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The Use of Natural Sorbents to Clean Oily Wastewater in The Reservoir Pressure Maintenance Systems.

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ABSTRACT

This article presents the research results and consideration of a possible use of cheap natural sorbent (tripolite) to clean water in the reservoir pressure maintenance systems at the oil production enterprises. Tripolite is fine-pored opaline sedimentary rock that is loose and very light; it contains up to 80% of amorphous silica (SiO_2). In order to evaluate the improvement of tripolite properties to clean water contaminated with oil products, the technology of its hydrophobization was used with the aim to make it water-repellent. The following water-repellent agents were used: oligo methyl hydride siloxane Penta-804, non-polar hydrocarbons and industrial oil. The efficiency of oily water treatment with modified tripolite-based sorbents was studied and evaluated at the specifically developed and constructed sorption-membrane system. The modified tripolite was tested with model solutions, most close to the real ones in terms of their oil-product contents. Oil concentration in the original and purified water was determined by the method of IR spectrophotometry. The comparative tests have demonstrated the efficiency of trapping oil products by the modified tripolite of the M80 grade.

Keywords: reservoir water, treatment, membranes, natural sorbents, sorbent modification, tests, sorbent capacity, hydrophobization, mining, recycled water.

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INTRODUCTION

One of the principal natural resources is oil, which in the course of mining, transport, reprocessing and consumption continuously comes in contact with the environment and pollutes it, especially water. One of the paramount tasks in the course of natural resources extraction is to protect the environment against oily wastewater. The measures aimed at oily water treatment will help to save a certain amount of oil and keep air and water resources clean.

In the course of the oil deposit development, significant volumes of natural or drainage waters are used to maintain the reservoir pressure, which makes it possible to extend the period of oil-well flowing and considerably increase oil and gas recovery factors.

In order to maintain the reservoir pressure, it is possible to pump natural (fresh or brackish) or waste (drainage) waters, which can contain organic and inorganic impurity, to this reservoir.

The sorption method of oily wastewater treatment has become the most widely spread as it is the most effective and environmentally-acceptable.

Currently the oily wastewater is cleaned to the concentration within the range of 0.5- 0.05 mg/l by means of the activated macro-porous carbon and mineral coal sorbents, coal of DAK, BKZ, MIU ranks and other sorbents; however these types of sorbents are expensive and not readily available.

So, the issue of efficient treatment of oily wastewater with new sorbents based on accessible, inexpensive, environmentally safe natural materials is still very topical.

The review of literature sources [1-7] has demonstrated that the most promising and available sorbents to clean oily wastewater are silica and aluminosilicates. However, natural sorbents have low natural oil sorption capacity that could be improved by modification of their surface with hydrophobic agents of various origins.

This paper considers a potential use of accessible and inexpensive natural tripolite-based sorbents.

Tripolite is fine-pored opaline sedimentary rock that is loose and very light. It is a natural sorbent that contains up to 80% of amorphous silica (SiO_2), actually without any organic residuals. Tripolite usually contains 3-10 % of Al_2O_3, carbonate impurities and 6-8 % of chemically bounded water. Besides, it may also contain oxides of ferrum – 0.8-6.0 %; aluminium – 8.4-10.1 %; calcium – 0.9-3.5 %; magnesium – 0.9-1.3 %; sodium – 0.18-0.29 %; potassium – 1.4-1.5 % and other elements. Tripolite contains the following micro-elements: copper – 300 mg/kg; manganese – 510 mg/kg; molybdenum – 25 mg/kg; fluoride – 90 mg/kg; boron – 75 mg/kg, and phosphorus (P_2O_5) – 3900 mg/kg [8-12].

The tripolite structure primarily consists of fine spherical particles with a size of 10-20 µm. Small quantities of clay matter, grains of glauconite, quartz and fieldspar are usually also present. The colour varies from white and grayish to dark reddish, red and black. The tripolite density is 2-3 g/cm^3; its porosity goes to 60.2-64%. Due to its fine porosity and high contents of activated silica, tripolite found its application as filtering and sorption material.

There are huge tripolite deposits in different regions of the Russian Federation (Zikeyevsk deposit in Kaluga region, Potanin deposit in Chelyabinsk region, Khotynets deposit in Orlov region, etc.).

The main enterprises involved in the natural zeolite mining and processing in the Russian Federation are OAO “Priargunsk Production Mining-Chemical Association (PGKhO), NPVO “Tseolit”, OOO “Alsiko-Resource”, OOO “Kholinsk Zeolites”, OOO “Primorskiy Zeolit”, OOO “Suntarzeolit”, OOO “Zeolit”.

Tripolite is not widely used in the processes of sorption purification of oily water as it has low natural oil sorption capacity.

In the course of development of the tripolite-based oil sorbent, tripolite should be modified (to be subject to chemical and thermal hydrophobization). It is rather promising to artificially make it water repellent by creating thin layers of water-repellent agents of organic or organic-silicon nature on the mineral surface. A water-repellent agent should have good adhesion to the material, should be uniformly spread and completely cover it, should not be washed out in the course of operation and should not dissolve in oil products.

Nowadays, paraffin, silicon oil or petroleum oil, high-molecular compounds, etc. are widely used for hydrophobization of various materials.

When any material is subject to modification, it becomes important not only to fix various compounds on the surface, but also to achieve the strongest possible bonds between the modifier and the substrate material (tripolite). Otherwise, under the influence of the environment it will be rejected and the product will stop performing its functions.

MATERIALS AND RESEARCH METHODS

To perform the studies, tripolite from the Zikeyevsk deposit in Kaluga region was used, of grades M-80 (particle size of 80 μm) and D-25 (particle size of 0.8-1.25 mm), produced by ZAO “Sorbent”, Kaluga. Tripolite was modified according to the techniques and procedures developed by a group of companies under OOO “OCST” [13].

The following substances were used as water-repellent agents: KOS- oligo methyl hydride siloxane Penta-804 produced by OOO “Penta-91”, Moscow; non-polar hydrocarbons –bitumen (BT) and industrial oil (IO). As a result of modification a few oil sorbents were made.

The model reservoir water was used as model solutions with addition of oil in the amount of up to 2000 mg/l.

A special sorption-membrane system was developed and manufactured to perform tests on efficiency of oily water treatment with different tripolite-based sorbents (Figure 1). It includes a sorption unit (1) where the model solution is treated with tripolite , a membrane unit (2) with a nanostructured membrane where the suspension is cleaned of tripolite, and a container for the filtrate (3).

1 – a container to treat water with sorbent (sorption unit);
2 – a filtering element with a nanostructured membrane (membrane unit);
3 – a container for filtrate

Figure 1 – Sorption-membrane system

Below there is a description of the oily water treatment research procedure with the use of tripolite:

- treatment was performed at the sorption-membrane unit (Figure 1);
- for each test, 10 dm^3 of the model solution was prepared in the following way:
- 20 g of tripolite was added to the water with the oil product concentration of 2000 mg/dm^3;
- sorbent : solution mass ratio was equal to 1:500 in each test;
- the model solution was poured into the sorption unit of the system (Figure 1,(1)) and held there for 1 hour under stirring;
- the model solution was filtered through the membrane unit that contained a filtering element with a nanostructured membrane (Figure 1,(2)).
- the filtrate was collected in a special container (Figure 1,(3)) and sampled to analyze the oil concentration in it;
- the oil sorption value was calculated (*A*, mg/l) with the formula:

$$A = (C_0 - C) * \frac{V}{m},$$

where C_0 and C are oil concentrations before and after sorption, respectively, mg/dm^3; m – sorbent weight mass, g; V –the volume of the solution under sorption, cm^3;

- the degree of oily water treatment (S, %) was calculated with the formula:

$$S = (C_0 - C) * \frac{100}{C_0},$$

- oil concentration in water was determined by the method of IR-spectrophotometry, by extracting oil components emulsified and dissolved in water with carbon tetrachloride; by means of chromatographic separation of oil products from associated organic compounds of other classes on the column filled with aluminium oxide, and the follow-up quantitative determination of their mass concentration on the basis of C-H bonds sorption intensity in the infrared spectrum region.

RESULTS

Table 1 presents the results of oily water treatment with modified tripolite at the sorption-membrane system.

Table 1- Modified tripolite sorption capacity and efficiency of oily water purification with tripolite

No.	Tripolite Grade	Name of the Modifier (concentration in the reaction mixture, %)	Sorption Capacity, A, mg/g	Degree of Purification, %
1	M-80	KOS (0.5)	30.1	84.5
2	M-80	KOS (1)	31.1	85.6
3	M-80	BT (0.5)	31.3	86.1
4	M-80	BT (1)	32.1	87.2
5	D-25	KOS (1)	30.7	85.5
6	D-25	KOS (5)	31.3	86.1
7	D-25	BT (1)	31.5	86.2
8	D-25	BT (5)	31.9	86.6
9	D-25	IO (5)	31.3	86.1

From Table 1 it is clearly seen that the tripolite modified with bitumen with its concentration in the reaction mixture of 1% demonstrated the best sorption properties with regard to oil. The purification degree of this sorbent is 87.2%.

The treatment time is one of the most important sorption parameters. To choose the optimum time of oil adsorption with the modified tripolite in the course of research into its sorption properties, the kinetics of oil sorption from the model reservoir water was studied (Figure 2). The graph shows that it takes 55-60 min to achieve the sorption equilibrium. The sorption time (mixing with tripolite) is assumed to be equal to 60 min.

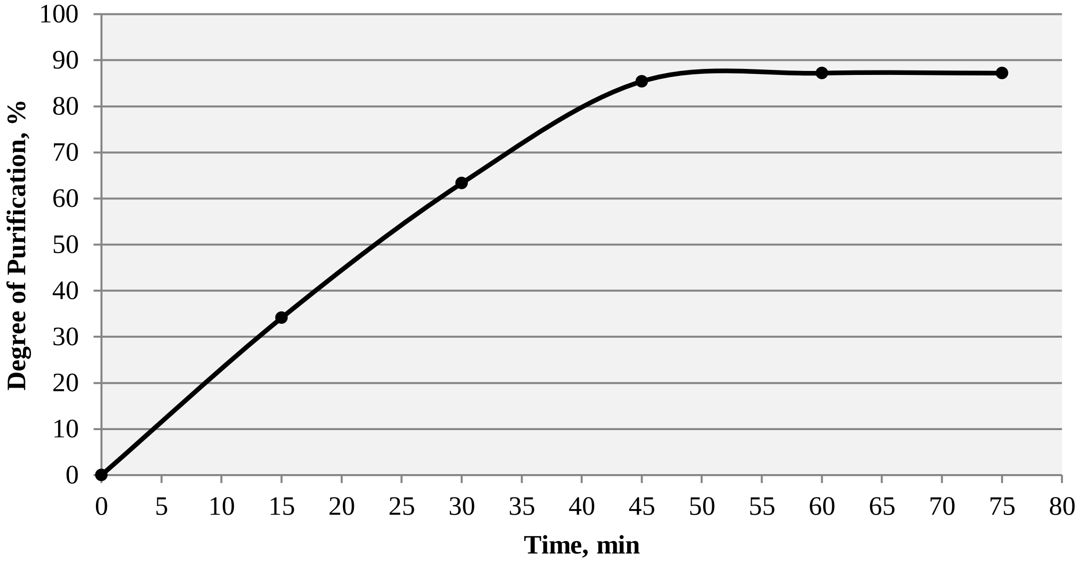

Figure 2- Kinetics of oil sorption with the modified tripolite.

CONCLUSIONS

Based on the data obtained in the course of performed studies of the oily water sorption purification, the conclusion should be made about the expedience to use modified tripolite as a highly efficient and inexpensive sorbent for oily wastewater treatment in the reservoir pressure maintenance system.

GRATITUDE

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