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ENGINEERING-GEOLOGICAL ASPECTS OF NEGATIVE CONSEQUENCES OF CONTAMINATION OF DISPERSIVE SOILS BY PETROLEUM PRODUCTS

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The article presents the features of transformation and migration of petroleum products in the underground environment, which are determined by the physical and physicochemical properties of petroleum hydrocarbons (density, viscosity, solubility in water, etc.) and their enclosing soils (sorption capacity, humidity, etc.). The main processes of degradation of oil products in the soil stratum are considered. The influence of oil products on the change in oxidation-reduction and acid-alkaline conditions of the underground space, development of activity of various forms of microorganisms is shown. The change in the composition and properties of dispersive soils of various degrees of water saturation is experimentally studied. The analysis of the causes of the reservoir destruction used for storage of fuel oil is given. It was established that the development of microbial activity at its base led to the transition of sands to quicksands, and moraine loams to quasi-plastic varieties. Intensive gas formation of methane and its homologues, nitrogen, carbon dioxide, hydrogen in sands was recorded.

Based on the analysis of the results of long-term monitoring of the effect of contamination of dispersive soils by oil products, their bearing capacity in the base of the structures has been reduced to 50% of the initial value. The role of microbial activity in the formation of an aggressive environment in relation to building materials is shown.

***Key words*:** underground space, petroleum hydrocarbons, contamination, microorganisms, sandy-clay soils, aggregates, biochemical gassing, quicksand, corrosion.

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Introduction. The problem of contamination of the underground space of urban and industrial regions with oil products is very relevant in connection with the extraction, processing and transportation of energy carriers, as well as their wide use in many technological cycles of industrial enterprises. The release of petroleum hydrocarbons into the underground environment leads to a change in oxidation-reduction and acid-alkaline conditions, to the activation or suppression of microbial activity in the water-bearing soil. The development of these processes is reflected in the stress-strain state of dispersive soils, their composition and physical-mechanical properties, and also intensifies a number of natural-technogenic processes, the orientation of which depends on the degree of water saturation of rocks.

In the soils of the aeration zone represented by sandy varieties the chemical oxidation of petroleum products occurs due to the presence of air oxygen, which results in their irreversible sorption on the surface of mineral particles, accompanied by the formation of aggregates. As a result of these processes, the sand deposits change into friable varieties ($p_d \geq$ 1.01-1.25 g/cm^3) with high water permeability ($k_f \geq 60$ m/day), which become «quick» when interacting with water. The release of oil products as nutrient and energy substrates in the water-bearing layer leads to their biochemical transformation under the influence of a microbial biocenosis consisting of natural and introduced microorganisms. The general orientation of this transformation is as follows: the starting hydrocarbon → ethanol (R – OH) → aldehyde (R – CHO) → acid (R-COOH) → gases.

The accumulation of living and dead cells of microorganisms, as well as the products of their metabolism, reduces the shear resistance of clay soils, the modulus of general deformation and increases the ability to develop plastic deformations. The dynamic activity of microorganisms in the sands shifts them into a state of quicksand. The result of complete biochemical degradation of petroleum hydrocarbons in a reducing environment is the generation of highly soluble (hydrogen sulphide, carbon dioxide) and low-soluble gases (methane, nitrogen, hydrogen). The formation of highly soluble gases along with organic acids increases the corrosive aggressiveness of groundwater, whereas the accumulation of poorly soluble gases in its turn leads to a significant decomposition of dispersive soils. The processes of degradation of sandy-clay soils significantly reduce their bearing capacity in the basement of structures for various purposes. In this connection, the structure of complex engineering-geological monitoring for the state of the components of the underground space un-

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der conditions of hydrocarbon contamination was proposed, the analysis of the results of which may promptly prevent the transition of the structure to a pre-emergency or emergency condition.

When studying the processes of contamination of the underground environment with oil products, it is necessary to analyze the forms of migration of petroleum products, their physicochemical, chemical and biochemical transformation in dispersive soils with varying degrees of water saturation. In addition, it is necessary to trace the influence of petroleum products on the promotion of microbial activity in the underground environment, depending on the degree of water saturation of the soils and their engineering-geological types, to reveal its positive and negative effect.

The geotechnical and engineering-geological aspect is to assess the reduction in the bearing capacity of sandy-clay soils in the basement of structures for various purposes under the combined effect of changes in physicochemical conditions and the activation of microbiota in the underground environment when they are contaminated with oil products.

Solving a complex problem – the consequences of contamination of the underground environment with oil products requires a variety of methodological approaches. At the same time, it is necessary to give theoretical analysis of the migration forms of petroleum products in soil, the characteristics of their chemical and biochemical transformation in dispersive soils with different degrees of water saturation: experimental studies of the influence of different types of oil products depending on the nature and completeness of their degradation in the underground environment on composition, – mechanical properties of sandy-clay soils; study of the impact of oil products (diesel oil) on sandy soils in the zones of aeration and water saturation; calculation methods for estimating and predicting the change in the bearing capacity of transformed sandy-clay soils in the basement of structures for various purposes.

Discussion of research results. More than 90-95 % of the oil is composed of hydrocarbons of four homologous series: paraffin (alkanes), naphthenic (cycloalkanes), aromatic (arenes) and hybrid – paraffin-naphthenic-aromatic. The total number of carbon atoms in petroleum hydrocarbons varies from C_1-C_4 (gases) to C_{60}. In addition to the chemical composition, the fractional composition of oil available from its distillation is also distinguished (see table).

The main fractional composition of oil [2]

Oil fractions	Index compounds	Hydrocarbon chain length
Petrols	Paraffins, naphthenes, arenas	C_3-C_{10}
Paraffin oils	Paraffins, naphthenes, arenas, alkenes	C_{10}-C_{16}
Diesel oils	Paraffins, naphthenes, arenas	C_{17}-C_{25}
Axle oils	High-molecular paraffins, polycyclic arenas, hybrid paraffin-naphthenic-aromatic hydrocarbons	$>C_{25}$

The transformation and migration of petroleum products in the stratum of rocks and underground waters is determined by their physical and physical-chemical properties: density, viscosity, solubility in water, the ability to sorb on the surface of mineral particles and aggregates, and volatility (boiling point). Basic physical properties of petroleum products [4]:

	Petrols	Paraffin oils	Diesel oils	Axle oil
Density, g/cm^3	0.700-0.780	0.775-0.800	0.795-0.850	0.879-1.030
Viscosity, mm^2/c	0.66-0.80	1.05-1.5	2.5-8.0	296-1021
Solubility in water at T = 20 °C and air pressure, mg/dm^3	9-505	2-5	8-22	–
Boiling point, °C	40-200	200-300	300-400	>400

In the process of migration of petroleum hydrocarbons in groundwater, their solubility, which is related to the chemical composition and increases in the following series, is of particular importance: paraffins-naphthenes-aromatic hydrocarbons [4, 14]. In general, the solubility of oil and oil products in water varies widely [9].

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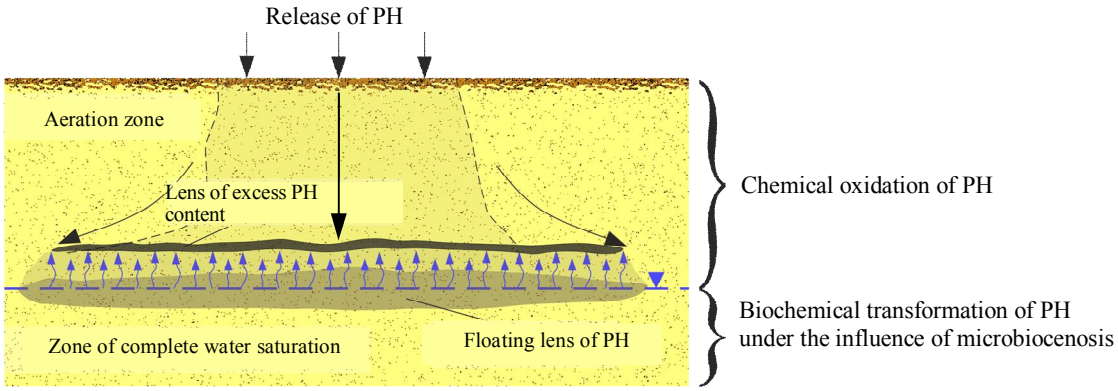


Fig.1. Flow chart of main processes of petroleum hydrocarbons (PH) transformation after release in soil

During interaction of petroleum hydrocarbons with soils, their transformation occurs as a result of chemical oxidation and biochemical destruction with the participation of various forms of microorganisms (Fig.1).

The products of chemical oxidation of hydrocarbons are alcohols, aldehydes, ketones, acids, resins, etc., which move into a gaseous or dissolved state and continue to migrate along the subsurface or accumulate in the fissured-porous space of soils and undergo further transformation with the participation of different groups of microorganisms in the water-saturated environment.

Various groups of microorganisms have ability to utilize petroleum hydrocarbons, they develop both in oxygen (aerobic) and anoxic (anaerobic) conditions. It is established that microorganisms can use practically all kinds of organic matter from C_1 to polymers. Microorganisms are relatively easy to utilize kerosene (C_{10}-C_{16}) and diesel oils (C_{16}-C_{25}), and the light-boiling hydrocarbons with a chain length up to C_8 are more difficult to be used. Naphthenic and polycyclic aromatic compounds decompose only in co-oxidation cycles in environments with a rich biocenosis. Hybrid polycyclic compounds - fuel oil and others, with a chain length $C > 25$ are assimilated less well [4, 5, 13, 16].

In the process of hydrocarbon degradation in the soil stratum, both natural microorganisms and those released as compounds of petroleum hydrocarbons, including sulfate-reducing, iron-reducing, fermenting bacteria, aceto- and methanogens, take part [1, 15]. The presence of polar groups (–OH, –COOH, $–NO_2$, etc.) in the oxidized hydrocarbons leads to an increase in their sorption capacity [10]. When considering the sorption of petroleum hydrocarbons, the preservation of the structure plays a major role in the interaction with a solid surface of dispersed particles. A feature of the sorption of polyelectrolytes is its irreversibility. The increase in the dispersity of soils during the transition from coarse-grained sands to clays in the aeration zone leads to an increase in sorption capacity from 8 to 40 l/m^3 [4]. The presence of an organic component increases the sorption capacity of dispersive soils in relation to petroleum hydrocarbons, especially with the content of $C_{org} \geq 1.2$ % [5].

The release of petroleum hydrocarbons into the groundwater changes the direction of oxidation-reduction reactions. For groundwater, the redox potential values range from +860 to –600 mV. The values of the oxidation-reduction potential of groundwater containing oil hydrocarbons are +100 ÷ 350 mV and in some cases can decrease to –400 ÷ –500 mV [3, 7, 8]. The magnitude of the acid-base potential (pH) of groundwater varies from 0 to 12.5, but in most cases is within 6-8.5 [11]. However, the oxidation of natural organic matter and especially the formation of organic acids reduces the pH to 5 or less (as it was determined in field tests).

To assess the effect of petroleum hydrocarbons on the sandy soils of the aeration zone, laboratory studies of air-dry sands with a different content of OH (diesel oil) from 20 to 100 mg/kg were carried out. The performed experiments made it possible to evaluate the transformation of the composition, state, water and physical-mechanical properties of the sands as the hydrocarbon content was increased. Sorption of petroleum hydrocarbons on air-dry sands is accompanied by aggregation of particles during the formation of hydrogen bonds in chain structures of diesel oil (C_{16}-C_{25}).

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The formation of aggregates contributes to an increase in the total porosity and pore sizes, which causes an increase in the total water capacity (the ability of the ground to contain only water) and the sand filtration coefficient (Fig.2, 3).

The appearance of oxidized hydrocarbons leads to an increase in the number of chain carriers, which increases the hydrophilicity of the sands, and accordingly, the maximum molecular moisture capacity (Fig.4).

Reduction of the dry unit weight of sandy differences is associated with an increase in their porosity and a change in the material composition due to the irreversible sorption of oxidized hydrocarbons (Fig.5).

The presence of hydrogen bonds characterized by flexibility in chain structures provides a pronounced ability of sands to develop plastic deformations, which is manifested when studying their strength under long-term testing conditions in single-plane shear devices (Fig.6).

The contamination of water-saturated sands with oil products leads to the promotion of microbial activity by the supply of nutrient and energy substrates, as well as microorganisms introduced with petroleum hydrocarbons. Since in the water-saturated sands there is no sorption of oil hydrocarbons, the main processes of changing the composition, condition and properties of the sand will be associated with the promotion of microbiological activity in the presence of petroleum hydrocarbons in groundwater. It is known that even the most durable benzene rings in aromatic hydrocarbons are able to rupture under influence of microbiological hydroxylation.

The studies of the Department of Hydrogeology and Engineering Geology of the Mining University of water-saturated sandy soils containing oil hydrocarbons showed that medium-grained sandy varieties have passed into sands with a predominance of fine and fine-grained fractions in their composition. In the sands moisture-holding capacity w_{mm} from 0.10 to 0.19 unit fractions and

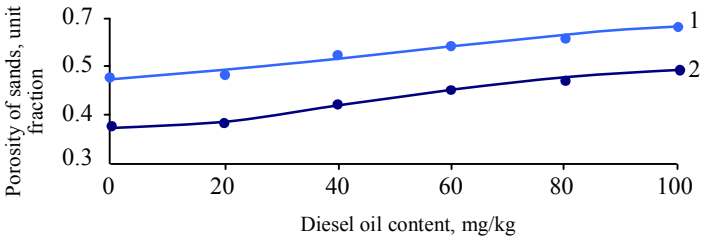


Fig.2. Change in the porosity of sands in loose (1) and dense (2) state with different contents of the diesel oil

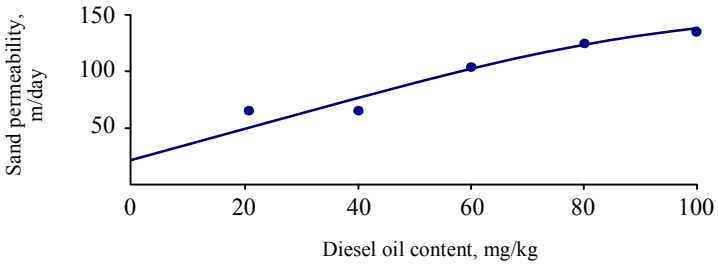


Fig.3. Change in the filtration coefficient of sands with different contents of the diesel oil (with a pressure gradient I = 3)

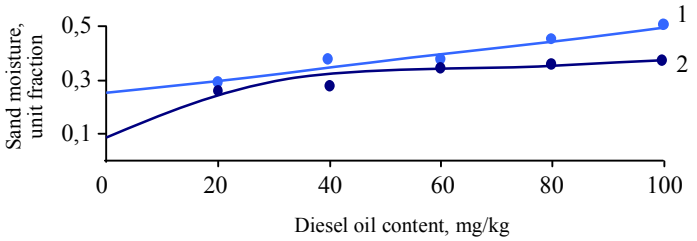


Fig.4. Change in the water capacity w_p (1) and the maximum molecular moisture capacity w_{mm} (2) of sands with different content of diesel oils

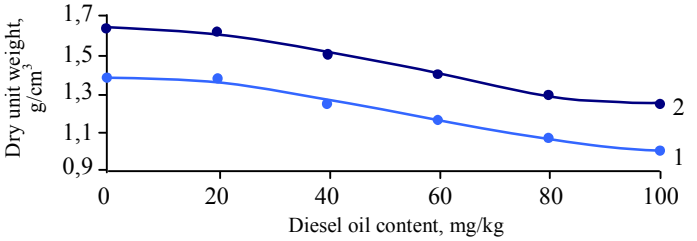


Fig.5. Change in the density of dry unit weight of sands in loose (1) and dense (2) state with different contents diesel oil

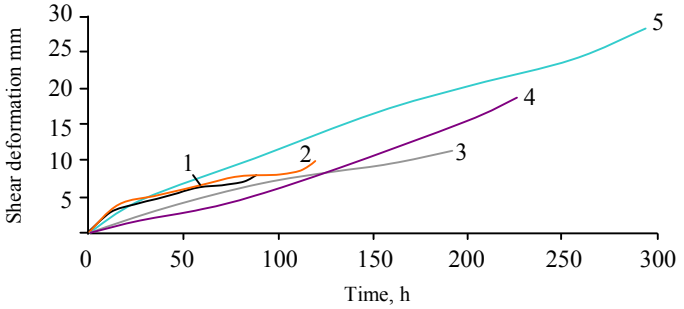


Fig.6. The nature of development of shear deformations of air-dry sands with different contents of the diesel oil (at a normal pressure of 0.15 MPa)
1 – 20; 2 – 40; 3 – 60; 4 – 80; 5 – 100 mg/kg

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water permeability decreased compared to the initial value $k_ф$ = 3 m/day to 0.4 m/day, as well as the internal friction angles (≤12 degrees.). As it was established earlier, when the microbial mass content is more than 40 μg/g sands begin to show floating properties [5].

In the presence of petroleum hydrocarbons in groundwater, all indicators determining the content of organic compounds (permanganate oxidability, chemical oxygen demand) are substantially increased, and the activity of microorganisms is activated, which is recorded by increasing the amount of biological oxygen demand BOD_5 for 5 days. Generation of organic acids by microorganisms leads to a decrease in pH to 4 or less. Results of studies of the content of organic compounds in water: oil products – 55 mg/dm^3; permanganate oxidability – 390 mgO_2/dm^3; COD – 770 mgO_2/dm^3; BOD_5 – 310 mgO_2/dm^3; pH – 6.7 (laboratory tests); pH – 3-4 (field tests).

Experimental studies of the composition, state and physical-mechanical properties of sandy fluvial soils and loams, lacustrine (mIVlt), glaciolacustrine (lgIIIbl) and glacial origin (gIIIos) in conditions of a high degree of groundwater contamination by oil hydrocarbons and microbial impact made it possible to reveal the following regularities: absence of cementation bonds in the soils due to iron hydroxides; low values of the modulus of general deformation and shear resistance in comparison with the engineering-geological characteristics of the same soils in unpolluted areas. The hydrocarbon pollution has a particularly great effect on lacustrine-glacial and moraine deposits. Despite stable forms of consistency, such moraines exhibit pronounced plastic properties when studying their mechanical properties.

The microbiological studies of clay soils under conditions of contamination with petroleum products made it possible to establish a relatively high number of different groups of microorganisms (10^5-10^7 cells/g) – saprophytes, ammonifying, iron-reducing, sulfate-reducing, thionic, etc., among which heterotrophic forms of microbiota, including generating hydrogen sulphide, which was clearly recorded during well testing.

Everywhere in the sandy-argillaceous soils the formation of hydrotroilite was observed throughout the depth of the well. In addition to bacterial forms, a high content of micromycetes, the number of which reached 7000 CFU/1g, was found. Eighteen species of fungus cultures were found in the cross-section of the territory, most of which belonged to active destructors of petroleum hydrocarbons and were aggressive towards building materials (*Aspergillus*, *Fusarium*, *Penicillium*, etc.).

In the practice of design and operation of facilities that involve the processing, storage and use of petroleum hydrocarbons, the assessment of their long-term stability and operation safety is conducted without taking into account the effect of contamination of dispersive soils with petroleum hydrocarbons.

The largest impact on the underground environment due to leakage is provided by reservoirs for storage of petroleum hydrocarbons, the volume of which currently can reach 200,000 m^3. When designing reservoirs, it is assumed that the change in the state and properties of dispersive soils in the base occurs only under the action of cyclic loads during hydrotesting in the first years of their operation. It is believed that the cycles of «filling-retrieval» of hydrocarbons shift soils into a «quasi-elastic» state [12]. A comprehensive analysis of the cause of the crash of fuel oil reservoir that collapsed after 19.5 years of operation showed that the longitudinal rupture of the reservoir wall was due to the development of large and uneven deformations of the base due to a negative change in the state and properties of sandy clay soils when they are contaminated with fuel oil, active development of microbiota, biochemical gassing, which facilitate the transition of sandy soils to the state of quicksand and clay deposits into plastic differences [6]. Determination of the calculated resistance of the sandy-clay soils of the base made it possible to establish that its value at the end of the life of the tank became significantly lower than the effective pressure at full capacity filling (p = 0.12 MPa): the sands lost their bearing capacity, and the value of the calculated resistance of argillaceous soils decreased to 0.09 MPa. The inclination of the tank was due to the boiling of quicksand and amounted to 0.027.

When designing structures in areas subject to long-term hydrocarbon pollution, it is necessary to take into account not only a decrease in the load-bearing capacity of soils in the base of a struc-

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ture due to microbiological activity, gas generation and the transition of sandy clay soils to a group of unstable, plastic differences with a high content of organic compounds of abiogenic and biogenic genesis, but also the formation of an aggressive environment in relation to concrete structures. First of all, this refers to auger cast piles, their production technology implies their hardening in the soil column. If the traces of petroleum products are contained in the composition of groundwater, the permanganate oxidability exceeds 15 mgO_2/dm^3, and the pH value is < 4, then in this hydrochemical setting the hardening of concrete based on Portland cement will not occur. These conditions were traced within the cross-section of the territory of construction of the residential complex «Ilmatar», located in the south-western part of Vasilievsky Island between Kosaya street and 26th line street.

Conclusions

1. The peculiarities of transformation and migration of petroleum hydrocarbons in the underground environment, which have various organic compounds with a length of the carbon chain from C_1 to C_{60}, are determined by their physical and physicochemical properties: density, viscosity, water solubility, volatility, sorption ability on the surface of mineral particles.

2. The transformation of petroleum hydrocarbons in the strata of rocks can occur as a result of chemical oxidation (aeration zone) and biochemical destruction with the participation of natural and introduced microorganisms (the water saturation zone). The main degradation products of petroleum hydrocarbons under the action of these processes are alcohols, aldehydes, acids and gases.

3. The migration of petroleum hydrocarbons in sandy-argillaceous soils is accompanied by their sorption, the magnitude of which is determined by the granulometric composition and moisture of the soils, the presence of organic matter. The increase in the dispersity of deposits, along with the increase in the content of the organic component in the aeration zone, leads to the increase in the sorption capacity of soils relative to petroleum hydrocarbons, and growth of their moisture content reduces the activity of this interaction.

4. The presence of petroleum hydrocarbons in the composition of water-saturated sandy-clay soils predetermines the change in their oxidation-reduction ($Eh \leq 0$ mV) and acid-alkaline conditions (pH <5) due to microbial activity and the formation of metabolic acids.

5. The sorption of petroleum hydrocarbons on air-dry sands is accompanied by the aggregation of particles during the formation of hydrogen bonds in chain hydrocarbon structures, an increase in the total porosity, the total and maximum molecular moisture capacity, and in the sand filtration coefficient. The appearance of an organic component in the sands reduces the value of the density of the mineral part, and the presence of hydrogen bonds in the chain structures contributes to the appearance of pronounced plastic properties of sands under the conditions of long tests in determining the shear resistance.

6. The release of petroleum hydrocarbons as nutrient and energy substrates to water-saturated dispersive soils promotes the activity of microorganisms, primarily heterotrophic forms, which adversely affects the condition of soils, the permeability of sands and their water yield, as well as the mechanical properties: the decrease in the angles of internal friction and adhesion, the modulus of general deformation. Complete biochemical degradation of petroleum hydrocarbons in a reducing environment leads to the generation of various gases – carbon dioxide, methane, hydrogen sulfide, nitrogen, and hydrogen.

7. When designing facilities in the technological cycle of which there is a possibility of petroleum hydrocarbons leakage even in small quantities, forecasting their long-term stability should be carried out on the basis of a gradual decrease in the load-bearing capacity of sandy-argillaceous soils at the base. Analysis of the experience of plant accidents and the results of long-term monitoring of changes in the state and properties of dispersive soils makes it possible to quantify the reduction in their design resistance to 50 % of the initial value for clay deposits, and for water-saturated sands, complete loss of their bearing capacity is possible due to transition to a state of quicksand in case of increase of microbial activity in the conditions of the release of petroleum hydrocarbons.

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