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Conference Paper

Theoretical Bases of Electrochemical Cleaning of Oil-contaminated Soil

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Abstract

This study developstheoretical bases for the electrochemical process of cleaning soils from oil, oil products and highly mineralized reservoir water. The article experimentally and theoretically reveals patterns of reducing the content of polluting oil products in soils of various types during the small voltage passing. The optimal amount of electricity for the effective removal of various types of pollution was required. For the implementation of a electrochemical soil cleaning process a scheme of an original installation with placement of electrodes in the soil was studied. It reduces the resistance between the electrodes. The technical and economical calculations to determine energy costs of the electrochemical installation for cleaning oil-contaminated soils included: the number of electrodes; the voltage depending on the properties of the soil; the area; the depth of contamination of the soil to be treated;azndthe parameters of the electrodes. This allowed us to determine and develop the required degree of cleaning.

Keywords: electrochemical process, charge, soil, oil products, voltage, cleaning

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A large amount of oil-containing waste is generated annually in the oil and oil refining industry. According to the State Report "About the State and Environmental Protection of the Russian Federation in 2017", about 10 million tons of waste are generated by the country's largest oil producing enterprises, of which 945,8 thousand t arethe oil sludge [1]. One of the types of generated waste is soil contaminated with oil and oil products. It belongs to III or IV hazard class depending on the content of oil products (medium hazardous and low hazardous waste). The area of land contaminated by oil companies in 2017 amounted to more than 3410 ha [1]. The development and improvement of methods of oil-contaminated soil cleaning is an actual problem.

Electrochemical cleaning of oil-contaminated soil is a universal and interesting method and it is possible to use it for soil treatment throughout the depth of pollution without excavation and transportation, as well as to partial removal of polluting

components. Electrochemical cleaning is a set of processes that occur under the influence of an electric current at a relatively low density.
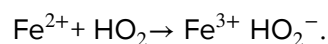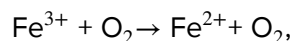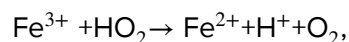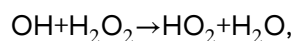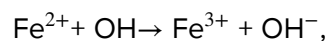
Electrokinetic reactions are the transferring of pollutant particles in a liquid or solid phase towards one of the electrodes. Usually electroosmosis, electrophoresis, flow potential and sedimentation potential ate separated. Electroosmosis and electrophoresis are considered predominant. In the case of a high concentration of contamination the oil moves to the cathode with electrokinetic transfer and can be pumped out of the electrode well.

Oxidation reactions occur in the soil under the influence of an electric current and are subdivided into direct and indirect. Direct oxidation of pollutants include gaseous substances formed at the anode (such as chlorine, oxygen, etc.), however, it does not play a leading role in soils.

In the presence of oil products in the soil the indirect oxidation have greater importance [2]. Hydrogen peroxide H_2O_2 is formed at the cathode and can either directly participate in soil redox reactions or transform into a hydroxyl radical (OH). The formation of the latter occurs in the presence of iron (II) ions:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH + H_2O.$$
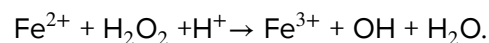
In this case, we should talk about the emergence of the Fenton system, which includes a number of chemical reactions with the formation of radicals [3]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-,$$
$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^-,$$
$$OH + H_2O_2 \rightarrow HO_2 + H_2O,$$
$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + H^+ + O_2,$$
$$Fe^{3+} + O_2 \rightarrow Fe^{2+} + O_2,$$
$$Fe^{2+} + HO_2 \rightarrow Fe^{3+} HO_2^-.$$

Hydroxyl radical will have the greatest activity in the oxidation of organic compounds in soils. It can oxidize hydrocarbons, ideally to carbon dioxide and water, as well as to intermediate oxidation products depending on the conditions.

The possibility of occurrence of these electrooxidaton processes in the soil is largely due to the presence of particles capable of conducting electric current which are calling "microconductors", on the surface of which radicals are also forming [2]. Such particles include iron-containing minerals, graphite, and some others. Thus, electrooxidative processes can occur not only on the electrodes, but also in the entire soil volume between them.

These electrooxidative processes, in contrast to kinetic ones, require different conditions: lower voltage and current density (approximate current density about 1 mA/cm^2) and can reduce the concentration of many organic pollutants, but require long-term processing. They are called "advanced oxidation processes", and in the soils - Electro-Chemical GeoOxidation (ECGO) [4].

Other processes, such as electrocoagulation, electroflotation, and evaporation of polluting components at high voltages and heating may occur in the soil too. The identification of all processes occurring in the soil under the influence of an electric current is extremely difficult due to the variety of conditions and natural soil physicochemical and biological processes.

For the studying of electrochemical cleaning of oil-contaminated soil in laboratory conditions similar to oil spills during production were simulated by the adding of oil products and salt solution of formation water of the field (containing NaCl, CaCl$_2$, MgCl$_2$, Na$_2$SO$_4$, NaHCO$_3$) in an amount of 408,9 g/kg. We studied various levels of contamination of loam, clay and sand with oil, the most part of the experiments was carried out at contents of 1,1 g/kg and 11,0 g/kg.

Contaminated soil was placed in a plexiglas cell, where graphite electrodes were immersed and a current with different densities (40<j<350A/m^2) was applied. In all cases, an exponential dependence of the the oil products content decrease of in the soil on the amount of missed charge q was observed [5]:

$$\frac{C\left(t\right)}{C_{max}} = \left(1 - b\right)e^{-\alpha q} + b,\tag{1}$$

where C (t) is the concentration of petroleum products at time t,

Cmax - initial concentration of oil products,

α, b - coefficients depending on the type of soil.In particular, $\alpha \sim$ 3-5 $\cdot$ 10^{-3} C^{-1}, and b $\sim$ 0,1-0,35.

$$q = \int_0^t I\left(t\right)dt.\tag{2}$$

After the passing an electric charge exceeding a certain value through contaminated soil, the concentration of oil products practically does not change. The limiting specific charges of electric treatment are 0,63 $\cdot$ 10^7 for clay, 0,93-0,96 $\cdot$ 10^7 for loam, 1,34 $\cdot$ 10^7 C / kg of oil products for sand [6].

A comparison of the efficiency of the process of electrochemical purification of loam of varying degrees of contamination is presented in Figures 1 and 2.

The cleaning efficiency varies depending on the type of soil. So the level ofcleaning for oil products in clay was approximately 84%, in loam - 76%, in sand - (69%). The high intensity of the process in clay can be explained by the high dispersion of the
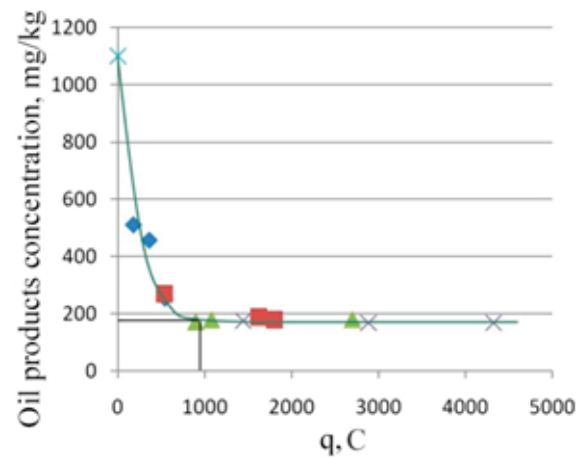
Figure 1: Change in the content of oil products as a result of passing of electric current in loam with a low oil content.
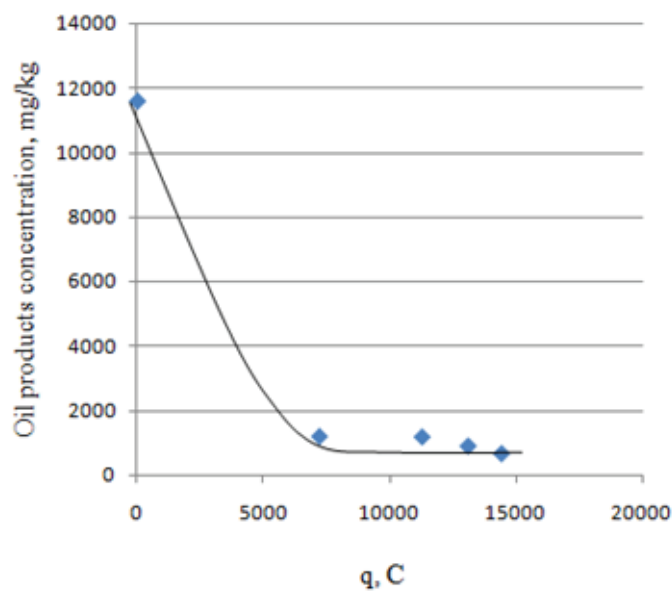
Figure 2: Change in the content of oil products as a result of passing of electric current in highly contaminated loam.

medium, which is an important indicator for electrokinetic processes. In addition Fe^{+2} ions are practically absent in the sand, which significantly limits the occurrence of redox reactions.

The placement of cathodes and anodes in parallel batteries, each connected by its own bus is more efficient and economical. The electric field created in the interelectrode space is close to uniform, which allows reducing the resistance of the medium. The specific resistance of soils depends on the pollution degree, moisture and soil type. In real conditions the resistance varies widely depending on the time of year and weather conditions. For soils with a moisture content of about 40%, containing more than 1000

mg of oil products per kg, this value varied from 0,93 Ω · m for sandy soil to 1,069 Ω · m for chernozem.

The density of the electric current passing between the electrodes is determined by the specific resistance of the soil ρ and the electric field strength E:

$$j = \frac{1}{\rho}E. \tag{3}$$

To determine the electric field generated by the electrodes, we use the first Maxwell equation:

$$\int \vec{E}d\vec{S} = \frac{\sum q}{\varepsilon\varepsilon_0}, \tag{4}$$

where q is the charge covered by a closed surface around the electrode;

ε is the relative dielectric constant of the medium (soil);

ε0 = 8,85 · 10^{-12} F/m - electric constant.

Integration is carried out over a cylindrical surface of radius R≤r≤L, the axis of symmetry of which coincides with the axis of symmetry of the positive electrode (anode), and the height is equal to the immersion depth of the electrode.

From the symmetry of the lines of force of the electric field:

$$E \bullet 2\pi rH = \frac{\sigma \bullet 2\pi RH}{\varepsilon\varepsilon_0}, \tag{5}$$

where σ is the surface charge density of the electrode;

R is the radius of the electrode.

From the last equation:

$$E = \frac{\sigma R}{\varepsilon\varepsilon_0 r} \tag{6}$$

Expressing the surface charge density σ through the potential difference between the electrodes, we obtain:

$$E = \frac{U}{rln\frac{L}{R}} \tag{7}$$

Thus, the density of electric current in the space between the electrodes is determined by the ratio is

$$j = \frac{U}{\rho rln\frac{L}{R}}, \tag{8}$$

and electric current of one anode is:

$$I = \int jds \approx \frac{2\pi H}{\rho ln\frac{L}{R}}U. \tag{9}$$

It can be seen from the last equation that at a given voltage between the electrodes the amperage decreases with increasing distance L, and increases with increasing immersion depth.

The "elementary" cell amount is k = S / 4L^2. Sothe number of anodes required to treat a plot of soil contaminated with oil products with area S will be: Z_A = 2k=S/2L^2.

The total current between the electrodes is adopted by the equation

$$I_s = \frac{\pi S H}{L^2 \rho ln\frac{L}{R}}U,$$ (10)

then the power consumption will be

$$W_s = I_s U t,$$ (11)

where t is the treatment time of the oil-contaminated area, determined by the initial concentration of oil products in the soil [7].

Thus the technology of electrochemical cleaning of oil-contaminated soil is most suitable for clay and loamy soils. For the cleaning of sandy soils it is better to reduce the oil content by other methods primary (for example, using sorbents), or additionally introduce Fe^{2+} ions into the soil to intensify electrochemical oxidation.

The derived dependences allows to calculate the number of electrodes and the voltage between them, the treatment time for a given area and contamination depth, the properties of the contaminated soil and the required cleaning degree.

Funding

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