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Complex Oil-containing Waste Treatment by Applying Solar Energy

Maral ABDIBATTAYEVA[1]*, Kylyshbay BISSENOV[2], Zheniskul ZHUBANDYKOVA[3], Raigul ORYNBASSAR[4], Lyazzat TASTANOVA[5]

[1, 4]*Al-Farabi Kazakh National University, 71 al-Farabi Avenue, 050040, Almaty, Republic of Kazakhstan*

[2]*Korkyt Ata Kyzylorda State University, 29A Aiteke Bi Street, 120014, Kyzylorda, Republic of Kazakhstan*

[3, 5]*K. Zhubanov Aktobe Regional State University, 34 A. Moldagulova Avenue, 030000, Aktobe, Republic of Kazakhstan*

***Abstract* – The article describes in detail the complex oil-containing waste treatment by applying solar energy. The developed Helio devices are equipped with concentrating elements to extract oil in the purification of dump oil. The questions of practical application of pre-treated oil-contaminated soils and oil sludge to strengthen road surfaces are considered. The results of the experimental study on the production of soil concrete is based on oily dump. The structures of the soil concrete made on the basis of oil-contaminated soils and oil sludge are investigated and relevant proposals are made.**

***Keywords* – Cleaning of waste oil; disposal of oily waste; concentrating elements; oil extraction; structure of soil-concrete**

1. INTRODUCTION

The ever-increasing volume of oil-containing waste generation as a result of production activities in the extraction, transportation and processing of oil strongly dictates the need to search for new and optimization of existing technologies for the effective utilization of this type of waste, which is currently one of the most urgent environmental problems in the world [1].

Oil industry is characterized by the scale of the formation of oil waste, clogging not only the soil but also the air and water basins, which adversely affects the ecology of the territories. In the development of technology for cleaning oil waste solid residues can be obtained that can serve as a unique raw material for the manufacture of road construction materials [2]. The oil industry is one of the major sources of environmental pollution. The production activities of oil refining and oil and gas production enterprises inevitably have a man-made impact on the natural environment, so the issues of environmental protection and rational use of natural resources are important. One of the most dangerous contaminants in almost all environmental components – surface and groundwater, soil-vegetation cover, atmospheric air, are the slimes [3]. A wide range of oil sludge composition requires the development of efficient and cost-effective technologies for their processing [4], [5]. At the initial stage of development of oil sludge disposal destructive methods were the main ones. New methods of waste processing

* Corresponding author.
E-mail address: maral.abdibattayeva@kaznu.kz

should include resource recovery and exclude the loss of valuable components of waste from resource turnover [6], [7].

Every year about 3 million tons of sludge in the world is being produced; over 100 thousand tons is being produced in Kazakhstan. Significant loss of oil from oil sludge and their negative impact on the environment of the region creates the need to develop technologies for processing sludge. Sludge processing methods involves their thermal, chemical or biological treatment, which in turn is characterized by the release of large quantities of toxic gases, the use of expensive chemical reagents or biological strains. The authors of the current study propose a method of cleaning oil contamination of waste with the use of solar energy. To carry the process out, the Helio device equipped with concentrating elements has been developed.

According to the aggregate state of oily waste can be divided into:

- liquid, formed in the process of operation of technological installations, as well as in sludge storage tanks and ponds-settling tanks, for which it is advisable to separate the phases by centrifugation into oil products, water, and a solid residue;
- solid and high viscosity (heavy oil fractions), which include bottom sediments of oil storage tanks and sediments formed during the treatment of oil-contaminated wastewater (excess activated sludge of biological treatment facilities) [8].

Ground oil sludge is formed during the spill of oil products in emergency situations, tank oil sludge, due to the chemical interaction of oil products with the walls of the tank, water and air [9]. Each method of waste disposal and the technology based on it have a certain niche [10], which allows to achieve the greatest profit or minimal costs for the disposal of a certain type of waste with the least environmental damage to nature. Disposal of such hazardous waste as oil sludge is unacceptable, as it leads to serious environmental pollution, which is the case in many regions of oil production [11]–[13].

According to the mineral composition of oil sludge, dumb is similar to the raw mixture components, and according to the fractional composition of the organic part, they are similar to expansion admixture [14].

The removal of municipal solid waste from urban areas is an element of life support, an important environmental problem of creating conditions for sustainable urban development [15]. The rational use of industrial waste allows to solve many economic and environmental problems [16], [17].

The oil industry is potentially dangerous for the environment due to its specific activities. This is due to the toxicity of hydrocarbons and related substances used in technological processes and related to 3–4 hazard classes [18]. In the process of exploitation of deposits, the formation of oil waste, which is a persistent oil-water emulsion, is inevitable. Their properties depend on various factors: gas content and water content of oil wells, mineralization of formation waters, production method, component composition, physical-chemical and colloidal-chemical properties of oil and their natural stabilizers, the presence of particles of mechanical impurities, composition, and temperature [19], [20]. ‘Aging’ of emulsions, compaction and hardening time of booking shells on drops of water, evaporation of light fractions, blending of petroleum products, and increase of mechanical impurities due to the atmospheric dust that occurs [21].

The emulsion in a broad understanding is usually called a dispersed system consisting of two mutually soluble or slightly soluble liquids, one of which is distributed to the other in the form of small drops [22]. There is oil disperse systems, they can be divided into high and coarse [23], [24]. Dispersion can be determined by different methods. The simplest and reliable method is sedimentation, based on the dependence of the particle sedimentation rate on their size [25], [26].

2. MATERIALS AND METHODS

Helio device that allows you to clean 10 kg/h oil-contaminated dump consists of the following parts: 12 series-connected solar panels; a controller; monitoring devices with the software; batteries; capacity for cleaning oil-contaminated waste; inverter; Helio tracker; cylindrical parabolic concentrator; electric heater; actuator arm.

Cleaning of dump by Helio device equipped with concentrating elements is as follows:

– Compiling waste

Every year up to 4300 tons of sludge is being produced at oil production facilities. Purification sludge of tanks and pipelines from oil generated dump from the places of formation is pumped out and removed to the territory of which there is a waste storage facility – a sludge collector.

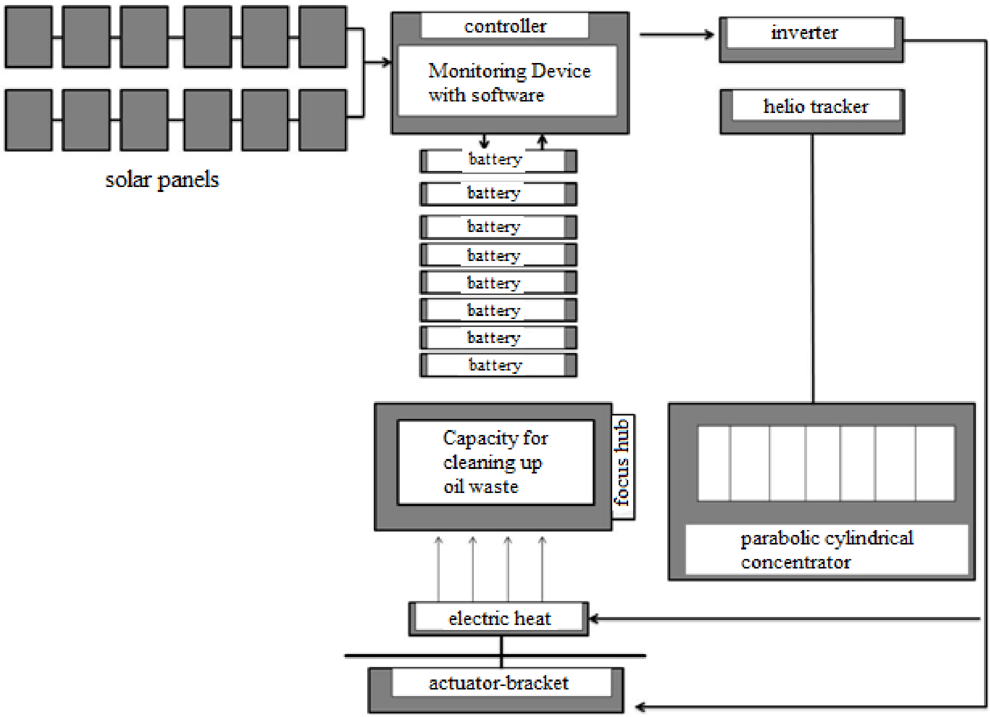


Fig. 1. Helio devices equipped with concentrating elements.

The first phase of the first cycle of cleaning soil from oil starts with pre-treatment of contaminated soil (soil, sand). The preparation of the contaminated material is loading and sorting it from large inclusions (e.g. stones) and their removal. For this purpose, the bolting machine is widely used in the mining industry.

Then, the contaminated material is stirred with water. For this purpose, a milling jet mill MJM-7 is used, that is widely used for the preparation of drilling fluids during drilling for oil and gas. Thus, there is a thinning and grinding lump of contaminated material, grinding of small wood residues and vegetation.

Thus, there is sorting, shredding or removing of large particles, such as stones larger than 100 mm; wood and vegetation removal, grinding and liquefaction lumps of contaminated soil (ground, sand), bitumen inclusions. Then the liquefied mass is subjected to sorting with the removal of stones larger than 5 mm. To do this, a bolting machine with a funnel tray located under it is used.

– Purification of Waste on Helio Device

Waste treatment is carried out on a Helio device equipped with a cylinder fixed inside the radiator solar collector. The radiator is represented in tube form, made of copper and is used for circulating the coolant (a mixture of antifreeze and water), having an inner diameter of 30 mm or more. Helio device is further equipped with a solar panel, that is made of concentrator photovoltaic modules placed on a mechanical system that provides additional warmth missing in the overcast and cold season, as well as parabolic hub, which in turn virtually lossless collects all the sun energy that falls on it in the focal point, where the copper pipe, with the orientation of the sun with the help of the tracking system. Thus, a device for collecting solar heat promotes maximum temperature of coolant at a given time. After heating by means of the heat carrier, the received productive oil merges into the tank for oil collection, through the pipe, which connected to the case of devices.

The work is carried out as follows: In order to create conditions of displacing oil from waste, contaminated soils or oil sludge mixed with water, which is first in the unit volume of 30 dm^3 filled with 20 litres of water, and laid on top of 10 kg of polluted soil or sludge. In the focus of the case on a metal frame mounted cylindrical parabolic concentrator equipped with a tracking system of the sun, which is the maximum focus straight and diffuse solar radiation, collects all the incident solar energy on it. As solar energy concentrator used stainless steel radius of 2.0–2.5 m.

After saturation of the soil with water by means of a mixer, channels are formed, through which in the process of heating due to solar energy, oil fractions with water begin to be released. The resulting productive oil with water through a pipe connected to the body merges into a separation column, where the oil fraction is separated from the aqueous solution. After draining, the water solution is sent again to the device for cleaning the next batch of waste. The time of phase separation string is 10–15 minutes. That is, every 15 minutes it will be ready to return the water to clean the waste. The separation column is made of heat-absorbing material so that the temperature of the liquid in the column is kept within 60–800 °C, which allows an efficient separation of oil products, mainly high-viscosity oil. Water having a temperature of 60–800 °C is sent to the device thereby providing a rapid release of oil from waste. 6–8 parties download oil waste device per day (60–80 kg/day) in the active time of day. After passivation of solar radiation clean up the work is completed.

When the oil-contaminated soil is heated, the temperature in the device reaches 850 °C at an ambient temperature of 28 °C, heating is carried out for 1 hour, and when using additional energy accumulated by the solar panel, the heating time is reduced by 2–2.5 times. Loading and unloading of oil-contaminated and treated soils and oil sludge are carried out by the mechanized method.

The main purpose of the Helio device is to impact natural solar radiation flux density varying with significant involvement in this process is solar energy concentrator provided with a system for tracking the sun, the maximum of the focusing solar rays, where in the heat sink in the form of a copper tube located on the focus of the cylinder is cooled, absorbs and stores the heat. Practical implementation of the optimal combination of concentrator solar energy in the form of cylindrical shape equipped with the tracking system of the sun, which collects all the incident solar energy to it, promotes maximum focus of direct and diffuse solar radiation, even a low density, and additionally used solar panel provides the missing heat in cloudy and cold seasons, thereby improving the heating and shrinking process [27], [28].

2.1. Practical Application of Oil-contaminated Soil and Sludge to Strengthen Pavements

For the manufacture of soil-concrete as oil polluted soil and oil sludge are being used as a raw material, which are a source of environmental pollution on the Atyrau region in Kazakhstan. In the production process in the preparation of oil industrial waste containing oil products is up to 10 %, suspended solids – up to 90 %. The main pollutants in waste oil, waste toxicity class – 4. The annual output amounts to 4,500 tons. Size distribution of the soil is determined according to SST 12536 – 79 by sieving the sample in an amount of one kilogram of a standard set of sieves. To solve the problem of disposing of oil-contaminated soil, we carried out experimental studies on the use of pre-treated contaminated soils and sludge as secondary raw materials as the most rational way of recycling.

On the one hand, it allows to reduce the environmental burden on the environment (reducing or eliminating oil waste disposal sites); on the other – to provide a more rational use of scarce and non-renewable natural resources, replacing the primary to the secondary raw materials, which enables the use of oil-contaminated soils as a secondary raw material in the manufacture of soil concrete [29].

Using a new method of pre-treatment of oil-contaminated soil and sludge using solar energy and saving petroleum products (in the cleaning process oil is further obtained) and astringent, which are used in road construction, reduces the cost of processing of liquid and solid oil waste disposal, to minimize transportation costs and other. The technology of soil-concrete manufacture for road construction observes the following order. First, oil-contaminated soil or slime is pre-treated with the use of solar energy in the device with the elements concentrating solar energy to separate the contaminated soils from heavy fractions of the hydrocarbon. We have created a new technical solution aimed at obtaining high-quality soil-concrete with the use of solar energy and expanding resource base of soil due to the use of oily waste production and reducing the consumption of cement and lime exceptions. The developed soil-concrete includes oily waste, cement and sand, characterized in that the oil-containing waste is used as sludge and oil-contaminated soil containing up to 10 % of oil products and up to 90 % of suspended substances, and as a mineral filler-sand at this ratio of components in the soil concrete, mass. The percentage of oily waste (oil-contaminated soil and oil sludge) is 60 %; sand – 27 %; cement – 13 %.

Oily waste is generated during the extraction, preparation, and transport of commercial oil field and main pipelines, tanks for oil storage and pumping stations. The main difference between the organic component of oily waste, defining the physical properties and chemical reactivity is tar and asphalt; and mineral part of – ion-exchange complexes and $Ca^{2+}$and Mg^{2+}. Stabilization of oily wastes is Portland cement PC 500. Production and testing of soil-concrete were carried out in accordance with the instructions [30]–[32].

To prepare the soil concrete mixture, pre-cleaned oil contaminated soil or oil sludge was first stirred, and then mixed with sand by dosing. Next, it was mixed until a homogeneous mixture, and then binders were added, and stirred again. Next, the concrete additive was introduced, stirred and moistened for moulding with the required degree of homogeneity. The consistence of the investigated soil-concrete composite mixture on the basis of oil-contaminated soil and sludge: structure is 1:4:2. In formulations based on oil-contaminated soil and sludge used concrete admixture based on a sulfonic synthetic polymer that provides super strength, decreases in the largely water content rheoplastic concrete containing no chlorine, which initially accelerates and increases the strength of concrete.

3. Results and Discussion

To conduct an experimental study, we have developed experimental and control samples from two compositions for the production of a soil concrete mixture, using oil-contaminated soil and oil sludge. In order to heat treatment, the test samples were subjected to heat treatment in an apparatus with elements of concentrating solar energy and control samples hardening occurred in vivo.

TABLE 1. CONSISTENCE OF SOIL-CONCRETE ON THE BASIS OF OIL-CONTAMINATED SOIL AND SLUDGE

Number of samples	The consistence of soil-concrete (experimental sample-heat treatment with the use of solar energy)	Number of samples	The consistence of soil-concrete (control – hardening in vivo)
With the use of oil-contaminated soil			
2	contaminated soils cement sand water concrete additives	22	contaminated soils cement sand water concrete additives
Using oil sludge			
4	Oil sludge cement sand water concrete additives	44	Oil sludge cement sand water concrete additives

After the heat treatment in the soil-concrete Helio device with a translucent shell, physical and mechanical properties of experimental samples of soil-concrete had the following values shown in Table 2. As can be seen from the results in Table 1, soil-concrete consistencies 2 and 4 on the quality of instruction to meet the requirements of the stabilized soil two strength class.

TABLE 2. PHYSICAL AND MECHANICAL PROPERTIES OF THE EXPERIMENTAL AND CONTROL SAMPLES OF SOIL-CONCRETE AFTER 28 DAYS OF HARDENING

Name indicators	According to building codes and regulations, 2 strength class	The value of technical indicators			
		Contaminated soils		Oil sludge	
		2 experimental	22 control	4 experimental	44 control
1	2	3	4	5	6
The compressive strength of saturated samples, MPa	6–4	5.73	3.1	5.33	3.70

The tensile strength in bending samples saturated with water, MPa, not less	1.0	1.6	0.86	1.50	0.76
Coefficient of frost, not less than	0.75	0.81	0.55	0.80	0.53

A large compression strength of soil-concrete second consistence on the basis of oil-contaminated soil, and forth consistence on the basis of sludge is due to the selection of the correct consistence: complex sand and additives, the presence of an organic part of the compounds with unsaturated chemical bonds, which increases their reactivity, as the use of pre-treated contaminated soils or sludge, as after pre-treatment molecular weight hydrocarbons close in magnitude to the bitumen, and the ratio of carbon to hydrogen varies according to the given row, bitumen (6.29–10.7) > polluted soil and oil sludge (8.56–8.79). In soil-concrete made on the basis of oil-contaminated soil or sludge priority tensile strength in bending is due to tar providing adhesion, elasticity and cohesive bonds (Table 3).

TABLE 3. SOIL-CONCRETE STRENGTH BY HEAT TREATMENT USING SOLAR ENERGY

Number of the mixture	**W/C**	**Tensile strength in bending**	**Compressive strength, MPa age day**			
			1	**7**	**14**	**28**
1	2	3	4	5	6	7
Contaminated soils						
2	0.5	1.6	1.07	1.7	3.74	5.73
22	0.5	0.86	0.11	0.75	1.55	3.1
Oil sludge						
4	0.5	1.50	1.01	2.36	3.70	5.33
44	0.5	0.76	0.13	0.93	1.85	3.7

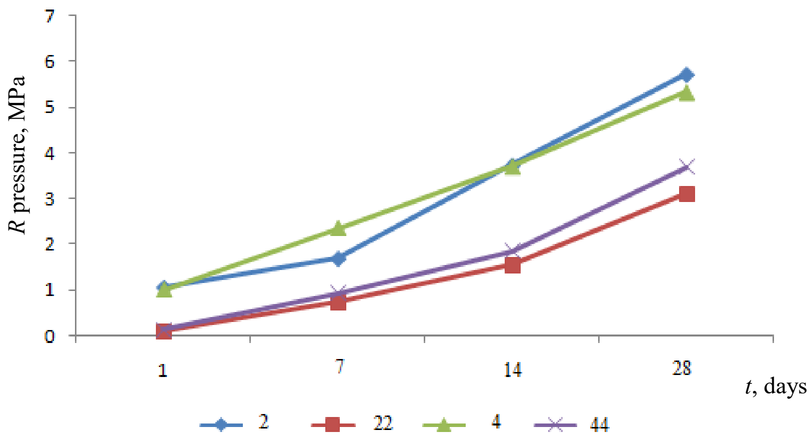


Fig. 2. The strength of soil-concrete with the use of solar energy.

In accordance with the above stated optimum consistence can be recommended according to the instructions for building a foundation or as a coating of local roads. They can also be recommended as a basis, performing the function of a crack soil-concrete consistencies – interrupting layers. This improves the technological properties: workability due to the presence of plasticizers – oil, and hence the homogeneity and workability. Increase operational performance: compressive strength and tensile, frost resistance and deformation capacity through the use of cement, providing crystal structure space frame which occurs in soil stabilization. This is due to the fact that the oil has a coagulation structure, and the presence in it of cement provides mixed coagulation – crystal structures of soil with a real possibility of obtaining soil-concrete with high physical and mechanical properties.

3.1. Investigation of Soil-Concrete Structure, Made on the Basis of Oil-Contaminated Soil and Sludge

Properties of oily waste (oil sludge, drilling wastes, contaminated soils) are determined by mineral, particle size distribution, number and size of soil aggregates, density, viscosity, water-holding capacity, pH of the medium. The structure of oily wastes and materials based on them can be coagulation, condensation, and crystallization.

Coagulation structure is the source of oily waste (i.e., water-saturated). Connectedness of oily wastes is provided by molecular forces of adhesion occurring between the surfaces of solid particles through the layer of water. Oily waste has sticky properties, prone to sedimentation (precipitation) in the course of which the grain size up to 5 mm "fall" into the sediment in a shorter shelf life, fine particles of clay minerals (mainly montmorillonite) are suspended in the surface layers. Accordingly, during a prolonged storage of oily waste differs inconstancy of consistence and particle size, respectively, adjustment storage properties.

The condensing structure has great strength in the dry state. However, when moisture condensation structure dramatically (approximately 10 minutes), passes into a coagulation, which is unacceptable for use as a main component of the pavement.

The crystallization structure is formed in the event of supersaturated solutions of crystals and their coalescence with each other. In oily waste, crystallization structure is underdeveloped (due to oil-well cement or salts). The mixture was dried oily waste and cement, mixing with water as a result of chemical and physical processes acquires a solid structure, however, along with a large amount of crystal accounts for condensation. It is possible that the cement stone with sandy, mudstones and other cuttings forms a kind of frame, which causes dry strength. However, when using the original mud, high turnover of the strength of the mixture at equivalent dosages of cement is negligible, due to the large thickness of water films. Therefore, to address recycling and organic components integrated approach is needed.

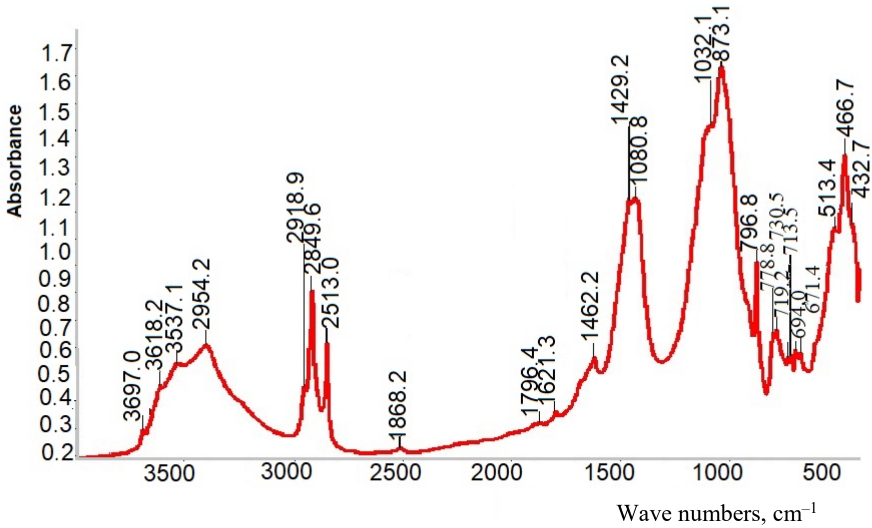
Complex physical and chemical interactions occur when the cement is incorporated into the oil-containing waste. As is well known, Portland cement is a complex mineralogical consistence polydisperse powder. Stone formation is due to the occurrence of hydration and hydrolysis and subsequent crystallization processes of structure formation. Process efficiency is determined by the state of a supersaturated solution, which can indirectly have expressed in units of pH 12.5–13.2. In the presence of oily waste, the particles of which are characterized by a high specific surface area and activity are lowering the pH – the liquid phase. In this case, the exchange capacity greater than 40 mg/00 g. At the initial stage of cement hydration calcium hydroxide released. In a subsequent step the interaction with the drilling fluid $Ca(OH)_2$ and the individual constituents of the clinker minerals hydrated. Large surface area clays and the flow of cement contributes vigorous physical and chemical reactions. Due to the presence of a pronounced alkaline medium capacity clays to ionic exchange reactions increases sharply (in the case of the presence of peat lignitic material increases). This leads to the absorption of Ca^{2+}, to reduce the alkalinity of the system and violate the cement hardening process and hence the formation of low-strength structure. Thus, the required degree of saturation can be achieved by a ship of 30 % or more of the cement. At lower doses (as determined experimentally) is compacted mud, but the structure of crystallization does not occur, therefore, the "soil stabilization" is not sufficient water resistance, low modulus of deformation. The surfactants contained in the oily waste focusing on the interface, change the molecular nature and properties of surfaces. Additives surface active agents (surfactants) can control the stability or destruction of disperse systems. Therefore, the presence of surfactant in the oily waste has a positive effect on the rheological properties of the resulting mixtures and elastic – deformation properties of hardened consistencies. Also, oily waste can include oil. In this case, the water absorption of the prepared consistence s markedly decreases due to the clogging (partially filled), then the oil, and also due to the formation of calcium salts of fatty acids, gives hydrophobic properties to the consistence [33].

It was established that favourable temperature and humidity conditions of hardening and heating soil-concrete for soft modes at a rate of 4–5 °C from an hour to a temperature of 65 °C with conventional isothermal exposure at these temperatures and slow cooling of soil-concrete at a speed of about 1.5–2.5 °C per hour should have a positive impact on the formation of the structure and physical mechanical characteristics of soil-concrete. This is due to the fact that the thermal energy, influence the formation temperature in the soil-concrete, consists of simultaneous exposure to heat energy transferred by radiation from the environment; heat extracted due to the exothermia. Soil-concrete heat dissipation depends on the chemical and mineralogical consistence of cement used and polluted soil, the subtlety of his grinding, water-cement ratio, temperature and duration of concrete hardening, heat accumulated soil-concrete for daylight.

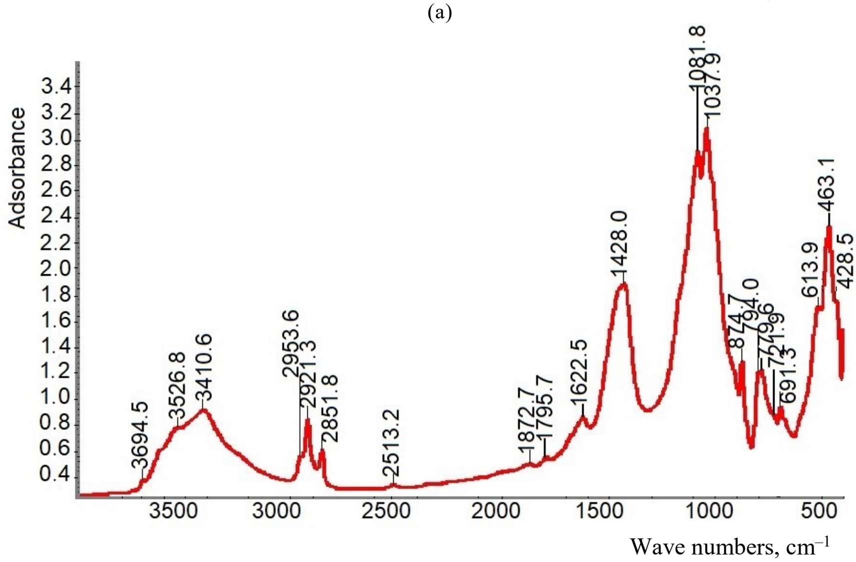
The aim of the study was to investigate the features of the structural characteristics of soil-concrete heat-treated with the use of solar energy in comparison with the structural characteristics of soil solidified under normal conditions. To study the influence of external environmental factors, such as solar energy by heat treatment on the mineralogical consistence of soil-concrete on the basis of oil-contaminated soil or sludge, complex physical and chemical methods of research have been used: thermal, X-ray and infrared spectroscopy. Heat treatment, using the solar energy is connected, firstly, to the transfer of high energy, leads to heating of the objects. Secondly, it is accompanied by ultraviolet irradiation of the latter.

According to the results of X-ray and IR-spectroscopic analysis methods established mineral phase consistence, as well as the organic consistence of soil-concrete. To study the phase consistence and structure of cement stone and soil-concrete method, infrared spectroscopy, X-ray diffraction, differential thermal and microprobe analysis, and electron scanning microscopy, which allow to evaluate the degree of hydration of cement binder and the condition of the cement stone have been used.

Investigations were carried out on IR-spectrometer “Nicolet 5700” Corporation “Thermo Electron Corporation” (USA) in the range of 400–4000 cm^{-1}. It has been established that the tested samples have absorption bands characteristic for both organic and inorganic objects. Thus, the organic components are represented aliphatic hydrocarbons. Absorption bands in the 2840–2960 cm^{-1} correspond to asymmetric and symmetric vibrations CH_2 and CH_3 groups in the 1440–1470 cm^{-1} – bending vibrations of these bands at ~ 720 cm^{-1} – vibrations – $(CH_2)_n$ – groups. IR-spectrum revealed that in the presence of residual paraffin oil structure. The inorganic part consists of quartz SiO_2 (466, 513, 694, 778, 796, 1080 cm^{-1}), calcite $CaCO_3$, (719, 873 cm^{-1}), gypsum dehydrate (671, 1030, 1621 cm^{-1}). Inorganic part corresponds silicates, alum inosilicates, and materials of this type. Most characteristic for these silicates is a strong absorption band at 1100 cm^{-1} (up to 1030 cm^{-1}), which, depending on the nature of the mineral, can manifest itself in the form of a singlet, and multiples. The absorption bands in the region 3400–3700 cm^{-1} (smooth humps) and 1640 cm^{-1} correspond to the associated water molecules as crystallization and crystalline hydrate.



(a)

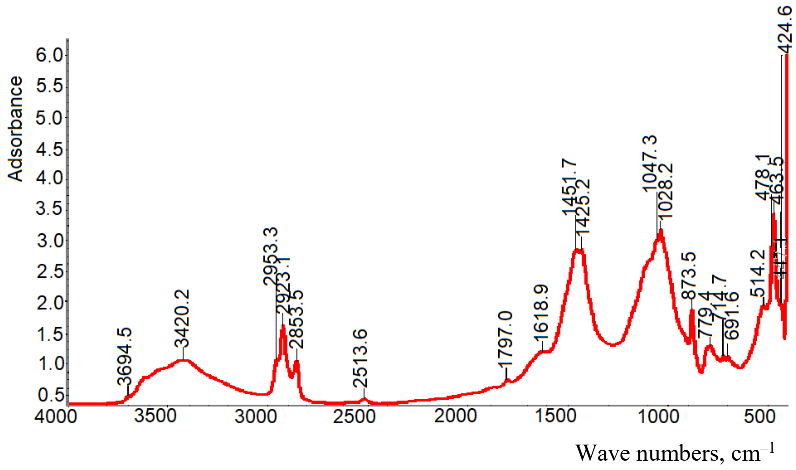


(b)

Fig. 3. The IR spectra of soil-concrete produced on the basis of oil-contaminated soil with an additive: a) experimental, b) control.

Based on the convergence criteria according to the analytical program "*OMNIC*" Corporation "Thermo Electron Corporation" Comparative description of the experimental (a) and control (b) samples made of oil-contaminated soil, which showed their identity to each other and the convergence of 86 %. Similar results were obtained for pairs of samples 2 and 22 compounds (Fig. 3).

X-ray diffraction analysis was carried out on a diffractometer: *XPERT-PRO*. For X-ray analysis of fragments of plates cut from three different sections of the samples (from the surface layers and volume) powders were prepared by rubbing in a porcelain mortar. Radiographs of the samples on the basis of soil – sludge different from the X-ray samples from contaminated soils by the presence of diffraction peaks characteristic of clay minerals. It should be noted that the decrease in the intensity of the diffraction peaks of quartz indicates the intensification of the process Hydro silicates education in soil – with his participation and the formation of a stronger skeleton of the silicate and silica component of soil-concrete (Figs. 4–5).



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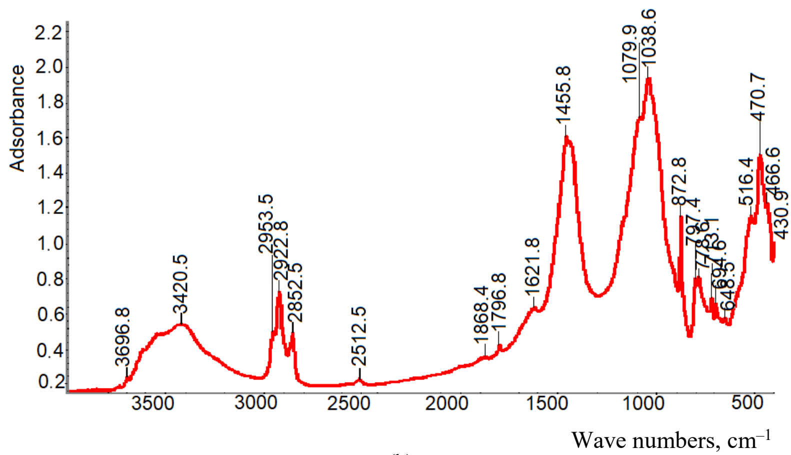
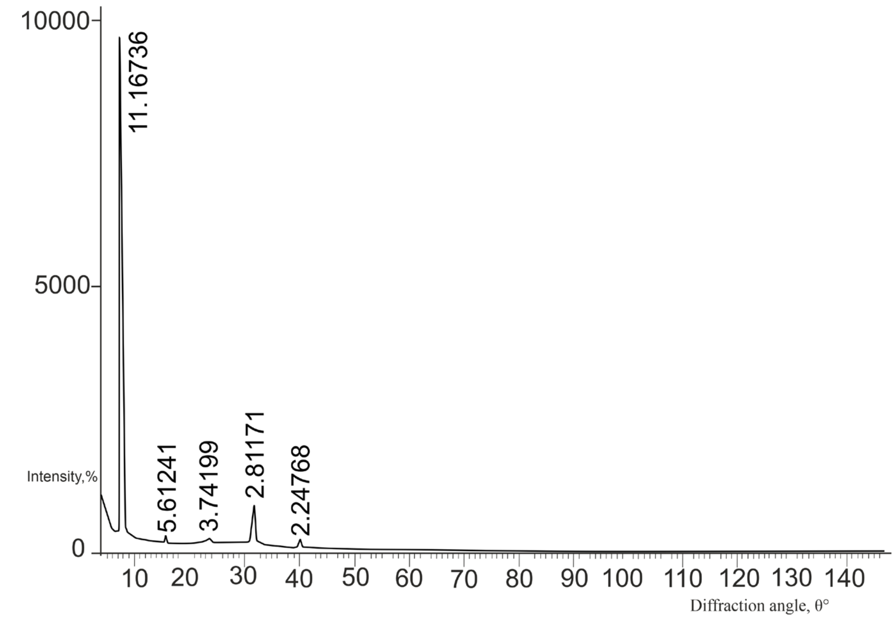


(b)

Fig. 4. The IR spectra of soil-concrete produced on the basis of sludge: a) experimental, b) control ones.



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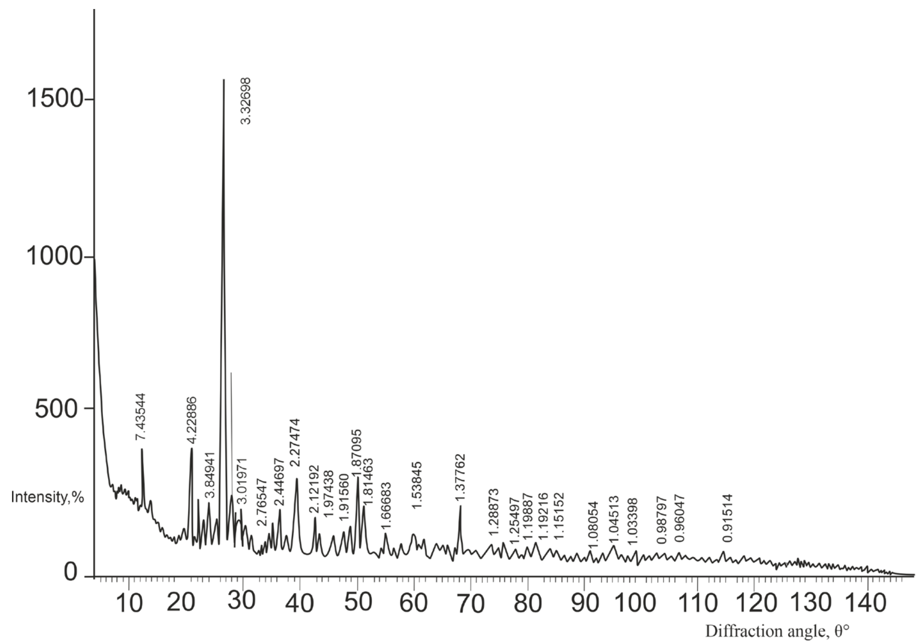
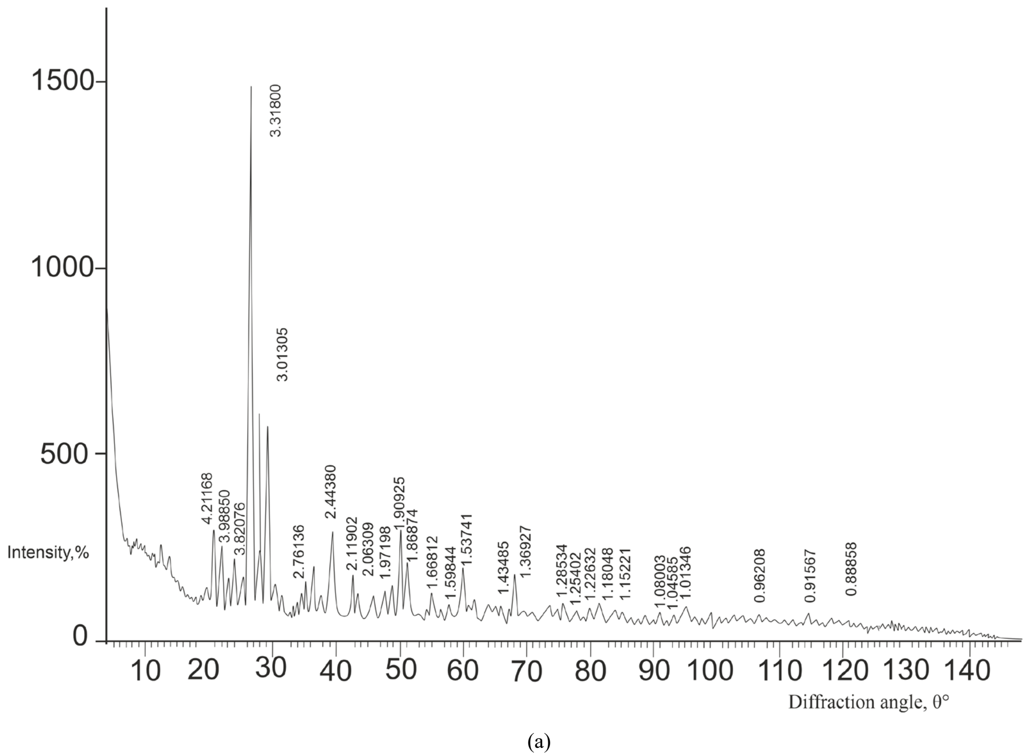


(b)

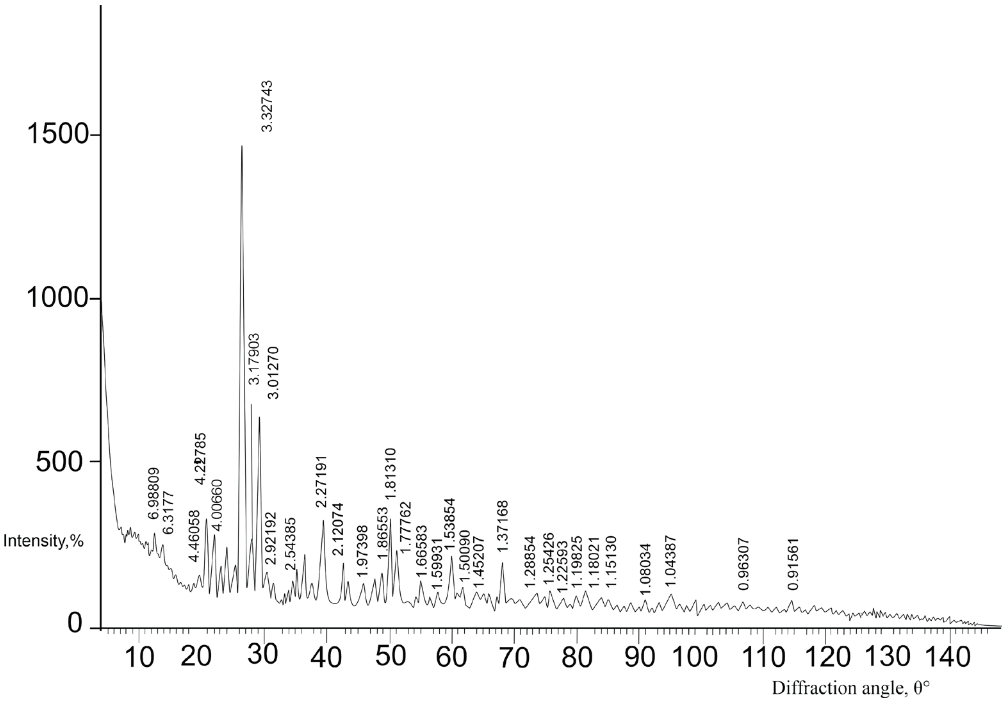
Fig. 5. Radiographs of experimental: a) and control, b) soil-concrete samples of polluted soil (with a concrete additive) (XRD).

The complex addition of sand and modifier leads to the strengthening of the gel formation process and amorphization of the system, which contributes to the compaction and increase the density and, consequently, the strength of the samples. Infusion additive enhances the process of phase formation and the appearance of additional diffraction maxima on the radiograph of the sample, the heat-treated with the use of solar energy (in the 2 and 22). According to XRD on radiographs fixed line quartz SiO_2: 4.24 – 3.326 – 2.45 – 2.286 – 2.232; calcite $CaCO_3$ – 3.86 – 3.037 – 1.917 – 1.873; gypsum dehydrate – 7.6 – 4.27 – 3.79 – 3.06 (Fig. 5).

According to X-ray diffraction analysis, in addition to SiO_2 and quartz-feldspar present in the sand, fixed line $CaCO_3$ calcite and dolomite $CaMgCO_3$, line of tricalcium silicate, a component of cement, have a small intensity. This indicates that curing has not ended. Lines portlandite $Ca(OH)_2$, 4.88 and 4.92 indicate that it is a portion of the hydrated cement. As part of portlandite 2 has a higher intensity than the consistence 22. Lines 5.6 ettringite hydrocortamate consisting of 2 more than in the consistence of 22. The results of X-ray analysis can give a comparative assessment of the intensity of phase formation processes in the soil-concrete. Since X-ray-based soil samples of contaminated soil indicate that the reduction of the intensity of the diffraction peaks of quartz (3.34; 4.24) and some increase in the intensity of the diffraction peak characteristic of the calcium hydro silicate, suggests that the method of heat treatment using solar energy intensify the process of hydro silicate formation (Fig. 6).



(a)



(b)

Fig. 6. Radiographs: a) experimental and b) control samples of soil-concrete sludge (with a concrete additive) (XRD).

Thermal analysis revealed the influence of solar energy in the heat treatment on the consistence of soil-concrete. A comparison of the curves of differential thermal analysis of soil – structure 22 (control) and 2 (after heat treatment with the use of solar energy) showed similarity. Endoeffects (–) 120 °C and (–) 140 °C due to the dehydration of calcium hydro silicates. On the heating curve DThA endoeffects (–) 120 °C and (–) 130 °C decomposition of gypsum dehydrate $CaSO_4 \cdot 2H_2O$, naphthenic hydrocarbons of C_nH_{2n}. Exoeffects (+) 220 °C – methane-naphthenic components naphthenic hydrocarbons series. And exoeffects (+) 320 °C and (+) 660 °C waxy structure of the organic component of soil samples. Exoeffects (+) 340 °C and (+) 400 °C due to the presence of oil residues (naphthenes) and (+) 500 (+) 610–630 °C aromatic oil component. Endoeffect (–) 420 °C and (–) 450 °C – decomposition of potassium and sodium nitrate KNO_3 and $NaNO_3$. Endoeffect (–) 810 °C – decomposition of calcium carbonate $CaCO_3$. But the intensity of the low-temperature “hump” exoeffects associated with a number of naphthenic hydrocarbons with maxima (+) 340 °C and (+) 400 °C decreased. This was due to the heat treatment using solar energy samples that led to oxidation (burnout), naphthene series hydrocarbons. Having a double endoeffects thermograms indicates the presence of both moisture-absorbent samples and adsorption-related ones. Endothermic effects on the thermogram in the 250–290 °C are associated with the processes of burnout in samples of organic soil-bituminous oil component. Endoeffect intensity and temperature are indicators of quantity, the degree of connectivity of the skeleton, the influence on the physical and chemical processes of soil-concrete curing.

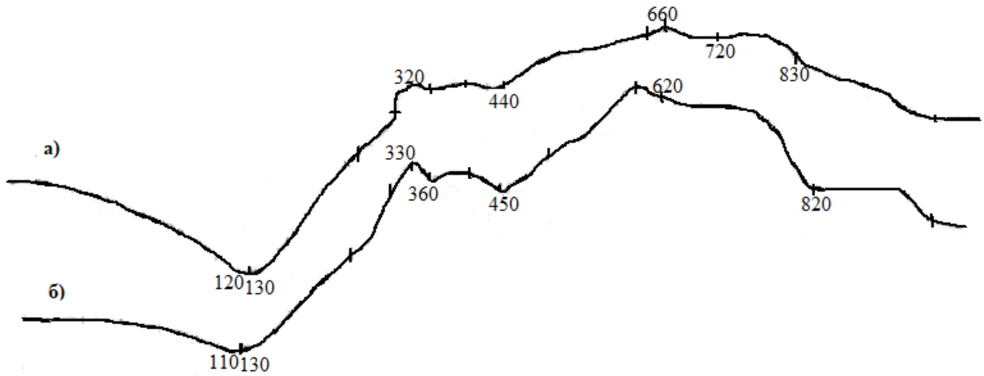


Fig. 7. Derivation of soil-concrete consistencies: a) experimental and b) control soil-concrete samples (DThA) (consistence 2).

To study the effect of heat treatment using solar energy on the hardening of soil concretes on the basis of oil-contaminated soil, cement, and sand, 2 series of consistence using concrete additives have been formed. Under the code 22, samples were formed, hardening in natural conditions. Under the code 2, the consistence s subjected to heat treatment with the use of solar energy are indicated (Fig. 7). To study the effect of heat treatment with the use of solar energy in the mineralogical consistence of the soil-concrete were moulded for samples consisting of sludge, cement, and sand. The control sample under code 44 hardened in vivo, as an experimental model under code 4 is heat treated using solar energy. According to the thermal analysis results can be seen that the DThA – endoeffect curve (–) 100 °C removal of free water. Exoeffects (+) and 320 (+) 410 °C burning hydrocarbon components of the sludge. Exoeffects (+) 220 °C – consistence of hydrocarbons and methane series (+) 320 °C – waxy structure of the organic components of sludge. Endoeffect (–) 480 °C, associated with the expansion of portlandite intensity. It also points to the beneficial effects of heat treatment with the use of solar energy in the soil-concrete hardening.

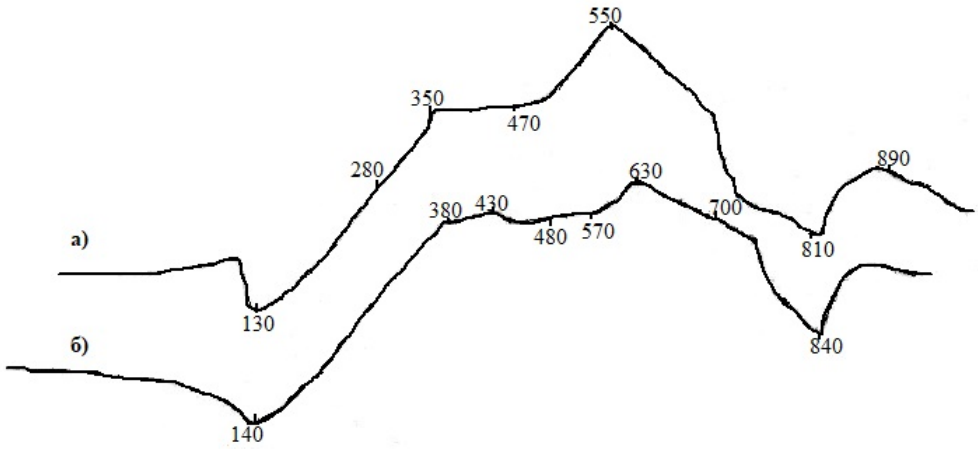


Fig. 8. Derivation: a) experimental and b) control soil-concrete samples (DThA) (consistence 4).

Three points of structural soil-surface of each sample have been investigated by elemental microprobe analysis. Table 4 shows mass content (%) of the element at the point of microprobe analysis. Values of mass content of elements are listed, whose participation in the formation of phases uniquely hydro silicate (Ca, Si, O). In addition, the table shows the values of carbon content in the area of microprobe analysis. These values allow us to indirectly assume the nature of the distribution of the organic component in samples.

Comparison of the mass content of calcium in the soil-concrete samples based on oil-contaminated soil showed that a uniform distribution is characteristic for the samples containing only the cement component. The introduction of sand, additives, complex sand and additives leads to the appearance of non-uniformity in the distribution of calcium, which may be explained by processes of redistribution of elements as a result of coagulation and crystallization hydro silicate components of the system. It is important to note that the silicon component has the lowest number of samples at the points of microprobe analysis, regardless of the consistence and soil-hardening conditions.

On the other hand, the weight content of the predominant calcium point of microprobe analysis for the samples of soil-concrete content of silicon (Si) indicates a predominance of carbonate component samples over silica and indicates the intensity during the curing process. A comparison of the nature of the distribution of elements depending on the curing shows that soil-concrete samples for oil-contaminated soils uneven distribution of mass element content is more significant than the sample on the basis of sludge that may be due to a greater dispersion of sludge. Comparison of the mass content of elements in samples of contaminated soils (compounds 2 and 22) shows (Table 4), the total distribution of elements depends on the consistence of the sample, and the conditions of hardening. It draws attention to the fact that the smallest mass content in samples, regardless of the point of the microprobe analysis, curing conditions, the consistence of the sample is characterized by silicon (Si), where in the marked points at which it is not detected (consistence 2 and 22) or its minimum content. Thus, the use of microprobe elemental analysis of soil-concrete samples allowed to determine the degree of homogeneity of the distribution of the elements according to the imposed conditions and hardening additives.

TABLE 4. ELEMENTAL MICROPROBE ANALYSIS OF THE MAIN COMPONENTS OF SOIL-CONCRETE COMPONENTS, MADE ON THE BASIS OF OILY WASTE FROM CONCRETE ADDITIVES

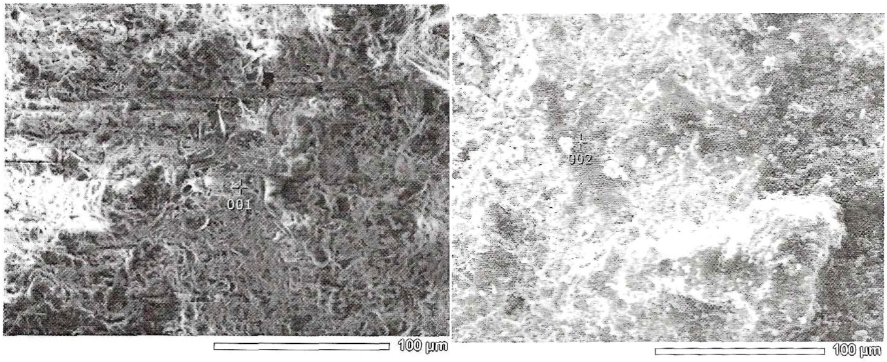
Element	The weight content of at microprobe analysis					
	Experimental	**Experimental**	**Experimental**	**Control**	**Control**	**Control**
	On the basis of oil-contaminated soil					
	2	2	2	22	22	22
C	46.02	17.79	31.09	20.62	47.91	24.53
O	30.46	52.18	40.21	44.67	35.29	45.36
Si	6.32	1.13	3.21	9.20	6.08	12.27
Ca	4.06	14.41	9.19	18.89	6.89	10.43
On the basis of oil sludge						
	4	4	4	44	44	44
C	21.78	17.66	19.25	30.83	1.96	38.65
O	37.59	42.19	25.97	46.36	12.91	17.56
Si	10.73	6.61	7.20	5.17	1.18	6.55
Ca	21.50	26.75	41.63	14.55	82.77	33.67

By electron scanning, microscopy allows samples to establish the laws of structure formation processes in the soil-depending on the consistence and conditions of curing. Electron-scanning microscopy has been performed on the electron microscope – microprobe: *JED-2300 Analysis Station* in modes of the study of the morphology, microanalysis and plot points. The microstructure of the soil-concrete shows its structure, due to the shape, size, and nature of accretion of mineral grains with each other and astringent, as well as their relationship. The addition of cement in the soil-based oil-contaminated soils is an important part that contributes to their physical and mechanical properties. Electron-scanning microscopy microstructure of soil-concrete showed that the hydration products of Portland cement are able to grow together with the mineral soil skeleton. And the products of hydration of cement reacts with minerals in soil-concrete structure, forming micro-aggregates. The adhesion force of hydration products to soil particles depends on the nature of the mineral surface caused by crystallochemical and mineralogical characteristics. In addition, the presence of organic component dramatically changes the normal course of hydration and hydrolysis cement minerals.

Strengthening Portland dispersion systems caused by the fact that the hydration products of cement particles interact with the surface of the mineral particles, coagulated dispersion are aggregated the most part of the system in the process of growth and crystallization to form a solid structure irreversibly. When a chemical reacts with water clinker minerals in the early periods of hardening soil-concrete consistences, soil-forming hydration produces colloidal forms depending on the mineralogical consistence of cement, fineness, water-cement ratio, temperature, etc. Calcium hydrosilicates formed in the early periods of hardening in a gelatinous mass during further hardening the microparticles formed of different morphology – the needle plate, oval grain. By law, they are aggregated colloidal systems, fused with each other to form a solid structure, providing performance characteristics of soil-concrete. The microstructure of the bulk of the soil is incorporated in the closed area size – 2.3 mm, which includes a grain having an average size of 20–30 mm. Grains, in turn, are combined into larger aggregates of up to 100 mm. Rich content boundaries of structural components within the borders creates favorable conditions for interaction with the binder, which ultimately serves as an additional source of increasing the strength properties of soil-cement with the additive. Strengthening grained soils Portland happens because the hydration products of cement particles (evenly spaced between the soil particles by mixing and compaction) interact with the surface of mineral soil particles coagulate, aggregate dispersed most of the soil in the process of growth and crystallization form a solid structure irreversible. The degree of dispersion of soils have a great influence on the bond strength of their case – hardening. With the increase of specific surface area and the surface energy of the soil particles to a certain extent increased the strength of the concrete ground, but to create a frost-resistant material requires an increase in the dosage of binder and the infusion of cold-resistant additives. Since the presence of montmorillonite clay requires a considerable increase of cement dosage. The mobility of the crystal-structure of montmorillonite and its large exchange capacity, in contrast to kaolinite and hydromicas more strongly violates the normal course of hydration of Portland cement (actively absorbed Ca^{2+}), in order to create a water- - and frost-resistant material of clay containing montmorillonite, require large quantities of binder administering or activating additives (consistence 2).

The microstructure of hardened montmorillonite clay (reinforced Portland cement dosage) crystallization, aggregate, cement, or contact cement particles have a dense shell of montmorillonite particles, resembling in form sheets of tissue paper. This structure of reinforced montmorillonite clay does not make it water- and frost-resistant. The structure of the kaolinite clay (reinforced cement dosage) also has a crystallization-aggregative character.

Particles of pseudo hexagonal kaolinite forms highly aggregated, mainly oriented perpendicularly relative to their most advanced edges. In some places, there are areas where kaolinite particles are located at different angles. Cement is mostly of contact and sometimes of filling type. Hydrated cement clinker minerals particles coated with particles of kaolinite, which are oriented parallel to its most developed faces.



1 – cemented clay; 2 – crystallization-aggregate sample.

Fig. 9. The microstructure of cemented clay and crystallization-aggregate sample: a) experimental and b) control soil-concrete samples made on the basis of polluted soil with concrete additive (×500).

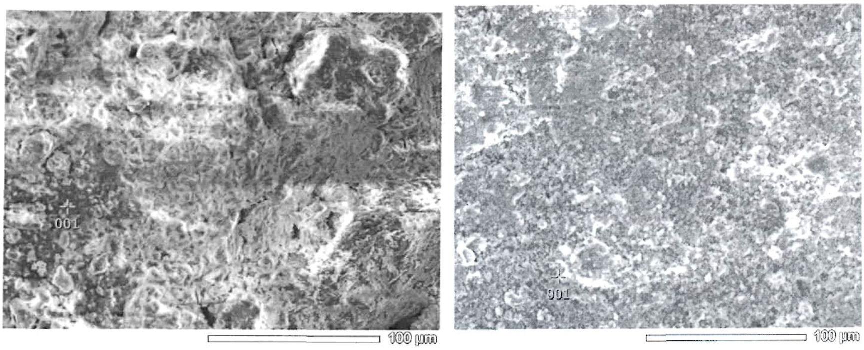


Fig. 10. The microstructure: a) experimental and b) control soil-concrete samples made on the basis of sludge with a concrete additive (×500).

- The study of the morphology and microstructure of hydrated Portland cement in the consistence of soil does not always correspond to existing structural types of crystals, characteristic of hardening cement paste.
- The strength and durability of fine-grained soil are caused by the crystallization and aggregation – crystal structure (a type of cement with the basal or fill the pores). Crystallization – aggregative structure because of its reversibility does not provide soil reinforcement strength and durability.
- The process of hydration and structure of soil reinforced with cement, shows that

hardening occurs as a result of:

1. Surface adhesion forces of various forms of highly dispersed crystalline hydrates;
2. Chemical forces (covalent bonds), leading to the imposition of direct and structural mutual growth surface crystalline lattice;
3. The strength of gelation and crystallization of cement hydration products of $Ca(OH)_2$;
4. Recrystallization forces of $Ca(OH)_2$ to $CaCO_3$. As a result of these processes is formed heterogeneous, mostly crystallization structure.

The nature of the interaction of soil with astringent is determined by the degree of surface soil, which determines the intensity of the adsorption processes occurring during their interaction with the cement, i.e. adhesion traction plays a significant role in shaping the mechanical strength of soils. In this regard, the presence of oil-contaminated soil and oil sludge oil and bituminous component contributes to a decrease in water-repellence and hydrophilic particles of soil, which provides the appearance of active sites and the formation of strong and adhesive bonds with the binder (cement), the formation of cement stone, soil-concrete structure reinforcement. Comparison of soil-strength characteristics shows that they depend on both the consistence of the raw soil and the type and amount of additive (sand, additive). Influence of cement strength depends on the mineralogical and particle size distribution of the original soil. Because of the high amount of hydrophilic mineral soil – strength is reduced, and when administered with sand fineness modulus Mgradation = 2.5, the soil-concrete strength increases.

4. CONCLUSION

The results of the studies of the effect of sand and additive, hardening conditions (use of solar energy) and the type of organic contaminants (fuel oil, oil) according to physical methods (XRD, DThA, elemental microprobe analysis, electron scanning microscopy) on the processes of hydration and phase formation in hardening systems showed:

- technological factors listed do not have a significant impact on the phase consistence;
- the use of solar energy increases the hydration process and phase formation, helps to seal and streamline microstructure, provides uniform distribution.

Practical task – to create conditions for the formation of microstructures, which allow a reduction in the retarding influence of organic matter (fuel oil, oil) on the process of curing the binder, but it will help to manifest positive and repellent effect.

Extensive use of recycled materials, such as waste oil production is dictated by both the feasibility and the modern environmental requirements. Economic and environmental feasibility of recycling waste, including oil-contaminated soil and sludge increases, since they contain more components suitable for highly sought-after building materials, road-building materials (soil-concrete). At present, the growing importance of lightweight, transitional and lower road types with the use of soils and soil-reinforced mineral binder. The development of the road network in the regions of Kazakhstan refineries due to the use of local materials, which include overburden for oil, waste drilling mud, sludge oil production and transportation of oil. Such waste is usually deposited in open areas, landfills, occupy large areas, environmentally unsafe and processing is becoming increasingly important.

Social benefits achieved improved ecological conditions of area of oil through the utilization of oil-contaminated soil and sludge and reduce the environmental impact on the environment, rehabilitation of areas polluted by oil waste, as well as appeal to non-traditional sources observed around the world, explains how limiting traditional energy sources are, and more critical environmental conditions, caused by the burning of fossil fuels and the emergence of the so-called ‘greenhouse’ effect. The use of renewable energy and converting them in the most convenient forms: electricity and heating costs today is extremely expensive [34]. However, the difficulties that await humanity in the case of increasing or maintaining the rate of growth of the negative impact on the environment as a result of industrial activity and energy production, and are forced to seek means to develop research aimed at improving the efficiency of clean energy, primarily solar. Soil-structure based on the proposed use of different renewable energy sources, including solar energy, reducing energy consumption, low cost, and decides on disposal of oily waste. Developed environmentally friendly soil-concrete can be used in building a foundation of roads with minimal energy and labour costs.

A significant role in the formation of chemical technology as a scientific basis of chemical production was played by the organization of a network of scientific institutions in the country, in which the theory of chemical processes of specific industries was developed [35].

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Maral M. Abdibattayeva. Doctor of technical science, Associate Professor of the UNESCO Chair in Sustainable Development of the Department of Geography and Environmental Sciences KazNU named after Al-Farabi. She is a scientist and a teacher, whose works are known at the international and national level. She trains highly qualified engineering and scientific personnel. Abdibattayeva M. M. is a corresponding member of the Russian Academy of Natural Sciences (RAE) in the section 'Earth Sciences'. By the decision of the Presidium of the Russian Academy of Natural Sciences, she was awarded the honorary title 'Honoured Worker of Science and Education', and she was also awarded the diploma 'Golden Department of RUSSIA' of the series 'Golden Fund of Russian Science'.

Maral M. Abdibattayeva actively conducts scientific and educational work. During her work at the university, she published more than 100 scientific works, including 7 textbooks, 20 educational and methodological complex of disciplines, 13 innovative patents for inventions, 8 in journals and conference proceedings with an impact factor, 10 in foreign journals. Maral M. Abdibattayeva has experience in implementing projects of an innovative nature, for a number of years she has been engaged in practical and theoretical research in the field of using solar energy, utilizing oily waste and obtaining new materials from natural and man-made waste.

E-mail: maral7676@mail.ru
ORCID iD: https://orcid.org/0000-0001-5736-4268

Kylyshbai Bissenov is a Kazakh scientist in the field of construction, founder of a scientific school for the development and improvement of energy-saving technologies for the production of new building materials, 'Honoured Worker of the Republic of Kazakhstan' (2012). Rector of the Kyzylorda Polytechnic Institute (1996-1998), Rector of the Korkyt Ata Kyzylorda State University (1998–2007 and 2011–2017). Doctor of Technical Sciences (1995), Professor (1992), Corresponding Member of the National Academy of Sciences of the Republic of Kazakhstan (2017), Honorary Rector of the Korkyt Ata Kyzylorda State University (2019), Secretary of the Kyzylorda Regional Maslikhat.
Author of over 260 scientific papers, including 35 patents, 12 monographs, 3 textbooks, 20 scientific and teaching aids. He prepared 3 doctors of sciences, 7 candidates of sciences, 4 doctors of philosophy (PhD).
K. A. Bissenov has published more than 280 articles, about 100 interviews dedicated to improving the national education and science system, topical problems of socio-economic development, socio-political and spiritual life of the country.
E-mail: Bisenov_KA@korkyt.kz
ORCID iD: https://orcid.org/0000-0002-0167-3560

Dr Zheniskul Zhubandykova received her PhD degree (Geoecology) from K. Satpaev Kazakh National Technical University in 2009. She is presently working as Associate Professor of Metallurgy, Mining and Oil and Gas Industry Department at Aktobe Regional State University, Aktobe, Republic of Kazakhstan. She has teaching experience of 30 years. She is an author of more than 30 scientific papers, 5 certificates of authorship for intellectual property, author of 1 textbook, 6 manuals, developer of 3 new educational programs 'Electric Power Engineering', 'Low Voltage Networks', 'Hybrid Power Engineering'. She has a number of awards: Certificate of Honour of the Minister of Education and Science of the Republic of Kazakhstan, certificate for outstanding achievements and contribution to the modernization of educational programs of the Minister of Labour and Social Protection of the Republic of Kazakhstan and the World Bank, Certificate of Freelance Coach of 'TALAP' Holding.
E-mail: tima2001@inbox.ru
ORCID iD: https://orcid.org/0000-0003-2028-9262

Dr Lyazzat Tastanova received her PhD degree (Catalysis) from D.V. Sokolsky Institute of Organic Catalysis and Electrochemistry in 2008. She is presently working as Associate Professor of Chemistry and Chemical Technology Department at Aktobe Regional State University, Aktobe, Republic of Kazakhstan. She has teaching and administrative experience (Head of Department, Dean of Technical Faculty, Head of Scientific Innovations Department) of 23 years. She has contributed research papers in International Journals and International Conferences. Previous publications were in such journals as Journal of Applied Polymer Science, News of the Academy of Sciences of the Republic of Kazakhstan, Polymers and Polymer Composites, Polymers, Materials. Her scientific interests include improvement of composites properties, development of polymer modified Nano catalysts, study of combined and complex impact of different pollutants on environment.
E-mail: lyazzatt@mail.ru
ORCID iD: https://orcid.org/0000-0002-9236-5909

Raigul Orynbassar obtained her PhD degree at the V. Sokolsky Institute of organic catalysis and electrochemistry in the direction of "Petrochemistry and Catalysis" in 2010. She was a lecturer and head of Oil and Gas Department in Aktobe Regional State University after K. Zhubanov (2010–2020), where she conducted lectures, practical and laboratory classes on 'Structure and properties of oil and gas', 'Protection of oil and gas equipment from corrosion', "Chemistry and physics of oil and gas", 'Thermodynamics and heat engineering' for students of educational program 'Oil and Gas Business'. She has 18 years' experience of scientific and pedagogical work. Since September 2020, she is an acting Associate Professor of the Department of Physical Chemistry, Catalysis and Petrochemistry at the Al-Farabi Kazakh National University. The results of her research work are published in 35 articles in domestic and international journals confirmed. She participates in national and international conferences. Orynbassar R. has one innovation patent of the Republic of Kazakhstan and one monograph.
E-mail: raihan_06_79@mail.ru
ORCID iD: https://orcid.org/0000-0002-6198-3018