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Crude oil contaminated soil: neutralization and using

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Abstract: The paper represents the research results for the process of the crude oil-contaminated soil neutralization with the use of a neutralizer obtained on the basis of humine substances. Using the physical methods (gas and liquid chromatography, fluorimetry, atomic absorption spectrometry, IR spectrometry) the element and group compositions have been determined for the crude oil-contaminated soil, neutralizer and neutralized soil. Optimal parameters have been determined for the process of the crude oil-contaminated soil neutralization in laboratory conditions: weight ratios of the crude oil-contaminated soil, neutralizer and water, temperature and neutralization process duration. The technological scheme has been developed for neutralization of the crude oil-contaminated soil in the field conditions. It is found that low-boiling hydrocarbon fractions ($C_{12} – C_{17}$) disappear completely at neutralization of the crude oil-contaminated soil, high-boiling hydrocarbon fractions ($C_{20} – C_{23}$) are essentially increased; the content of oil components and metals including the toxic ones is decreased. The engineering characteristics for nine mixtures of the stabilized soil with the neutralized soil have been evaluated by laboratory methods and the conditions have been determined for their use in the road construction (road category, characteristic pavement layer, minimal air temperature). An experimental road section has been constructed with the use of the stabilized soil with neutralized soil (40%).

Keywords: crude oil-contaminated soil; neutralizer; neutralized soil; stabilized soil; experimental road section

1. Introduction

Crude oil spill occurs on the earth surface at its production, transportation and storage. Soil contaminated with oil (crude oil-contaminated soil) is dangerous for human health, flora and fauna. Therefore one of the actual problems for normal functioning of biological and ecological systems in the regions with oil production is efficient remediation and utilization of crude oil-contaminated soil.

The most important genetic soil characteristics are disturbed at oil contamination: content and composition of humus, nitrogen, phosphor and microelements vary; soil adsorption complex is declined, volume weight is increased (density is increased), aeration and water penetration are reduced, and moisture available for plants is decreased [1, 2].

Natural self-purification of natural objects from oil contamination is a time-consuming process. Therefore short-time efficient artificial methods are required for purification. At present the following methods are known for remediation of crude oil-contaminated soil: biological [3-8], chemical [9-17], thermal [18], ultrasound [19] and mechanical [20, 21]. The purpose of the most of remediation methods mentioned above is to extract oil from a crude oil-contaminated soil. As a rule these methods are expensive.

This paper suggests a method for neutralization of crude oil-contaminated soil with the use of neutralizer produced on the basis of a sodium humate, and the possibility is shown for the use of the neutralized soil in road construction.

2. Materials and Methods

2.1. Crude oil-contaminated soil

Crude oil-contaminated soil (Figure 1, a) belonging to JSC "Ozenmunaigas" (Mangistau region, Kazakhstan) has been taken for further purification and improvement of the properties with the purpose of its use in a subbase of a highway. A storage facility for crude oil-contaminated soils is shown in Figure 2.

2.2. Neutralizer

To purify the crude oil-contaminated soil from oil components a neutralizer has been used (Figure 1 b), a composition material produced on the basis of humine substances which has the following content (% by weight): humic acids – 72.40; moisture – 15.25; ash – 12.35.

2.3. Chemical analysis methods

Fractional composition of oil components in the crude oil-contaminated soil and the neutralized soil has been determined by the methods of gas and liquid chromatography (Chromatograph "Agilent 6890", USA) and fluorimetry ("Fluorat-02", Russia, Moscow, RF) [22, 23]. N-hexane has been used as an extract. Accuracy for determination of fractional composition content is (1.5-2.0) $\cdot 10^{-3}$ mg/ml.

Content of metals in the crude oil-contaminated soil and the neutralized soil has been determined by the method of atomic absorption spectrometry [24, 25] (spectrometer AA-240 "Varian Inc. Scientific Instruments", Australia). Analysis of organic fraction of the crude oil-contaminated soil and the neutralized soil has been performed on IR-spectrophotometer of the model Nicolet 5700 (company "Termo Electron", USA) within the range of wave numbers 4000-400 cm^{-1}. The analyzed soil samples have been prepared with KBr.

Quantitative content of metal oxides was determined by the spectral method (Spectrophotometer Lambda-35 "Perkin Elmer", USA) [26].

2.4. Neutralization of crude oil-contaminated soil

Due to multicomponent (complexity) of the crude oil-contaminated soil composition, polyfunctionality and nonstoichiometry of the neutralizer composition it is difficult to represent the chemical mechanism of the process for neutralization of the crude oil-contaminated soil. However we suppose that neutralization of the crude oil-contaminated soil on the basis of the humate provides oxidation of hydrocarbons in oil components and bonding of heavy metals into safety non-soluble complexes. Toxic cations of metals (Pb^{2+}, Cr^{3+}, V^{5+}, As^{2+} and others) in the process of neutralization are bonded into humates, become inactive and less dangerous for the environment. Methane hydrocarbons (paraffins), complex alicyclic resins and asphaltenes are formed.

2.4.1. In laboratory conditions

Neutralization of the crude oil-contaminated soil in laboratory conditions has been performed by joint mixing (rate is 400 rotations per minute) of the crude oil-contaminated soil, the neutralizer and water in the specified ratios in a mechanical mixer with a thermostatical beaker of model "Eurostar 20 digital" (Figure 3). Ratios of weights for the neutralizer and water to the weight of the crude oil-contaminated soil in the tests varied from 0.05 to 1 and from 0.1 to 1 respectively. The temperature and process duration varied from 20°C to 80°C and from 5 to 60 min respectively.

The neutralized soil has a form as in Figure 1, c.

Figure 1. a – crude oil-contaminated soil; b – neutralizer; c – neutralized soil.

Figure 2. Storage facility for crude oil-contaminated soil.

Figure 3. Mechanical mixer.

2.4.2. In production conditions

Neutralization process in the production conditions can be performed on standard equipment of chemical manufacturers according to the following technical scheme (Figure 4): the crude oil-contaminated soil from a tank (2) by a belt conveyor (6) is supplied into a crusher (5); the crushed (up to 0.5 mm) crude oil-contaminated soil by a belt dozer (7) and a belt conveyor (6) is supplied into a reactor (1); the neutralizer is supplied from the reactor (1) into a tank (3) by the belt dozer (7); water is also supplied into the reactor (1) from a tank (4) by a pump (8) and a dozer (9); the neutralized soil is supplied by a belt conveyor (10) into a tank (11).

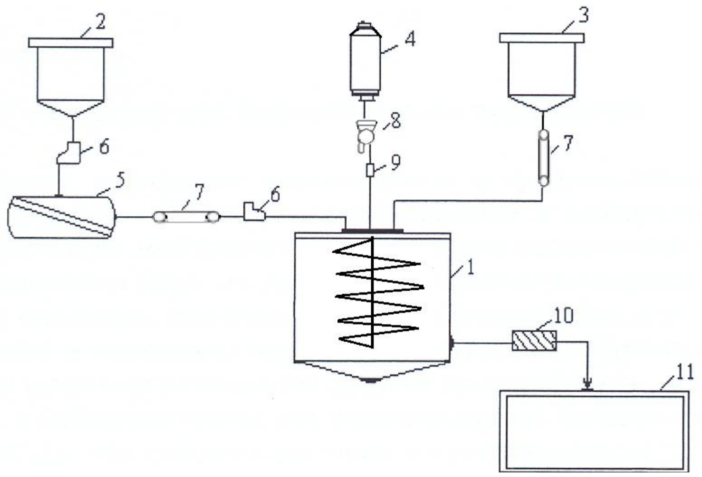

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Figure 4. Technological scheme for the neutralization process of a crude oil-contaminated soil: 1 – reactor; 2 – tank for crude oil-contaminated soil; 3 – tank for neutralizer; 4 – tank for water; 5 – crusher; 6 – belt conveyer; 7 – belt dozer; 8 – pump; 9 – dozer; 10 – belt conveyor; 11 – tank for neutralized soil.

2.5. Engineering characteristics

2.5.1. Granularmetric composition

When determining granularmetric compositions of the neutralized soil and stabilized soil mixes under the standard ST RK 1273-2004 [27] the specimens and the mixes have been dried before in a drying oven at the temperature of $105\pm5^{\circ}$ C up to constant weight. Then the specimens have been sifted through a set of sieves. The sieves with dimensions 1.25; 0.63; 0.315; 0.16; 0.05 mm and 20; 10; 5; 2.5; 1.25; 0.63; 0.315; 0.16 mm have been used for the neutralized soil and the stabilized soil mixes respectively.

2.5.2. Content of organic substances

Content of organic substances in the neutralized soil has been determined under standard ST RK 1280-2004 [28] by incineration of the soil sample (30 g) in a muffler at the temperature of 550° C for 2 hours up to constant weight. The soil sample has been dried before in a drying oven at the temperature of $105\pm5^{\circ}$ C up to constant weight and cooled up to a room temperature in an exicator.

2.5.3. Preparation of stabilized soil

To study the possibility for the use of the neutralized soil in the road construction it was proposed to consider different mix compositions of the stabilized soil containing crushed stone (5-20 mm), sand (0-5 mm), Portland cement (grade M 400) and water. Preparation of the stabilized soil mixes was performed under standard ST RK 1218-2003 [29] in the following way: the required quantity of crushed stone, sand and Portland cement were added to the neutralized soil of the pre-determined weight; the mixture was carefully mixed in a mixer (rate 90 rotations per minute) for 3 minutes; then after reaching of homogeneity of the dry mixture water was added during mixing; mixing of the wet mixture was in progress up to reaching of its homogeneity; due to the fact that neutralized soil contains organic substances and a hydrophobic one the wetter has been introduced in the ratio of 1/15 by weight.

2.5.4. Sample preparation

From prepared mixtures of the stabilized soil according to the standard ST RK 1218-2003 [29] cylindrical samples with dimensions d = h = 71.4 mm for compression test and samples in the form of a beam with dimensions 40x40x160 mm for bending test were made. The samples were compacted in appropriate molds under the stress of 20 MPa for 3 minutes. The prepared samples were in a wet environment for 28 days prior to testing.

2.5.5. Compression strength

Strength of the stabilized soils at compression was determined according to ST RK 1218-2003 [29] by testing the cylindrical samples with dimensions d = h = 71.4 mm at the temperature of 20 °C. The sample was deformed during the test at a constant rate of 3 mm/min to failure.

Compression strength was calculated by the formula:

$$R_c = \frac{P}{F},$$

(1)

where *P* is load at which the sample has been failed; *F* is an initial cros sectional area of the sample.

2.5.6. Bending strength

Strength of the stabilized soils at bending was determined according to ST RK 1218-2003 [29] by testing samples in the form of a beam with dimensions of 40x40x160 mm at the temperature of 20 °C. The tests were performed on the three point bending scheme. The sample was deformed during the test at a constant rate of 3 mm/min to failure.

The bending strength was calculated by the formula:

$$R_b = \frac{3 \cdot P \cdot l}{2 \cdot b \cdot h^2},$$

where *P* is load at which the sample has been failed; *b, h* are width and height of the sample respectively; *l* is length between supports.

2.5.7. Frost resistance

Frost resistance of the stabilized soil in accordance with ST RK 973-2015 [30, 31] is determined by the maximum number of freezing and thawing cycles, which it resists without significant (not more than 25%) reduction of compression strength.

Cyclic freezing and thawing is carried out in the following way: pre-water-saturated soil samples are placed in a freezer and held at the temperature of -18±2 °C for 4 hours; then the samples are placed in a water bath at the temperature of +18±2 °C for 4 hours. Further, the next freezing and thawing cycle is performed.

3. Results and discussion

3.1. Group composition of crude oil-contaminated soil

The results for determination of the chemical composition of the oil components contained in the crude oil-contaminated soil by the gas and liquid chromatography and fluorimetry showed that the oil components in the crude oil-contaminated soil composition are in dissolved, emulsified and solid states. Total hydrocarbon content in the crude oil-contaminated soil varies in wide range (5-69%) depending on sampling point. But the fractional composition of the oil components is relatively uniform. As shown in Table 1, the main part of the oil components are represented by complex acetylene hydrocarbons (65-74%), the content of resins, paraffinic and naphthenic hydrocarbons varies from 20 to 33.5%, and the amount of light hydrocarbons is only (0.5-6.0%). Thus, it can be assumed that 70% of the oil components are complex acetylene hydrocarbons and 30% of them are resins, medium and light hydrocarbons.

Table 1. Total content of hydrocarbons and group composition of oil components in the crude oil-contaminated soil.

Total content of hydrocarbons, %	**Content of fractions, %**		
	complex acetylene hydrocarbons	**resins, paraffinic and naphtenic hydrocarbons**	**light hydrocarbons**
5	65	33.5	1.5
8	71	28.5	0.5
69	74	20.0	6.0

3.2. Neutralization of crude oil-contaminated soil

Table 2 shows the results of the multivariate process for neutralization of the crude oil-contaminated soil at different weight ratios of the crude oil-contaminated soil, the neutralizer, water and at different temperatures. Neutralization process duration is 60 min.

Table 2. Variation of neutralization degree of the crude oil-contaminated soil at different ratios of the neutralizer and water (process duration is 60 min).

Relative content			**Neutralization degree at temperature of (°C), %**			
oil components	**neutralizer**	**water**	**20**	**40**	**60**	**80**
1	0.05	0.1	61.31	69.11	75.45	83.07
1	0.05	0.5	66.04	73.84	80.18	87.80
1	0.05	1.0	70.96	78.76	85.10	92.72
1	0.1	0.1	73.32	81.12	87.46	95.08
1	0.1	0.3	78.24	86.04	94.03	100.0
1	0.1	0.5	75.33	83.13	89.47	97.09
1	0.1	1.0	73.07	80.87	87.21	94.83
1	0.3	0.3	69.85	77.65	83.99	91.61

1	0.3	0.5	72.79	80.59	86.93	94.55
1	0.3	1.0	71.26	79.06	85.40	93.02
1	0.5	0.5	67.95	75.75	82.09	89.71
1	0.5	1.0	56.46	64.26	70.60	78.22
1	0.7	0.5	56.41	64.21	70.55	78.17
1	0.7	1.0	51.31	59.11	65.45	73.07
1	1.0	0.5	47.29	55.09	61.43	69.05
1	1.0	1.0	40.52	48.32	54.66	62.28

It can be seen from Table 2 that the neutralization process depends either on the neutralizer or on water content and temperature. The neutralizer content and temperature are the dominant ones. It is established that the greatest degree of neutralization (100%) is achievable and it takes place at weight ratios of the crude oil-contaminated soil, the neutralizer and water equal to 1:0.1:0.3.

All options for neutralization of the crude oil-contaminated soil, the results of which are given in Table 2, are performed with duration of 60 min. Since the longer the duration of neutralization process, the higher the costs, it is necessary to study its effect on the degree of neutralization of crude oil-contaminated soil. Figure 5 shows a graph of change in neutralization degree of the crude oil-contaminated soil depending on duration of neutralization process. As can be seen, it turned out that 15-20 minutes were sufficient to achieve the maximum possible degree (100%) of neutralization of the crude oil-contaminated soil.

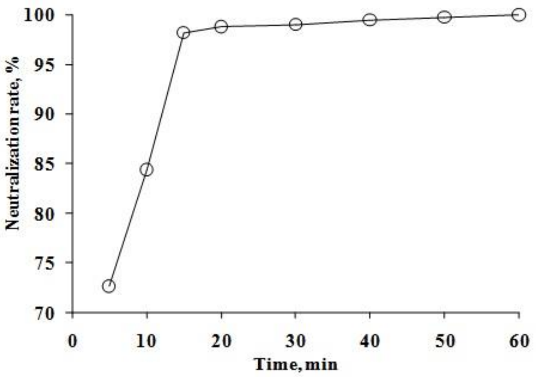


Figure 5. Dependence of neutralization degree for the crude oil-contaminated soil on the process duration.

3.3. Chemical composition of crude oil-contaminated soil and neutralized soil

Comparative analysis of fractional composition of oil components in the crude oil-contaminated soil and the neutralized soil has shown (Table 3) that there are practically no low boiling fractions (C_{12} – C_{17}) in the neutralized soil, but the content of high boiling fractions (C_{18} – C_{23}) is significantly increased. This shows that neutralization of the crude oil-contaminated soil by the proposed method reduces significantly its toxicity.

Table 3. Content of paraffins and alkanes in the crude oil-contaminated soil and the neutralized soil.

Paraffins, alkanes	**Content, mg/kg**	
	in the crude oil-contaminated soil	**in the neutralized soil**
Paraffins	68-70	-
Alkanes:		

C_{12}	1.56	0.07
C_{13}	2.90	0.08
C_{14}	20.98	0.11
C_{15}	80.44	0.15
C_{16}	69.47	0.09
C_{17}	77.40	0.56
C_{18}	80.44	0.72
C_{19}	53.36	0.43
C_{20}	34.35	134.37
C_{21}	19.01	119.01
C_{22}	17.53	117.55
C_{23}	9.54	229.51
Amount of alkanes	466.98	602.65

It should be also noted that the neutralization of the crude oil-contaminated soil involves an oxidation process whereby low boiling acetylene hydrocarbons are converted to high boiling hydrocarbons – paraffinic, naphthenic hydrocarbons, bitumen and asphaltenes (Table 4).

Table 4. Content of hydrocarbons in the crude oil-contaminated soil and the neutralized soil.

Hydrocarbons	**Content, mg/kg**	
	in the crude oil-contaminated soil	**in the neutralized soil**
Acetylene	192 300	-
Paraffinic and naphtenic	10 100	53 194
Bitumen and asphaltenes	4 300	6 870

In neutralizing of the crude oil-contaminated soil the total content of oil components and metals is decreased: the content of oil components is decreased more than 260 times. The metal content is decreased from 2.4 times (Mo) to 20,000 times (V); the content of highly toxic metals (Pb, Cr and As) is reduced by 5.6; 3.1 and 1500 times respectively (Table 5).

Table 5. Content of oil components and metals in the crude oil-contaminated soil and the neutralized soil.

Oil components, metals	**Content, mg/kg**	
	in the crude oil-contaminated soil	**in the neutralized soil**
Oil components	242 205.00	927.00
Pb	5.30	0.95
Cr	2.10	0.68
As	1.50	0.01
Mn	6.50	1.90
Cu	12.80	1.70
Ti	22.00	6.10

Mo	11.00	4.50
Ni	1.30	0.20
V	2.00	0.0001

Table 6 shows the chemical compositions of solid particles for the crude oil-contaminated soil and the neutralized soil. The solid particles of the soil consist generally of silica oxide (SiO_2 - 50.2%), calcium oxide (CaO - 19.4%) and ferrum oxide (Fe_2O_3 - 15.2%) total content of which is 84.8% (almost 85%). The rest of solid particles for soil (15.2%) is presented by magnesium oxide (MgO - 4.8%), potassium oxide (K_2O - 4.1%), aluminum oxide (Al_2O_3 - 3.1%), sodium oxide (Na_2O - 2.1%) and phosphorus oxide (P_2O_5 - 1.1%). As can be seen from this Table, the neutralization process does not practically change the chemical composition of the soil.

Table 6. Content of metal oxides in the crude oil-contaminated soil and the neutralized soil.

Metal oxides	Content, mg/kg			
	in the crude oil-contaminated soil		in the neutralized soil	
	mg/kg	%	mg/kg	%
SiO_2	472 800	50.2	470 100	49.1
Al_2O_3	29 110	3.1	32 000	3.3
Fe_2O_3	142 800	15.2	143 100	15.0
CaO	182 500	19.4	205 800	21.5
MgO	45 500	4.8	27 500	2.9
Na_2O	20 200	2.1	17 500	1.9
K_2O	39 100	4.1	46 800	4.9
P_2O_5	10 263	1.1	13 800	1.4

3.4. IR-spectra

Interpretation of IR-spectra of the investigated objects (Figure 6) has been performed with the use of well-known monographs [32-34]. There are absorption peaks at 1364.9 cm^{-1}, 1362.1 cm^{-1} and 1358.5 cm^{-1} in IR-spectra of the crude oil-contaminated soil, the neutralized soil and the neutralizer respectively, characterizing the symmetrical deformation variation of *C-H* bond in methyl (CH_3) groups. More intense absorption peaks were found at 1477.9 cm^{-1}, 1478.5 cm^{-1} and 1483.1 cm^{-1} corresponding to the *C-H* bond deformation variation in methylene (CH_2) groups. Two groups of absorption peaks at 2856.1 cm^{-1}, 2859.2 cm^{-1}, 2892.8 cm^{-1}, and 2923.3 cm^{-1}, 2925.6 (2959.7) cm^{-1}, 2967.4 cm^{-1} indicate valence variations of the *C-H* bond in methyl and methylene groups. A comparison of the corresponding absorption intensities showed that after neutralization the methyl and methylene group content was reduced by an average of 30-40%.

It is known that the symmetrical deformation variation of the *C-H* bond in methyl groups is shown about 1375 cm^{-1}, but in the composition of complex compounds it moves towards low frequencies and has a higher intensity due to the neighborhood with the carbonyl group (*C=O*) [33]. Absorption peaks at 1797.2 cm^{-1} and 1790.9 cm^{-1} correspond to valence variation of carbonyl group of a high-molecular hydrocarbons fragment. No infrared absorption frequencies have been determined in the neutralizer spectrum in this area. In addition, the absorption degree of the carbonyl group in the crude oil-contaminated soil is 29% higher than in the neutralized soil, which can give information on reduction of asphaltenes content after neutralization.

Absorption peaks of 1415.3 cm^{-1}, 1415.5 cm^{-1}, and 1411.3 cm^{-1} on the spectra of the crude oil-contaminated soil, the neutralized soil and the neutralizer indicate the availability of carbonate-anion $\left(CO_3^{2-}\right)$. Content of carbonate-anion is less in the neutralized soil by 33% than in the crude oil-contaminated soil. This can be explained by the decomposition of carbonates during the neutralization process:

$$MeCO_3 + 2OH^- \leftrightarrow Me(OH)_2 + CO_3^{2-}, \quad (3)$$

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2\uparrow. \quad (4)$$

The remainder of these anions is in the neutralized soil in the form of metal carbonates, mainly calcium carbonate, since the calcium content is substantially higher than that of sodium, potassium and magnesium (Table 6):

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O. \quad (5)$$

The availability of carboxylic acids (*-COOH*) having an internal hydrogen bond is confirmed by peaks at 1649.9 cm^{-1} (crude oil-contaminated soil), 1652.7 cm^{-1} (neutralized soil) and 1651.8 cm^{-1} (neutralizer). The availability of the carboxylic acid absorption band is due to the presence of humic additives in the reaction mixture. At the same time their content is more by 47% and 29% in the neutralizer and the crude oil-contaminated soil respectively than in the neutralized soil.

The availability of acetylene compounds is confirmed by valence variations of *C≡C* bonds in monosubstituted alkynes and disubstituted alkynes, in which the substituents are different, by absorption peaks respectively: 2139.5 cm^{-1} (crude oil-contaminated soil), 2140.1 cm^{-1} (neutralized soil), 2141.7 cm^{-1} (neutralizer) and 2195.3 cm^{-1} (crude oil-contaminated soil), 2196.4 cm^{-1} (neutralized soil), 2197.8 cm^{-1} (neutralizer). At the same time it turned out that the number of bonds of *C≡C* in mono- and the disubstituted alkynes in the crude oil-contaminated soil and the neutralized soil is the same and almost three times less than in the neutralizer.

Absorption peaks of 2025.9 cm^{-1} and 2062.0 cm^{-1} (crude oil-contaminated soil), 2025.8 cm^{-1} and 2062.6 cm^{-1} (neutralized soil), 2025.8 cm^{-1} and 2062.6 cm^{-1} (neutralizer) fall into the band of overtones (2222-2000 cm^{-1}) characterizing the combination of antisymmetric deformation and torsional vibrations of NH_3^+ groups. The group content in the neutralizer is on average two times more than in the crude oil-contaminated soil and the neutralized soil.

Peaks 870.9 cm^{-1} (crude oil-contaminated soil), 860.7 cm^{-1} (neutralized soil) and 854.0 cm^{-1} (neutralizer) falling into the absorption band 900-675 cm^{-1} correspond to out-of-plane deformation vibrations of *C-H* bonds in mono- and polynuclear aromatic compounds. The amount of this type of bonds in the crude oil-contaminated soil is more by 50% compared to the neutralizer and the neutralized soil.

Presence of heterocyclic aromatic compounds in the investigated object compositions is indicated by availability of peaks on their band absorption spectra 1100-1000 cm^{-1} and 1580-1520 cm^{-1}. The first of them, which characterizes deformation vibrations of *C-H* bond in heterocyclic aromatic compounds, includes peaks equal to 1061.0 cm^{-1} (crude oil-contaminated soil), 1070.2 cm^{-1} (neutralized soil) and 1068.5 cm^{-1} (neutralizer). In the second of them, which characterizes valence variations of bonds *C=C, C=N* in heterocyclic aromatic compounds, peaks are shown at 1567.4 cm^{-1} (crude oil-contaminated soil), 1573.1 cm^{-1} (neutralized soil) and 1575.1 cm^{-1} (neutralizer). After neutralization, the first kind of bonds is reduced by 20%, and the second kind remains practically constant. This fact suggests that in the neutralization process the content of heterocyclic aromatic compounds with substituted nitrogen atoms is not varied, but heterocycles with substituted atoms of other elements (e.g. O, S, V, Ni, Ti) are decreased.

The availability of silicates was found in the neutralizer (954.7 cm^{-1}) and the neutralized soil (954.8 cm^{-1}). These peaks characterize variations in *Si-O-Si* bonds (970-940 cm^{-1}).

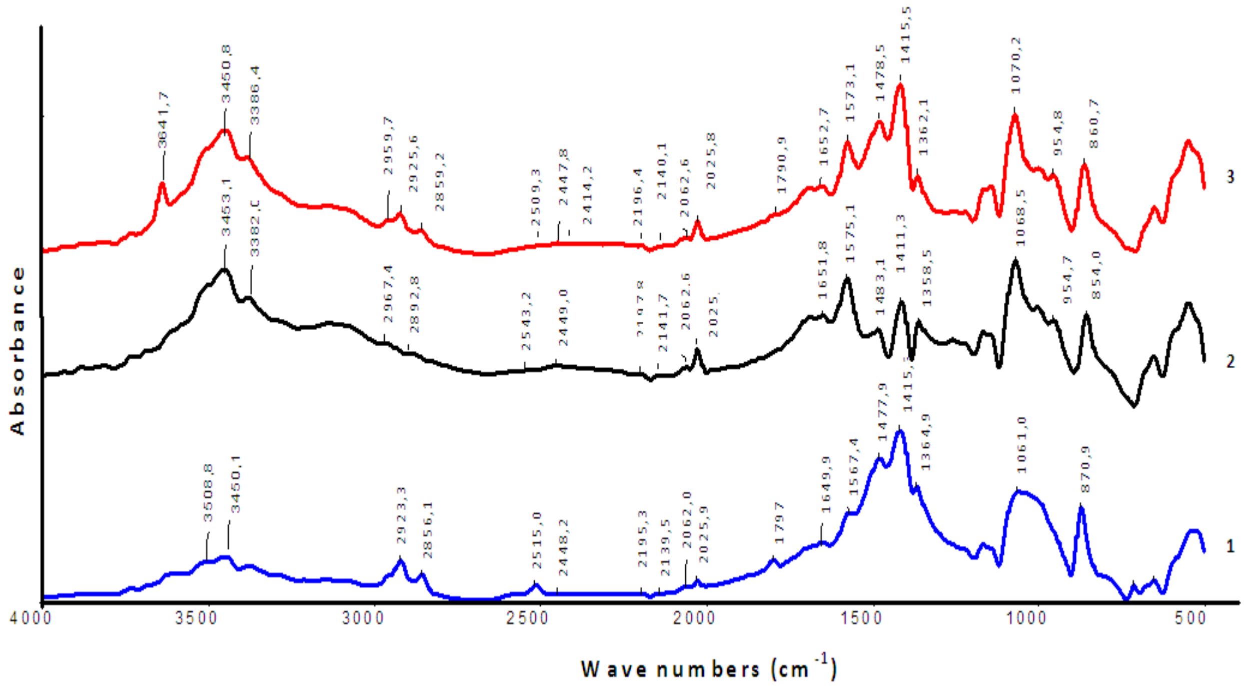
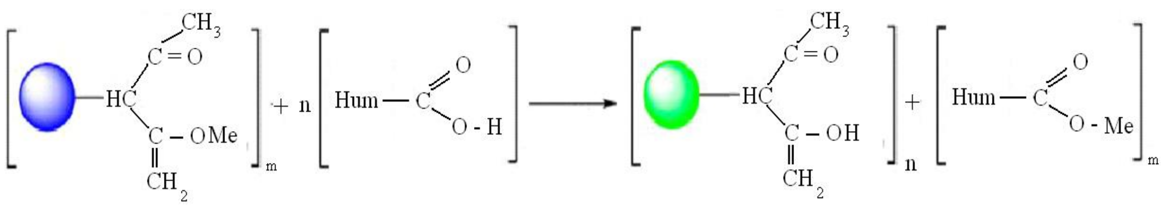


Figure 6. IR-spectra of samples: 1 – crude oil-contaminated soil; 2 – neutralizer; 3 – neutralized soil.

The crude oil-contaminated soil contains unsaturated toxic hydrocarbons which react with the neutralizer. At the same time, the chemism of the current processes at neutralization of the crude oil-contaminated soil can be described by the following equation:



(6)

where  are hydrocarbons and heterocyclic compounds before neutralization;

 are hydrocarbons and heterocyclic compounds after neutralization.

Thus, when neutralizing the crude oil-contaminated soil heavy oil fractions can be subjected to chemical degradation with forming of low-toxic hydrocarbons.

3.5. Stabilized soils

In order to study the possibility for the use of the neutralized soil in road construction, nine mixtures of stabilized soil have been considered (Table 7). As can be seen, the first three mixtures contain 60% of crushed stone, 15% of sand and 25% of neutralized soil. Their Portland cement content is 6%, 7% and 8%, respectively. They also contain different amounts of water. The other six mixtures do not contain sand. In the second and third triple of mixes the content of crushed stone and the neutralized soil is 50%, 50% and 30%, 70% respectively. Content of Portland cement is equal to 9%, 10% and 11%.

For visual reference the granularmetric curves of the neutralized soil and one of the stabilized soil mixes are represented in Figure 7.

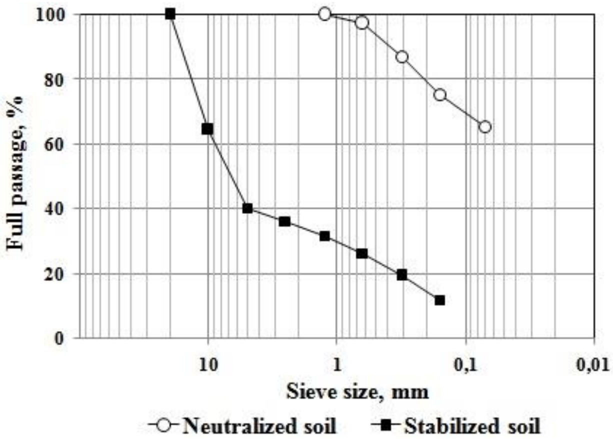


Figure 7. Granularmetric curves for the neutralized soil and the stabilized soil.

Engineering characteristics of the stabilized soils are given in Table 8, from which it can be clearly seen that all strength indicators are increased with the increase of crushed stone and Portland cement content in the mixtures. As expected, compression strength is decreased in all cases as the number of freeze and thaw cycles is increased. The reduction in strength after 10, 15 and 25 cycles of freezing and thawing is on average 16%, 38% and 53%, respectively.

Table 7. Composition of the stabilized soil mixes.

Mix No.	Composition, %				
	stone	sand	neutralized soil	Portland cement	water with wetter
I-1	60	15	25	6	6.3
I-2	60	15	25	7	7.2
I-3	60	15	25	8	7.6
II-1	50	-	50	9	8.0
II-2	50	-	50	10	9.3
II-3	50	-	50	11	9.8
III-1	30	-	70	9	10.2
III-2	30	-	70	10	11.5
III-3	30	-	70	11	12.2

Table 8. Characteristics of the stabilized soil mixes.

Mix No.	Maximal density, g/cm³	Strength, MPa		Compression strength (MPa) after freeze-thaw cycles		
		compression	bending	10	15	25
I-1	2.11	4.0	1.0	3.5	2.0	1.8
I-2	2.08	4.5	1.2	4.0	3.5	3.0
I-3	2.07	4.8	1.3	4.2	3.6	3.1
II-1	2.00	2.8	0.7	2.4	1.8	1.2
II-2	2.03	3.5	0.8	3.0	2.0	1.4

II-3	2.05	4.0	1.0	3.5	2.5	1.6
III-1	2.04	2.0	0.6	0.6	-	-
III-2	2.06	2.5	0.7	0.8	-	-
III-3	2.07	3.2	0.8	2.0	1.6	1.0

According to the regulatory document [35] all public roads in the Republic of Kazakhstan are divided into five categories depending on traffic intensity (Table 9). The higher the road category, the more strong and durable materials are used for their pavements. At the same time for the roads of I-IV categories the surface (first) layer of pavement is arranged from an asphalt concrete. As the multiyear design practice shows, pavement of a road of the III category has two layers of the asphalt concrete with a total thickness of 10-12 cm, and roads of the I and II categories have three layers of asphalt concrete with a total thickness of 15-18 cm.

Table 9. Categories of automobile roads.

Traffic intensity, car/day	**I**	**II**	**III**	**IV**	**V**
Category of automobile road	>7000	3000-7000	1000-3000	100-1000	<100

Stabilized soils on roads of the I-IV category roads can be used as a base layer material and a subbase layer material, and on V category roads as a pavement material [36].

Table 10 shows the conditions for using of the stabilized soils with the neutralized soil of different composition. Figure 8 shows a map of isoline of minimal temperature of -30° C on the territory of Kazakhstan. A joint analysis of these Tables and the maps shows that the stabilized soil containing 70% of the neutralized soil and 9-10% of Portland cement cannot be used in road construction in Kazakhstan. The stabilized soils of all other compositions can be used as a material of the base layer for pavements. At the same time only the stabilized soils of I-1 and I-2 (60% of crushed stone, 15% of sand, 25% of the neutralized soil and 7-8% of Portland cement) can be used for roads of the III, IV and V categories, and all others can be used only for roads of the IV and V categories. According to climatic requirements only mixtures of I-1 and I-3 are allowed to be used in the areas with minimal temperature below -30° C, and the remaining mixtures can be used only up to -30° C.

Table 10. Conditions for the use of the stabilized soils with the neutralized soil.

Mix No.	**Road category**			**Pavement layer**		**Minimal temperature, °C**
	III	**IV**	**V**	**base layer**	**subbase layer**	
I-1		+	+	+		below -30
I-2	+	+	+	+		-30
I-3	+	+	+	+		-30
II-1		+	+	+		-30
II-2		+	+	+		-30
II-3		+	+	+		below -30
III-1	+	+	+		+	-5
III-2	+	+	+		+	-5
III-3		+	+	+		-30

Figure 8. Map of minimal temperature of -30° C on the territory of Kazakhstan.

3.6. Experimental section

An important stage in the implementation of new materials and technologies into road construction is the construction of an experimental section. The possibility for implementing of the proposed technologies and materials is checked during the construction of an experimental section.

In November 2014, near the city of Zhanaozen (Mangistau region), an experimental road section has been built using the stabilized soil with the neutralized soil. The test section has a length of 75 m and a pavement with a width of 3.5 m from the stabilized soil. The stabilized soil had the following composition: crushed stone of 5-20 mm fraction (50%), neutralized soil (40%), Portland cement of M 400 grade (10%), water with wetter (12%).

Crushed stone was supplied from “Shetpe” quarry, and the neutralized soil - from a storage site of the JSC “Ozenmunaigas”.

The technology for construction of the pavement was implemented in the following sequence: mixing of the crushed stone, the neutralized soil and Portland cement was performed at the storage site; the mixture of crushed stone, neutralized soil and Portland cement was brought to the experimental section and distributed on the surface of the subgrade (Figure 9); water with wetter is distributed from KamAZ tank truck (tank volume is 16 m^3); mixing of the mixture and water on the surface of the subgrade has been performed by an grader (Figure 10); pavement material - a graded mixture of the stabilized soil with the neutralized soil - is compacted by a smooth drum roller of Rascat brand (3 tons) (Figure 11).

As a result of the subsequent implementation of the above technology, a 15 cm thick pavement has been built (Figure 12).

Successful implementation of the project for the experimental section has shown the full possibility for the use of the neutralized soil in the road construction. Meanwhile the conventional machinery and road equipment are used for transportation, mixing, levelling and compaction.

Figure 9. Mixture of crushed stone, neutralized soil and Portland cement on the surface of subgrade.

Figure 10. Levelling of the stabilized soil layer.

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Figure 11. Compaction of the stabilized soil layer.

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Figure 12. The completed pavement from the stabilized soil.

4. Conclusion

In this work the following conclusions can be drawn on the basis of the obtained results on neutralization of the crude oil-contaminated soil and testing of the possibility for the use of the neutralized soil in the road construction:

1.The method has been proposed for neutralizing of the crude oil-contaminated soil using a neutralizer based on humine substances. The schemes have been developed for neutralization of the crude oil-contaminated soil in laboratory and production conditions. It is found that the maximal possible degree of neutralization (100%) is achievable at weight ratios of 1: 0.1: 0.3 for the crude oil-contaminated soil, neutralizer and water, and at the temperature of 80 ºC and duration of 15-20 minutes.

2.When neutralizing of the crude oil-contaminated soil, the low boiling hydrocarbon fractions (C_{12} – C_{17}) disappear completely, the high boiling hydrocarbon fractions (C_{20} – C_{23}) are essentially increased, the content of oil components and metals, including toxic ones, is decreased, i.e. the neutralization process reduces significantly the toxicity.

3.Laboratory methods evaluated the engineering characteristics for nine mixtures of the stabilized soil with the neutralized soil and determined the conditions for their use in road construction (road category, characteristic layer of pavement, minimal air temperature).

4.An experimental road section has been built using the stabilized soil with the neutralized soil (40%). Successful implementation of this project has shown the full possibility for the use of the

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