb, Ga, Mo, Co, Ni, Pb, Sn, Be
Of the order of 0.00001	Ag

For complex utilization of oil shale also trace elements were determined (Table 5). The Khoot deposit oil shale contains some rare elements such as yttrium, scandium and beryllium, and the content of poisonous and heavy elements is less than their permissible concentration.

Conclusions

1. The petrographic composition of oil shale from the Khoot deposit was determined as 51 % clay minerals, 25 % organic matter, 10 % calcite and dolomite, 5 % limonite, 5 % epidote, and 2 % getite, 1 % feldspar, 1 % quartz.
2. Mineral matter of oil shale from the Khoot deposit consists of calcite, dolomite, quartz, illite, smectite, getite, halloysite, feldspar, and hydromica. The Khoot oil shale belongs to the aluminosilicate-carbonate type of oil shales.
3. The Khoot deposit oil shale contains some rare elements such as yttrium, scandium and beryllium.

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