Diagnostics of Oil Pollution Zones by Electro-Physical Method

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Abstract. The article presents the rationale and development of electro physical methods of control of the degree of soils pollution with petroleum products. The ranges of variation for the parameters of the pore space structure and wettability for the Kuzbass conditions are determined by inverse calculations on the basis of experimental data. The theoretical dependences are shown which allow us to assess the degree of soil pollution with oil products according to the results of longitudinal and areal electrical sounding. The study confirms the possibility of rapid prediction of the degree of soil contamination by measuring its electrical resistance. The database has been compiled for interpretation of the results of experimental sounding when monitoring the changes in the degree of contamination. The use of the express forecast of numerical values of the contamination factor was studied.

1 Introduction

One of the most dangerous soil pollutants are petroleum products: lubricants and liquid fuel [1, 2]. The relevance of the problem of cleaning soils from oil pollution in mining industry (coal surface and underground mines, ore mines) due to large amounts of fuel consumption by road and rail transport, and lubricants in the operation of mining equipment, and technical oils in electric power plants. The refined petroleum products contain toxic water-soluble fractions [3, 4], also, gasoline, and especially motor oils contain up to 20% of additives, solvents, heavy metals. One liter of used oil may contaminate one million liters of water, not more than 60% of their volume being regenerated

One of the effective methods for managing the soil properties, especially of low permeability (filtration coefficient $K_f < 10-8$ m/s), is the method of electrochemical treatment [5, 6], its main impact on the contaminated soil being the electrical destruction of ecotoxicants and the electroosmotic displacement of the diluted pollutant in the area of mechanical removal (pumping). Experimental and theoretical bases of the electrochemical method were developed for the solution of problems of technical reclamation (drainage) and for stabilizing the unstable waterlogged soils. The criteria for the rational use of this method are determined: the ratio of the coefficients of electroosmotic activity and filtration $K_e/K_f > 10^7$ and electrical resistance (SER specific electrical resistivity) $\rho < 8$ Ohm·m.

Direct and indirect methods are applied to control the processes of cleaning of soils from pollution. Direct methods [7-9] (infrared spectrophotometry, ultraviolet luminescence,

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gas and gas-liquid chromatography) require sophisticated equipment, significant duration of the analysis and extraction of soil samples, the measurement error can reach 40-50%.

2 Materials and methods

Diagnosis and ongoing monitoring of soil condition, properties and physico-chemical processes in the area of electrical treatment can be provided by geophysical methods that are effective supplement to geotechnical investigations. Very promising for the study of contaminated soils are electrical and electromagnetic methods [10] based on the measurement of electric fields, because oil and petroleum products exhibit pronounced dielectric properties and therefore they are electrically contrasting.

To control the degree of soil pollution with oil products, it is advisable to use the dependence of electrical resistivity of the three-phase medium on porosity, moisture and electrical resistivity of the pore filler that is used in electrical prospecting and includes structural-textural empirical parameters [11, 12]:

$$\rho_k = \frac{\alpha \cdot K_n}{m^\beta \cdot W^\gamma} \cdot \rho_{\rm B} \tag{1}$$

where m is porosity (pore cavitation); W – coefficient of the saturation space of the pores and cracks; ρ_{e} – electrical resistivity of the solution, filling pore space, Ohm m; K_{n} , α , β , γ are empirical parameters that depend on the structural and textural features of the studied soils; K_{n} – is the parameter that takes into account the surface conductivity of clay microlayer on the surface of the pores; α – is the parameter depending on the type of geological deposits; β is the parameter determined by the structure of the pore space (mainly by tortuosity of the channels); γ – parameter that depends on the wettability of surface pores by the solution.

The ranges of variation of the parameters of the pore space structure $\beta = 1.3-2.2$ and wettability $\gamma = 1.8-3.3$ should be taken for conditions of Kuzbass on the results of the inverse calculations based on experimental data; and electrical resistivity of the pore filler is calculated by the formula of harmonic weighted average for the two-component media [13]:

$$\rho_{\rm B}^{-1} = \sum_{i=1}^{n} V_i \cdot \rho_i^{-1} = V_{\rm g} \cdot \rho_{\rm g}^{-1} + V_{\rm H} \cdot \rho_{\rm H}^{-1}, \qquad (2)$$

where ρ_{θ} , ρ_{μ} , ρ_{γ} – electrical resistivity of, respectively, weighted, oil and electrolyte, Ohm m; V_{μ} , V_{γ} – volume fraction in the solution, respectively of the oil and electrolyte.

Theoretical dependence (1) and (2) basically allow us to assess the degree of soil pollution with oil products according to the results of single measurements, longitudinal and areal electrical sounding [14].

To further analyze the process of electrochemical treatment of contaminated soils, it is necessary to have information about the electrophysical properties of natural aqueous solutions and liquids containing contaminants or saturated soils. Experimental studies of electrical properties of electrolyte solutions, containing oil-products, with the measurements at permanent and variable electric current.

Figure 1 shows the measurement results of the electrical resistivity ρ_9 of the NaCl solution depending on the salt concentration in solution and the a. c. frequency, and Figure 2 shows the same dependence of the specific electrical resistance ρ_{μ} of motor oil and gasoline. It follows from these data that all petroleum products are electrically quite contrasting, because their electrical resistivity is by at least 3 orders of magnitude higher than electrical resistivity of natural water solutions.



Fig. 1. The dependence of the electrical resistivity of solution ρ_3 on the salt concentration C in the solution: 1 – constant current; 2 - alternating current, f=10 Hz; 3 – 200 Hz; 4 - 1000 Hz.



Fig. 2. The dependence of the electrical resistivity ρ_{μ} of motor oil and gasoline on the frequency of the alternating current:1 - G-Energy F Synth 0W-40; 2 - Mobil Synt S 5W-40; 3 - Shell Helix Ultra (spent); 4 - Shell Helix Ultra; 5 - gasoline AI-92.

By substitution into equation (2) the data of Figure 1 and Figure 2, the dependences of the average values of ρ_e on the relative content of petroleum products V_{H}/V_{3} for DC (Fig. 3) and AC (Fig. 4) currents.



Fig. 3. The dependence of the average values of ρ_s on the relative content of the petroleum products when measured at DC current: 1 - the salt concentration in the solution C = 0.1 g/l; 2 - 0.5 g/l; 3 - 2 g/l; 4 - 10 g/l.

The given dependences allowed us to form the database for interpretation of the results of experimental sounding when monitoring the changes in the relationship V_{H} / V_{5} e by ρ_{κ} value [15].

To quantify the degree of saturation by the pollutant, the coefficient of soil contamination k is introduced that is equal to the ratio of the volume of oil contained in the soil pores to the total volume of the pore fluid. By transformation of equations (1) and (2) it is possible to obtain the following expression:

$$V_{\rm H} = \frac{\rho_{\rm H} - \frac{\alpha \cdot k_n \cdot \rho_{\rm g}}{\rho_{\rm k} \cdot m^{\beta} \cdot W^{\gamma}}}{\rho_{\rm H} + \rho_{\rm g}} \approx 1 - \frac{\alpha \cdot k_n \cdot \rho_{\rm g}}{\rho_{\rm k} \cdot m^{\beta} \cdot W^{\gamma}}, \qquad k = m \cdot V_{\rm H}$$
(3)

where $V_{\rm H}$ – the volume fraction of the pores filling with oil.



Fig. 4. The dependence of the average values of electrical resistivity on the alternating current frequency and concentration of salt in the electrolyte C = 0.5 g/l (a); 10 g/l (b): 1 - f= 10 Hz; 2 - 200 Hz; 3 - 1000 Hz

The theoretical dependence (3) allows us to estimate the degree of soil pollution with oil products according on the results of single measurements, profile and areal electrical soundings using cyclic algorithms that are implemented in the software package created in the software product Lazarus (environment Free Pascal).

3 Results and discussion

To control the processes of cleaning soil of oil pollution by the electrophysical parameters, it is recommended to use two schemes of sounding from the earth's surface: for partially open facilities and for closed facilities. When using the four-electrode method of sounding from the earth's surface, standard metal feeding electrodes are grounded in the soil beyond the treated area boundaries, using electrodes-injectors as measuring ones. The location of the electrodes-injectors and feeding electrodes for partially open and closed objects is shown in Fig.5.



Fig.5. Circuit that control the processes of electrical treatment for partially opened (a) and closed (b) objects: 1 – pollution zone; 2 – feeding electrodes A, B; 3 – electric power unit; 4 – electrical exploration equipment; 5 – area of contamination; 6 – structure

The control results are used to plot the graphs of change in the effective electrical resistivity ρ_{κ} along the main axis of the electrical treatment and depending on the power consumption or time (Fig.6).

The main purpose of monitoring is to identify points of correction of the modes or the termination of electrical treatment, as well as the calculation of the coefficients of pollution before and after treatment.

For Express forecast of the numerical values of the contamination factor, they use four design dependences obtained in the processing of the data received from experimental field studies: linear, logarithmic, parabolic and exponential. The constants a_1 - a_4 were determined for a known initial contamination factor $k_0 = 7$ % that is equal to the ratio of the volume of contaminant to volume of contaminated soil. According to the equations given in the table, the contamination factor k was found at each point in time of the measurement of the effective resistivity.



Fig.6. Graph of changes in time *t* of the relative effective electrical resistance ρ_{κ} at electrical sounding in the process of experimental electrical treatment: 1 – clean clay massif; 2 – contaminated array treated with oil; 3 – array contaminated with gasoline; 4 - array contaminated with used oil and treated with solvent, 5 - array contaminated with gasoline and treated with solvent

 Table 1. The dependence of the contamination factor k on the relative change of the effective resistivity of the soil in the treatment area (experimental data)

Equation	The value of the constant <i>a</i> at pollution		The value <i>k</i>		
			initial <i>k</i> 0, %	final k_{κ} , %	
	oil	gasoline	, ,	oil	gasoline
$k = a_1 \cdot \frac{\rho_{\kappa}}{\rho_{\kappa 0}}$	<i>a</i> ₁ =2.8	<i>a</i> ₁ =3.5	7	3.64	4.55
$k = a_2 \cdot \ln(\frac{\rho_{\kappa}}{\rho_{\kappa 0}})$	<i>a</i> ₂ =7.64	<i>a</i> ₂ =10.1		2	2.65
$k = a_3 \cdot (\frac{\rho_{\rm K}}{\rho_{\rm K0}})^2$	<i>a</i> ₃ =1.12	<i>a</i> ₃ =1.75	,	1.9	2.96
$k = a_4 \cdot exp(\frac{\rho_{\kappa}}{\rho_{\kappa 0}})$	<i>a</i> ₄ =0.575	<i>a</i> ₄ =0.95		2.11	3.49

Fig.7 presents the change in the coefficient of pollution k_3 (concentration of oil) in time. The graph shows that the coefficient of pollution k_3 with time decreases until t = 48-72 h, and then stabilizes. The time of stabilization of the calculated value of k is an objective criterion for the termination of electrical treatment as any further exposure of the array does not give any significant positive effect.



Fig.7. Graphs of change in concentrations of waste oil (a) and gasoline (b) during electrical treatment depending on time t: 1 – linear dependence; 2 – logarithmic dependence; 3 – parabolic dependence; 4 – exponential dependence.

4 Conclusions

The dependence of electrical resistivity (electrical resistivity) of the three-phase medium on porosity, moisture and electrical resistivity of the pore filler, calculated according to the formula of the harmonic weighted average is the physical basis of electrophysical methods of control of the degree of pollution of soils with petroleum products, while for the conditions of Kuzbass the ranges of change in structural parameters of the pore space and wettability are, respectively, $\beta = 1.3$ -2,2 and $\gamma = 1.8$ -3.3. On the basis of experimentally established ranges of change of the resistivity of an aqueous solution ($\rho_{\rm B} = 0.2$ -80 Ohm m) and major types of petroleum products (fuel, engine oil) ($\rho_{\rm H} = (0.2$ -1.1)¹⁰⁶ Ohm m), the databases were calculated for dependences of the effective specific electric resistivity $\rho_{\rm K}$ on the ratio of the volumetric proportion of oil and moisture in the range of V_H/V_B = 0-20.

Express-control of changes in contamination factor k in the process of electrical treatment of the soil is ensured according to the value of the effective electrical resistivity ρ_{κ} for the scheme with the zone-by-zone integral sounding using as electrodes-injectors as the measuring ones. During the experimental trials after treatment for 168 h, the value of k when contaminated with used oil declined from 7 to 2.11 %, and when polluted with gasoline – to 3.49 % (exponential dependence). Stabilization of the k value at a minimum level is a criterion for the transition to a more intensive mode of electrical treatment or, if the capacities of the power electric unit are exhausted – this is a sign that further treatment makes no sense.

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