

## Natural Zeolites as Petroleum Product Adsorbents

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### Abstract

Physicochemical and adsorption properties of natural zeolites of the Sakhaptinsk (Krasnoyarsk Territory), Kholinsk (Chita Region) and Khonguruu (Yakutia) deposits have been studied. Changes in the zeolite characteristics in contact with alkaline and acid solutions have been established. The efficiency of the zeolites studied in the process of adsorption of petroleum products from gaseous and aqueous media has been compared. A correlation between the adsorption activity and efficiency of natural adsorbent zeolites with Na, K-components and molar Si/Al ratio in their composition has been found. The results obtained have made it possible to recommend the zeolites studied for development of adsorbent materials.

### INTRODUCTION

One of the methods of purification of gases and waters from petroleum products is their extraction with the help of adsorbents with subsequent regeneration [1, 2]. In connection with the increase in environment pollution with petroleum products, the search for new efficient and cheap fillers for adsorbents and filters retaining their properties under various conditions of purification of water and gaseous media is very important. The discovery of great reserves of natural zeolites characterized by adsorption and ion exchange capacities has made it possible to study them in the process of purification of waters and gases from oil pollution. The reserves of zeolite raw materials in CIS estimated totally at about 3.5 billion tons are contained in more than 60 zeolite ore deposits in the Transcaucasian and Transcarpathian regions, Middle Asia, Siberia, and the Far East [3]. At present, a series of works are known in which physicochemical foundations of the use of natural sorbents, including zeo-

lites have been created for purification of various media from dispersed admixtures, surfactants, substances of protein nature, petroleum products, cations, and for deactivation of solutions and equipment. On the basis of zeolites, new efficient catalysts and adsorbents for many technological processes have been developed [4, 5]. However, each type of zeolite raw material possesses individual properties, including those of adsorption.

The degree of study of physicochemical and adsorption properties of zeolites from various deposits is different. Poorly studied ones are the ores from zeolite deposits in Yakutia, Primor'ye, Sakhlalin, Krasnoyarsk Territory, among which there are large deposits Khonguruu (Yakutia), Kholin (Chita Region), Sakhapta (Krasnoyarsk Territory) [6]. The goal of the present work was to study the possibility of using natural zeolites of these deposits as adsorbents of petroleum products, to elucidate the general patterns of adsorption of petroleum compounds on natural and modified zeolites.

TABLE 1  
Physicomechanical and adsorption properties of zeolite rocks

Parameter	Zeolite		
	Sakhapta	Kholin	Khonguruu
Colour	Light brown	Gray	Light green
Real density, kg/m <sup>3</sup>	2200	2380	2410
Bulk density, kg/m <sup>3</sup>	1850	1940	1680
Total porosity, %	19	19	31
Abradability, %	8	4	0.4
Humidity, %	18.5	13.5	8.0
Equivalent cation-exchange capacity, mmol/100 g of rock	45	73	50
Adsorption in terms of water vapours (P/P <sub>s</sub> = 0.4), %	6.2	8.2	7.8

#### CHARACTERISTICS OF NATURAL ZEOLITES

It has been established that zeolite rocks of the Sakhapta, Kholin and Khonguruu deposits are composed mainly by zeolite minerals of heulandite – clinoptilolite group [3, 6, 7]. Physicomechanical and adsorption properties of zeolite rocks are presented in Table 1.

The values of the real and bulk density of the zeolites studied are similar. The difference in the cement contents determines the high strength of the Khonguruu zeolite (khongurine) and the high abrasibility of the Sakhalin zeolite. The high mechanical strength of khongurine may be used in devices with moving layers. Khongurine is characterized by the highest porosity (31 %). Cation-exchange capacity is correlated with equilibrium adsorption of water vapour. The specific surface of zeolites changes as a result of crushing and heating within the limits of 0.35–0.75 m<sup>2</sup>/g. This is linked with dehydration and destructurezation processes resulting in amorphization of the rock. The loss of zeolite mass in heating due to dehydration processes amounts to 9–10 %. The optimal dehydration temperature is 350–400 °C. The high cation-exchange and absorption capacities belong to characteristics determining the practical utility of the zeolites under study.

On the surface of zeolite rocks there are water molecules tied by various bonds. This can be seen in IR spectra of zeolites recorded on the device Specord M80 (Fig. 1). Absorption

bands at 3700 and 3400 cm<sup>-1</sup> characterize the ν<sub>B</sub> of OH-groups of water molecules localised on cations. The blurred band in the region of lower frequencies corresponds to water molecules bound to surface oxygen ions by hydrogen bonds. The narrow band at higher frequencies belongs to hydroxyl groups of water molecules not bound to the surface of zeolites [8]. Hydroxyl-hydrate components on the surface of zeolites influence considerably their adsorption properties.

Zeolites represent fine-porous ionic crystals with a definite size of inlet windows, built of alternating tetrahedrons SiO<sub>4</sub> and AlO<sub>4</sub> joined with each other by their apices. For heulandite-clinoptilolite zeolites, the window sizes are 0.40 × 0.55, and 0.44 × 0.72 nm [6]. In Table 2, chemical characteristics of the zeolites studied

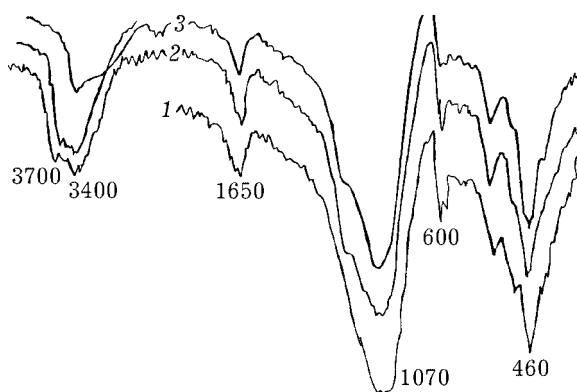


Fig. 1. IR spectra of zeolites from the Sakhapta (1), Kholin (2) and Khonguruu (3) deposits.

TABLE 2

Chemical characteristics of zeolite rocks

Parameter	Zeolite		
	Sakhapta	Kholin	Khonguruu
Total SiO <sub>2</sub> and Al <sub>2</sub> O <sub>3</sub> content, %	78.52	79.69	82.24
Molar ratios:			
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	8.94	9.64	9.34
Si/Al	4.4	4.87	5.14
Total R <sub>2</sub> O content, %	4.28	6.15	5.26
Molar ratio:			
Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	0.14	0.34	0.49
K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	0.29	0.33	0.12
Total R <sub>2</sub> O and CaO content, %	6.55	7.52	6.46
Total R <sub>2</sub> O and RO content, %	8.21	7.94	6.74

are presented. Molar Si/Al ratios have been calculated by RFA spectra obtained on an X-ray fluorescence spectrometer VRA-30. The zeolites indicated may be considered as high-silica compounds. Khongurine is characterized by the highest total content of silicon and aluminium oxides, by the highest Si/Al molar ratio and considerable sodium content.

#### INTERACTION OF ZEOLITES WITH WATER, ALKALI AND ACID SOLUTIONS

It is known that acid treatment of clinoptilolite increases its adsorption capacity with respect to benzene, *n*-heptane and other molecules. In a long-term contact of some zeolites with aqueous solutions, their swelling and decationization take place [6, 7]. We studied the interaction of zeolite rocks with water, and hydrochloric acid and sodium hydroxide solutions under static conditions for 1–20 days and in boiling for 1 h.

In Fig. 2, curves of pH change in long-term contact of zeolites with water in the system of 50 ml of water – 1 g zeolite are presented. The greatest pH change is observed in the Kholin zeolite. This can be accounted for by the higher Na, K-component content of the zeolite rock from the Kholin deposit. The highest alkalization of the medium in the khongurine – water system seems to be due to rock hydrolysis.

The mechanical strength of zeolite in water is conserved, and specimens do not become swollen. In boiling, a partial dissolving of zeolites, especially Sakhapta zeolite (up to 0.5 %) is observed, and cations go to the solution, their proportion changing in the following order: Sakhapta zeolite > Kholin zeolite > khongurine. By the calculated SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio in alkaline and acid extracts one may conclude that the greatest influence is exerted by alkaline medium on the Sakhapta zeolite. The most susceptible to acid medium is khongurine (Fig. 3). Acid-alkaline treatment of zeolites can be used for modification of natural sorbents for making them selective with respect to a concrete type of adsorbates.

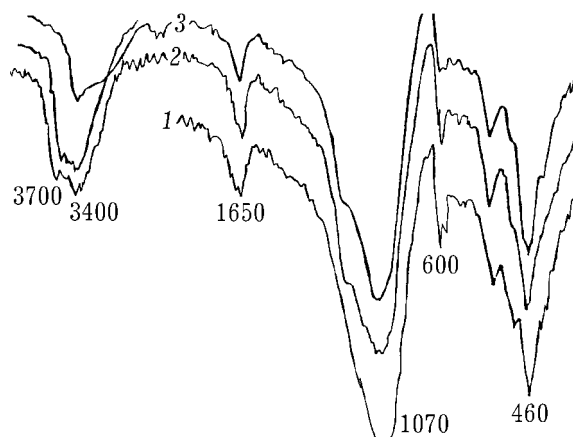


Fig. 2. Changes of pH values during a long-term contact of 50 ml of water with 1 g of zeolite: 1 – Kholin, 2 – Sakhapta, 3 – khongurine.

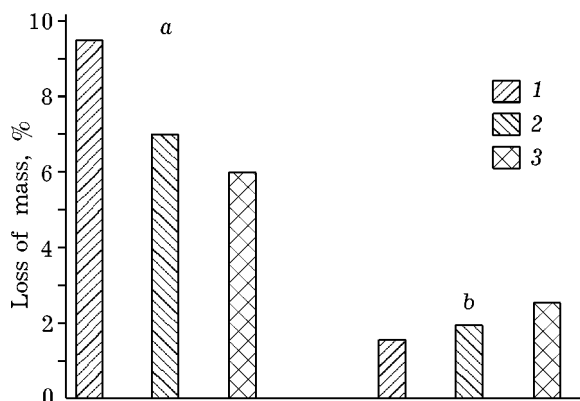


Fig. 3. Diagram of changes of zeolite mass in 20 days in a medium of 1 M NaOH (a) and 1 M HCl (b): 1 - Sakhapta, 2 - Kholin, 3 - khongurine.

#### KINETIC PARAMETERS OF SORPTION OF PETROLEUM PRODUCT VAPOURS

The use of adsorbents depends on the adsorption dynamics when gas flow or air-vapour mixture is run through the adsorber containing a layer of adsorbent grains. Therein, the adsorption process on zeolites consists of the following stages [9]:

- 1) substance supply to the external surface of zeolite crystal;
- 2) diffusion of molecules across windows on the external surface of the crystal;
- 3) migration of molecules inside the zeolite crystal.

When elucidating the adsorption kinetic pattern, only the 2nd and the 3rd stages were considered, since the 1st stage is determined by external diffusion factors and is of no special interest. Desorption of hydrocarbons from the zeolite surface was studied under non-isothermic conditions.

As a result of the experiment, it was established that Khonguruu zeolite with the highest molar Si/Al ratio was the most efficient in adsorption of petroleum compounds. On the example of this adsorbent the kinetic parameters of adsorption and desorption of Talakan petroleum vapours and its fractions were estimated, the optimal characteristics of the adsorption process were calculated and the conditions of the most efficient regeneration of the adsorbent were found.

For studying the isotherms and the kinetics of adsorption of Talakan petroleum vapours

and fractions, a device was used whose scheme is shown in Fig. 4. Compressor 1 supplied air to flask 2 containing the petroleum product at the rate of 1 m/min; this air carried the petroleum product vapours to adsorber 3 filled with zeolite. The temperature of the flask and of the adsorber was set by thermostats 4. At the outlet of the adsorber, the petroleum product vapours were trapped by trap 5. In order to fill up the adsorber, zeolite fractions of 0.5–0.25 mm with the mass of 10 g were selected. At the adsorbent temperatures of 20, 40 and 50 °C adsorption was carried out on fresh zeolite portions for 0.5–6 h. The temperature of the flask with the petroleum product varied within the interval of 20 to 50 °C. After the experiment, a 2 g mass of used-up zeolite was treated with 50 ml of CCl<sub>4</sub> in which the petroleum products were assayed by the spectral method [10].

Adsorption isotherms are presented in Fig. 5. One can see that the increase in temperature is accompanied by a decrease in adsorption of vapours of the petroleum fraction (200 °C) from the maximal value of 30 mg/g at 20 °C (see Fig. 5, a). This can be accounted for by the increase in contribution of diffusion processes at increasing temperature and by the decrease in the time of exposure of adsorbate molecules in the pores of the adsorbent. The isotherm at room temperature goes up sharply, the heat of adsorption of hydrocarbons by the zeolites is rather large. The presence of the convex region on the isotherm may be accounted for by an intermolecular adsorbate – adsorbate interaction at room temperature. As the temperature increases, no association of adsorbed molecules takes place.

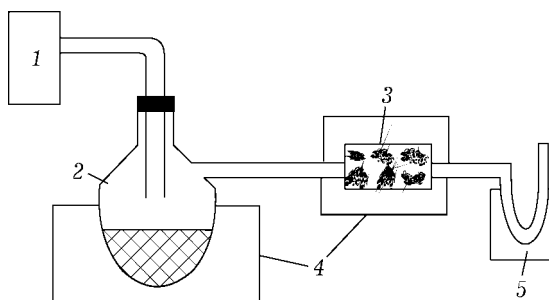


Fig. 4. Scheme of device for studying the adsorption of petroleum product vapour under dynamic conditions: 1 - compressor, 2 - flask with the petroleum product, 3 - adsorber, 4 - thermostats, 5 - trap.

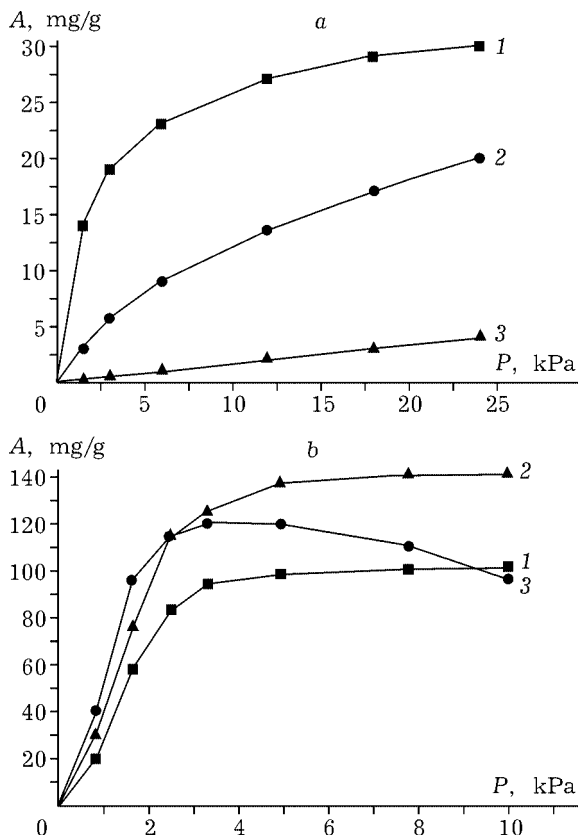


Fig. 5. Isotherms of adsorption of vapours of 200 °C fraction of Talakan petroleum (a) and Talakan petroleum vapours (b) on Khonguruu zeolite at 20 (1), 40 (2) and 50 °C (3).

Petroleum vapour adsorption isotherms shown in Fig. 5, b have a more complicated pattern. One can see two regions convex with respect to different axes. Such a course of isotherm may be accounted for not only by retention of hydrocarbon molecules in adsorbent pores, but also by a specific interaction of some petroleum compounds with active centres of the zeolite surface. It is known that zeolites somewhat polarise any molecules (induction electrostatic interaction) and interact specifically with polar molecules (oriented electrostatic interaction) [11]. One can see that the contribution of specific interaction increases as so does the temperature. At 50 °C, the isotherm passes its maximum, because the retention of light petroleum hydrocarbons under these conditions decreases. The maximal adsorption of petroleum vapours amounts to 140 mg/g at 40 °C. On the basis of the experiment results, one may conclude that the process of adsorption of petroleum compounds is

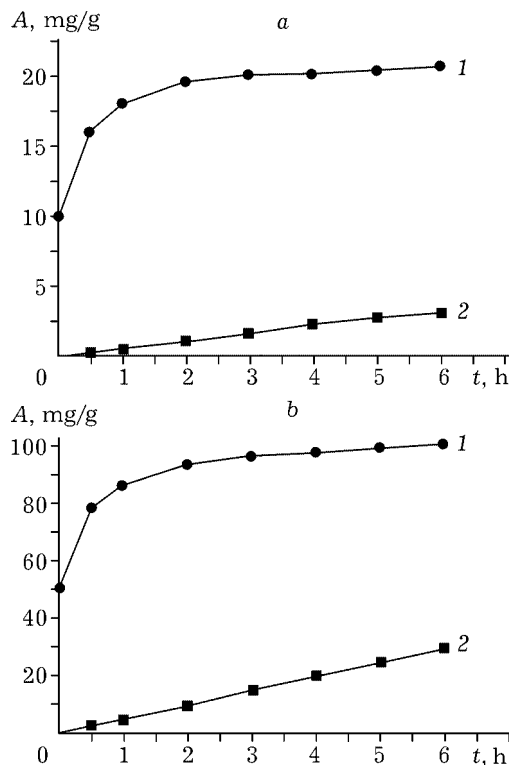


Fig. 6. Kinetic curves of adsorption of 200 °C fraction of Talakan petroleum (a) and Talakan petroleum vapour (b) under static (1) and dynamic (2) conditions on Khonguruu zeolite.

activated and seems to have chemisorption character.

In Fig. 6, kinetic curves of adsorption of light petroleum fraction vapours and petroleum vapours at room temperature under static and dynamic conditions are presented. Under static conditions, after attaining 10 mg/g, a linear dependence of adsorption of light fraction vapours on the square root of time is observed. In this region, the process rate is determined by the rate of migration of molecules adsorbed in the sorbent cavities. Under dynamic conditions, the adsorption rate is much lower and depends linearly on the time for a long time stretch. In [12] it is demonstrated that the dependence of vapour adsorption rate on pressure ( $p$ ) obeys an equation formally analogous to Langmuir's equation:

$$\frac{da}{dt} = \frac{kp}{1 + k'p} \quad (1)$$

In the case of adsorption of petroleum vapours on zeolite, a similar kinetic dependence is observed. One can see that under dynamic

TABLE 3

Results of desorption of Talakan petroleum vapours from the surface of Khonguruu zeolite

Petroleum products	Desorption, %, at the temperature of, °C			
	40	50	80	100
Vapours of light petroleum fractions (200 °C)	50	80	100	100
Petroleum vapour	5	40	80	100

conditions the rate of adsorption of petroleum compounds vapours decreases by 8–10 times.

#### DESORPTION OF PETROLEUM PRODUCT VAPOURS UNDER NON-ISOTHERMIC CONDITIONS

Desorption of vapours of petroleum products was carried out in airflow at heating the adsorbents in the adsorber. The airflow rate was 50 m/h, the temperature varied from room temperature to 100 °C. For estimation of desorption, the mass of adsorbents was controlled, and after the experiment the adsorbents were treated with carbon tetrachloride, whereupon petroleum products were assayed in it by the spectral method. In Table 3, results of desorption of Talakan petroleum vapours at heating of Khonguruu zeolite in airflow are presented. One can see that a complete regeneration of the adsorbent is achieved at heating to 100 °C. As the experiment shows, at heating in airflow, 20–30 min are sufficient for full regeneration.

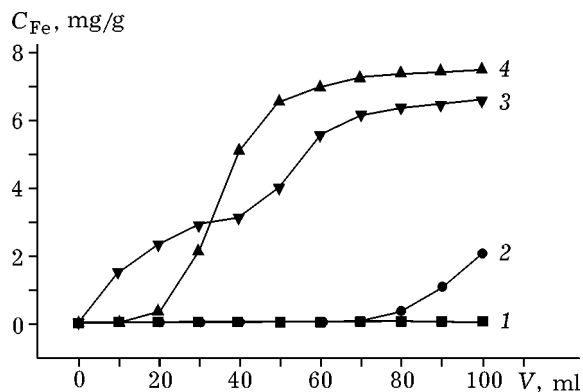


Fig. 7. Curves of filtration of waters polluted with iron through columns packed with Kholin (1, 3) and Sakhapta (2, 4) zeolites at pH 2 (3, 4) and 7 (1, 2).

#### ADSORPTION OF PETROLEUM PRODUCTS ON ZEOLITES FROM AQUEOUS MEDIA

Waters polluted by petroleum products were run through adsorption columns packed with zeolites. Besides, an experiment was carried out under static conditions, wherein a certain amount of zeolite was added to the polluted water sample with subsequent separation of filtrates. The purification efficiency was estimated by the difference of the pollutant concentrations between the initial sample and the filtrate. Petroleum products were assayed by means of spectral method after extraction with carbon tetrachloride. It was demonstrated that when purifying water from petroleum products zeolites worked both in the microemulsion coalescence and in adsorption regimes. Using zeolites, it was possible to purify polluted waters from emulsified petroleum products by 100 % and from dissolved petroleum components by 80 %.

Interesting results were obtained when extracting petroleum products from waters also polluted with inorganic substances, particular-

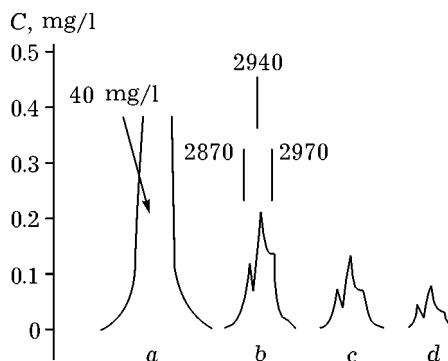


Fig. 8. IR spectra of extracts in  $\text{CCl}_4$  for the initial sample (a) and filtrates using Sakhapta (b) and Kholin (c, d) zeolites.

ly iron compounds. In Fig. 7, curves of filtration of waters polluted with iron at different pH values are presented, which permitted calculating the adsorption capacity of materials with respect to iron. One can see that the most complete purification was achieved at pH 5–7, the Kholin zeolite being characterized by the highest adsorption capacity (20 mg/g). Figure 8 presents IR spectra of filtrates after purification of waters from transformer oil and iron and their extraction in  $\text{CCl}_4$ . One can see that the best results of purification from petroleum products were obtained using the Kholin zeolite. Especially high purification efficiency with the Kholin zeolite was achieved when petroleum products and iron were simultaneously presented in the polluted water. The use of the Kholin zeolite considerably diminishes the solution pH (see Fig. 2). This seems to contribute to retention of iron in ionic form and ensures the participation of iron in ion exchange with the adsorbent. Adsorbed iron forms can play the role of supplementary centres of adsorption and coagulation of petroleum products. The results obtained confirm the data that an increase in Si/Al ratio in the zeolite skeleton leads to an increase in adsorption activity.

## CONCLUSIONS

As the carried out studies demonstrate, natural zeolites characterized by a high molar Si/Al ratio manifest a considerable adsorption activity with respect to light petroleum fraction vapours and petroleum vapours in their extraction from an air-vapour mixture. Such zeolites can be used as adsorbents in air purification plants and for prevention of hydrocarbon losses in evaporation. Zeolites are most active under static conditions. Charging of adsorbents is calculated by the formula  $M = P/(AK)$ , where  $A$  is the zeolite adsorption capacity, t/t;  $P$  is the presumed loss of petroleum products, t/year;  $K$  is the coefficient indicating the frequency of replacement of the adsorbent per year. The adsorption capacity of the most efficient Khonguruu zeolite under static conditions amounts to 30 mg/g for light hydrocarbons (the process temperature is 20 °C) and 140 mg/g for

petroleum vapours (40 °C). It is possible that at lower temperatures the zeolite is still more efficient; however, the region of lower temperatures has not been studied. The optimal contact time is 0.5–1 h at the proportion of volumes of the liquid phase, vapours and adsorbent of 5 : 5 : 1. During this time the saturation of the adsorbent reaches 80 %. It is expedient to study the filling of the adsorbent depending on various proportions of the liquid phase, vapours and zeolite. It is possible to carry out desorption of hydrocarbons from the zeolite surface and volume by heating the adsorbent in an airflow (of no less than 50 m/h) at 100 °C for 0.5–1 h.

It has been proposed to use the zeolite of Khonguruu deposit in combination with polymers for manufacture of microspheres floating on the surface of petroleum products in order to prevent their evaporation in reservoirs and oil storage, and as a load of floating roofs and pontoons in reservoirs for prevention of evaporation, in reservoir respirator devices (respiratory and safety valves etc.).

The results obtained permit considering the Kholin deposit zeolite as a promising adsorbent for purification of filters which can ensure a high capacity with respect to dissolved iron compounds and a high degree of purification from emulsified and dissolved petroleum products.

Zeolites can be modified by means of changing their properties *via* washing with water or treatment with acids and alkalis.

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