ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

UDK 544.46:665.75:662.7

K. K. KUDAIBERGENOV[1, 2], G. R. NYSSANBAYEVA[1, 2],
D. AMANJOLOVA[1], G. O. TURESHOVA[1], B. A. BAYTIMBETOVA[3],
E. K. ONGARBAYEV[1,2], Z. A. MANSUROV[1,2]

[1]Al-Farabi Kazakh National University, Almaty, Republic of Kazakhstan,
[2]Institute of Combustion Problems, Almaty, Republic of Kazakhstan,
[3]Satpayev University, Almaty, Republic of Kazakhstan

THERMODYNAMICS AND MECHANISM
OF OIL ADSORPTION PROCESS BY THERMOGRAPHITE

Abstract. In this work synthesis of the production of expanded graphite is proposed. It's used as a sorbent for the elimination of oil. It́s characteristics, kinetics, and properties were investigated. The mechanism of oil adsorption is established. The magnetic properties of thermographite were also determined.

Keywords: thermographite, thermodynamics, kinetics, adsorption, oil absorption, reagent composition, ferromagnet.

It is common knowledge that cleaning surface and wastewater from oil is one of the cardinal problems of environmental protection, since oil and oil products cause enormous damage to the biosphere [1]. A common and substantial lack of all the known ways of running can practically be described as the absolute impossibility of the recovery of the collected from the water surface of the oil. It is completely burned down (method of monitoring combustion), or it falls on the bottom and is subject to dissipation (disincentives, secondary coils), or it can be unjustifiably depleted or completely removed from the reagents, emulsified water (floating adsorbents), or civil, mechanical take (with the reduction of mechanical constitution), and such oil will undo by burning with a rubbish or coil [2, 3].

The new effective sorbent synthesized in [4] on the basis of thermographite (TEG) is devoid of the aforementioned shortcomings. In the studies, natural flake graphite of the Chelyabinsk deposit of grade GL-1 0.4-0.8 mm in size was used (GOST 5279-74), the swelling agent was six-water ferric chloride [FeCl3 · 6H2O] and the initiating agent was metallic magnesium. Synthesized during the combustion of oil sorbents possessed high sorption and hydrophobic properties. It has been established that they can be reduced to the use of non-refined products and other pollutants to 80 g per 1 g of corn, which is facilitated by such properties of the TEG as a high-speed surplus surface (50-150 m^2/g), low density (1-10 kg·m^{-3}), microcrystalline structure, to improve the resistance of large clusters of substances. It should be noted that an easy and hygienic thermomagnet stabilizes the rate of release on the surface of the water in the course of the day, and after the use of non-ferrous products in the course of several sideways. At this time it can wipe the water with the surface, as well as out of the water. It is hydrated, chemically inert, electrolytic, ecologic clean, removes non-ferrous products as if they are reconstituted or emulsified, as well as in a gasoline state.

In the next paper [5], the investigation of the kinematics of the thermogenesis of the reagent composition on the output of gaseous and solid products in the frames of the classical ways to the operation of the heterogeneous reactions of the type S1 → S2 + gas is given.

The obtained results allowed to evaluate the effective thermodynamic resistance for different temperatures (table 1).

Table 1 – Effective components of the rapidity of the reagent composition for various temperatures

Temperature of thermolysis, °C	Effective constant of shortly, k h[1]	Free member	Coefficient correlations
830	0,31 ± 0,01	0,23 ± 0,04	0,993
880	1,49 ± 0,04	-0,13 ± 0,06	0,990
1000	2,15 ± 0,09	0,43 ± 0,08	0,991

The calculated values of the effective energy of the activation of the reagent formulation are 176 kJ/mol and are close to the E_{act} values determined by other methods and presented in the literature.

The authors have proven that the main routes of the thermolysagic composition are the stages of dethermalization and ventilation (with the formation of OC and TRH, respectively), which appear paralleling. If we take into account the well-known literature [6, 7] and the obligatory for the synthesis of intercalated graphite compounds of the stages of electron transfer to the oxidizer and intercalation of graphite, it is possible to present the general scheme of the process and the destruction of SIG and, in the framework of this scheme, to consider this process as one.

The purpose of this study is to consider the thermodynamic possibility of forming thermographite using various crystalline hydrates at the interface: the solid surface of the reagent-air-oil film-water. Crystalline hydrates ($FeCl_3 \cdot 6H_2O$) can only be intermediate compounds and promote the formation of thermographite, and as the temperature rises, crystalline hydrates dissolve. Thermodynamic calculations of the values of the variation of isobaric-isothermal potentials at different temperatures.

At present, the most frequently used data are the changes in enthalpy (ΔH), heat capacity (Cp), entropy (S), Gibbs's energy (ΔG), and equilibrium constant (K) at constant pressure. Knowledge of such quantities, first of all, is necessary for determining the thermal balances of processes, in calculating the characteristics of equipment and for using them in theoretical works. Moreover, for the most part, on the basis of data on heat capacity, the effect of temperature on the enthalpy and entropy of substances and on their variation as a result of the reaction.

The values of the isobar potential are calculated for different temperatures by the formulas:

$$\Delta G_T = \left(\Delta H_{298} + \int\limits_{298}^{T} C_p dT \right) - T \left(S_{298} + \int\limits_{298}^{T} C_p \frac{dT}{T} \right) \tag{1}$$

$$\int\limits_{298}^{T} C_p dT = a(T - 298) + \frac{b}{2}(T - 298)(T + 298) + \frac{c}{3}(T - 298)(T^2 + 2 \cdot 298 T + 298 \cdot 298) \tag{2}$$

$$\int\limits_{298}^{T} C_p \frac{dT}{T} = a \ln \frac{T}{298} + b(T - 298) + \frac{c}{2}(T - 298)(T + 298) \tag{3}$$

$$\int\limits_{298}^{T} C_p \frac{dT}{T} = a \ln \frac{T}{298} + b(T - 298) + \frac{c}{2}(T - 298)(T + 298) \tag{4}$$

$$\int\limits_{298}^{T} C_p \frac{dT}{T} = a \ln \frac{T}{298} + b(T - 298) + \frac{c}{2}(T - 298)(T + 298) \tag{5}$$

The values of the standard values $\Delta H(298) = 0$, $S(298)$ and average molar heat capacity mean coefficients of the equation (mean = f (T) a = 4.1, b = 1.02·10^{-3} and c = -2.1·10^{-5}) are taken from the reference books [8-9]

Thermodynamic calculations of the values of the variation of isobaric-isothermal potentials at different temperatures (table 2).

Table 2 – Isobaric-isothermal potentials of ΔGT reactions of formation of thermogravenite and decomposition of crystalline hydrates at different temperatures.

T, K	$\int\limits_{298}^{T} C_p dT$	$\int\limits_{298}^{T} C_p \frac{dT}{T}$	ΔG_T, kcal/mol
873	-2581,6	-1,72	-2276,05
923	-3291,1	-2,36	-2377,33
973	-4100,8	-3,07	-2446,73
1023	5015,6	-3,82	-2509,21
1073	-6040,6	-4,61	-2564,10
1123	-7180,9	-5,46	-2587,88

As follows from the table, the formation of thermographites in the burning of oil at the interface between the solid surface of the reagent – air-oil film-water – is thermodynamically favorable and depends on the kinetic characteristics. The existence of crystalline hydrates at different ratios in natural graphite in the metastable state during the combustion of oil should be observed if the rate of formation of thermographite is sufficiently high. With increasing temperature, the dissolution rates of crystalline hydrates increase.

Thus, the thermodynamic characteristics of this process indicate its ability and direction towards the formation of individual compaction products, up to thermographite.

The establishment of the mechanism of the oil adsorption process, the nature of the adsorbing forces, is one of the important problems of physics and surface chemistry. Figure 1 shows a step-by-step sequence of interaction between the TEG and the oil film.
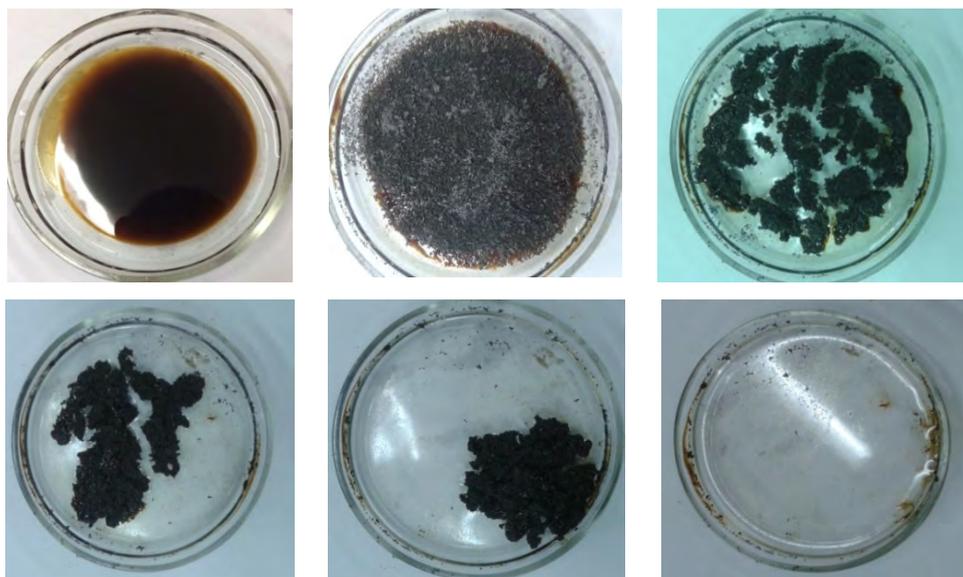
Figure 1 – Process of interaction of thermographite and oil film on the surface of water

The outer surface of the TEG is not homogeneous. In the places of contact of the particles of TEG and the oil film, interaction occurs due to intramolecular forces, which leads to a decrease in the density of the oil film. The increase in the magnetic moment of such sorbents enhances the effect of their attraction and the formation of dendrike-like structures. Such a structure ensures the stability of the position of the oil slick on the surface, at least in conditions of calm oil.

It is known [10] that the surface of any solid covers the double electrical layer, and the oil molecules are dipoles, and therefore there is interaction between the surface of the adsorbent and the oil film. Experimental studies of various adsorption cases show that the bond of the adsorbed molecule to the adsorbent can vary from weak molecular potentials to high values of chemical energy [11].

The whole process of water purification from oil contamination with an adsorbent can be presented in stages, beginning from the moment of the immersion of individual particles (or their conglomerates) of the sorbent into the oil film on water and interaction with it by the micellization scheme [12].

This process reduces to the fact that on the surface of a solid particle, due to its hydrophobicity, the process of adhesion of sorbate molecules (oil) begins and

pulls them into dense colloidal formations enveloping the adsorbent particles as the core of the micelle. In addition, for the aggregates of the adsorbent there is a process of displacement and The introduction of oil into micellar complexes. The film of oil becomes thinner. Since the adsorbent particles have magnetic properties, the micelles formed also exhibit magnetic properties. Primary complexes begin to shrink together, forming the structure of a mixture of oil + sorbent. Simultaneously, the process of oil absorption by moving micelles complexes continues. The particles of the magnetic adsorbent are aligned, forming an internal fairly rigid "dendrite-like" structure inside the remaining oil film on the water surface. The number and branching of such colonies of micelles is determined by the ratio of the amount of spilled oil and the powder scattered over thermographite. With complete exhaustion of the sorption capacity of thermographite particles, a stable oil-powder structure is formed, which ensures the stability of this mixture on water.

The molecule and the sorption surface polarize each other and the dipole-dipole van der Waals interaction between these induced dipoles generates the heat of adsorption. The heat of adsorption in such cases is usually of the order of 5 kcal/mol.

A feature of adsorption interactions is that the adsorbed molecule interacts not with one center on the adsorbent surface, but with many neighboring centers. In this case, the total interaction of the adsorbate molecules with the entire adsorbent, due to the dispersive forces, is always greater than the interaction with one center of the adsorbent, and the total electrostatic interaction can be less than the electrostatic interaction with one center of the adsorbent.

The oil film does not spread, but is fixed on the surface of the water and becomes magnetically controlled. The molecules of the surface layer belong to both phases. But they experience the effect of intermolecular forces more on the liquid phase side than on the side of the solid phase (figure 2).
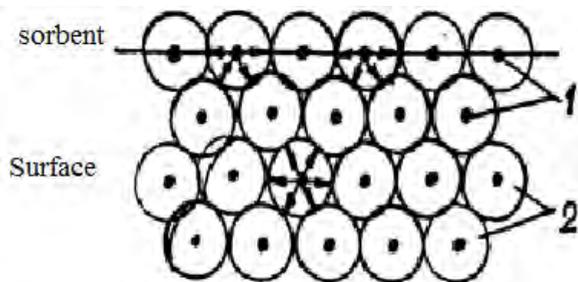
Figure 2 – Scheme of the action of intermolecular forces in the volume of a liquid and \on its surface: 1 – molecules; 2 – sphere of action of forces

To increase the effect of contraction and complete purification from oil, it is necessary either to add an additional amount of magnetic adsorbent, or to ensure the mobility of the remaining oil by "disturbing" the surface of the water. In this

case, the oil completely coagulates with the sorbent. The resulting mixture exhibits magnetic properties and can be easily controlled when moving through water and collecting in a container in various ways, including by means of a magnetic conveyor.

The proposed mechanism of interaction of thermographite and oil film on the surface of water was confirmed by extended pilot testing of the reagent composition, and also by the analysis of the obtained TRG with sorbed oil.

Initially, water with a volume of 50 liters is poured into a container, then an oil layer 0.5-1 mm thick is poured onto the water surface. On the surface of the oil, a small amount of flammable liquid is sprayed, in this case gasoline, after which it is ignited (figure 3a). On the surface of burning oil the reagent composition is scattered. The high temperature of the oil heats it, as a result of which thermogravenite is formed over the oil and the burning of oil gradually decreases (Figure 3b). At the same time, the formation of thermographite on the surface of the oil ends and after a few seconds a complete adsorption of the oil product takes place (figure 3c).

a   b   c

Figure 3 – Formation and use of innovative reagent formulations as a sorbent
for the elimination of oil in a pilot plant:a) burning of oil on the water surface
with different reagent compositions in the pilot plant; b) formation of thermogranite
and reduction of combustion; c) adsorption of petroleum products

The adsorption capacity of synthesized thermogranite is determined primarily by the state of the surface of the particles and by the dimensions of the adsorbing surface. Of the ophthalmic photographs, the thermographite, which is derived from the mechanical sample "20% graphite + 70% [$FeCl_3·6H_2O$] + 10% magnesium," can see that the size of its particles varies from 100 to 1200 μm (figure 4).

The amount of oil absorbed by thermogravenite also depends on the free area of the sorbent and the properties of the surface. The increase in the surface area of the sorbent can be achieved by increasing the porosity.

In figure 5 shown of IR-spectra termographite before and afther oil sorption.

Figure 4 – Optical microcirculation of the thermomagnetic image, emitted
from the mechanical "20% graphite + 70% [FeCl$_3$·6H$_2$O] + 10% magnesium"
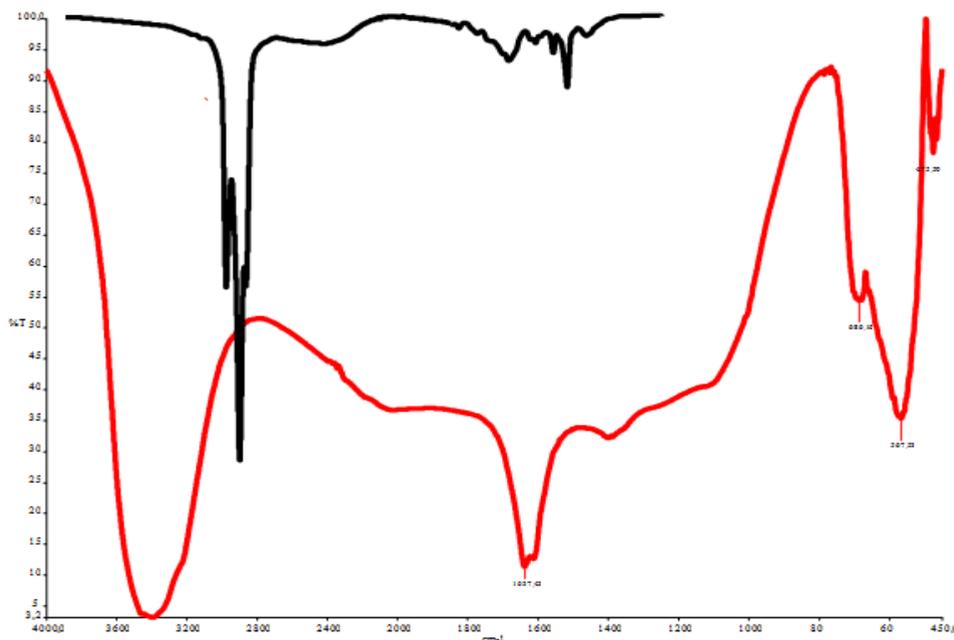
Figure 5 – IR spectra of thermographite before and after oil sorption

As it is seen, after the absorption of oil by thermogravenite, peaks with high inten- sity appear at the spectrum at 2955, 2923 and 2853 cm^{-1}, which are connected with symmetric valence and antisymmetric valence vibrations of the C-H bond on the surface. The presence of an impurity in these values of the alumina induces adsorption of the naphtha to thermogravenite. In addition, the method of IR spectroscopy established the presence of carbonylic, carboxyl groups on the surface of thermogravenite (intense absorption peaks in the 1600-1700 cm-region).

116

It was found that the properties of the carboxyl and carbonyl groups depend on such properties of thermogravenite as the capacity of absorption, the ability to exchange and form complex compounds, etc.

Additional orders on the structure of the samples of in-process and thermal gains are obtained by the method of retrogenic analysis. The retrograde phase analysis of the subterranean glare of the GL-1 mark (figure 6a) and the thermogranite obtained from the reagent composition grafit-FeCl$_3$·6H$_2$O (figure 6b) is shown on figure 6.
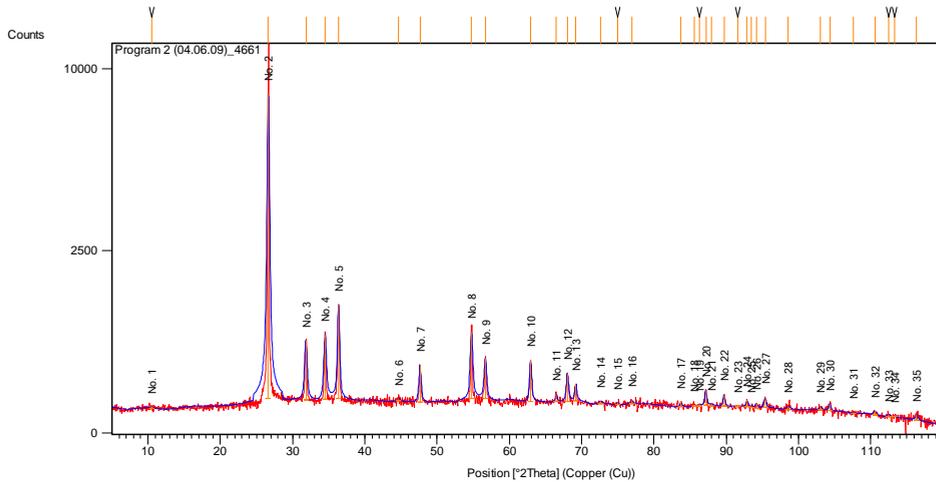
a – nature graphite
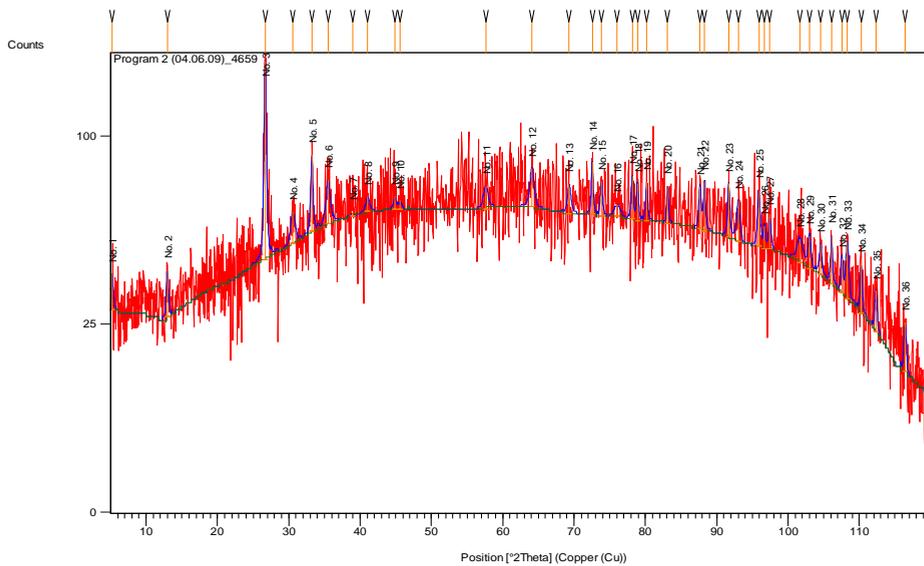
b – thermographite

Figure 6 – X-ray diffractograms of nature grafite and thermogranite

The blue Fourier line corresponds to the Bragg-Brentano transformation. The red line is an amorphous phase of carbon by the method of sliding X-rays. The trouble bumps of the diffraction are a characteristic black amorphous material, confirming that the thermodynamic transforms the crystal structure of the granite into an amorphous, exquisite (figure 6b) [13].

RFA also shows the magnitude of the defective phase of carbon along with the small crystal gland of the iron.

Thus, in the present study, thermodynamic calculations of the formation of thermogranite, as well as the mechanism of adsorption of oil on the surface of the synthesized sorbent, were proposed for consideration.

REFERENCES

[1] Siyavush Karayev Karam Shykhaliev. Environmental problems of transportation of oil and oil products and new methods of cleaning the water surface from oil and oil products. – Hannover: EAAEN, 2014. 44 p.

[2] Inagaki M., Toyoda M., Iwashita N., Nishi Y., Konno H. Exfoliated Graphite for Spilled Heavy Oil Recovery // Carbon Science. 2001. Vol. 2, N 1. P. 1-8.

[3] Toyoda M., Aizawa J., and Inagaki M. Sorption and recovery of heavy oil by using exfoliated graphite // Desalination. 1998. Vol. 4, N 115. P. 199-201.

[4] Thermally expanded graphite: properties and production. S.T. Tursynbek, G.O. Tureshova, K.K. Kudaibergenov, S. Lyubchik, E.K. Ongarbayev, Z.A. Mansurov. // Combustion and Plasma Chemistry. Almaty: Kazakh university, 2016. Vol. 14, N 2. P. 150-157.

[5] Kinetics of thermolysis of intercalated graphite compounds. K.K. Kudaibergenov, G.R. Nyssanbaeva, G.O. Turshova, G.A. Spapanova, E.K. Onangarbayev, Z.A. Mansurov, S.B. // Lyubchik plasmochemistry. Almaty: Kazak universiteti, 2016. Vol. 14, N 2. P. 144-150.

[6] Toyoda M., Aizawa J., and Inagaki M. Sorption and recovery of heavy oil by using exfoliated graphite // Desalination. 1998. Vol. 4, N 115. P. 199-201.

[7] Corinokina N.N., Avdeev V.V. The commemorative nano-emotional nature of the internal grafit: training. 2010. 100 p.

[8] Baron N.M., Ponomareva A.M., Ravdel A.A. A short reference book of physical and chemical quantities. L.: Chemistry, 1983. 232 p.

[9] Kireev V.A. Methods of practical calculations in the thermodynamics of chemical reactions. M.: Chemistry, 1985. 536 p.

[10] Levy E. Crystallography and crystal chemistry of a material with layered structures / Ed. Dordrecht. Holland Reidel publ., 1976. P. 422.

[11] Burleshin M. Grafitprichoditna the name of the act // Vecnik Mochenergo. 2001. N 9. P. 3-4.

[12] Mofa N.N., Chervyakova O.V., Ketegenov T.A., Mansurov Z.A. Magnetic sorbents. Received by mechanochemical treatment of quartz-containing mixtures // Chemistry for Sustainable Development. 2003. N 11. P. 755-761.

[13] Ubellov A.D., Lewis F.A. Grafit i ego kristallicheskie coedyneniya. M.: Mir, 1965. 265 p.

Резюме

К. К. Құдайбергенов, Г. Р. Нысанбаева, Г. О. Төрешова,
Б. А. Байтимбетова, Е. Қ. Оңғарбаев, З. А. Мансұров

ТЕРМОГРАФЕНИТ КӨМЕГІМЕН МҰНАЙ СОРБЦИЯСЫ ҮРДІСТЕРІНІҢ
МЕХАНИЗМІ ЖӘНЕ ТЕРМОДИНАМИКАСЫ

Жұмыста кеңейтілген графит алу синтезі және оны мұнайды сіңіру сорбенті ретінде пайдалану ұсынылады. Оның сипаттамасы, кинетикасы және қасиеттері зертелінді.Мұнда мұнай адсорбциясы үрдісінің механизмі көрсетілген. Сондай-ақ, термографениттің магниттік қасиеттері анықталынды.

Түйін сөздер: термогранит, термодинамика, кинетика, адсорбция, мұнай сіңі-ру, реагент композициясы, ферромагнит.

Резюме

К. К. Кудайбергенов, Г. Р. Нысанбаева, Г. О. Турешова,
Б. А. Байтимбетова, Е. К. Онгарбаев, З. А. Мансуров

ТЕРМОДИНАМИКА И МЕХАНИЗМ
ПРОЦЕССА АДСОРБЦИИ НЕФТИ ТЕРМОГРАФЕНИТОМ

Предложен синтез получения вспученного графита и использование его как сорбента для ликвидации нефти. Были исследованы характеристики, кинетика и свойства. Установлен механизм процесса адсорбции нефти. Также были определены магнитные свойства термографенита.

Ключевые слова: термографенит, термодинамика, кинетика, адсорбция, нефтепоглощение, реагентный состав, ферромагнит.