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# Application Prospects of a Mineral Sorbents in Yakutia

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**Abstract.** The subject covered in the paper is practical application of ecologically and economically proved methods to restore the disturbed soil ecosystems in Yakutia after emergency oil spills. Experimental studies have been performed on the development of a new petroleum biosorbent based on a mineral composition. The natural zeolite from the Khongurru deposit (Sakha Republic (Yakutia), Russia) is used as a base for obtaining the new petroleum biosorbent. A brief description of the material composition and physico-chemical characteristics of various types of zeolite raw material is given. We present the results of the experimental application of hydrocarbon oxidizing microorganisms (HOM) immobilized on zeolite (clinoptilolite-geylandite series) from the Khongurru deposit in oil-contaminated soils. It has been established that the obtained biomineral compositions provide a significant activation of the biodegradation of petroleum hydrocarbons (HC) in the soil. The most intensive processes occur at the first stage of the treatment activities (up to 90 days from the experiment's start). The effect of the zeolite with fraction size less than 0.25 mm on the intensity of the destruction of oil is somewhat higher, compared with fraction size 0.5-3.0 mm. During one growing season, the degradation of petroleum hydrocarbons in soils treated with HOM was 36-54%; in soils treated with HOM immobilized on zeolite - 71-99%; in control variants not treated with biological preparations, the degradation coefficient of oil contamination is not significant. In general, the technology of using zeolite raw materials for cleaning up oil spills from different types of permafrost soils provides a significant ecological and economic effect, thus contributing to the reduction of the time for rehabilitation of disturbed lands and the improvement of the environment in the disturbed territory.

## 1. Introduction

At present, the situation with the production and consumption of petroleum biosorbents in Russia is characterized both by the expansion of the volumes of their use and by the continuous increase in the deficit of their production. In Yakutia, petro-biosorbents for environmental purposes - liquidation of oil spills and oil products (OP) - are purchased mainly by the companies OJSC Sakhaneftegazsbyt and JSC NC Tuymaada-neft in volumes that can not satisfy the needs of all filling stations, fuel depots and oil depots of the Republic [1].

It should also be noted that the problem of restoring disturbed lands on the territory of the Sakha Republic (Yakutia) is very acute, which is primarily due to the specific nature and climatic conditions of the region. The duration of the cold period, which lasts 7.5-8.0 months, is practically a period of biogeochemical dormancy for pollutants. Therefore, it can be assumed that oil pollution in the conditions of the permafrost zone can become a large-scale factor of the negative impact on the environment. For this, it is necessary to create new technologies based on advanced scientific concepts



capable of capturing, processing, utilizing pollutants or toxicants, mitigating or preventing the effect of environmentally unsafe enterprise on the environment [2].

For the permafrost soils of Yakutia, the choice of oil destructors that work effectively in the climatic conditions of the North requires special studies and tests [3]. Therefore, the scientific studies of the Institute of Oil and Gas Problems of the Siberian Branch of the Russian Academy of Sciences (IPNG SB RAS, Yakutsk, Russia) aimed at developing biotechnologies for neutralizing oil and oil product spills based on the use of local natural raw materials proved to be in demand in modern conditions.

The potential and perspective of the biotechnological approach to the rehabilitation of oil-contaminated lands in the conditions of the cryolithozone are obvious and are a priority in the studies of most scientific institutions of the Sakha Republic (Yakutia), as evidenced by innovative products of local producers, including sorbents and biologics for the rehabilitation of anthropogenic-disturbed territories [4].

The first approbation of the biotechnological method of soil purification from oil pollution based on the use of natural raw materials of local deposits in Yakutia was carried out in 2006.

The emergency sections of the Talakan-Vitim temporary oil pipeline route laid the first experimental sites to study the effect of vermiculite from the Inagli deposit (South Yakutia) and native microorganisms on the biological degradation of oil pollution. The works were conducted under the supervision of Petr Gavrilovich Novgorodov, the Leading Researcher, Head of the Ecology Sector of IPNG SB RAS, candidate of geological and mineralogical sciences, in cooperation with scientists from the Yakut Research Institute of Agriculture and the Institute of Biological Problems of the Cryolithozone of the Siberian Branch of the Russian Academy of Sciences.

In 2008, a group of scientists from the Siberian Research Institute of Agriculture and Peat of the Siberian Branch of the Russian Agricultural Academy (Tomsk, Russia) joined the researchers. The specialists have studied the effect of zeolites on the activation of biochemical oxidation of oil. The research was carried out within the framework of the State Contract No. 611 of March 27, 2008, "Development of technology for neutralizing oil and oil product spills based on the use of local sorbents activated by microorganisms-oil destructors".

The stimulating effect of the zeolite on the process of degradation of petroleum hydrocarbons (HC) was evaluated by microbiological and enzymatic activity of soils, as well as by changes occurring in the composition of petroleum hydrocarbons. It was found that the degree of degradation of oil contamination in variants with the addition of zeolites to the soil was higher than in the control variant, without adding zeolites to the soil. The dynamics of degradation of oil hydrocarbons correlated with a change in the activity of oxidation-reduction enzymes (catalase, dehydrogenase) and the degree of accumulation of HC-oxidizing microorganisms in the soil [5].

Thus, studies of natural resources of local deposits and their role in bioremediation and restoration of anthropogenic-disturbed lands are among the priority ones that ensure the safety of development of the entire oil and gas complex of the Sakha Republic (Yakutia).

The purpose of the present studies is to develop an ecologically and economically feasible method for the restoration of disturbed ecosystems, following an accidental oil spill.

## **2. Materials and methods**

As source material for the production of biosorbent, a natural zeolite from the Honghuruu field (Republic of Sakha (Yakutia), Russia) and HOM isolated from the permafrost soils of Yakutia was used.

The deposit is located 22 km east of the village of Kempendyai (Western Yakutia, Russia), in the spurs of the eponymous ridge. In the structural plan, the deposit is located on the southeastern board of the Taas-Tuus salt-anticoloured structure, where four layers of zeolite rocksgenerally form elevated forms of relief and form the spurs of the Honguruu ridge. The strata have a simple structure and are laid according to the sedimentary rocks of the Upper Devonian and Lower Carboniferous. The bulk of the zeolite rock consists of vitroclastic and crystallo-nitro-clastic tuffs, replaced almost completely by

cryptocrystalline isotropic aggregates of clinoptilolite-geyländite. Crystalloclastic material (2-25%) is represented by quartz, feldspar, fragments of siliceous rocks and biotite plates, etc. The thickness of the beds varies from 6.5 to 13 m and is traced to a distance of 8.5 km, their structure has been studied to a depth of 100-160 m. The content of zeolites in the rock is 70-98% [6]. Mining geological conditions of bedding are favorable for open development. Currently, the deposit is being developed in insignificant volumes by LLC "Suntarzeolit" [7].

At this stage of the study, two types of raw materials are distinguished at the deposit, differing mainly in cationic composition: clinoptilolite-geyländite composition (extracted in quarry 1) and geyländite composition (extracted in quarry 2) [8].

The average chemical composition of zeolites for two types of raw materials, (%): SiO<sub>2</sub> -66.43; TiO<sub>2</sub> - 0.18; Al<sub>2</sub>O<sub>3</sub> - 12.03; Fe<sub>2</sub>O<sub>3</sub> - 0.92; FeO - 0.26; MnO - 0.03; MgO: 1.47; CaO- 2.50; Na<sub>2</sub>O - 1.75; K<sub>2</sub>O - 1.35; P<sub>2</sub>O<sub>5</sub> - 0.14; pp. - 6.2.

Physicochemical properties of zeolite rocks from the deposits by types of raw materials varies: content of zeolites in the rock, % - 70-98; ion-exchange capacity, mg-eq/g – 0.16-1.91; adsorption properties for water at P/Ps=1.0, % - 10.34-12.03; thermal stability, °C - 700; the optimum temperature of dehydration, °C - 300-550 [9].

Field experiments were carried out at the emergency facilities of the oil and gas complex of Yakutia: a section of the temporary oil pipeline Talakan-Vitim, South-West Yakutia, (N 59°33,840', E 112°06,656'), petroleum depot of the Amga village, Central Yakutia, (N60°54,067'; E 132°03.060'), fuel and lubricant storage in the village of Khonuu, in the North-East Yakutia (N 66°27'18.63 ", E 143°13'58.64") and the territory of the diesel power plant in the village of Chapchylgan, Central Yakutia (N 60°69'069 ", E 132°09'062").

Sampling and sample preparation were performed according to generally accepted procedures [10, 11].

To isolate HOM, the method of accumulation cultures on the mineral environment with oil of Muntz was used [12, 13, 14].

Specific identification of the isolated microorganisms was carried out using the Bergey's guide [15], using the analysis of the nucleotide sequences of the 16S rRNA gene [16, 17, 18, 19, 20].

The emulsifying activity of the isolated HOM cultures was determined by the Cooper method [21].

Investigation of the sorption properties and petrofluidity of materials was carried out with oil from the Talakanskoye field (Yakutia, Russia) using the methods of Anufrieva et al. [22].

Determining the content of petroleum products in the soil was carried out in accordance with the generally accepted methods in geochemistry [23].

### 3. Results and discussion

Experimental work on testing the sorption-biological method of clearing frozen soils of Yakutia with the use of local zeolite was carried out on permafrost-taiga soil. Mineral compositions of the screen fraction 0.01-1.0 mm have been used [24, 25].

At the initial stage of work accumulating cultures of microorganisms (ACM) were received from the oil-contaminated permafrost soils. Obtaining ACM from oil-contaminated soils in a mineral medium with oil allowed for creating elective conditions for preferential growth of microorganisms capable of absorbing and using petroleum hydrocarbons as the sole source of carbon and energy.

The process of accumulation of microorganisms proceeded at room temperature for 3-5 days under conditions of constant aeration. By this time, the disappearance of oil stains, the formation of a turbid emulsion, the pigmentation, the precipitation of flakes, and (or) the saponification and disintegration of the oil layer were noted in the culture flasks.

The resulting ACMs were introduced into the soil of the test sites in two versions: in the form of a liquid suspension and after immobilization on a natural zeolite of the Honghuruu field. Areas of the soil that were not treated with ACM, as well as soils with the introduction of pure zeolite-containing crumb without bacteria (Table 1) were used as a control.

**Table 1.** Biodegradation of petroleum products in soils of experimental sites

Option of experience	Content of OP (g / kg)		Degradation of OP, %
	Before cleaning	Afterc leaning	
Sod-meadow loamy soil, recent pollution (Central Yakutia)			
Control(S+O)	0.608	0.512	15.7
S+O+Z	2.432	1.889	22.5
S+O+ACM	1.987	1.071	46.1
S+O+ACM+Z	4.269	0.298	93.0
Permafrost-tundra soil, 1 year after the spill (Northeast Yakutia)			
Control (S + DF)	25.823	21.247	17.7
S + DF + Z	3.260	2.494	23.5
S + DF+ACM	5.275	2.412	54.3
S + DF+ACM + Z	19.803	2.875	85.5
Permafrost-taiga, 5 years after the spill (South-Western Yakutia)			
Control (S+O)	364	361	0.8
S+O+Z	1621	1093	32.6
S+O+ ACM	1616	1030	36.3
S+O+ ACM+ Z	4.269	65	96.9

Note: S - soil; O - oil; Z - zeolite; ACM - accumulation cultures of hydrocarbon oxidizing microorganisms; DF - diesel fuel.

As a result of the conducted studies, it was established that during one growing season, the degradation of the PP in the soils of the experimental sites treated with ACM in the form of a liquid suspension was 36.3-54.3%; in the soils treated with accumulative cultures immobilized on zeolite - 71.8-99.4%; in control soil samples, not treated with biopreparations – just 0,8-23,0%.

#### 4. Conclusion

Thus, the conducted studies have shown that the use of the zeolite of the Hongurru deposit in the purification of permafrost soils from oil contamination is an effective and promising method for bioremediation of oil-contaminated soils in the soil-climatic conditions of Yakutia.

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