

FEATURES OF THE INFLUENCE OF MECHANICAL AND CHEMICAL IMPACT ON THE TREATMENT PROCESS OF OIL CONTAMINATED SOILS

Gahraman Hasanov, Soltan Aliyev, Ruslan Hasanov, Vaqif Valiyev,
Ismail Aliyev

•

Azerbaijan State Oil and Industry University

gaman51@mail.ru

soltan15041953@gmail.com

gasanov935@gmail.com

vaqifveliyev1953@gmail.com

ismaileliyev51@gmail.com

Abstract

The paper examines the issues of replacing residual oil from fine pores of oil contaminated soil under gradientless pressure conditions. It was shown that the replacement of residual oil from fine pores of oil contaminated soil can be possible because of their unavailability for displacing water. Therefore, in addition to others, destruction degree of the system of pores and capillaries in aggregated structure of oil contaminated soil is considered as an efficiency criterion of an impact on disperse system in oil flushing process, and optimum destruction – as an optimum degree of these impacts. The aim is solved by using the complex methods of joint chemical, physical-chemical and mechanical impact on structured disperse systems of mineral particles of soil. It was shown that in the same chemical-mineralogical composition of oil contaminated soil the efficiency of its treatment increases with the growth of dispersity of its mineral particles. Increasing methods of their dispersity are related to the impact on various forces connecting mineral particles in a single system of structural formations, such as coagulative, condensation-crystalline, and mixed - coagulative -crystalline macro- and microaggregates. To ensure the possibility of realizing mass exchanging processes under the influence on washing water solution on oil surface it is important to destruct the structure, disperse all aggregates from particles by separating them (breaking of contact) and releasing unevenly distributed immobilized liquid phase (oil and water). Under intense mechanical impacts the bond strength between particles is destroyed using adsorption decrease of structure strength in surface-active medium. In this case, aggregates are destroyed into initial particles and structural bonds are broken. Dispersion (peptization) or spraying of microaggregates can be caused by changing the composition of the dispersion medium, using a chemical method of impact. An example of a chemical method of influencing oil contaminated soil is the displacement of Ca^{2+} u Mg^{2+} ions from the exchange complex of clay minerals and their replacement with Na^+ ions, which leads to the spraying of water-resistant and true aggregates cemented with calcium and magnesium. Increasing the pH of soil suspension medium to 8.0-8.5 and recharging of electropositive hydrates of Al and Fe oxides leads to the destruction of isoelectric aggregates formed by them with electronegative particles such as silica and clay minerals. In the treatment of oil contaminated soil by washing the surface of mineral particles with washing water solution to prevent oil resorption and coalescence of its droplets, hydrophilization of soil particles is a determining process.

Keywords: oil contaminated soil, mineral particles, aggregation, dispersion, treatment, mechanical and chemical impacts, residual oil.

I. Introduction

Oil contaminated soils consist of mineral particles combined into aggregates with intermediate pores and capillaries partially or completely filled with water and oil. The washing of oil contaminant film from the surface of mineral particles is a result of a complex joint action of molecular surface phenomena (selective wetting, surface energy gradient) and mechanical forces of water washing stream. A washing process is a complex of complicated phenomena with a great variety in the composition and nature of pollution, in the different nature of washed surfaces and a variety of changes in the physicochemical properties of washing agents. General ideas about the role of wetting and adhesion in the washing action are developed and physical and chemical analysis of forces arising at three-phase interface in washing agent-washed surface-oily contamination system is given in the works [1-5].

The quantitative bond of the process energy - necessary mechanical work of treatment - with the main physical and chemical properties of washing agents and washed surfaces is shown. The known results of numerous studies, the conclusions and technical substantiations are related to the study of washing processes of oily contaminants from fabric and polished metal surfaces, washing of bituminous sands, or the processes of oil displacement from oil-saturated sands at deep oil production under conditions of high pressures and temperatures.

A feature of oil-contaminated soils of ecologically unfavorable territories of the oil and gas production division of Apsheron Peninsula is that their components: residual oil, mineral, organomineral and organic particles are in long-term contact of natural occurrence for many decades under climatic conditions of Apsheron. A new substance "oil-contaminated soil of long duration" with features of composition, structure and properties is formed. Utilization of oil-contaminated soils, based on their washing with washing water solution of surfactants using an organic solvent, is a complex of complicated phenomena with a wide variety of composition and nature of contaminants, with a wide variety of nature of washed surfaces and the variety of washing agents.

The methods are based on understanding and knowledge of the nature of oil-contaminated soil and the properties of residual oil, which is part of it and is located on particle surfaces of minerals constituting the soil in the form of a film of a boundary layer with a strong molecular bond and oil coating layer on top of it [6]. Therefore, the restoration of soil ecology destroyed by oil pollution, the development of a treatment technology of oil-contaminated soil require special approaches, considering the characteristics of their composition and properties, and considering the understanding of their formation conditions, the migration of oil-contaminated soil in the soil body, the location of oil-contaminated soil and its location in soil structure.

Displacement of oil with water from the surface of oily soil particles is a complex process, which depends on many factors: on the surface properties and chemical composition of oil and its wash out water; on the granulometric composition of mineral solid phase of soil, especially on the amount of clay fraction in it; on the structure of pore space and a number of other factors. In addition, it is important to break down the aggregated soil structure by available technological methods in order to provide the aqueous detergent solution with maximum access to the oil contaminant of mineral particles. Along with the listed factors, to provide the mineral particles maximum access to oil pollutant, the destruction of the aggregated structure of soil by available technological methods is important. The article presents the results of studies that have formed a rational direction for treatment oil-contaminated soils and determined the necessary methods for influencing them using the technology for their utilization.

II. Methods

For experiments, oil-contaminated soil with a mass fraction of oil of 10% was used as a study object, obtained by applying an oil sample from its benzene solution to clean, dry soil, followed by evaporation of benzene. Granulometric composition of clean soil was determined, according to GOST 12536-79, the chemical composition using an X-ray spectrometer S8 TIGER (Germany, BRUKER), and the mineralogical composition using X-ray diffractometer «MiniFlex 600» (Rigaku Corporation, Japan). Table 1 shows the results of analyses and some physical and chemical properties of pure soil. From the data in Table 1 it can be seen that the pure soil used to obtain the research object is a silty loam containing mainly quartz of various dispersions and up to 15% clay minerals smaller than 0.001 mm.

Pure soil is a polydisperse polymineral mass with a certain water content, and if it is oil-contaminated, then with a certain content of oil and oil products. To maintain the average constancy of the granulometric composition of soil samples in different experiments, they were selected for analysis according to the standard method to obtain a sample with an average particle size distribution. The physical and chemical parameters of oil, which is part of oil-contaminated soil, are presented in Table 2.

Table 1: *Physical and mechanical properties, mineralogical and granulometric composition of pure soil.*

Granulometric composition, mm		Mineralogical composition	
Fraction composition, %			
	1.0 – 0.25	6.43	Quartz
	0.25 – 0.05	57.73	-----
	0.05 – 0.01	11.68	-----
	0.01 – 0.005	5.16	-----
	0.005 – 0.001	4.44	-----
	≤0.001	14.56	montmorillonite
	<0.01	24.16	
Liquid limit, %		33.0	
Amount of carbonates, %		11.25	
Specific surface, m ² /g		3.88	
Specific weight, g/sm ³		2.66	
Volume weight, g/sm ³		1.35	
Porosity, %		49.0	
Full water extract, salt amount, %		0.053	
pH of water extract, unit.		7.9	

The results of analysis of the residual oil that is part of oil-contaminated soil, shows that the oil does not contain light fractions, is weathered, contains resins, asphaltenes, organic acids and hydrocarbons, which boil at a wide temperature range.

III. Results and Discussion

In nature, there are no clean crystal surfaces or soil particles. Finely dispersed particles of clay minerals and larger sandy ones are covered with films of various colloids firmly bound to them: iron hydrates, silicic acid, organic and organomineral substances. Soil formation processes continuously occurring in nature, leading to the destruction of rocks under certain conditions, cause the reverse process of aggregation and cementation of fragments or particles into relatively stable micro- and macroaggregates, characterized by granulometric (aggregate) composition, degree of fragmentation, percentage of particles with different sizes.

Table 2: Physical and chemical indicators of residual oil released from oil-contaminated soils of Absheron Peninsula in Balakhani region.

Name	Value	Test method
Fraction composition, °C/% vol.	100 -260/4,0	GOST 2177
	>260- destruction	
	32-110/13	
	110-155/17	ASTMD 1160
	155-220/9,5	
>225- destruction		
Content, % mass:		
asphaltene	6,2	IP143
resin	8,71	GOST 11826
paraffin C ₁₉ – C ₃₅	1,16	GOST 11821
Acidity, mgKOH/g	0,168	ASTMD 664
Viscosity at 50°C, kinematic, cSt	76,0	ASTMD 445
Density at 20°C, kg/m ³	955	GOST 3900

The Apsheron Peninsula is characterized by the presence of cohesive clay soils - clay, loam, sandy loam. Much less often in large areas lie incoherent - sands. In this regard, it was shown in [6] that the formation of oil-contaminated soils is caused by the impregnation of crude oil with the main components of the soil body, which are in secular equilibrium—aggregates consisting of cemented natural elementary particles with water on their surface, in their pores and capillaries. Oil coating is layered on the “fur coat” of films consisting of colloids and water on the surface of mineral grains or aggregates cemented from them, Fig. 1 i.e., in the gap between oil layer coating and the surface of the natural elementary particle, there is a water film in the gap between them.

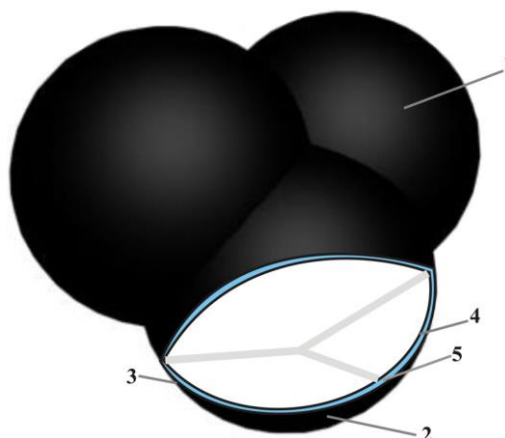


Figure 1: Scheme of an oil-contaminated aggregate, consisting of cemented natural-elementary particles of chipped soil: 1 - oil-contaminated aggregate; 2 - grain of an oil-contaminated natural elementary chipped particle; 3- oil on the surface of aggregate; 4 - the surface of a natural elementary particle, covered with a colloidal particle film; 5 - gap in the interval between the particle surface and oil shell filled with water film.

In addition, it was found that in order to effectively clean the surface of aggregated oil contaminated soil particles, it is necessary to provide water-washing solution an access to them. It is necessary to disperse, spray oil contaminated aggregates of dust-clay particles and destroy aggregates consisting of grains of oil polluted natural elementary sand particles.

The oil coating layer of residual oil from the surface of dust and clay particles and grains of

natural elementary sand particles is washed out using an organic solvent and an water surfactant solution with destruction of oil polluted aggregates.

To treat the grains of natural-elementary sand particles from boundary layer film of residual oil, it is enough to chip or crush them into two small parts, which occurs due to the established laws of washing oil-contaminated glass and quartz plates. Indeed, it is necessary to disperse the cemented oil-contaminated granules consisting of grains of natural-elementary sand particles and split them, then by wedging action of water-washing stream, with its power vector directed into the intermediate gap between particle surface and the film of residual oil boundary layer, the latter will be torn and is removed from the surface in the form of oil droplets by water-washing stream. The described mechanism of washing the oil-contaminated surface of a soil particle is schematically shown in Fig.2.

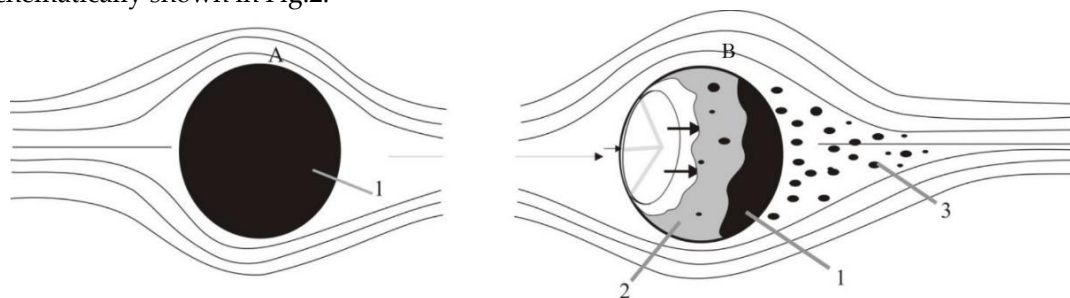


Figure 2: Scheme of oil-contaminated soil natural-elemental particle and with chip in water-washing solution stream (water + surfactant + organic solvent). A – oil-contaminated particle; B - oil-contaminated chipped particle; 1 - layer of oil coating on particle surface; 2 - film of a boundary layer of residual oil; 3 - oil drops from particle surface chipped during crushing.

Soils, especially cohesive soils, are polymineral and polydisperse bodies. Its separate particles have a very high strength. Sand particles consisting mainly of quartz are characterized by compression strength $\sim 1500\text{-}2000 \text{ kg/cm}^2$ [7].

Adsorption of surfactants from environment can significantly reduce the flexibility limit, strength and hardness, facilitate the destruction of fine bodies and increase the flexibility of metals [8]. Water is the most active with respect to quartz surfactant [8]. The existence of three different experimentally established effects of the influence of the environment is stated. Depending on the specific conditions of the experience, the effect of the medium acts either in plasticization, or in increasing brittleness, or gives solids the ability to spontaneously disperse.

The addition of surface-active medium or adsorbent additives can cause spontaneous dispersion of aggregates without external mechanical influences. Such spontaneous dispersion or peptization (with internal stresses in aggregates) leads to a significant increase in the volume of the number of free particles. Fine dispersion is generally impossible without surface-active medium and adsorptive additives [9]. It was found that grinding a quartz powder with water with an optimal content of 30-50% increases specific surface area compared to the specific surface area of powders of the same length in dry air grinding.

Difference in dispersion of powders of dry and wet grinding increases with the growth of dispersion duration (the average optimal value of wet dispersion duration of quartz is 4-8 minutes). Quartz powder crushed with paraffin becomes hydrophobic, but actively disaggregates when it is crushed with water [10]. Water in disaggregation process creates obstacles for close approach of particles and, due to this, reduces the area and number of contacts between them. The specificity of the dispersing action of water is based on its ability to form hydrate shells on particle surfaces, as well as the high wetting energy of many solid (hydrophilic) bodies by it and, the wedging effect. When quartz crystals are destroyed by a split, siloxane groups Si-O-Si , SiO^- and Si^+ ions are exposed on the surface.

During grinding in water, hydrogen ions or hydroxide ions attach to SiO^- and Si^+ ions,

forming silanol groups SiOH, [11] fig. 3. Quartz surface is represented by groups interacting with water in different ways: siloxane, silanol, and dissociated silanol. Silanol groups are partially dissociated upon contact with water. Unsaturated bonds of SiO⁻ groups actively interact with water molecules and mainly determine the wettability of quartz surface with water. All various types of amorphous and crystalline silicas, due to their origin from water solutions (silica gels), when milled in water (crystalline silicas), carry on their surface the so-called "structural water". Based on chemical and adsorption data in [12] this structural water represents silicic acid hydroxyl groups chemically bonded to surface silicon atoms. Structural water is released when silica is heated at 500-700°C.

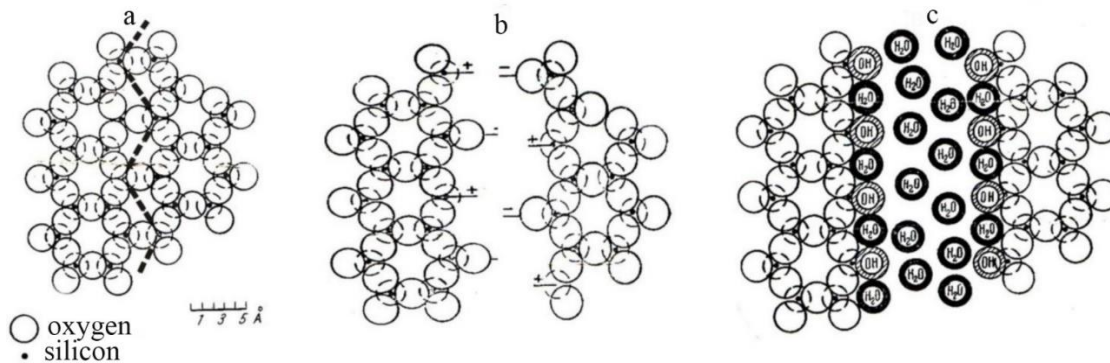
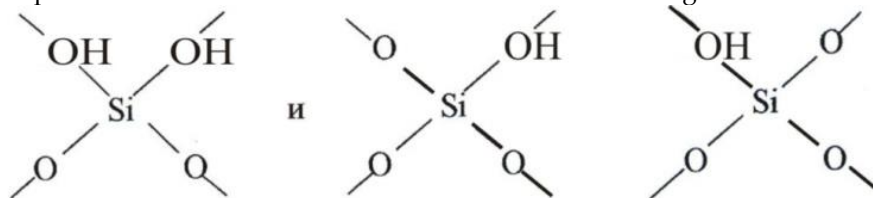


Figure 3: Scheme of exposure of bonds during splitting of quartz crystals: a - scheme of splitting; b - scheme of a split on air; c - diagram of a split in water.

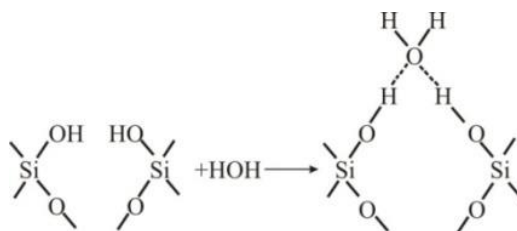
Hydrated silica surface contains mainly silanol groups of two types: [13]. Hydroxyls of these groups, located at suitable distances, partially interact with each other. All this creates a chemical and geometric nonhomogeneity of the surface. As a result, on silica surface there are both "free" hydroxyl groups which are remote from each other and not interacting with each other, as well as



closely spaced and favorably oriented to form a mutual hydrogen bond hydroxyl groups. A hydroxyl cover also exists on the surface of other oxides, such as Al₂O₃ [14] and TiO₂ [15].

Direct and most reliable information on the mechanism of physical adsorption on hydroxylated surfaces was obtained by spectral studies of the interaction of hydroxyl groups on the silica surface with adsorbed molecules. A typical occurrence of adsorption interaction due to the formation of a hydrogen bond with surface hydroxyl groups is observed during the adsorption of water.

The adsorption of water molecules on two adjacent, closely located, and favorably oriented hydroxyl groups of the surface is most energetically favorable [16]. Research results allow us to consider that the hydroxyl groups of fully hydrated silica are the main centers of reversible physical adsorption. Water adsorption is associated with the formation of hydrogen bonds between the hydroxyl groups of the surface and the oxygen of adsorbed water molecules. The predominant interaction of adsorbed water molecules with a hydrated surface is close to that expressed in the scheme [17, 18]:



Protection of the surface of a split quartz particle from resorption of washed oil drops on it and suppression of particle flotation (sticking to air bubbles) can be ensured by introducing colloidal SiO₂ in the form of liquid glass into the composition of the water-washing stream. Facilitating the hydrophilization of a split particle surface, colloidal SiO₂ will give it protective properties from hydrophobic interaction with releasing oil drops.

Processes of dispersion and spraying of aggregates formed by silty-clay particles are traditionally used in soil science for the preparation of soils for granulometric dispersion analysis. When developing the technology for treatment oil-contaminated soil, this experience in the rational use of methods for its dispersion was taken into account. To treat effectively the surface of dusty-clay particles from an oil pollutant, it is necessary to provide a water-washing solution an access to it, by weakening coagulation bonds, dispersing aggregates and releasing particles from an aggregation state.

By controlling hydrophobic coagulation adhesion between particles, peptization and changes in the interaction of water (dispersion medium) with cohesive soil with the addition of electrolytes, surfactants, organic solvent, it is possible to regulate the adhesion properties of dusty clay particles in suspensions by facilitating dispersion process by mechanical interactions into coagulates, particle aggregates.

When the soil is stirred with water, false aggregates formed by the coagulation of particles with Na⁺ cation are destroyed. More energetic effect is required for aggregates formed by coagulation of particles with 2^x valent cations. The destruction of such aggregates can be achieved by grinding a highly concentrated water suspension of a soil sample. Thus, with a more energetic mechanical action, in addition to the destruction of false aggregates, water-resistant and true aggregates are sprayed. High dispersing effect is achieved by grinding a thick mass (clay, loam) with liquid glass as a dispersing agent [19].

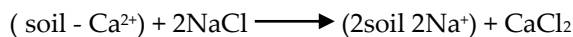
The efficiency of soil dispersion depends on the stabilization of the suspension of sprayed particles. An increase in the stability of colloidal systems is due to the electric charge of their dispersed phase: colloidal particles, carrying the same charge, repel each other when they meet. Thus, the electric charge is a factor stabilizing the colloiddally dispersed state of a substance. Most of the colloids in the soil are negatively charged, so the presence of salt anions is a stabilizing factor for them. Salt cations will reduce or destroy the negative charge of colloidal particles, promoting their coagulation. In this case, cations are a destabilizing factor.

The stabilizing effect of cations depends on their valency and atomic weight. The higher the valency and atomic weight of the cation, the greater its precipitating ability. An exception is H⁺, coagulating capacity of which is greater than all other monovalent cations and even surpasses divalent cations in this respect. the calcium ion has the highest coagulating ability among the cations found in natural water in soils. Therefore, in non-saline soils, the main role of the coagulator of colloiddally dispersed particles belongs to this cation.

In acidic soils, the hydrogen ion is of great importance. In salina Na⁺, Ca²⁺ and Mg²⁺ can be the main coagulators, depending on their predominance in salina. The hydroxyl ion (OH⁻) increases the stability of negatively charged atomized colloidal particles and greatly reduces the coagulating ability of electrolytes. Soils containing oxide hydrates of monovalent cations contain colloids in a dispersed state, while divalent cations (especially Ca(OH)₂) have colloids in a coagulated state.

In granulometric analysis, the physical chemical method of soil preparation is widely used, in

which Na^+ and OH^- ions, transforming into an absorbed state, disperse natural soil aggregates according to the reaction:



NaCl is introduced into the soil based on the cation exchange capacity value of soil. At the same time, Na^+ , passing into the absorbing complex, disperses the soil.

To prepare a soil suspension, low-mineralized waters (dry residue less than 100mg/l) are most favorable, in which the content of monovalent cations is higher than multivalent ones.

An important role in dispersion processes of clay soils can be played by their absorption capacity, based on the formation of low-soluble compounds, as a result of which both anions and cations are absorbed in equivalent amounts. Ca^{2+} , Mg^{2+} , Fe^{3+} and Al^{3+} are most often found in soils from cations that give insoluble compounds. The first two ones (Ca^{2+} and Mg^{2+}) play the most important role. Low-soluble compounds with listed cations can give CO_3^{2-} , PO_4^{3-} and SO_4^{2-} . As a result of the exchange, cations that are in the adsorbed state and capable of forming low-soluble salts with anions of the solution release into the solution.

The action of Na_2CO_3 solution on a carbonate soil and be an example. In this case, the Na^+ cation will enter the absorbing soil complex and displace an equivalent amount of Ca^{2+} and Mg^{2+} from there. These two cations give with the anion CO_3^{2-} low-soluble carbonates CaCO_3 and MgCO_3 which precipitate in solid state.

IV. Conclusion

Thus, chemical methods of soil preparation, when combined with methods of mechanical action, it is possible to spray true aggregates with a large yield of fine particles. With dispersion method of analysis all aggregates are destroyed due to:

- displacement of Ca^{2+} and Mg^{2+} cations from the exchange complex and their replacement with Na^+ cations,
- increase of pH of the suspension above 8.0-8.5 and, as a result, recharging the electropositive hydroxides Al and Fe by destruction of aggregates formed by them with electronegative colloids - silica, humus and clay minerals.

On the basis of the data, the techniques and methods of mechanical, chemical and physico-chemical effects are substantiated, which are the essence of the developed technology for treating oil-contaminated soils, based on the washing off with a water washing solution of an oil pollutant concentrated in hard-to-reach, hydrophobized areas of pores and capillaries of the aggregated structure of soils. The set of techniques and methods of influence used is determined by the necessity of providing the washing agent with favorable conditions for treating the surfaces of soil mineral particles, as well as its maximum access to the oil pollutant, while ensuring high efficiency of mass transfer in dispersed systems.

References

- [1] Rebinder P. A. Physics-chemistry of washing agent. M.: Publishing House «Food Industry», 1935. p.210
- [2] Adam N. K. (1937) Detergent Action and its Relation to Wetting and Emulsification. *Society of Dyers Colourists*. 53, pp.121-129
- [3] Kling W, Longe. (1955) *Kolloid Z. Energetik des Waschvorganges bei oligen Anschmutzungen*. 1, p.142
- [4] Koretskiy A.F., Kolosanova V.A., Smirnova A.V., Koretskaya T. A. (1972). To the theory of washing action. I. Role of energy in treatment processes of surfaces from oily pollutants. *Bulletin of the Russian Academy of Sciences. Chemistry*, issue 1, № 2, p. 32

- [5] Koretskiy A.F. (1974). To the energy of washing action. *Bulletin of the Russian Academy of Sciences. Chemistry*, issue 6, № 14, p. 28
- [6] Hasanov K.S., Abdullayev F.Z., Latifov F.I. (2006). *Processes of petrochemistry and oil processing*. № 2 (25). p. 62.
- [7] Bezruk V.M. Strengthening of soils. M.: Transport. 1965, 340 p.
- [8] Shukin E.D., Rebinder P.A. (1958). Formation of new surfaces during deformation and destruction of solid states in surface active medium. *Colloid. journal*. 1958, vol. 20, № 5, p. 645-654
- [9] Khodakov G.S., Rebinder P.A. (1960). On the impact of medium on amorphization of quartz in its mechanical dispersion. *Proceedings of the USSR Academy of Sciences*, 131, p. 1316-1318
- [10] Khodakov G.S. Fine crushing of construction materials. M.: Stroyizdat, 1972, p. 38
- [11] Streltsin G.S. (1968). Surface properties of a quartz. *Colloid. journal*. vol. 30, № 4, p. 592-595
- [12] Kiselyov A.V., Ligin V.I. (1962). The use of IR – spectroscopy for the study of compound surfaces and adsorption. *The Russian Chemical Reviews*. vol. 31, issue. 3, p. 351-363
- [13] Kiselyov A.V. (1961). Energy of interaction adsorbate-adsorbent and adsorbate-adsorbate in monolayers on surfaces of solids. *Russian Journal of Physical Chemistry*, vol. 35, p. 233-257
- [14] Peri J., Hannan R. (1960). Surface hydroxyl groups on γ -alumina. *J. Phys. Chem.*, v. 64, pp. 1526-1530
- [15] Yates D. (1961). Infrared studies of the surface hydroxyl groups on titanium dioxide, and of the chemisorption of carbon monoxide and carbon dioxide. *J. Phys. Chem.*, v. 65 (5), pp. 746-753
- [16] Kiselyov A.V., Ligin V.I. (1959). IR-spectra of adsorption and hydroxyl coating in different degrees of hydration. *Colloid journal*, vol. 21, № 5, p. 581-589
- [17] Jigit O.M., Kiselyov A.V., Mutik G.G. (1961). Heat of adsorption of water steam on silica gel with hydrated and dehydrated surfaces. *Colloid journal*. 23, p. 553-557
- [18] Starshov M.I., Starshov I.M. Certificate of authorship of Method of extracting bitum. 1989
- [19] Hasanov G.S., Abdullayev F.Z. (2009). Selection of processing scheme of oil slums and oil-contaminated soils, pilot testing, technology of their utilization and neutralization. *Journal of Chemical Problems*, № 2, p. 213-227