The Electrochemical Cleaning of Various Types of Soils Contaminated with Reservoir Water and Oil

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Abstract. The constant development of the technosphere leads to negative consequences, such as environment pollution by components with toxic properties and violation of natural biosphere processes. The most significant negative effect of the functioning of the oil and gas production and processing complex is soil pollution. This article is devoted to the study of the features of the electrochemical cleaning process in various types of soils contaminated by oil and reservoir waters. The mechanisms of the hydrocarbons amount decrease are described. The greatest contribution is made by electrokinetic processes as well as by direct and indirect oxidation. The dependence of the content of petroleum hydrocarbons on the amount of transmitted electricity in several types of soil (clay, loam, chernozem and sand) is established. It has been established that there is the limit quantity of charge required for effective cleaning of each type of soil. This parameter primarily depends on the soil characteristics. It was revealed that at a high soil moisture the voltage differences are insignificant. The efficiency of cleaning for each type of soil was calculated. The clay soil has optimal conditions for electrical treatment (cleaning efficiency is 84.5%). The cleaning efficiency of sand soil was minimal.

1. Introduction

Oil contamination of soil is one of the most important ecological problems nowadays. There is a large number of technologies of oil-contaminated soils cleaning which differ in energy and efficiency. These are mechanical, thermal, sorption methods, bioremediation and phytoremediation among them [1, 2]. The electrochemical cleaning of oil-contaminated soils becomes more widespread.

The concept of "electrochemical cleaning" is quite broad and implies several processes simultaneously, which are initiated by electrotreatment of the contaminated medium [3-5]. In the case of soil cleaning the situation is more difficult because the soil is not only inert electrochemical cell, it is complex system with the large number of physicochemical and biological processes. So electrochemical soil processes are not completely known and are still studied by scientists. The study of the peculiarities of the electrochemical treatment is an actual problem.

There are several main directions of electrochemical processes [6].

The electrokinetic process is the processes of transportation of pollutant in a liquid or solid phase towards one of the electrodes. There are 4 types of electrokinetic processes: electroosmosis, electrophoresis, flow potential and sedimentation potential. The electroosmosis is the transfer of a liquid phase in the electric field. The flow potential is a phenomenon opposite to the electroosmosis. It is the potential difference which appears during the electrolyte flowing. The electrophoresis is the
movement of solid particles in the electric field. Clay particles detached from soil and move to the anode. The sedimentation potential is a phenomenon opposite to electrophoresis in which a potential forms during the charged particles sedimentation in the electrolyte medium.

Electro-oxidation is the next extremely important process that takes place in oil-contaminated soils. The electrochemical oxidation of oil products can be direct or indirect [7-11].

During the direct oxidation petroleum hydrocarbons are oxidizing by gaseous compounds produced at the anode (primarily molecular oxygen, chlorine and some other substances). Direct oxidation in soils is rather inefficient.

The greatest contribution is made by indirect oxidation [12]. In this case hydrogen peroxide H$_2$O$_2$ is produced at the cathode as a result of redox reactions, and in particular by the reduction of O$_2$ from air:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2.$$  

It can participate in soil redox reactions and also can be transformed into a hydroxyl radical (OH •). The formation of the hydroxyl radical occurs in the presence of iron (II) ions in Fenton reactions:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH^• + H_2O.$$  

The direct electro-generation of hydroxyl radicals from water at the electrodes has also been reported, with the following mechanism:

$$H_2O \rightarrow OH^• + H^+ + e^-.$$  

The hydroxyl radicals are highly active and oxidize organic substances in soils (oil products, PAHs) to carbon dioxide and water, as well as to intermediate oxidation products.

The most important feature of the soil oxidation processes is the ability of a number of particles (for example, some iron-containing minerals) conduct amperage. Such particles are microconductors which contribute to the occurrence of oxidation in the entire volume of the soil but not only at the electrodes [13].

Another advantage of electrochemical soil treatment (at low voltages) is the stimulation of native species of oil-oxidizing microorganisms by the temperature about 40 °C because of increase of nutrient transport and bioavailability.

The predominance of a particular process of the removal of oil products depends on many factors, primarily the characteristics of soils, the humidity of the environment, the concentration of electrolytes, the voltage and the processing time.

2. Practical part

The features of electrochemical cleaning of varieties of oil-contaminated soils named red clay, loam, sand and chernozem have been determined during the experimental studies [14].

The model soil was prepared with 408.9 g/kg of a concentrated salt solution (NaCl, CaCl$_2$, MgCl$_2$, Na$_2$SO$_4$, NaHCO$_3$) and 1.1 g/kg of oil. The amount of pollutants is the same as in the soil contaminated during an emergency spill at the oil producing field. The oil had the following characteristics: density 0.876 g/cm$^3$, kinematic viscosity at 20 °C 17.85 cSt, sulfur content 3.32%, water content 2.4%, mechanical inclusions 0.0204%, paraffin content 1.6%, asphaltenes content - 2.3%.

The salts solution was poured into the soil, everything was thoroughly mixed, then oil was added, after this the sample was mixed again. The soil was placed into the plexiglass electrochemical cell of rectangular shape of 161 cm$^3$. Two flat graphite electrodes connected to power supply with digital indication were placed in the cell. The electric treatment was carried out with amperage of 0.1 A, 0.3 A, 0.5 A and 0.8 A; experimental treatment time was 30 min, 60 min and 90 min.
The content of oil products in the soil was measured by infrared spectrometry according to the document "Determination of the total content of oil products in soil samples by infrared spectrometry" after the electrochemical treatment [15].

3. The experimental results
The determining of the efficiency of oil-contaminated soil cleaning showed significant differences. The best results of cleaning are in the clay, medium - in chernozem and loam, the lowest - in the sand (Table 1).

| Soil      | Cleaning efficiency (%) |
|-----------|-------------------------|
| Clay      | 84.52                   |
| Chernozem | 77.1                    |
| Loam      | 75.67                   |
| Sand      | 69.03                   |

The high intensity of the process in clay can be explained by the high dispersion of the medium, which is an important parameter of electrokinetic processes. This is consistent with the results of other researchers [16].

In addition indirect oxidation of oil products requires the presence of Fe$^{+2}$ ions in the soil, which are practically absent in the sand, so it limits the redox reactions significantly.

In all cases the exponential dependence of the content of oil products on the amount of electric charge transmitted through the soil was observed during the research (Figures 1-4).

![Figure 1](image1.png)  
**Figure 1.** The dependence of concentration of oil products on quantity of the skipped electricity in clay.

![Figure 2](image2.png)  
**Figure 2.** The dependence of concentration of oil products on quantity of the skipped electricity in sand.
It has been established that when the electric charge passed through the polluted soil exceeds a certain value, the concentration of oil products practically does not change. This value of the charge (the ultimate specific charge of electric treatment) was determined for all of the studied varieties of soil. The specific energy consumptions for cleaning have been additionally calculated too (Table 2).

**Table 2.** Specific limit charges and energy consumption of electrochemical treatment

| Type of contaminated soil | The limit specific charge of electrochemical treatment (coulombs/kg of oil products) | Specific energy inputs (MJ/kg of oil products) |
|---------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------|
| Chernozem                 | $0.96 \cdot 10^7$                                                                | 47.04                                         |
| Clay                      | $0.63 \cdot 10^7$                                                                | 28.98                                         |
| Loam                      | $0.93 \cdot 10^7$                                                                | 45.29                                         |
| Sand                      | $1.34 \cdot 10^7$                                                                | 59.9                                          |

The dependence of oil products concentration on the electrical charge ($q$) passing through the soil was established:

$$C(t) = C_{\text{max}}[(1 - b)\exp(-\alpha q) - \alpha q + b]$$

(1)

The coefficient $\alpha$ is characterized by the value of the limiting specific electric charge, and the coefficient $b$ is the ratio of the residual and initial content of oil products in the soil.

Studies have shown that voltage in the various soil types change insignificantly because of large content of water-salt solution (Figure 5).
Figure 5. Volt-ampere characteristic of soils.

The salt solution acts as the electrically conductive medium which neutralizes the influence of soil characteristics on the voltage. When the content of the electrolyte solution decreases, the process should intensify with an increase of the soil dispersity.

The analysis of the conducted experiments indicates the expediency of using electrochemical cleaning at oil-contaminated soils. The authors propose the location of electrodes for cleaning in practice (Figure 6) [17]. Electrodes are put into the ground wells which are drilled to the depth of contamination. Anodes are graphite to prevent their oxidation and destruction. It is advisable to make cathodes out of steel.

Figure 6. The electrodes location scheme.

The distance between electrodes depending on the amperage and voltage will be determined by the depth H, the electrodes radius R and soil resistivity ρ:

\[ l = R \cdot \exp \left( \frac{2nHU}{1p} \right) \]  \hspace{1cm} (2)

Electrodes location will significantly reduce the voltage between the electrodes and accordingly reduce the energy and material expenditure for the cleaning.
4. Summary
The electrochemical cleaning of soils contaminated with oil and reservoir water is the effective method of remediation. The maximum cleaning efficiency is in clay (84.5%), the least efficiency is in the sand (69%).

The analysis of the obtained results allows formulate recommendations for the practical use of the electrochemical cleaning of oil-contaminated soil. This technology is advisable at clay and loam. Its recommended to use additional remediation methods in sands before electrochemical treatment (for example sorption). It is perspective to use phytoremediation after the electrochemical cleaning of oil-contaminated soil which helps to restore disturbed ecosystems [18-21].

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