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CHEMISTRY

Functional Groups in Leningradsk Fuel Shales

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Abstract—This research focuses on the phase composition of Leningradsk fuel shales and its variation on heat treatment in the range 25–1100°C. The characteristic functional groups in the organic composition of Leningradsk fuel shales are C–C, CH_2, CH_3, and SH. The main minerals present are carbonates, silicates, hydroxides, sulfides, and sulfates. Phosphates are also present in small amounts. The mineral composition of the fuel shales is determined after heat treatment at 1100°C

Keywords: fuel shales, functional groups, mineral components, organic components, shale ash
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Interest in fuel shales is rising in parallel with the continuing growth of energy consumption, decrease in known accessible petroleum reserves, and increase in the sulfur and water content of petroleum [1]. The processing of fuel shales to produce electric power and chemicals has been adopted in Brazil, Estonia, the United States, China, and elsewhere [1, 2]. Mineral components constitute up to 50% of the fuel shales. Therefore, they must be taken into account in shale processing.

In the past decade, interest in the processing of shale and its ash has sharply risen. Many researchers acknowledge the need for detailed study of how the mineral components affect the behavior of fuel shales in processing, as well as study of the shale ash [2].

The ash contains the free oxides CaO and MgO as well as hydrating silicates, aluminates, and ferrites of calcium. For example, ash from Leningradsk fuel shales in the Pribaltiisk Basin contains around 36% CaO, of which around 20% may be free.

The main component of shale ash is slag glass SiO_2 [3]. Given that it contains aluminate slag glass, free lime (in variable amounts), and anhydride, the shale ash may be regarded as natural sulfate–slag binder, which may be used in the production of constructional materials and cement, in highway construction, and in agriculture to neutralize acid soil [4, 5].

The mineral composition of Leningradsk fuel shales was studied in [5]. The dominant components are as follows: 28% calcite $CaCO_3$; 25% quartz SiO_2; 17% illite $(K_{0.75}(H_3O)_{0.25})Al_2(Si_3Al)O_{10}((H_2O)_{0.75}(OH)_{0.25})_2$; and 11% microcline $K[AlSi_3O_3]$. In the present work, we study the functional composition of the organic and mineral components in Leningradsk fuel shales and its dependence on the temperature. We also study the mineral composition of the fuel shales after heat treatment at 1100°C.

XPERIMENTAL METHOD

We investigate Leningradsk fuel shales from the Pribaltiisk Basin, furnished by OAO Zavod Slantsy (≤25 mm fraction).

An IR Fourier spectrometer is used to determine the functional groups present in the fuel shales and their thermal destruction. To determine the functional groups, potassium-bromide tablets containing the samples are prepared. The dependence of the absorption intensity I_{abs} (%) on the frequency ν (cm^{-1}) is presented. The samples are manufactured by means of a press for the manufacture of potassium-bromide tablets in the analysis of solids by IR Fourier spectroscopy.

For X-ray phase analysis, we use a sample of shale ash obtained after heat treatment in nitrogen at 1100°C. The sample consists of finely ground gray powder of uniform grain size (mass 5 g). The mineral composition of the sample is studied on a DRON-6 X-ray diffraction system equipped with a cobalt-anode X-ray tube and with a secondary graphite monochromator. The diffraction patterns are analyzed by means of PDWin-4 software and the international JCPDS cards. The Rietveld method is used for quantitative determination of the phases.

RESULTS

The IR spectrum of Leningradsk fuel shale from the Fourier spectrometer is shown in Fig. 1.

Analysis of the IR spectra indicates that the characteristic functional groups in the organic composition of Leningradsk fuel shales are C–C, CH_2, CH_3, and

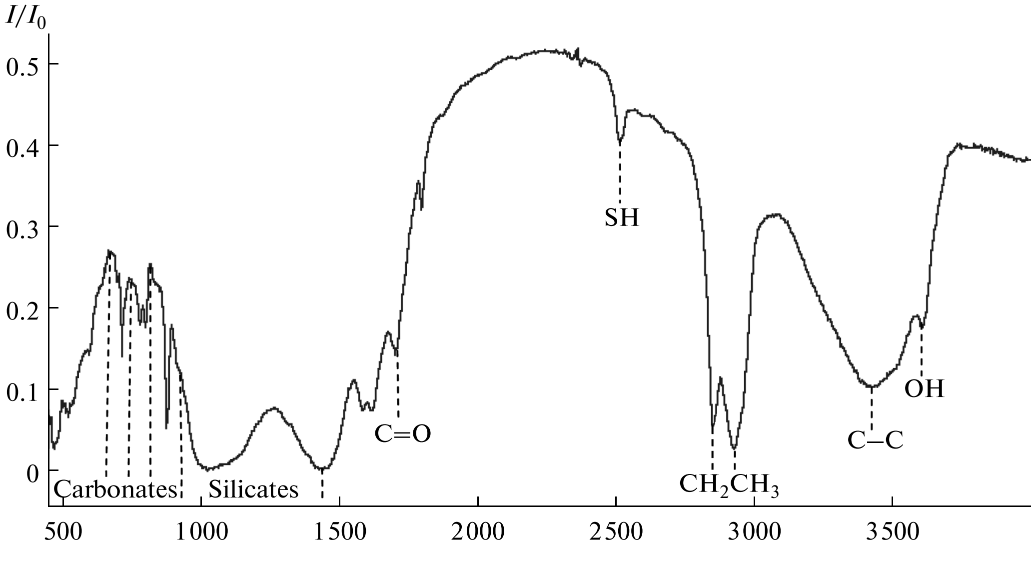

Fig. 1. IR spectrum of Leningradsk fuel shales.

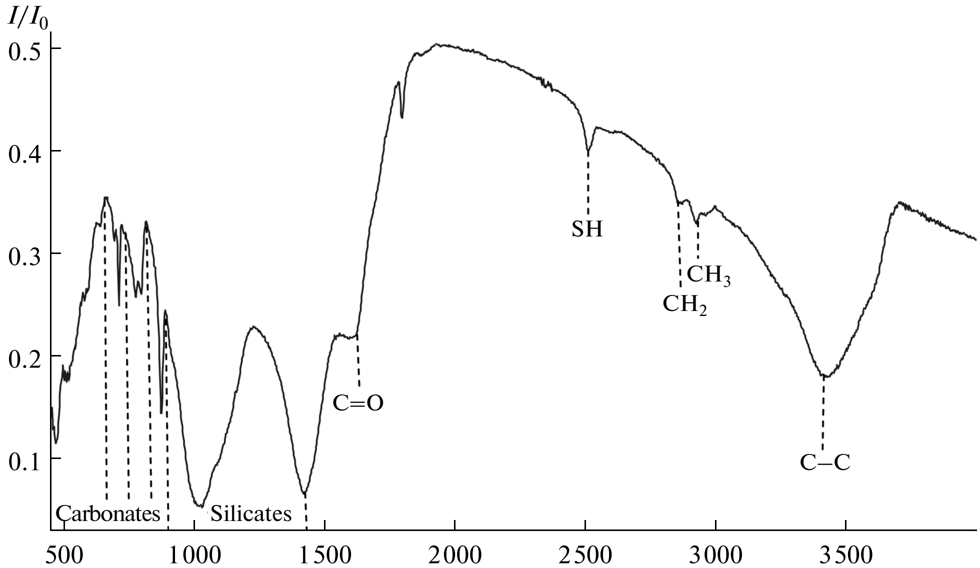

Fig. 2. IR spectrum of shales after heat treatment at 400°C.

SH. The main minerals present are carbonates, silicates, hydroxides, sulfides, and sulfates. Phosphates are also present in small amounts.

From these results, we conclude that fuel shales may be used in adsorption and filtration.

The IR spectra of the fuel shales after heat treatment at 400, 900, and 1100°C are shown in Figs. 2–4. Analysis permits the following conclusions.

(1) With increase in temperature to 400°C, free water is removed. At 1100°C, the chemically bound water is removed.

(2) With increase in temperature, the SH functional group disappears from the organic composition.

(3) With increase in temperature, the content of groups such as C–C and C–H declines.

(4) With increase in temperature from 900 to 1100°C, the intensity of the carbonate peaks is reduced. That may be attributed to the decomposition of carbonates.

In Fig. 5, we show the diffraction pattern of the shale ash. Before the diffraction pattern is recorded, the fuel shale is heated at 1100°C for 50 min in a PTK-1.2-40 tubular furnace, in nitrogen.

The table summarizes the composition of the shale ash. The predominant minerals are as follows: larnite Ca_2SiO_4 (42%); gehlenite $Ca_2Al(Al;Si)_2O_7$ (18%); aker-

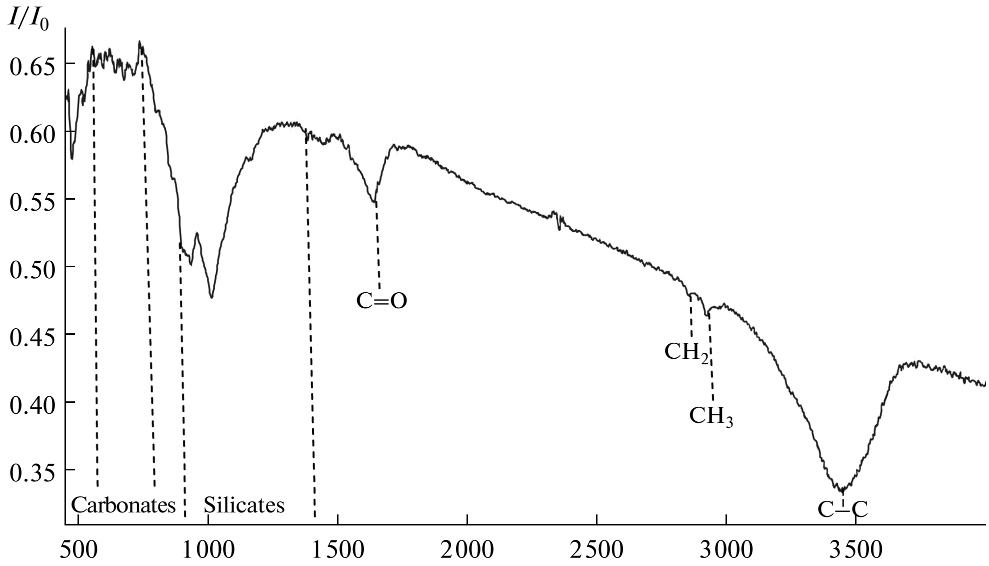

Fig. 3. IR spectrum of shales after heat treatment at 900°C.

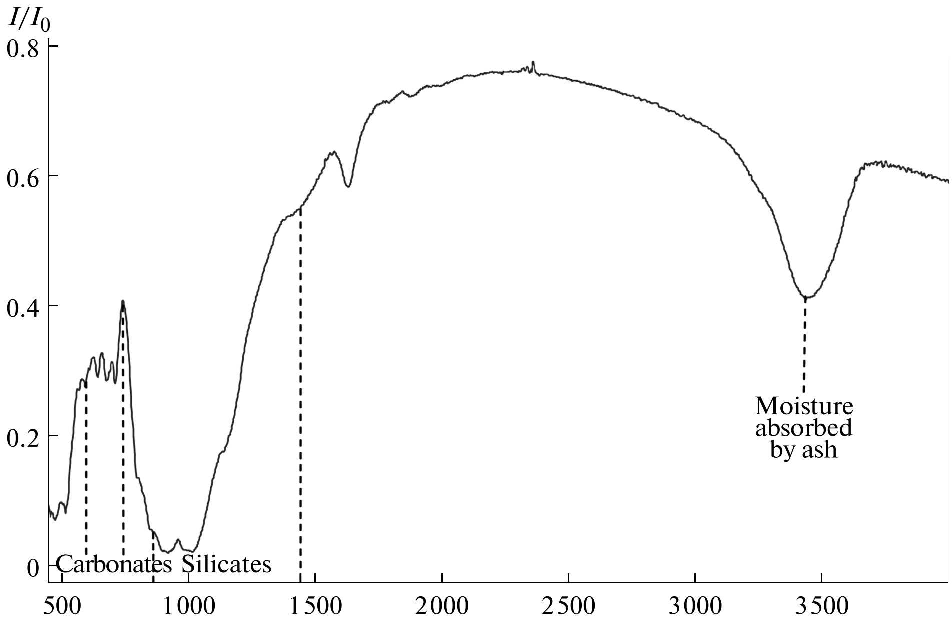

Fig. 4. IR spectrum of shales after heat treatment at 1100°C.

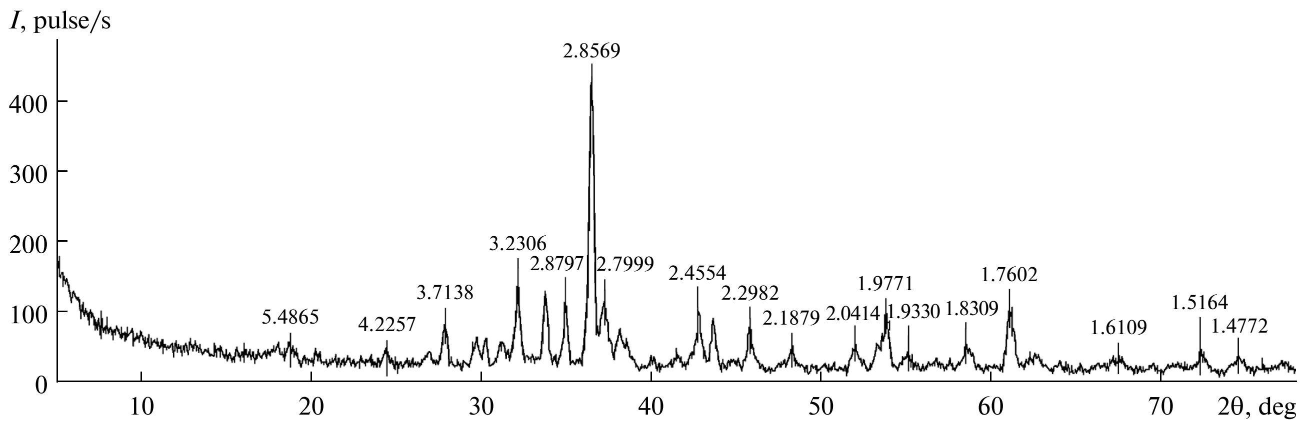

Fig. 5. Diffraction pattern of shale ash after heat treatment of shale at 1100°C.

Results of quantitative X-ray phase analysis for shale ash after gasification

Phase composition		Content, wt %
Larnite	Ca_2SiO_4	42 ± 5
Gehlenite	$Ca_2Al(Al;Si)_2O_7$	18 ± 4
Akermanite	$Ca_2MgSi_2O_7$	15 ± 5
Wollastonite	$CaSiO_3$	15 ± 4
Fayalite	$(Fe,Mg)_2SiO_4$	10 ± 3
Hematite	Fe_2O_3	≈1

manite $Ca_2MgSi_2O_7$ (15%); wollastonite $Ca^2MgSi_2O_7$ (15%); and fayalite $(Fe,Mg)_2SiO_4$. Small quantities of hematite are present.

The changes in the mineral composition on heating to 800°C were described in [5]. Further heating to 1100°C results in the formation of fayalite $(Fe,Mg)_2SiO_4$ from magnesite $MgCO_3$ and periclase MgO, with the participation of quartz SiO_2 and hematite Fe_2O_3. Gehlenite, akermanite, and wollastonite also appear.

CONCLUSIONS

We have determined the functional composition of Leningradsk fuel shales and its change on heat treatment at 400, 900, and 1100°C. The characteristic functional groups in the organic composition of Leningradsk fuel shales are C–C, CH_2, CH_3, and SH. The main minerals present are carbonates, silicates, hydroxides, sulfides, and sulfates. Phosphates are also present in small amounts.

With increase in temperature to 400°C, free water is removed. At 1100°C, the chemically bound water is removed. With increase in temperature from 900 to 1100°C, the intensity of the carbonate peaks is reduced. That may be attributed to the decomposition of carbonates.

The predominant minerals in shale ash are as follows: larnite, gehlenite, akermanite, wollastonite, and fayalite. Small quantities of hematite are present.

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