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Estimation of the Migration Processes of Kumkol Oil in Different Types of Soil of South Kazakhstan Oblast

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***Abstract* – It was established that the sorption processes and migration of Kumkol oil in various types of soils of South Kazakhstan oblast (SKO) depend on their physical and chemical properties and temperature.**

All types of soils, except for desert sand and red-ferralitic clays have a high sorption capacity for the volume of Kumkol oil. Compact placic horizons of takyr and gray-brown soils obstruct the filtration of oil on the profile, and the desert-sandy soil and red-ferralitic clays, due to the large volume of their total porosity have the ability to pass the oil into deeper layers of the horizon. At low temperatures, the depth of migration of oil depends on the porosity of the soil, excess of oil on the surface of the soil forms a thick bitumic crust, which negatively affects the water and air regime of soil.

***Keywords* – Oil Migration, Soils, Sorption Capacity.**

I. INTRODUCTION

One of the main sources of environmental pollution by organic xenobiotics is oil and oil products. According to the International Economic Agency, the oil resources in the future will remain to be the main type of fuel in total energy consumption. In 2020, at an average annual growth rate of 1.9%, they will retain their share on the current level of 40%. According to proven oil reserves Kazakhstan occupies the 10th place in the level of oil production - 17 th place. Recoverable reserves of 214 domestic oil and gas fields, including 169 confirmed fields are estimated in 2.2 mldr. tons, condensate is about 700 mln. tons. The main reserves of Kazakh oil (90%) are concentrated in 15 major fields: Tengiz, Kashagan, Karashyganak, Uzen and others. In 1992, 25.8 million Tons were extracted, in 2000 - 35.3 million, In 2010 - 73.7 million. Tons. It is expected that by 2015 this number will rise up to 95 million .Tons., and according to estimates, in 2020 oil production will reach 140 million Tons. According to the results of the strategic development of the oil and gas industry for 2010 and plans for 2011(2011) in Kazakhstan in 2010 the three main enterprises processed 13.7 mn tons of oil, including the Shymkent oil refinery plant - 4.58 million tons, the Pavlodar Petrochemical Plant - 4.5 mln., Atyrau oil refinery plant - 4.2 million tons. Moreover, in the Republic of Kazakhstan there are 32 mini - oil refinery plants, the capacity of which allows to produce 28 tons of engine oil and 365 tons of diesel annually. Unfortunately, the extraction and processing of oil is associated with environmental problems. contamination by organic xenobiotics (Loosaar J. et al., 2010).

Strategy of Kazakhstan's transition to a green economy will involve solving water issues, urgent environmental issues, the development of green energy, reducing effects of environmental pollution. Analysis of the situation shows that the difficulty in assessing the impact of organic pollutants on ecosystems are connected, first of all, with the lack of study of migration processes in different types of soil (Grimaz S. et al., 2007), which determined the selection of research topics. Jain et al. (2011) believe that the currently used physical and chemical treatments are effective for the degradation of petroleum products but they lag behind in the desired properties, apart they frequently produce many hazardous compounds which are potent immunotoxicants and carcinogenic for living beings. Required for this purpose for the foreseeable future, long term tolerance studies are needed before being recommended for large scale use.

In assessing the migration of oil in the soil, various methods for the identification of petroleum products in the different soils. For example, in studies Lemke et al. (2005) evaluated the migration processes on a brown sandy loam soils with LIF (laser-induced fluorescence) analysis. Sotnikova E.G., Lipatov D.N. (2010) investigated Oil hydrocarbon migration in soils of the northeast of Sakhalin Island. Kudryavtsev et al., (2012) studied water migration and degradation of shaimskoy oil in the soil of bogs of the Khanty-Mansi Autonomous District. It is established that oil (up to 2 g/kg) is retained by the humic matrix of peat and does not pass into water. In studies of Halmemies et al., (2003) studied time and the penetration of oil into the soil, Semple et al. (2003) established the bioavailability of possible intermediates of oil degradation in the soil. Walter et al., (2000) identified features of sorption processes of selected polycyclic aromatic hydrocarbons on soils in oil-contaminated systems. According to the literature, in Kazakhstan, the study of migration of oil in the soil were carried out.

II. MATERIALS AND METHODS OF THE RESEARCH

2.1 Soils

The object of study is based on eight types of soils of the South Kazakhstan Oblast (SKO): typical loamy gray (serozems), light gray, mountain-brown, mountain light brown, desert sand, gray-brown, and red ferralitic clays and takyr, which are similar by physical and chemical properties and mechanical structure to characteristics of the main soil types, common in the territory of Kazakhstan

2.1.1 Soil types SKO On the territory of South Kazakhstan Oblast there are 19 types and subtypes of soils. Among them, the mountain and black brown, mountain light brown meadow-gray soils and gray soils

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irrigated soils, compared with others, which are less common. If the first two types of soils are found only on high submontane areas of the oblast, the latter two types - mainly on the plains that are surrounding the river basins. Other types of of soils towards the geographic drain forms a conditional series of horizontal zones in the following order: the typical gray soils →light gray soils →gray-brown → desert-sandy→ saline and solonets soils→ takyr soils. The above conventional number is defined by the dominant soil type.

All these horizontal soil zones, significant territories occupied by red-ferralitic clays characterized by the absence of differentiated genetic horizons of the profile. Typical gray soils soils are confined to the higher areas of the piedmont plains and foothills of the South Kazakhstan region. In this area there are main fields of industrial sites like refineries LLP "PetroKazakhstan Oil Products", JSC KP "Southpolimetall" and a number of municipal enterprises of the oblast. Gray-brown desert sand and takyr soil, saline, solonetsic soils common on plains areas of the oblast are located along the left bank of the Syrdarya River, which are zones of extraction and transportation of minerals and intensive development of animal husbandry. "KazMunaiGaz" company's pipeline penetrates through the mentioned territories, where there is a high probability of spills of crude oil.

2.2 Oil.

In this work there was used composite sample of Kumkol oil with the following characteristics: The content of oil products in the composition of the soil was determined by fluorometric method (PND F 16.1: 2.21-98, 1998).

2.3 *Determination the sorption capacity.*

To determine the sorption capacity of the soil adsorption complex (SAC) for Kumkol oil, we conducted laboratory experiment with composite samples of disturbed horizon of studied soil types. Analyzed samples to eliminate the influence on soil capacity of total and noncapillary porosity (which are native horizons for various reasons can vary significantly and thereby distort its true value), previously passed through a standard set of sieves. In In the experiment there were selected the combined fractions of mechanical elements ranging from 0.0001 to 3 mm, which corresponds to a mixture from colloidal particles to the gravel. The combined fractions of studied types of soil were placed in transparent plastic containers by 100 g in each container with a diameter of 10cm, and the height of12 cm and in which there were installed metal sieve instead of the bottom. Oil was added to the soil by 1-5 ml before its full saturation determined by the appearance of the first drop of oil through the lath bottom of vessel. To set the value of the index of influence temperature factor on the adsorption capacity of soils, the experience was repeated at 28, 20, 17 and 10 ° C, which corresponds to the temperature conditions in summer, autumn and spring periods of the year.

2.4 Statistical analysis.

Statistical analysis of the results was carried out by calculating arithmetic mean value and the standard deviation at 0.95> P> 0.80. All determinations were carried out in 3 and 5-fold reiteration. The data were processed using a personal computer IBM "Pentium" based on software packages "Excel".

III. Results of the Research and Discussion

3.1 Dependence of sorption capacity of soils on the type SKO

As a result of studies it was found that the studied types of soils, ascending indicators of Kumkol oil sorption capacity at 28°C, located as follows (Figure 1).

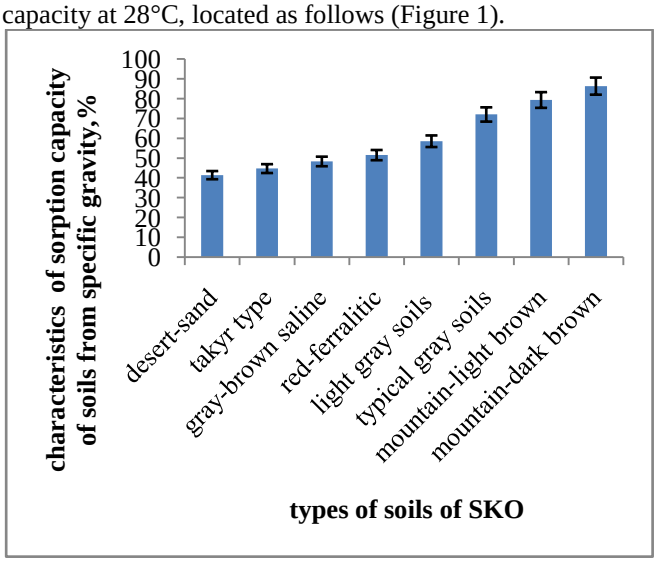


Fig.1. The dependence of the sorption capacity of soils of SKO on their type

At the same time studied types of soils also differed significantly in terms of duration of complete saturation process of their sorption capacity, turned out to be unrelated to the latter is directly proportional. The studied types of soils according to ascending of this indicator arranged in a row, hours: desert- sand – 2.4 ± 0.2, typically-gray soils – 3.3 ± 0.3, light-gray soils – 4.2 ± 0.3, mountain dark brown – 5.5 ± 0.2, mountain light brown – 5.7 ± 0.3, red-ferralitic – 6.5 ± 2.2, gray-brown – 8.6 ± 0. 4 and takyr – 10.3 ± 0.5.

3.2 Effect of soil texture on the sorption capacity

It is known that the volume of the sorption capacity depends on the combined effect of ion exchange, chemisorptive, complexing and capillary mechanisms of absorption of the soil adsorption complex (SAC).

Consequently, the amount of oil associated with the soil by using these mechanisms is a specific organic and mineral compound, interconnected by hydrogen bonds and bridges of polyvalent cations. These compounds are stably retained in a given volume of the soil against the forces of gravity and the pressure gradient. This means that the significant differences in terms of capacity and the duration of sorption process of oil of studied soil types is due to the activity of the above-mentioned mechanisms of soil-absorption complexes. At the same time, high indicators of the sorption capacity of typically-gray,

mountain light brown and mountain dark-brown can be explained as the result of interaction of oil with a full range of the above mechanisms. And in the case of previous types of soil capillary forces and low humus content, the predominance of sand and colloidal particles caused adsorption of oil through the expansion of the crystal lattice of clay minerals that adsorb organic substances with not so high molecular mass. On the boundary of interaction of solid particles of the soil and oil there takes place the fractional division. The light fractions of oil are quickly absorbed by the solid phase of the soil where in soil pores increases the proportion of heavy fractions, that are quickly filtered through a profile in the desert- sand and much more slowly in red ferralitic clays, gray-brown saline and takyr soils . This is due to the predominance in their mechanical composition of small dust and clay particles and it explains the longer period of saturation by sorption capacity of the latest types and subtypes of soils.

This is confirmed by the results of experiments on the study of oil filtration processes by profiles of these soils. As shown in Figure 2, when the dose is increased above the volume of oil of the sorption capacity at 50 and 100% the duration and depth of migration depending on types of soils varied considerably.

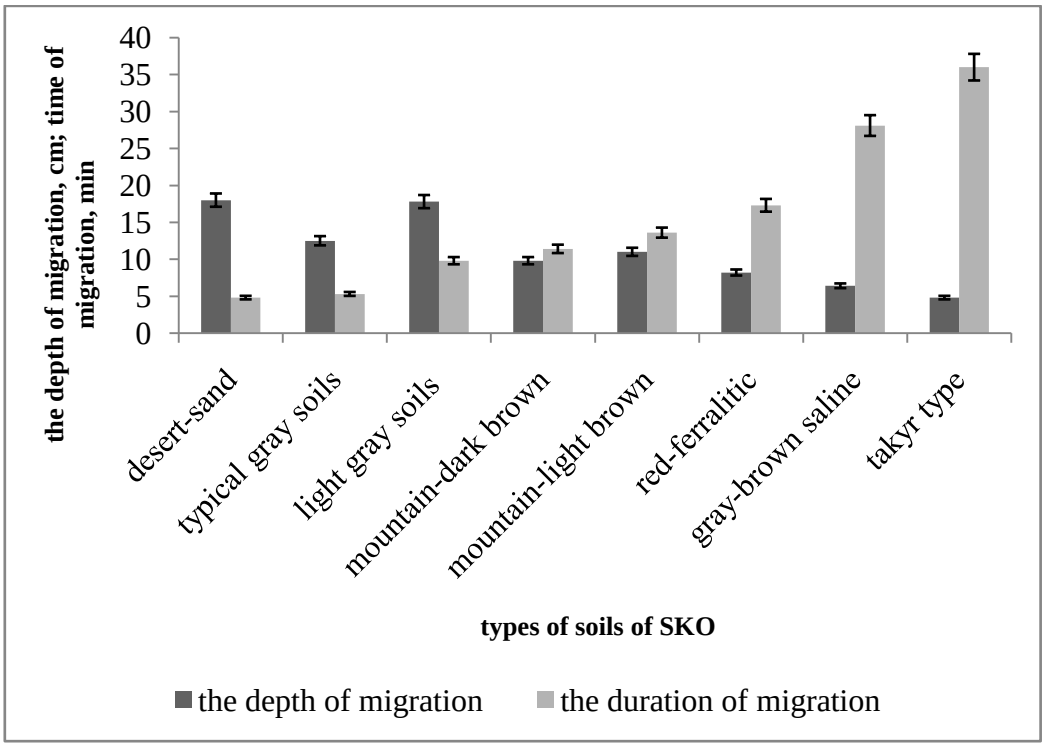


Fig.2. Indicators of the depth and duration of the migration of oil on the profile of different types of soils with a load higher than their sorption capacity by 50%

It was found that with increasing of amount of oil by 50%, the duration of the migration of oil on the profile directly linked to the duration of the period saturation of sorption capacity of soils and the depth of migration - inversely proportional. For the deadline of duration of migration in all soil types, except for the gray-brown saline and takyr soils the entire amount of additional portions of oil completely migrated to the lower layers. The latter two types of soil on the surface had the formed bitum crust of not absorbed amount of oil, of the hight of 3.5 ± 0.2 mm, further increase in load of oil tup o 100% led to formation of crusts with height of 5.0 ± 0.2 mm for all types but desert-sandy soils. bitum crusts survived for 65 days of the experiment. It was found that there was the increase of fractional separation of oil during its vertical migration. In the deeper layers of the soil the migration of light oil continued which occurred intensively in desert-sand, light gray soils and red-ferralitic soils.

3.3 Effect of temperature on the sorption capacity of soils

Analysis of the results shows that when the air temperature is 28 ° C and above, the characteristics of sorption processes of oil in the studied soil types are similar to the processes of moisture sorption. It was found that mountain and dark brown, mountain gray-brown and of typically gray soils soils have the largest amount of moisture in which the figure was 63.4 ± 3.3%, 53.7 ± 2.4% and 51.2 ± 2.2% of the specific gravity, respectively. The lowest volume of water capacity is set at the red-ferralitic and desert-sandy soils: 42.1 ± 1.9% and 26.2 ± 2.0%, respectively. These results are consistent with theoretical expectations associated with a high content of humus in the first three and a low content of organic components in the latter two types of soils. Indicators of gray-brown and takyr soils were close to moisture capacity of typically gray soils and mountain-gray-brown

soils, in which the duration of the process of complete saturation of moisture capacity was 7.5 ± 0.4 minutes. However, unlike them, the process of complete saturation of moisture capacity in the first two types of soil lasted by 30.6 times longer that was due to the rapid dissolution of the colloidal elements of soils, which during the subsidence was sealed capillary pores and create obstacles to the filtering of water down the profile. From these results it is clear that the value of oil capacity of studied soil types are slightly higher than the indicators of their moisture capacity that was, in our opinion, due to the presence in the noncapillary pores certain proportion of unrelated with set volume of the sorption capacity of oil, which is held against the forces of migration gradient due to sticking of heavy fractions to the large mechanical elements (Figure 3).

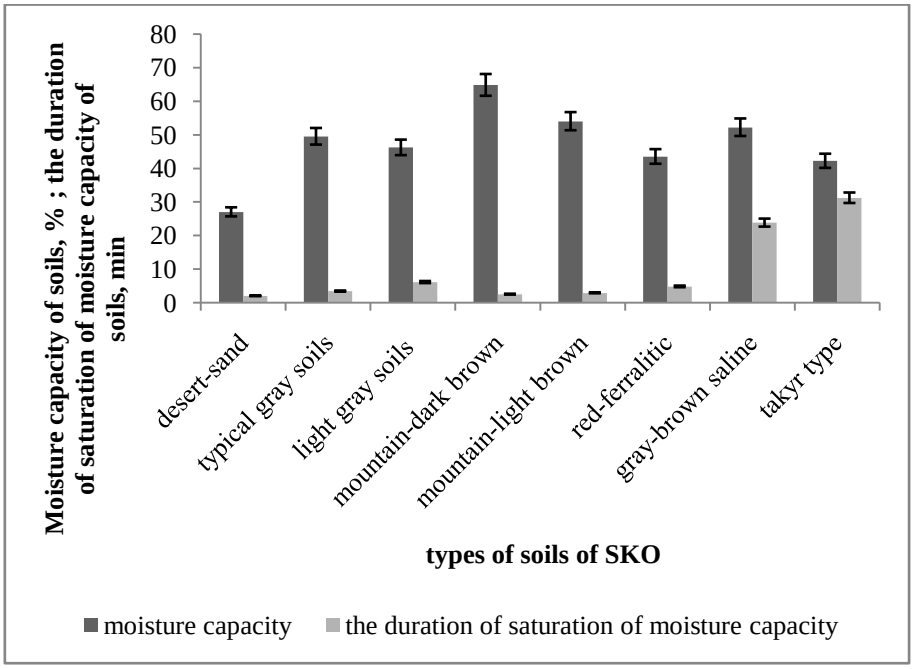


Fig.3. Characteristics of the studied types of soils by volume and duration of saturation of their moisture capacity

From these results it is clear that the value of oil capacity of studied soil types are slightly higher than the indicators of their moisture capacity that was, in our opinion, due to the presence in the noncapillary pores certain proportion of unrelated with set volume of the sorption capacity of oil, which is held against the forces of migration gradient due to sticking of heavy fractions to the large mechanical elements.

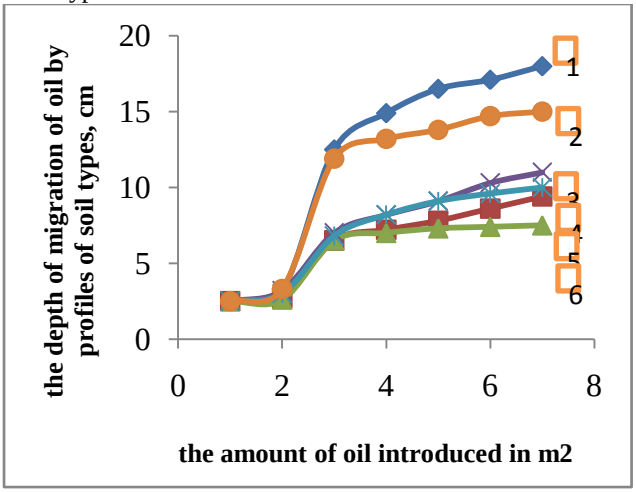
The results of laboratory studies conducted at 20.0 ± 1.0, 17.0 ± 1.0 and 10.0 ± 0.5°C showed that the lowering of temperature below 20°C dramatically increases the viscosity of Kumkol oil. Among the studied soil types statistically it was found that only typical gray soils and mountain - gray-brown soils have significant differences from the rest by the volume of oil sorption capacity. The volume of absorpted oil of the above types of soil was 28.5 ± 1.2% and 23.4 ± 1.6°C at 17.0, 15.6 ± 1.3 and 12.5 ± 1.0% at 10.0 ° from their indicators in the experiment at a temperature of 28 ° C. At 20.0^0C the results of sorption capacity is a bit higher, 65.4 ± 3.2 and 58.6 ± 4.3% respectively, for each of the soil, wherein the saturation rate of sorption capacity increased by 18.1 ± 1.2 and 10.4 ± 1.0 times. The volume of the sorption capacity ranged from 13.5 ± 1.1 to 19.4 ± 1.2% from the figures of experience at 28°C. On the surfaces of all the soils was formed crust of bitumen.

Based on these results it can be concluded about that the amount of soil sorption capacity for oil depends on the cumulative effect of all kinds of mechanisms of adsorption of soil SAC by which studied soil types vary significantly at environment temperature is 25^0C and above. Lowering of the temperature below 20°C leads to a dramatic increase in the viscosity of oil, which is the reason for decrease of sorption parameters and its migration into depth in all cases of studied soils.

3.4 Study of sorption properties of soils in the model conditions

Experiments conducted with monolithic soil samples showed a significant difference between the studied parameters of oil pollution in conditions of native horizons and parameters of experience with tests of combined fractions of mechanical elements. The oil in volume 2.0 and 4.0 ± 0.2 / m^2 was absorbed by all types of soils at 28°C almost instantly, the rate of total oil sorption by the top layer of the soil was 0.16 ± 0.01ch. The depth of the oil migration in the studied types did not differ statistically. However, from 5.50 ± 0.3 l / m^2 in the gray-brown saline and takyr soils the process of further sorption of oil, compared to other soil types, slowed down considerably. If a dose of 5.0 l / m^2, it was 0.76 ± 0.03ch, and at 6.0 liters – 0.91 ± 0.03ch and there were marked the signs of complete saturation of the absorption capacity of the upper layer. Further increase of the dose of oil to 8.0 ±

0.4l led to the formation of bitum crust, which remained on the soil surface for 20 days. The total depth of the oil migration in the profiles of these soils was 4.5 ± 0.1 and 4.3 ± 1.2sm respectively. It should be noted that under the black of oily top layer there was observed the migration of light fractions oil on 1.3cm. It should be noted that under the black of oily top layer there was observed the migration of light fractions oil on 1.3cm. This is because the load oil 6.0 l / m^2 was complete saturation of the sorption capacity of the upper swallowed and mud crust of soils, after which, upon further increasing of the dose to 8.0 ± 0.4 l / m^2 ; filtering of the excess quantity of oil into lower horizons was considerably difficult. On the contrary, in other types of soils dose of oil in an amount of 2-8 l / m2 were completely absorbed for 0.15 ± 0.01 – 0.75 ± 0.04ch. The highest rate of sorption of oil at a dose of 8.0 l / m^2 is set for desert-sand soils and red-ferralitic clays. As shown in Figure 4, the depth of oil migration by profiles of these soils also significantly higher than parameters of other types of soils.



1. Desert-Sand Soils, 2. Typical Gray Soils, 3. Light Gray Soils, 4. Mountain Dark Brown, 5. Mountain Light Brown, 6. Red-Ferralitic Clays

Fig.4. The impact of quantitative indicators of oil pollution on the depth of its migration in different types of soil profiles of SKO

Increasing the dose oil led to further lowering of migration rate into the depths in all types of soils, as compared with similar indicators at 8.0 l / m^2. The experimental results showed that in the conditions of oil pollution of native horizons parameters of absorption capacity are much higher than the true sorption capacity of the studied types of soil , due to the volume of their total porosity. In the mechanical composition of the desert-sand soils fractions of medium and large sand particles predominate, the space between them forms a significant amount of the total porosity of this type of soil. The high rate of migration and the amount of oil absorption by red ferralitic clays can be explained by the presence of large and deep cracks in their profiles, the formation of which is related to the processes of wind and water erosion.

The study of these indicators at temperatures of 17.0 and 10.0^{0}C confirmed the conclusions drawn on the basis of experiment samples of combined fractions of mechanical elements of soils. Later Kumkol oil viscosity increased and the bulk of it concentrated in the upper layers of studied types of soil. The rate of remaining saturation and migration greatly slowed when 17,0^{0}C and practically did not occur at temperature of 10,0^{0}C. The established difference in the depths of the oil migration by the profile in the studied types of soil is explained by the degree of permeability and general porosity of their upper horizon which caused initial depth of penetration at the moment of oil spill into the soil.

3.5 Study of sorption properties of soils in the field

These results were confirmed under field experiments, where the highest rate of sorption and migration of oil was set for desert sand and red ferralitic clays. But their parameters were somewhat lower compared to the results of experience with monolithic samples. The reduction of depth of oil migration indicators were also noted in other types of soil.

Results conducted experiments showed that the capillary effect is clearly seen at large permeability and porosity of the soil. Sand and gravel grounds are favorable for oil migration, but clay and silt limit the distance over which it can be moved. Oil moves on cracks in rocks. The most deeply oil products move in light-textured substrates - gravel sediments, sands, sandy clays, and fractured rocks.

IV. CONCLUSION

On the basis of the research we reached the following conclusions:

- The processes of sorption and migration of Kumkol oil by different types and subtypes of soils of SKO significantly affect their physical and chemical properties and temperature regime of period of oil pollution; All types and subtypes of soils, except desert- sand and red ferralitic clays have high enough volume of sorption capacity for the Kumkol oil;
- Dense stratified horizons of takyr and gray-brown soils prevent oil filtration on a profile that significantly reduces their true sorption capacity, which is the cause of bituminous crusts on the surface of the soil, starting with a dose of oil 8.0 ± 0.4 l / m^2;
- Compared with other types of soils, desert-sand soils and red ferralitic clays, due to the large volume of their total porosity have the ability to let the oil pass into deeper layers of the horizon;
- The established indicators of dynamic characteristics of the oil pollution in soil all types vary dramatically with increasing of viscosity of Kumkol oil at 20.0 ± 1,0^{0}C and lower.
- At low temperature conditions the depth of migration of oil depends on the porosity of the soil, and the excessive amount of oil on the surface of the soil forms a thick crust of bitumen, which negatively affects the water-air regime soils. The established patterns of research results are important information in the design of adapted bioremediation technologies of oil-contaminated soil to the conditions of different types of soil

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