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INVESTIGATION OF PURIFICATION PROCESS OF OIL-CONTAMINATED SOILS

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Abstract: *The work deals with the purification process of the oil-contaminated soils. Methods of intensification of molecular surface phenomena when exposed to oil-polluted soil were shown. Removal of the oil pollutant from the surface of mineral particles is a result of a complex action of molecular-surface phenomena (selective wetting, surface energy gradient) and mechanical forces of the aqueous solution flow. In order to increase the efficiency of their purification, the work considers methods of enhancing the molecular-surface interaction phenomena effect on oil pollutant of contaminated soils. Our experiments revealed interfacial surface tensions that drop on the oil-water interface during the dilution process with an organic solvent. The organic solvent used in the process dissolves the oil contaminant, reducing its viscosity many times and formed the optimum concentration of surfactants in the oil pollutant. It found that the organic solvent and non-ionic aqueous surfactant solutions, as well as alkaline medium reduced interfacial surface tensions that lead to the enhancement of molecular-surface interaction phenomena effect on the oil pollutant of contaminated soils and raise effectiveness of their cleanup.*

Keywords*: oil-contaminated soil, contaminant, solvent, the interfacial tensions, surfactants, treatment.*
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Introduction

It is well-known that all stages of oil use starting from exploration and production up to consuming oil products result in environmental contamination. Oil and oil product spills into the environment is accompanied by environmental safety violation, transformation in the composition and functions of elements of environment occurs with harmful changes of all natural biocoenosis [1]. In the course of developing the washing technology for recycling oil-contaminated soils with organic solvent-based aqueous surfactant solutions, we used theoretically grounded methods of mechanical, physical and chemical technological impact on oil-contaminated soils based on characteristics of oil-contaminated soils and properties of a contaminant “residual oil” on the surface of soil particle in the form of sold film with an interfacial layer of active components (acids, resin, asphaltene etc.) and an oil coating layered on it [2-3]. Only forced dispersing of the above can clean adhering layers of oil contaminant from the surface of particles of contaminated soils. Dispersion degree of oil contaminant till droplet state in the course of its treatment from the surface of minerals will depend on both excess mechanical work over the washing system and on emulsifying capacity of the washing solvent. Along with mechanical impact of flow, molecular-surface phenomena such as adsorption of surfactants with changing the interfacial tensionss have an effect on adhering layer [4]. Molecular-surface phenomena are determined by intensity of the interaction between molecules of different substances in the composition of solid and liquid phase of technological suspension [5]. During cleanup of oil contaminated soils, the role of molecular-surface phenomena proved to be a determining factor while methods on their intensification will increase an effectiveness of its cleanup which is the aim of this paper.

Experimental part

"Residual oil" isolated from oil-contaminated soil of Buzovna and Balakhany region of the Absheron peninsula served as a research object for investigation of washing process of oil-contaminated soil with aqueous cleaning solution. Preliminarily dried benzene AR was used as an extracting agent for the extraction of "residual oil" from soil. Benzene extract of oil was isolated from benzene by evaporating in water bath while the oil was analyzed by standard test methods. Chemical composition and physical-chemical parameters of residual oil are given in Table 1. Results of the "residual oil" analysis in the composition of oil-contaminated soil show that they do not contain light fractions; they are weathered, contain resins, asphaltenes, organic acids and hydrocarbons that are on the boil in a wide temperature range. Toluene AR was used to study the laws of effect of organic solvent on molecular-surface phenomena during cleanup of oil-contaminated soil with aqueous cleaning solution. The interfacial tensions of toluene solutions of "residual oil" on borders with distilled water at 20 ± 1 ^{0}C was studied. The interfacial tensions of toluene solutions of oils with mass share of oil 25% on borders with aqueous solutions of sodium hydroxide and non-ionic surfactants OP-10 at 20±1 ^{0}C was studied. Non-ionic surfactant OP-10 used in experiments conforms to GOST-8433-81 standards. The interfacial tensions on the border of two immiscible fluids (σ_{ow}, erg/cm^2) was determined by measuring drop volume [6-7]. In experiments the study of surface properties was conducted on systems consisting of two immiscible liquid phases – distilled water (aqueous solutions of sodium hydroxide and surfactant OP-10) and toluene solution of "residual oil".

Table 1. Physical and chemical parameters of residual oils isolated from oil-contaminated soils of Absheron peninsula in Balakhany and Buzovna regions

Name	Parameters of residual oil		Test method
	Balakhany	Buzovna	
1. Fractional composition, ^{0}C/% cap.	100 -260/4,0 >260-decomposition } atm	100 -160/2,5 >160-decomposition } atm	GOST 2177
	32-110/13 110-155/17 155-220/9,5 >225-decomposition } 3 mm	34-110/16 115-155/2 155-158-decomposition } 3 mm	ASTMD 1160
2. Chemical composition, mass. %			
asphaltenes	9.3	6.2	IP143
resins	4.95	8.71	GOST 11826
paraffin $C_{19} - C_{35}$	1.23	1.16	GOST 11821
3. Acidity, mg KOH/g	0.168	0.097	ASTMD 664
4. Viscosity at 50 ^{0}C, kinematic, cSt	76.0	50.9	ASTMD 445
5. Density at 20^{0}C, kg/m^3	955	957	GOST 3900

Measurements of the interfacial tensions on the border of two immiscible phases were conducted for systems with equilibrium distribution of components (water, aqueous-alkaline solution, toluene solution of oil) between phases at 20 ± 1 ^{0}C. Equilibrium is achieved by multi-day settling of phases.

Results and discussion

Study of surface activity of residual oils expressed by the dependence of interfacial tension on the border of oil – water (σ_{ow}) at 20 ±1 ^{0}C on the concentration of these oils in toluene are given with isotherm of surface tension in figure 1. As these data show at low concentrations of oil in toluene till mass share of 0.2 % interfacial tension for solutions of these oils does not almost change and nearly is equal to interfacial tension for pure toluene 36.6 erg/cm^2. At higher concentration of oil in toluene over 0.2 mass% interfacial tension starts to fall till the concentration of 23.1mass%, corresponding to minimum value of interfacial tension equal to 20.0 erg/cm2 for oil solution taken from the soil of Buzovna region and 11.5 erg/cm2 for oil solution taken from Balakhany region. Beginning from the concentration of oil in toluene equal to 23.1 mass %, the surface tension for both oils solution begins to increase.

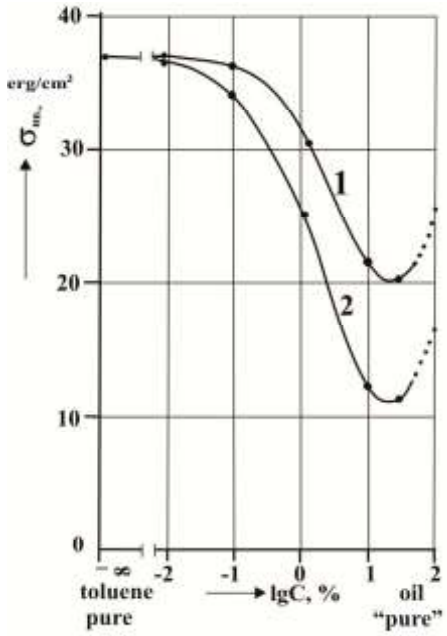

Fig.1. Dependence of the interfacial tensions of toluene solutions of oils on the border with distilled water upon the concentration of oil in toluene at 20±1^{0}C: 1, for oil from soil of Buzovna district; 2, for oil from soil of Balakhany district.

Rise in the surface tension was traced until the concentration of analyzed solutions of oils equal to 50.0 mass% with the value along the abscissa axis ℓgC being 1.699.

Study of σ_{ow} oils for their solutions with oils concentration higher than 50% stemmed from difficulties in passing these solutions through capillary of the stalagmometer due to the increased viscosity of the system. Therefore, the surface tension of oils at their concentration of 100% free from toluene, the so-called clean oils, was determined by extrapolation (Fig.1) of results σ_{ow} in line with the concentration of their solutions in toluene equal to 50 % of 100 % concentration. It turned out that the surface tensions on the border with distilled water for "clean" "residual oils" taken from soils in Buzovna and Balakhany region at 20±1^{0}C, are equal to 25.0 and 17.5 erg/cm^2, correspondingly.

Thus, results of experiments (Fig.1) allowed tracing changes in the surface activity of the reviewed oils to confirm both rise and fall of its values depending on dilution degree of oil with organic solvent. A value of the interfacial tensions on the border of oil-water depends on the amount of surfactants in oils [8-10]. According to the data in the Table 1,

the reviewed "residual oils" differ with surfactants' content which is resins, asphaltenes and organic acids. The"residual oil" isolated from oil-contaminated soils in Buzovna region contain 1.7 times more resins and 1.5 times less asphaltenes than the "residual oil" taken from the soil in Balakhany district. The latter contains 1.7 times more organic acids. These essential differences in the content of the surfactants in the composition of the reviewed oils allow concluding the effect of the surfactants of these oils on their surface activity and identifying laws of changes $\sigma_{нв}$ shown in Fig. 1. Comparative high surface activity of "residual oils" taken from soils in Balakhany region can be explained by a comparative content of organic acids in their composition. Obviously, high content of organic acids in these oils is a more significant factor affecting its surface activity than higher content of resins in oils taken from soils in Buzovna region. The revealed pattern of a decrease in interfacial surface tension at the interface with distilled water for both oils with an increase in their concentration in toluene solution when studying the curve of Fig. 1, starting from pure toluene, can be explained by a change in their surface activity.

Indeed, at high concentration of "residual oils" in the toluene solution the concentration of surfactants in the composition of these oils increases both in volumes of the toluene solution and on the interphase boundary of oil and water which causes the reduction of the interfacial tensions.

Trend of decreasing surface tension is kept with the growth of concentration of oils till certain value of their concentration and the rise of surface tension is observed. Evidently it is due to the decrease of concentration of surfactants in the composition of these oils both in toluene solution and on interphase boundary due to association of their functional groups with participation of hydrogen bond in intramolecular interaction.

Based on the results it should be noted that by diluting oil with organic solvent covering the surface of mineral particles of oil-contaminated soil we might increase its surface activity due to the formation of optimum concentration of surfactants in its composition. In particular, free compounds that are associated with intramolecular impact both in its volume and interphase boundary oil- aqueous cleaning solution. Active components of oil-contaminants of mineral particles of soil (resins, asphaltenes, acids etc.) are located on their surfaces in the form of solid films of a boundary layer. Efficiency of washing out mineral particles depends on breakthrough of such film by flow of aqueous cleaning solution. For effective use of the results of experiments through the developed technology of washing out of oil-contaminated soil, we considered mechanical destruction of oil film while grounding mineral particles of soil on their further contacts with aqueous cleaning solution-based organic solvents.

Also, the interfacial tensions on the boundary oil-water depends on the content of surfactants in the composition of oil, and the lesser its content, the higher is the concentration of adsorbed surfactants on the boundary of two immiscible phases. Concentration of surfactants in the boundary layer depends not only on their content in oil but on their content in water as well. Accordingly, we studied the interfacial tensions of toluene solutions of "residual oils" with a mass share of oil 25% taken from contaminated soils of Buzovna and Balakhay regions on the boundary with aqueous solution OP-10. Earlier we have established (Fig.10) that the interfacial tensions on the boundary with distilled water of toluene solutions of "residual oils" with mass share of oil 25% from Buzovna region is 20.05 erg/cm^2 whereas, from Balakhany region is about10.3 erg/cm^2. Addition of 0.10 mass % surfactants OP-10 into aqueous phase causes a major reduction of surface tension of toluene solutions of oil on the boundary with aqueous solution OP-10. Thus, the interfacial tensions on the boundary oil-water solution OP-10 for oil taken from oil-contaminated soils in Buzovna region dropped from 20.05 erg/cm^2 to 6.4 erg/cm^2, i.e. 3.1 times; however, a figure for oil taken from oil-contaminated soils in Balakhany region dropped from 10.3 erg/cm^2 to 5.3 erg/cm^2, i.e.1.9 times.

Concentration of surfactants in the

boundary layer depends on water's ability to leach organic acids in oil, as well as on the content of surfactants in their volume and on the interface phase boundary. Saponification of these acids with aqueous solution of sodium hydroxide should cause the formation of well-soluble sodium soap of organic acids – known as highly active surfactants. Accordingly, we studied the interfacial tensions of toluene solutions of "residual oils" with a 25% mass share of oil on the boundary with aqueous solution of sodium hydroxide. Study into the interfacial tensions of toluene solutions of reviewed oils from concentration of sodium hydroxide in aqueous solutions forming alkaline medium and considerably affecting the reduction of the interfacial tensions. Thus, the interfacial tensions on the boundary of oil and water for diluted organic solvent of oil taken from oil-contaminated soil of Buzovna region in concentration of sodium hydroxide of 0.06 mass% in aqueous solution decreased from 20.05 erg/cm^2 to 1.60 erg/cm^2. Nevertheless, for diluted organic solvent of oil taken from oil-contaminated soil of Balakhany region the interfacial tensions decreased from 10.30 erg/cm^2 to 0.80 erg/cm^2. The results of experiments on the impact of alkaline water on the reduction of interfacial tension for the system diluted with organic solvent "residual oil"– alkaline water can be explained with enrichment of aqueous phase of this system with surfactant, sodium soaps formed during saponification of organic acids in the composition of oil, sodium hydroxide.

Wash out of oil film from the surface of mineral particles is the result of joint action of molecular-surface phenomena and mechanical efforts of water washing flow. According to the results of researches washing out mechanism of the surface of mineral soil particles with aqueous cleaning solution using organic solvent can be expressed by the following way. Purification of the surface of mineral particles from "residual oil" provides removal of film of boundary layer of active components of oil (resins, asphaltenes, acids, etc.) and oil coating layer on it, mainly non-polar compounds (high molecular hydrocarbons). Oil-contaminant focuses on the surface of particles in hard-to-reach hydrophobized areas of pores and capillaries of aggregated structure of soil. Displacement of «residual oil» from small pores becomes impossible due to their unavailability for displacing water. Destruction degree of the system of pores and capillaries in aggregated structure of oil-contaminated soil can be considered as criteria effectiveness of impact on disperse system in washing out of oil.

Thus, in the preparation process of oil-contaminated soil to purification aqueous cleaning solution and organic solvent are provided with favorable conditions for working and maximum access to oil-contaminant.

Furthermore, along with the increase of dispersion of mineral particles of oil, even redistribution of different phases and components in microvolumes of disperse system and achievement of its maximum homogeneity is ensured. On exposure of flow of aqueous surfactant solution and organic solvent of oil layer on the surface of minerals are liquefied by the reduction of viscosity Organic solvent and aqueous surfactant solution decrease the interfacial tensions and the penetration of water solution into oil on the surface of minerals. As a result, oil layer is dispersed and emulsified with entrainment of its droplets by washing flow. The results of researches formed the basis for the development of purification technology for oil-contaminated soil of Absheron peninsula.

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NEFTLƏÇİRKLƏNMİŞ TORPAQQRUNTLARIN TƏMİZLƏNMƏSİ PROSESİNİN TƏDQİQİ

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İşdə neftləçirklənmiş torpaqların təmizlənməsi prosesi tədqiq edilmişdir. Neftçirkləndiricinin mineral hissəciklərin səthindən yuyulması molekulyar-səth hadisələrinin (selektiv islatma, səth enerjisi gradienti) kompleks birgə fəaliyyətinin və su təmizləyici axının mexaniki səylərinin nəticəsidir. İşdə onların təmizlənməsinin effektivliyini artırmaq üçün çirklənmiş torpağın neft çirkləndiricisinə təsir edən molekulyar-səth proseslərinin gücləndirilməsi üsulları nəzərdən keçirilmişdir. Təcrübələrlə göstərilmişdir ki, üzvi həlledici ilə durulaşdırma prosesində neft–su sərhəddində fazalararası səthi gərilmə azalır. Mineral hissəciklərin səthinin yuyulması prosesində istifadə olunan üzvi həlledici neft çirkləndiricisini durulaşdırır, onun özlülüyünü dəfələrlə azaldır və həcmdə neftçirkləndiricinin özünün səthi-aktiv maddələrinin optimal qatılığını yaradır. Bu qanunauyğunluq durulaşdırılmış neftçirkləndiricinin tərkibində SAM-ların optimal qatılığının yaranması ilə əlaqədardır. Müəyyən edilmişdir ki, su yuyucu məhlulunun tərkibində üzvi həlledici və qeyri-ionogen SAM, eləcədə onun qələvi mühiti fazalararası səthi gərilməni azaldır, bu da neftlə çirklənmiş torpağın çirklənməsinə təsir edən molekulyar–səth proseslərinin güclənməsinə gətirib çıxarır və onun təmizlənməsinin səmərəliliyini artırır.
Açar sözlər: *neftləçirklənmiş torpaqlar, molekulyar–səth hadisələri, həlledici, səthi gərilmə*

ИССЛЕДОВАНИЕ ПРОЦЕССА ОЧИСТКИ НЕФТЕЗАГРЯЗНЕННЫХ ПОЧВОГРУНТОВ

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В работе исследован процесс очистки нефтезагрязненных почвогрунтов. Показаны методы интенсификации молекулярно-поверхностных явлений при воздействии на нефтезагрязненую

почву. Отмыв пленки нефтезагрязнителя с поверхности минеральных частиц является результатом сложного совместного действия молекулярно-поверхностных явлений (избирательного смачивания, градиента поверхностной энергии) и механических усилий водного моющего потока. Экспериментами показано, что в процессе разбавления органическим растворителем снижается межфазное поверхностное натяжение на границе нефть – вода. Используемый в процессе отмыва поверхности минеральных частиц органический растворитель разжижает нефтезагрязнитель, снижая многократно его вязкость, и образует оптимальную концентрацию поверхностно-активных веществ самого нефтезагрязнителя в его объёме. Такая закономерность коррелируется с образованием оптимальной концентрации ПАВ в составе разбавленного нефтезагрязнителя. Было установлено, что органический растворитель и неионогенный ПАВ в составе водного моющего раствора, а также его щелочная среда снижают межфазное поверхностное натяжение, что приводит к усилению молекулярно–поверхностных процесссов воздействия на нефтезагрязнитель нефтезагрязненный почвы и повышают эффективность её очистки.

Ключевые слова: *нефтезагрязненные почвогрунты, молекулярно-поверхностные явления, растворитель, поверхностное натяжение.*