The Study of Processes of Electrochemical Treatment of Soils at the Pilot Test Site

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Abstract. The techniques of field testing of controlled electrochemical cleaning of soil from oil pollution and the experimental setup are described. The results of engineering-geological surveys of groundmass artificially saturated with petroleum products (used oil, gasoline) are presented. The processes of formation of zones of drying, accumulation of petroleum products in electroosmotic transport, changes in the structure of soil as a result of the phase transformation and dissolution of petroleum products are shown in detail. The phenomenon was established of oil coagulation in the pores of the soil when subjected to electric treatment leading to an increase of particle size of sand and clay components of the soil and contributing to its deactivation. The efficiency of electrochemical treatment of tight sand and clay soils was proved experimentally. Experiments confirmed the effectiveness of the integrated electrophysical control of soil properties changes in the process of treatment, and in combination with the previously established correlation dependencies – the possibility of the average assessment of the contamination factor change.

1 Introduction

Intensification and globalization of human impact on the surrounding natural environment is a characteristic feature of our time, causing its negative consequence in terms of the environment pollution [1-4]. Petroleum products (fuel, oil and lubricants) [5] are among the most common pollutants of soil in Kuzbass.

Functionally, the methods of purification from oil pollution fall into four main types: physical, chemical, physicochemical [6, 7], and biochemical [8-10]. There are three main approaches to combating pollutants: immediate removal of oil by means of its extraction from the ground; inactivation (detoxification) of oil directly in the solid mass, localization of oil products by creating of a protective screen around the anomaly preventing the further spread of oil spills [11, 12].

When processing low permeability clayey soils, a very promising method of electrochemical cleaning is used based on the integrated impact by the active substance and electric current. The main physical processes in electro treatment are as follows:

- electrothermal stimulation resulting in the change of the pollutant phase state;
- dissolution of the contaminant into light fractions followed by evacuation.

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When dispersive soil is exposed to electric current, its microstructure and its physical characteristics [13] change to a certain degree, including the conductive and dielectric properties [14, 15].

To identify patterns of changes of physical properties of soil in the electrochemical purification from oil pollutions, there were studies conducted in the KuzSTU laboratory which yielded the following main results:

- on a one-dimensional physical model, the phenomenon was established of the coagulation of oil in the soil pores during electro treatment leading to an increase in grain size of sand and clay components and correlated with the changes in the electrical resistance of the soil;

- the three-dimensional model confirmed that when electric current passed, it impacted the oil in the pores, and the oil moved in a solid cohesive state leading to an increase in the specific electrical resistance (SER) of the soil throughout the treatment area and to reduction in humidity.

In more detail the results of the laboratory studies are described in [16].

For industrial research of the processes occurring in the soil during the electrochemical cleaning from oil pollution the experimental plot of clay massif was prepared. The plan of the pilot area, the scheme of connection of electrodes and electric power installation are shown in Fig. 1.

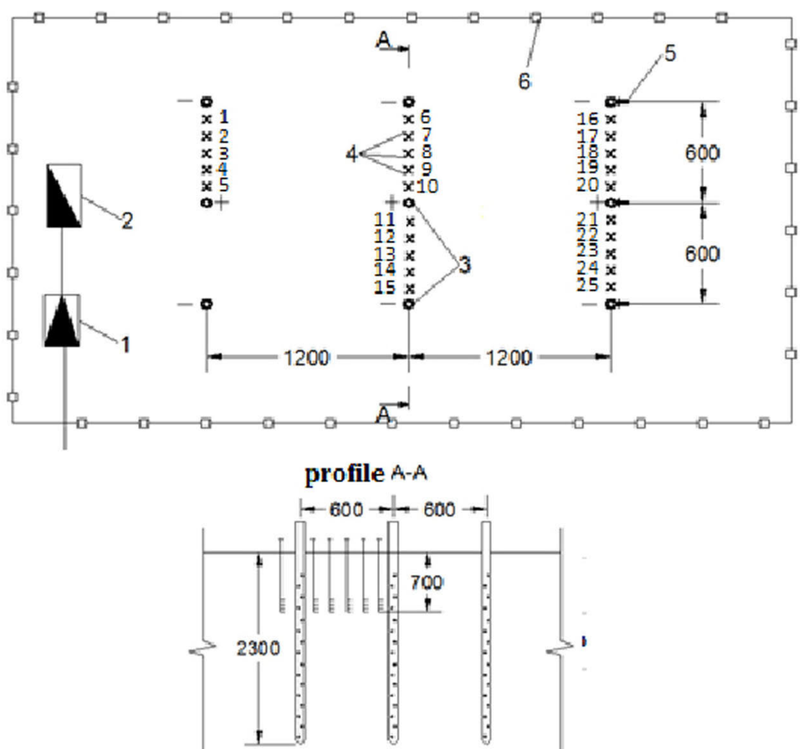

Fig.1. Diagram of the installation for field experiment: 1 – power transformer; 2 – rectifier-inverter; 3 – electrodes-injectors; 4 – microsensors of electrical resistance; 5 – feed of Hexane-n; 6 – temporary protective fencing; – electrodes-injectors; +, - polarity of the electrodes-injectors; x – SER microsensors

Near the place intended for cleaning there was installed an electric powertrain (power transformer TC-40, adjustable rectifier-inverter) and tanks for storage of polluting substances (waste oil and gasoline AI-80).

Direct current was supplied by cable type KG 4x25-0,66 from the installation to the electrodes. The range of the current intensity and voltages was from 0.1 up to 40 A and up to 360 V respectively. Perforated steel pipes with a diameter of 57 mm were used as electrodes-injectors. For electrochemical cleaning in series scheme of electrodes connection was used, with the polarity in the form: "cathode-anode-cathode". The distance between rows of electrodes was 1200 mm, and 600 mm between the opposite polarity electrodes.

The clay massif being in its natural state was artificially contaminated with oil for the experiment when the pollutant was injected in the blast holes with a 12 mm diameter to the depth of 700 mm (the cavity volume approximately 80 ml). The holes were placed every 80-100 mm uniformly in all directions. Oil contaminant from the cavities was absorbed into the soil, penetrating deeper and to the sides, thus having formed a contaminated area to a minimum depth of 2 metres, which corresponded to the parameters of soil contamination under natural conditions.

The main parameters of the experimental installation are the following:

- the total current consumption I·t – 3650 A·h;
- processing modes – electroosmotic mode for uncontaminated massif, electroosmotic mode for contaminated massif, electroosmotic with the dilution of the contaminant by the solvent "Hexane-n";
- polluting petroleum – gasoline A80; waste motor oil Shell Helix.

At all stages of the experimental research a continuous physical and technical control was carried out of the processes in the area of electro treatment including engineering-geological surveys and geophysical monitoring, both local (by SER microsensors) and integrated (electric sounding and ground penetrating radar). The information about the physical and technical methods of soil control is given in Table.1.

Table. 1. Methods of physical and technical control of processes in the treatment zone

Methods of control	**Equipment**	**Tasks to be solved, parameters to be defined**
Engineering-geological surveys	Field laboratory PL-2: a set of boxes to determine moisture, electronic balance, oven, a set of sieves	Determination of physical and mechanical properties and granulometric composition of the soil at different points in time
The SER microsensors	A logging tool KP-2 Sensors-microsondes	Monitoring of changes in the true resistivity of the soil in increments of 0.1-0.15 m
Electric sounding	A logging tool KP-2 rod electrodes	Determination of the effective electrical resistivity of the soil at various stages of electro treatment
GPR	GPR OKO-2	Diagnosing anomalies by the depth and in plan by the radargram

After the start of the clay massif electro treatment, measurements of all main characteristics were carried out twice a day, at the time of measurement the electric power unit was disconnected. At the end of electro treatment of the soil, sampling in the most characteristic areas (clean area, area contaminated with oil and area contaminated with gasoline) was performed, and physical and mechanical properties and granulometric composition of the soil were determined.

The total time of soil electrical treatment was over 168 hrs at current consumption per one pair of electrodes-injectors more than 600 A·h. The first area of clean clay was processed by a method of electro-osmosis without the addition of liquids in the electrodes in order to compare the obtained data with the results of treatment of contaminated clayey massif. The second and third areas contaminated with used oil and gasoline were treated by electric current without the use of active substance – solvent. The fourth and fifth areas were also contaminated with used oil and gasoline and treated by electric current and active substance – solvent Hexane. The solvent was supplied to the electrode-anode at the time point = 48 and 60 hrs in a volume of 4 liters at a time.

2 Results and discussion

To determine the physical properties of soils, a series of samples was selected in these areas prior to contamination of the clay massif, after its pollution by the oil products, and after completion of electrochemical treatment.

The results of the study of physical properties of soils before and after treatment of the massif are given in Table 2, and the granulometric composition of soil – in Table 3.

Table 2. Change of physical parameters of the soil as a result of electro treatment

Sample number	Characteristics (before contamination/before treatment/after treatment)		
	Moisture, %	Density in wet condition, g/sm^3	Density in dry condition, g/sm^3
# 1, clean clay	19.7/19.7/14.6	1.82/1.82/1.73	1.52/1.52/1.51
# 2, contamination with oil	19.7/20.1/17.1	1.82/1.80/1.71	1.52/1.5/1.46
# 3, contamination with gasoline	19.7/19.8/15.5	1.82/1.82/1.71	1.52/1.52/1.48
# 4, contamination with oil using solvent	19.7/20.1/15.7	1.82/1.91/1.79	1.52/1.59/1.55
# 5, contamination with gasoline using solvent	19.7/19.8/14.8	1.82/1.87/1.77	1.52/1.56/1,54

Table 3. Change of granulometric composition of soil due to the electro treatment

Sample number	The contents of fractions (in mm), % (before/after treatment)				
	2	0.5	0.25	0.1	<0.1
# 1, clean clay	2/2.2	17.6/18.5	15.5/17.4	18.8/21.2	46.1/40.7
# 2, contamination with oil	2/3	17.6/20.2	15.5/21.3	18.8/27.9	46.1/27.6
# 3, contamination with gasoline	2/2.5	17.6/19.7	15.5/18.5	18.8/24.4	46.1/34.9
# 4, contamination with oil, using solvent	2/1.8	17.6/17.8	15.5/16.6	18.8/29.4	46.1/34.4
# 5, contamination with gasoline using solvent	2/2.8	17.6/19.3	15.5/19.2	18.8/27.7	46.1/31

From the data of Table 2 it follows that in the soil both clean and contaminated with various petroleum products, after the electro treatment chemical binding of moisture and oil takes place, resulting in an overall decrease in soil moisture by 3 to 6 % and decrease in its density by 3 to 7% in both wet and dry conditions. At pollution of soil with petroleum products there was an increase in moisture, as the content of pore fluid at the experimental soil plot increased. In comparison with the results of laboratory studies, the changes in moisture and density are less significant, because of the influence of the atmosphere and surrounding rock with natural moisture.

In the granulometric composition of the soil the significant changes were identified:

- in the clean soil a small decrease in the content of fractions < 0.1 mm, and the increase of fractions of 0.5 mm, 0.25 mm and 0.1 mm were identified;

- in the soil polluted with used oil there is a significant increase in the number of particles fractions of 0.1 mm, a small increase in the number of particles of fractions 0.25 mm, 0.5 mm, and thus there is a significant decrease in particles fraction < 0.1 mm due to the process of oil coagulation, adhesion of small particles, with a likely transition of oil from a liquid to a solid state, which is considered less toxic and environmentally harmful, and in electrochemical processing with a solvent, this process was less intensive than in processing by electric current without solvent;

- in the gasoline contaminated soil there also occurs a significant increase in the number of particles fractions of 0.1 mm, a small increase in the number of particles of fractions 0.25 mm, 0.5 mm and a significant decrease in particles fraction < 0.1 mm as in treatment with solvent and without solvent; increase in the number of larger particles in the soil polluted with used oil is more intensive than when contaminated with gasoline, as used oil is more dense and viscous than gasoline, it coats the particles of the soil to a greater degree during pollution and electro processing.

To determine objective quantitative indicators of the condition of the soil massif in electrochemical processing of oil-contaminated soil, the measurements were carried out of the effective resistivity ρ_k by the method of electrical sounding from the earth's surface.

Graphically, the results of the measurements are presented in Fig.2.

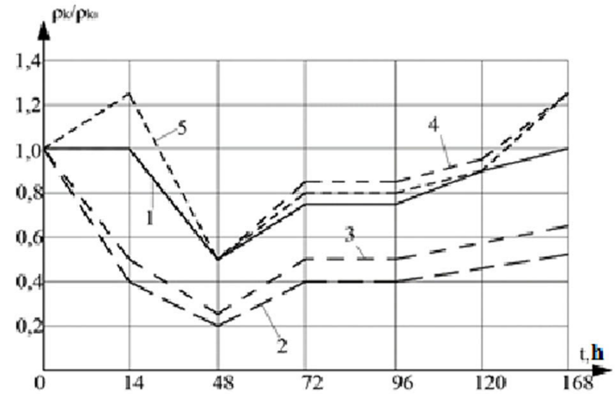

Fig. 2 The graph of changing of the relative effective electrical resistance in the electric sounding: 1 – clean clay massif; 2 – massif contaminated with used oil; 3 –massif contaminated with gasoline; 4 – massif contaminated with used oil processed with solvent, 5 – massif contaminated with gasoline processed with solvent.

In accordance with the theoretical background [17] outlined earlier, for transfer from the effective electrical resistance ρ_k to the contamination factor K_{cf} four dependencies were used: linear, logarithmic, parabolic and exponential. The equations shown in Table 4 were used to determine the coefficient of pollution in every moment of time measuring the effective electrical resistance ρ_k.

Table 4. The dependence of the rate of pollution K_{cf} on the relative change of the effective resistivity of the soil in the sample

Equation	Constant *a* when polluted by:		Primary K_{cf0}, %	Final K_{cff}, %	
	oil	gasoline		oil	gasoline
$k = a_1 \cdot \ln\left(\frac{\rho_k}{\rho_{k0}}\right)$	a_1=2.8	a_1=3,5	7	3,64	4,55
$k = a_2 \cdot \ln\left(\frac{\rho_k}{\rho_{k0}}\right)$	a_2=7,64	a_2=10,1		2	2,65
$k = a_3 \cdot \left(\frac{\rho_k}{\rho_{k0}}\right)^2$	a_3=1,12	a_3=1,75		1,9	2,96
$k = a_4 \cdot \exp\left(\frac{\rho_k}{\rho_{k0}}\right)$	a_4=0,575	a_4=0,95		2,11	3,49

The initial rate of pollution K_{cf0} (the ratio of volume of contaminant to volume of contaminated soil) was determined by the actual volume of the oil filled into the soil making $K_{cf} = 7$ %. Constants a_1-a_4 are included in the estimated equation.

Fig. 3 shows the change of coefficient of pollution in time. The graph shows that the rate of pollution over time decreases by the moment of processing time – $t = 48$ h, then increases until $t = 72$ h, and then almost does not change.

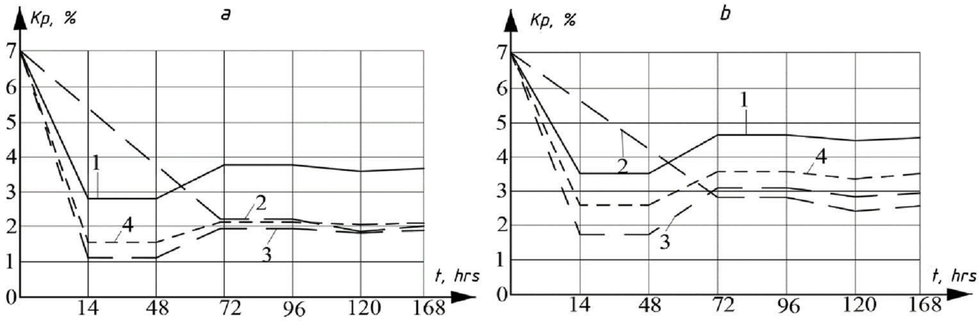

Fig. 3. Graph of changes in the concentration of used oil (a) and gasoline (b) in electro-processing depending on time t: 1 – linear relationship; 2 – logarithmic plot; 3 – parabolic dependence; 4 – exponential dependence.

The time of stabilization of value K_p is the criterion of the cessation of electro treatment, because the further electricity consumption does not lead to noticeable changes in the physical properties of soils.

3 Conclusion

Analysis of the results of engineering geological survey and geophysical soundings allowed us to make the following conclusions:

- when electric current passes and impacts oil products in the soil pores, they move in a solid cohesive state, and there is a decrease in moisture, which corresponds to the results of laboratory studies on one-dimensional and three-dimensional models, however, the ranges of these changes are lower, due to an additional supply of moisture from the atmosphere and surrounding soil with natural humidity;
- as a result of the electro thermal impact of direct current on the contaminated massif, the increase in the size of the particles and their adhesion take place, which leads to a change of granulometric composition of clay soil in the direction of increasing of the content of larger fractions and this increase is more intense in the contamination with more viscous oil products;
- in the processing of soil by electric current, the decrease in soil moisture and increase in the percentage of coarse particles lead to a decrease in soil density, both in wet and dry conditions;
- the process of phase conversion of oil-containing product in the soil pores due to electric and thermal coagulation occurs for any form of oil-pollutant, and when the solvent is used, the process of phase conversion is less intensive, however, this increases the volume of liquefied petroleum accumulated in the anode region;
- electrical sensing is provided by the integral control of changes of the soil properties during processing and in combination with the previously established correlation dependencies – the average assessment of changes in the rate of pollution. Electro treatment for 48-72 h reduces the degree of contamination of the soil by 2-3 times, while further dilution

of viscous oil by introducing into the electrodes of the solvent in the range of the ratio of pollution to 7% did not lead to noticeable positive effect.

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