Changes of Characteristics of Soil Contaminated by Oil Products during Electrochemical Cleaning

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Abstract. The article deals with the actual problem of cleaning and remediation of soils contaminated in oil industry. The transmission of a small electric current through polluted soil leads to a decrease of pollutants concentration because of various processes. The paper presents the results of the study of changes in soil characteristics as a result of passing the electric current. Such parameters as the content of chlorides and organic matter of the soil (humus), electrical conductivity, density and soil moisture were studied. The research showed that carrying out low amperage electricity through the soil contaminated with oil and highly mineralized reservoir waters using does not entail critical changes in the soil properties. It was proved that this method can be effectively applied on various soils of oil fields and will not impede the subsequent restoration of plant communities at the treatment site.

1. Introduction

Nowadays cleaning technologies for soils contaminated with oil and oil products are actively developing. The specificity of pollution at oil production is that soil can be polluted not only by oil, but also by reservoir and formation water. Such water is characterized by a high content of various salts. In this regard, the priority is given to technologies that allow the comprehensive cleaning of soils with the removal of both groups of pollutants – petroleum hydrocarbons and mineral salts. One of the methods for solving this problem is the electrochemical soil cleaning.

The method of electrochemical soil cleaning is universal and can be used for desalting and removing a complex of substances (oil products, heavy metals, phenols, etc.) \cite{1-5}. To implement this method electrodes connected to a constant voltage source are immersed in the soil to the depth of contamination. Also drainage can be additionally installed in the electrode wells. Electric current contributes to the directional movement of salt ions and oil products in aqueous phase to the corresponding electrodes. They can be pumped out in the form of aqueous solutions \cite{6, 7}. There are parallel electrochemical reactions leading to the pollutants transformation \cite{8-12}. The nature of these processes is determined by the soil characteristics, pollutants, weather conditions and other factors.

Electrochemical cleaning impact not only on the pollutants, but also on the soil, its properties and composition. It is necessary to implement such treatment regimes that would not cause degradation processes and secondary pollution, but on the other hand did not weaken the effect of soil cleaning. So it is very important to study the soil properties before and after the electrochemical cleaning.
2. Practical part
In the works [13-15] the results of laboratory studies of the efficiency of the use of electrochemical cleaning of various soils contaminated by oil and highly mineralized reservoir waters are presented. Contaminated soil from the oil spill at the oil deposit (named “chernozem”) and model soil based on clay, loam and sand contained 1100 mg / kg of oil products and 408900 mg / kg of salt solution. The composition of the salt solution corresponded to the formation waters of the field and is given in the table 1.

Table 1. Composition of the salt solution.

| Component     | Content (mg/kg) |
|---------------|-----------------|
| NaCl          | 86000           |
| CaCl₂         | 10500           |
| MgCl₂         | 5200            |
| Na₂SO₄        | 4000            |
| NaHCO₃        | 400             |

The treatment was carried out in the plexiglas cell with square graphite electrodes and included series of experiments with an current density of 42.55, 127.66, 212.77, 340.43 A / m² and treatment time varying from 30 to 90 minutes. The oil products content was determined by infrared spectrometry IKN-025. A decrease of oil products for clay was 84.52%, for chernozem - 77.1%, for loam - 75.67%, for sand - 69.03%. At the same time, to obtain such a result, it was necessary to pass a certain amount of electric charge through the soil: for chernozem it was $0.96 \cdot 10^7$ C / kg of oil products, for clay - $0.63 \cdot 10^7$, for loam - $0.93 \cdot 10^7$, for sand - $1.34 \cdot 10^7$ C / kg. The oil products decrease occurred according to the exponential law [16].

This study included changes in such soil characteristics as the content of total organic matter, chloride ions, density and humidity, and electrical conductivity of the aqueous extract.

The main soil characteristic, which determines its fertility and the possibility plants growing, is the amount of organic matter. In natural uncontaminated conditions organic matter is present in the composition of humus, including humin, humic acids and fulvic acids. The organic matter content determination was carried out in accordance with state standard GOST 26213-91 “Soils. Methods for the determination of organic matter” [17]. The method is based on the organic matter oxidation with a solution of potassium dichromate in sulfuric acid and the subsequent determination of trivalent chromium, equivalent to the content of organic matter, on a photocell calorimeter.

Samples of soil contaminated with oil and saline were placed in test tubes installed in racks, into which 10 cm³ of chromium mixture was added. After mixing the contents the tubes were placed in water bath, where they were heated for 1 hour after boiling water. Every 20 minutes the contents of the tubes were stirred using glass rods. Then the tubes were cooled and 40 cm³ of water were added to them. The mixture was thoroughly stirred by sparging and then filtered to remove solid particles. For subsequent photometry parallel reference solutions were prepared from a chromic mixture with distilled water and a reducing agent solution in accordance with the procedure.

Photometry of the solutions was carried out in a cuvette with a translucent layer thickness of 2 cm at a wavelength of 590 nm.

In addition the content of chlorine ions in the water extract from the soil was determined. A method based on the titration of chlorine ions with mercury nitrate (II) was used, in the course of which difficultly dissociated HgCl₂ is formed [18].

Water extract for analysis was prepared in accordance with GOST 26423-85 "Methods for determining the specific electrical conductivity, pH and dense residue of the aqueous extract " [19]. Samples of contaminated and cleaned soil with the weight of 30 g were placed in conical flasks with 150 cm³ of distilled water and mixed for 3 minutes.
To determine the chlorides, an extract with an indicator (diphenylcarbazone) was titrated with a solution of mercury nitrate. Then the mass concentration of chlorine ions in the aqueous extract (g/dm$^3$) was calculated.

Additionally the electrical conductivity of the water extract of the soil was determined using an ANION 4100 pH-meter according to the method of GOST 26423-85 [20].

Humidity was determined by the ratio of the mass of water removed from the soil to the dried soil mass.

The portion of contaminated or cleaned soil was placed in a pre-dried, weighted and numbered glass with a tightly closed lid. Then the cylinder with the soil was weighed. The soil was dried to constant weight at a temperature of about 105 °C for 5 hours (sandy soil - 3 hours according to the method), followed by weighing and further drying to constant weight.

Another important characteristic is the density of the soil. The soil before and after cleaning has significantly different humidity, so two methods were used: for dry soil it is determination of the density by the cutting ring method (according to GOST 5180-2015), and for highly wet soil it is the ratio of weight to volume occupied in the vessel. In the first case, the metal ring-sampler was manually pressed into the leveled soil, the ends were closed with slabs. Then the ring with the soil and the slabs were weighed and calculated.

3. The experimental results

The results of organic matter analysis are shown at Figure 1. Electrochemical treatment which significantly reduces the amount of oil in the soil, does not cause a significant change in the total organic matter of the soil. This suggests that the small amperage treatment does not cause a noticeable weakening of the fertile properties of the soil.

![Figure 1. The organic matter content in the soil before and after the cleaning.](image)

The results of the experiments are shown in Figure 2 and indicate chlorides concentration decrease (more than twice).
Figure 2. The chloride ions content in the water extract of the soil before and after cleaning.

Chlorine in contaminated soil is present in the composition of sodium chloride, calcium and magnesium chlorides. The predominant sodium chloride undergoes electrolytic dissociation, and the resulting Cl\(^-\) ions are transferred to the anode, where they are converted into chlorine gas and evaporated. They can also partially take part in oxidation processes interacting with hydrocarbons. Some chlorine-containing compounds can be sorbed by soil complexes [8, 22]. This causes a significant reduction in the content of chloride ions.

There is significant electrical conductivity decrease due to the positive metal and negative chloride ions concentration decrease (Table 2).

Table 2. Some characteristics of the soil before and after cleaning.

| Parameter                  | Soil from the oil spill | Clay | Loam | Sand | Soil from the oil spill | Clay | Loam | Sand |
|----------------------------|-------------------------|------|------|------|-------------------------|------|------|------|
| Electrical conductivity (mS/cm) | 89.5                    | 91.2 | 91.2 | 93.3 | 13.2                    | 14.6 | 14.9 | 14.5 |
| Humidity (%)               | 40.9                    | 40.9 | 40.9 | 40.9 | 15.0                    | 10.0 | 14.0 | 26.0 |
| Density (g/cm\(^3\))      | 1.224                   | 1.261 | 1.241 | 1.230 | 1.258                   | 1.637 | 1.281 | 1.723 |

The analysis showed that there is some compaction as a result of the electrochemical treatment with such conditions. However treatment modes with relatively large values of current density can cause more significant compaction. In this situation it is important to improve the soil structure.

4. Summary
The presented studies have shown that electrochemical cleaning of soil contaminated with oil and highly mineralized reservoir waters using small amperage does not entail critical changes in soil properties. The total organic matter decrease is insignificant. The a small amperage treatment does not lead to a deterioration of soil fertility. Electrochemical processes contribute to the active reduction of
soil chloride ions, reducing moisture and electrical conductivity. The soil density increases, which should be taken into account in treatment regimes with higher currents and can be compensated by improving the soil structure. Thus the electrochemical cleaning method can be effectively applied on the oil fields soils of the and will not impede the subsequent restoration of plant communities at the place of processing [21], which will make it possible to successfully restore disturbed lands.

5. References

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