УДК 53.082.36:531.755

THE INVESTIGATION OF STRUCTURAL AND ADSORPTIONAL CHARACTERISTICS OF GLAUCONITE IN RELATION TO HYDROCARBON MIXTURES

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The task of improving already existing ecologically safe and technological combined process of adsorptional purification of hydrocarbon mixtures in systems with natural disperse sorbents that ensure compliance with the formats of prevention of environmental impact and human activity have been definitely relevant nowadays. The range of industries that already use natural adsorbents with different types of activation is very significant and increases every year due to the development of new deposits. In the research work for the purification of hydrocarbon mixtures, the glauconite rocks of the Karachiivetsky deposit in Khmelnitsky region, which provide a complex potassium-containing water aluminosilicate, a mineral from the group of hydrides of the subclass of layered silicates of a non-permanent and complex structure. It is expressed by averaged formula, which has a composition $((K,Ca,Na)<1(Al,Fe^{3+},Fe^{2+},Mn)_2[(OH)_2]A_{l0}$, $35Si_3$, $65O_{10}$, SiO_2 – 44-56; Al_2O_3 – 3-22; Fe_2O_3 – 0-27; FeO – 0-8; MgO – 0-10; K_2O – 10%, H_2O – 4-10% [1]. According to research results, the fractional and elemental composition of mineral raw materials has been established. Spectra of X-ray diffraction (the original samples of clay) reflect amorphous structure, low degree of crystallinity and small size of sample particles. The mineral composition of raw materials is represented mainly by glauconite 70-75 mass. %, quartz 20 wt. %, and feldspar about 4%. There are also some insignificant amounts of carbonates (calcite) and titanium oxides presented in the samples, which totally does not exceed 1–2% by weight. The morphology of the original samples of glauconite is represented by a layered structure in the form of isometric finely dispersed tiled particles [2]. Samples of thermally activated glauconite differ in the dispersion of clay aggregates and a significant increase in small elastic aggregates of crystallites. Infrared Fourier spectra indicate coexistence of Fe and Mg saturated phases in octahedral layers of clay minerals and the presence of isomorphous aluminum substitutions in the tetrahedral layer for natural glauconite. The physico-chemical properties of glauconite clay from group of deposits in Adamivka, Khmelnytskyi Oblast, are: solidity − 1.7÷1.8; density − 2200 ÷ 2900 kg/m^3; effective specific surface area of natural glauconite − 112 mg/g; cation exchange capacity of natural glauconite − 15 mg-eq; capacity of natural glauconite monolayer − 1.73 mmol/1g. Was established high efficiency of glauconite at water purification from salts of heavy metals as well as from a number of organic and inorganic compounds and radionuclides. In the process of filtration of contaminated water through activated glauconite, it almost completely retains iron and ammonia. Nearly at an order of magnitude reduces petroleum products from water and in 25-50 times reduces the content of radioactive isotopes of caesium-137 and strontium-90[3].

Electron microscopic images (Fig. 1) show the characteristic morphology for that clay mineral, which is represented by a layered structure in the form of isometric finely dispersed tile parts. The sample of natural glauconite is characterized by the structure of a more amorphous-jelly-like mass. Microphotographs show the characteristic morphology of glauconite samples in the form of shapeless clustered aggregates composed of finely dispersed scaly clay particles. The sizes of clay aggregates vary from 2 to 10 microns. In smaller aggregates, clay crystallites of glauconite show elasticity [4].

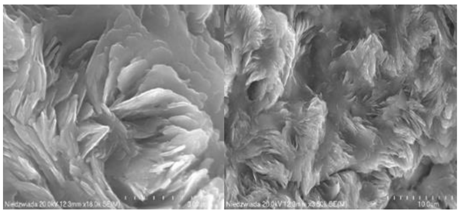

Fig. 1. Microphotographs of the sample of natural glauconite (100,000 times increase)

Determination of mineralogical composition was performed by X-ray phase analysis using an X-ray diffractometer DRON-3M. Phase analysis was performed using standard powder X-ray diffraction patterns of minerals collected in the PDF-2 of the International Center for Diffraction Data. On the radiograph of the natural sample of the rock are observed narrow diffraction lines with interplanar distances of 4,26; 3,344; 2,459; 2,238; 2,126; 1,98; 1,821; 1,673; 1,543; 1,454 and 1,419Å, which belong to quartz (Fig. 2). Diffraction lines with similar interplanar distances are also present on the X-ray diffraction pattern of the enriched glauconite sample, however in this case they are much weaker (Fig. 3), which is due to the lower content of quartz. On both radiographs is also present a narrow diffraction line with an interplanar distance of 3,247Å, which refers to feldspar. The intensity of this diffraction zone is about twice times lower than in the second sample. On the radiograph of the sample of enriched glauconite is observed a range of wide weakly intensed diffraction lines with interplanar distances of 10,12; 4,95; 4,53; 4,38; 3,713; 3,124; 2,577; 2,402 and 1,514 Å. In addition, on the radiograph of the sample of enriched glauconite there are very wide dome-shaped diffraction zones in the range of angles 2θ 45-50, 51-57, 62-67°. Such diffraction patterns are typical for poorly crystallized dispersed minerals. The position of the first diffraction reflex 10,12Å indicates that it is a micaceous mineral, and the value of the intense reflex in the angles 73 - 75°2θ, is equal to 1,514Å – what indicates that the mineral belongs to dioctahedral mica, which allows diagnosing it as glauconite. To confirm this, the mineral has a characteristic dark green color. Diffractograms of natural and magnetically enriched glauconite rocks from the Karachiyevetske deposit in Khmelnytskyi region are shown in Figures 2-3.

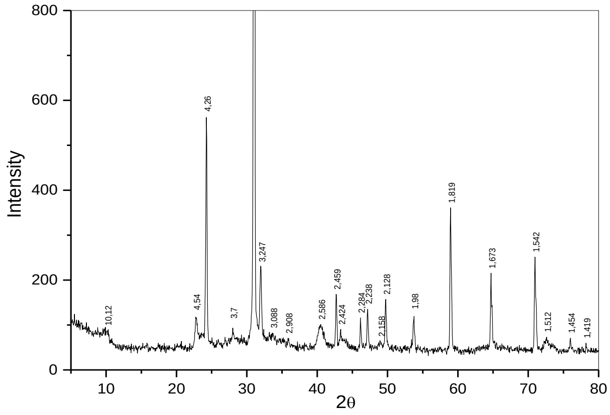

Fig. 2. Powder radiograph of glauconite rock in native form

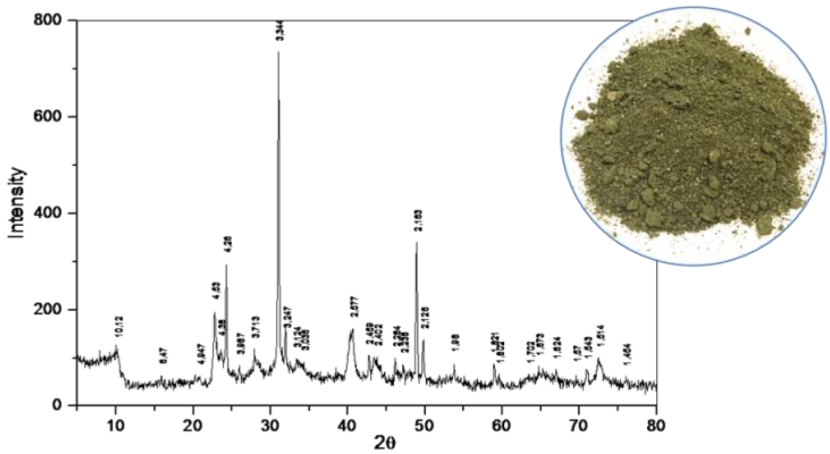

Fig. 3. Powder radiograph of glauconite rock enriched with magnetic separation

Thus, the mineral composition of the rock is following: glauconite 70-75 wt. %, quartz 20 wt. %, feldspar about 4%. The samples also contain minor impurities of carbonates (calcite) and titanium oxides, which in total does not exceed 1-2% of the mass. The investigated unleaded gasoline grade A-92 was investigated using high performance gas chromatography ("Crystal 5000.2"), where nitrogen was used as a carrier gas. The obtained results were processed in the GAZOLIN program. The results of the chromatographic study of gasoline A-92 are shown in Figure 4.

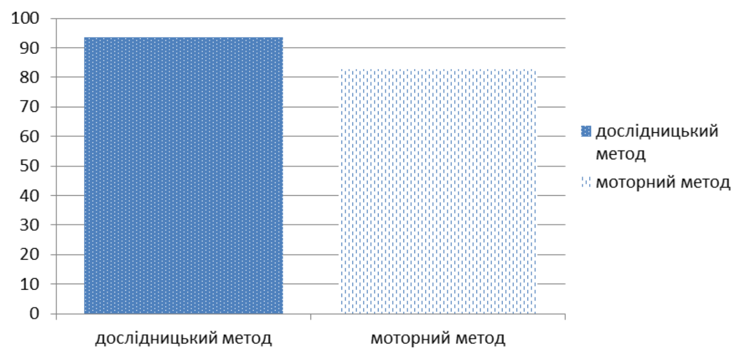

Fig. 4. Octane number indicators by research and motor methods of A-92 gasoline

To study the stability of glauconite granulate in samples of hydrocarbon mixtures were used two types of samples of granular natural glauconite with different sintering time and temperature, which are: granular natural glauconite (τ = 2 h, T = 500° C), and (τ = 1 h, T = 400° C). A sample of granular sorption material weighing 1 g was placed in a hydrocarbon mixture. Next, organoleptically observed changes in the granules of the sorbent. The studies were performed at different intervals: the first for 10 days and the second for 6 months.

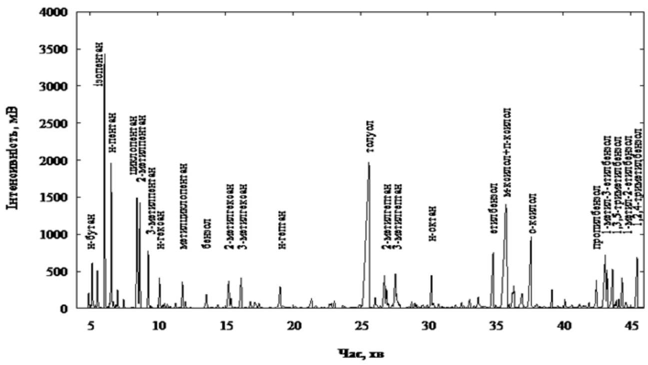

Fig. 5. Fragment of the chromatogram of a sample of a hydrocarbon mixture purified with natural glauconite calcinedat 400° C for 2 hours. (m = 0.3 g) with ultrasonic stirring τ = 5 minutes

The expediency of using ultrasonic mixing of hydrocarbon suspension is studied and experimentally substantiated in the work. In this case, one sample was examined chromatographically, without mixing it and leaving for 20 minutes; the second was stirred by ultrasound for 5 minutes, and the third was shaken for 20 minutes. The next step was to filter, centrifuge and chromatograph the purified sample of the hydrocarbon mixture. Therefore, according to research, after purification of fuel with natural glauconite, the CO content (%) decreases at blank mode for purified gasoline A-92 from 4.78 to 0.19, CO_2 content decreases from 12.18 to 8.56, and hydrocarbon content (ppm) decreases from 0.503 to 0.465. In the active mode of the engine, the CO content varies from 2.76 to 1.32, CO_2 from 13.37 to 10.24, and hydrocarbons from 0.377 to 0.299. The obtained results give grounds to claim that natural glauconites can be used in the production of high quality motor fuels and with reduced toxicity, which will improve environmental safety.

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