U.P.B. Sci. Bull., Series D, Vol. 72, Iss. 1, 2010 ISSN 1454-2358

ELECTROCHEMICAL REMEDIATION – EFFICIENCY VS TREATMENT CONFIGURATION

Irina Aura ISTRATE[1], Adrian BADEA[2], Gianni ANDREOTTOLA[3], Giuliano ZIGLIO[4], Tiberiu APOSTOL[5]

Conform Agenției Europene de Mediu, necesitatea decontaminării solurilor poluate apare la peste 250 000 din siturile prezente pe teritoriul Statelor Membre. Acest număr este asteptat să crească. Scopul cercetării experimentale este acela de a evalua fezabilitatea utilizării oxidării electrochimice, o tehnologie inovativă, în vederea degradării hidrocarburilor dintr-un sol contaminat artificial. Oxidarea electrochimică s-a dovedit a fi o tehnologie eficientă pentru remedierea solurilor contaminate cu motorină, chiar dacă s-au obținut eficiențe diferite pentru teste diferite. Toate testele au fost realizate pe o perioadă de 28 de zile folosind o tensiune specifică de 1 V/cm.

According to the European Environmental Agency, soil contamination requiring clean up is present at approximately 250,000 sites in the EEA member countries. And this number is expected to grow. The aim of this experimental investigation was to assess the feasibility of using electrochemical oxidation, an innovative technology, to degrade hydrocarbons from an artificially contaminated soil. Electrochemical oxidation proved to be an effective technology for diesel remediation; even tough different tests resulted in different removal efficiencies. All tests were done for a period of 28 days using a specific voltage of 1V/cm.

Keywords: electrochemical treatment, kaolin, sand, contaminated soil.

1. Introduction

According to the European Environmental Agency, soil contamination requiring clean up is present at approximately 250,000 sites in the EEA member countries. And this number is expected to grow. Potentially polluting activities are estimated to have occurred at nearly 3 million sites (including the 250,000 sites already mentioned) and investigation is needed to establish whether remediation is required. If current investigation trends continue, the number of sites needing remediation will increase by 50% by 2025 [1, 2]. Although the range of polluting

---

[1] Eng., Power Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: ia_istrate@yahoo.com

[2] Prof., Power Engineering Faculty, University POLITEHNICA of Bucharest, Romania

[3] Prof., Engineering Faculty, University of Trento, Italy

[4] Prof., Engineering Faculty, University of Trento, Italy

[5] Prof., Power Engineering Faculty, University POLITEHNICA of Bucharest, Romania

activities and their relative importance may vary considerably in each country, several main local sources of soil contamination can be clearly identified across Europe.

The industrial branches such as energy production, chemical industry, metal working industry and oil industry are contributing to more than 50% of total sources of pollution in each country, except in Finland where other industrial branches are more relevant [3].

2. Materials and methods

The base method for the current research, the electro-oxidation, is a branch of Direct Current Technologies (DCTs), which are remediation techniques for contaminated soils, in which an electrical field is created in the polluted medium by applying a low-voltage direct current to electrodes placed in the ground [3, 4]. Electric fields as well as electron transfer processes have been used for the decontamination of soils and underground water containing unwanted organic or inorganic substances [5, 6, 7]. The main phenomena involved here are [6]: electrolysis, geochemical reactions, electrophoresis, electroosmosis, and electromigration.

The samples were artificially contaminated with diesel fuel commercially available that was purchased from a gasoline pump at a typical refuel station. To prepare the diesel contaminated soil samples, the soil was at first dried and then spiked with diesel fuel. One kilogram of dry soil was mixed with about 100 mL of diesel fuel, and then the sample was stirred with stainless steel spoons in a glass backer, to ensure the contaminants to be evenly distributed trough the soil. After mixing, the sample was allowed to evaporate for about two weeks. Before the test, the spiked samples were saturated with demineralized water and allowed to evaporate overnight at room temperature before being inserted in the experimental setup. Two parameters were used to consider the contaminant content in the soil samples: TPH (total petroleum hydrocarbons), which refers to a family of many petroleum-based hydrocarbons, and TOC (total organic carbon), which represents the whole content of organic substances in the soil samples.

The experimental part was divided in three parts: (i) tests performed only on contaminated clay (kaolin); (ii) tests performed only on contaminated sand and (iii) tests performed with both layers in different configurations.

3. Experimental part

3.1. Electrochemical remediation applied on clay (kaolin)

The type of fine grain soil that was used to carry out the experimental investigation on diesel fuel remediation was speswhite kaolin. This type of soil could be classified as a silty clay, being mainly composed by particles having dimensions ranging between 2 µm and 75 µm (40%) or lower than 2 µm (60%). kaolin proved to be characterized by an iron content about 2794 mg/kg_{SS}. Before being mixed with diesel fuel, the TOC of the soil was negligible (about 0.01 mg/kg_{SS}). The test was called ISEO_K and was performed for a treatment period of 28 days, with an applied voltage of 10 V (1 V/cm).

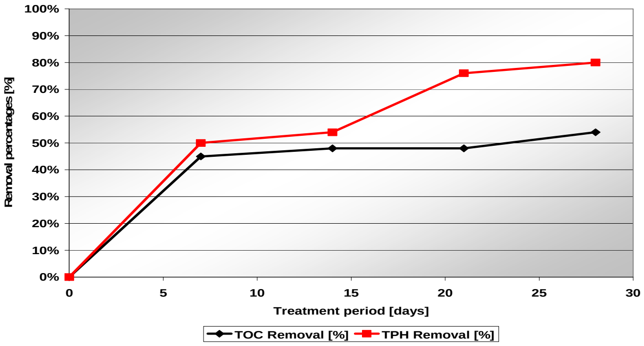

Fig. 1.Contaminant removal achieved during test ISEO_K

The removal percentages for test ISEO_K1 increased with the increase of exposure time, both for TOC and for TPH. As for the results obtained at the end of the test across the soil samples, it can be noticed that the pH decreases with the increase of distance from cathode on one hand and on the other hand the TOC and TPH increases with the increase of the distance.

3.2. Electrochemical remediation applied on sand

The test ISEO_S has been performed on a sample of sand Vaga 12 of about 1.8 kg, artificially contaminated by diesel fuel. During the test, on the sample was applied a constant potential difference of 10 V, which corresponds to a specific voltage of 1 V/cm, for a period of 28 days. The initial sample of soil had the humidity equal to 23.9% and a pH of 8.88. Contrarily with what was noticed with the clay, in sand case, the electroosmotic flux it is formed after some days from the beginning of the sample (more precise after 94 hours) and not in the first hours of the test as for the clay. The test ISEO_S involved the application of electrooxidation to a homogeneous matrix composed of only sand for 4 weeks, using a specific voltage of 1 V / cm. The concentration (in terms of TOC and TPH) and efficiency of removal obtained are presented in table 1 and figure 2.

Table 1

Contaminant concentrations and removal percentages obtained after test ISEO_S3

Time [d]	TOC [g/kg$_{ss}$]	TPH [g/kg$_{ss}$]	Removal TOC [%]	Removal TPH [%]
0	42.9	37.4	-	-
3	31.1	28.5	-	-
4	21.5	17.6	-	-
7	24.8	36.5	-	-
14	30.6	43.9	-	-
21	30.2	23.9	-	-
28	**34.4**	**27.3**	**20%**	**27%**

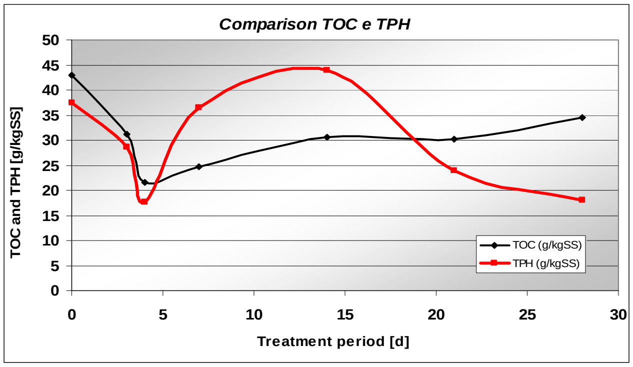

Fig. 2. Comparison between the TOC and TPH evolutions in time for test ISEO_S

3.3. Electrochemical remediation applied on a mixed sample (sand and kaolin)

Three types of experiments have been developed with a mixed matrix composed by sand and kaolin. The configuration for each test is presented in figure 3.

a) **b)** **c)**

Fig. 3. Configuration treatment for the electrochemical remediation of a mixed matrix: a) test ISEO_m1; b) test ISEO_m2; c) test ISEO_m3

The test ISEO_m1 has been performed on a sample of sand Vaga12 and white kaolin of the total weight of 1.9 kg, both artificially contaminated by diesel fuel. The test was performed in an experimental setup that had shaped cubic (10 cm x 10 cm x 10 cm).

The values of TOC and TPH decreased so evident in the two layers of sand, except for the data referring to the last samples where the phenomenon can be due to the migration of diesel, while n the kaolin, TOC and TPH decreased in the first four days of trial and after that increased in the remaining period of treatment. The removal percentages reached, can be considered quite high for the sand, (especially for the layer of sand 2), when compared with previous tests conducted on a sand matrix, where the removal was limited. In kaolin, however, the removal rate is very low. This fact can be justified by the phenomenon observed during this test, where it was noticed once the kaolin matrix releases the electroosmotic flux, succeed to each the initial humidity by taken the pore water contained in the two layers of sand. This exchange of pore water resulted in a transfer of diesel from the sand to the clay and this way the value of TOC and TPH increased. In fact the trend of humidity, TOC and TPH for kaolin were quite similar, showing a decrease in the first days of the test (when the flow is still present the electroosmotic flux) and increased after 4 days, as a result of the phenomenon described above.

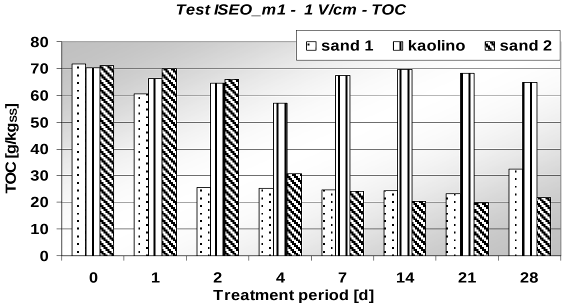

Fig. 4. Contaminant concentrations, in terms of TOC, measured during ISEO_m1

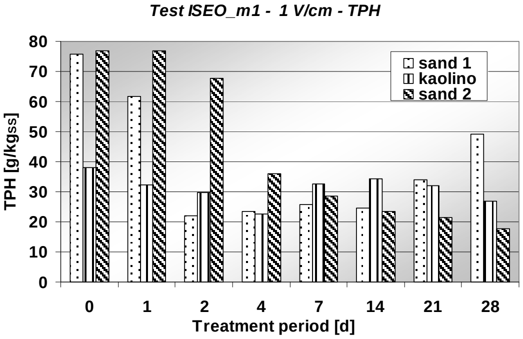

Fig. 5. Contaminant concentrations in terms of TPH, measured during test ISEO_m1

The test ISEO_m2 has been conducted, with the main purpose to see whether the configuration of sand and kaolin layers, compared to the position of electrodes, influence the behavior observed in test ISEO_m1. In this test, the reactor cell is divided into two equal parts; the layer of sand has been inserted at anode until the middle of the cell, while the layer of kaolin has been inserted from the middle of the cell to the cathode.

The electrooxidation, however, appears to have acted in the first week of the treatment in kaolin, so that after the exchange developed between the sand and the kaolin the final concentration of contaminant in kaolin was higher than the values from the beginning of the trial. Furthermore, regarding the electroosmotic flux, the solution resulted at the cathode was analyzed by measuring the values of TOC and TPH. The water presented a TOC value of 3.16 g/L and a value of 4.20 TPH g/L. Consequently, the total content of this TOC in the electroosmotic flux was of about 0.4 g, while the TPH was 0.6 g. The total mass of kaolin used for the test was equivalent to 0.7 kg and had a TOC equal to 64.1 g/kgSS and TPH of 39.9 g/kgSS, corresponding to a total of TOC equal to 24.5 g and 15.24 g TPH. Thus the fraction of contaminant removed through the electroosmotic flux is equal to 1.6% for the TOC and 4.5% for TPH, which can be considered negligible in the final removal of diesel.

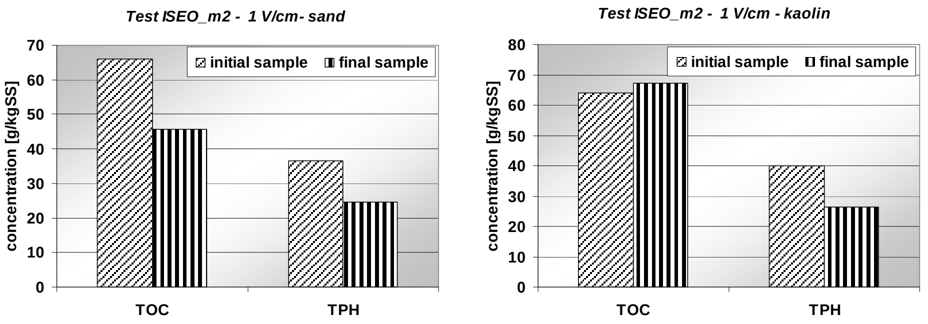

Figure 6. Contaminant concentration measured at the beginning and at the end of the treatment

The test ISEO_m3 is, as the two tests described above (ISEO ISEO_m1 and ISEO_m2), a test performed on stratified sample. This time, the layers of soil were placed horizontal in the electrochemical reactor, precisely on the bottom of the reactor we have sand until and on the top we have kaolin as shown in figure 3c. The removal percentages of the two matrixes are presented in the figure 7.

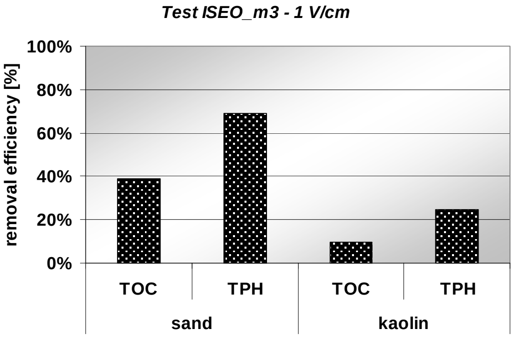

Figure 7. Comparison between removal percentages of the sand and kaolin

As it can be seen from the charts shown, the kaolin shows a modest decline in TOC and TPH at the end of treatment, while the sand shows a good removal. This fact leads us to believe that, again, has witnessed the phenomenon of exchange of pore water between sand and kaolin. During this test, the kaolin had a final humidity of about 8 percentage points lower compared to its initial humidity. Even the sand presents a decreasing in humidity at the end of the process. The fact that the kaolin has failed to recover all the quantity of water lost through electroosmosis underlines the fact that the clay is able to take the water from the sand, because the kaolin is located above the sandy layer and have to defeat the gravitation in order to move the water from one layer to another.

This most likely has reduced the exchange between sand and kaolin also in terms of the contaminant. In this way, the electrooxidation could act, however, leading to some removal of contaminants in kaolin.

4. Conclusions

A series of trials have been performed in order to assess the efficiency of the electrochemical treatment on different types of matrix: sand, kaolin and a mixed matrix composed of sand and kaolin. It was observed that the removal percentages obtained during the tests performed on a sand sample are smaller compared with the removal percentages reached in kaolin. In order to activate the electrooxidation processes it is not necessary the formation of electroosmotic flux (never registered in the sand).

It can be noted that the contaminant removal increases significantly with the duration of the process, or better said longer last the treatment, better are the results. Concentration profile along the sample is not always uniformly distributed; sometimes some areas present a higher remediation than others. This probably is also due to the fact that the diesel, in a matrix of sand, is characterized by a quite high hydraulic conductibility and because of that tends to migrate at the top of the sample.In the electrooxidation tests, conducted on a stratified sample composed by sand and kaolin in different configurations it was observed the fact that only electrooxidation, applied on a stratified sample, is not effective for removing the contaminant in the whole sample of soil, because it was created a strong non-uniformity in contaminant degradation favoring the remediation in sand and limiting the removal in kaolin. In fact, the sand has reached during the tests with only electrooxidation to an efficiency of about 31-69% in terms of TOC and 33-77% in terms of TPH. In addition, it was observed that the removal percentages in sand for this test are higher than the ones obtained at the end of a test performed with only electrooxidation, with the same voltage, on a sand sample (percentages ranging between 20-35% for both TOC that TPH). The non-uniformity in contaminant removal, which is observed between sand and kaolin, can be attributed to an exchange of interstitial flow that moves from sand towards kaolin, due to the formation of electroosmotic flux in kaolin, resulting in the creation of a negative pressure gradient. This exchange of pore water between sand and kaolin depends on the sand and clay distribution (vertical layers, horizontal layers, the kaolin position respect to the sand position).

Based on the results of this study, electrochemical treatments proved to be effective for kaolin when it is treated alone and for sand when is in a hybrid (sand and kaolin) sample. Some studies are still in progress in order to find a solution to remediate sand and both sand and kaolin in hybrid sample, using electrochemical methods.

REFERENCES

[1]. *T. Cairney*, Contaminated land: problems and solutions, Lewis Publishers, USA and Canada 1993.

[2]. *J.A.. Soesilo, Stephanie R.. Wilson,* Site remediation: Planning and management, CRC Press Inc., 1997.

[3]. *Y. B. Acar., R. J. Gale, A. N. Alshawabkeh, R. E. Marks, S. Puppala, M. Bricka, R. Parker* “Electrokinetic remediation: basics and technology status”, Journal of Hazardous Materials, no. 40, 1995, pp. 117–137.

[4]. *A. N. Alshawabkeh, T. C. Sheahan, X. Wu*, “Coupling of electrochemical and mechanical processes in soils under dc fields”, Mechanics of Materials, no. 36, 2004, pp. 453–465.

[5]. ***Environmental Protection Agency (EEA), Progress in management of contaminated sites (csi 015) assessment published aug 2007.

[6]. ***Environmental Protection Agency, How To Evaluate Alternative Cleanup Technologies For Underground Storage Tank Sites: A Guide For Corrective Action Plan Reviewers, EPA 510-B-94-003; EPA 510-B-95-007; and EPA 510-R-04-002, 2009.

[7]. *Irina Aura Oprea, A. Badea, G. Ziglio, M. Ragazzi, G. Andreottola, E. Ferrarese, T. Apostol*, “The remediation of contaminated sediments by chemical oxidation”, University Politehnica of Bucharest Scientific Bulletin, Series C: Electrical Engineering and Compter Science, **Vol. 71** , no. 1, 2009, pp. 131-142