Study of electroomosis technique for decontamination of stratified grounds

Inês Costa Feijão Borges

inescfborges@gmail.com

Abstract

This work studies the use of electrokinetic treatment, EKT, for the decontamination of stratified soils with layers of sand and clay. Tests were carried out on samples contaminated with leachate collected in a landfill from the Lisbon area, in Portugal. Two tests were performed, one in a sample of sand and the other in a sample with a layer of sand above a layer of compacted clay. A test with a sand sample prepared with tap water was also performed as reference. The relationship between chemical, electrical and hydraulic properties during treatment was studied. The degree of contamination was determined indirectly and in real time by monitoring the electrochemical properties of the soil and the pore fluid. This allowed the indirect determination of the decontamination achieved with EKT, because the relationship between increasing percentages of contaminant and the electrical conductivity of the fluid, or the electrical resistivity of the sand were determined. Chemical analysis performed to the soils before and after treatment showed that EKT was efficient. In addition, the presence of the sand layer had contributed to decontamination by promoting percolation due to the high saturated permeability of this material.

Key-words: Decontamination, Electroosmosis, Sand, Clay, Organic matter, Leachate

1. Introduction

Electrokinetics refers to the relationship between electrical potential and the movement of water and charged particles. Under an electrical gradient, water flows by electroosmosis from the anode (+) to the cathode (-). Electroosmotic efficiency is defined as the quantity of water moved per unit of electricity.

The theory of electroosmotic consolidation and the analytical solution for one-dimensional flow were presented in 1960's (Esrig 1968; Mitchell and Soga 2005). The electroosmotic volume flow rate can be described by eqn. (1).

$$Q_e = k_e \nabla E A \qquad (1)$$

where Q_e is the electroosmotic volume of water flow (m^3/s), k_e is the coefficient of electroosmotic permeability ($m^2/V/s$) already presented, ∇E is the gradient of the direct-current electrical field applied (V/m) and A is the total cross-sectional area perpendicular to the direction of flow (m^2). For unidirectional flow along the position x, the electroosmotic volume flow can be described by eqn.(2), where k_e is measured when water percolates the soil under constant voltage gradient dV/dx.

$$Q_e = k_e \frac{\partial V}{\partial x} A \qquad (2)$$

The previous equation is analogous to the well-known Darcy's law used to compute the volume flow of water Q_h driven by a hydraulic gradient in saturated soils (eqn. (3)) where k_h is the coefficient of hydraulic conductivity, or saturated permeability (m/s), and *i* is the hydraulic gradient given by the change in water head ∂H along the direction of flow ∂x, caused by changes in pore water pressure.

$$Q_h = k_h i A = k_h \frac{\partial H}{\partial x} A \qquad (3)$$

Eqn. (2) and (3) consider no coupling between the electrical and hydraulic characteristics. Considering that the application of $\partial V \,/\, \partial x$ causes generation of pore pressure ($\partial u \,/\, \partial x$), which induces a flow in the opposite direction, it is possible to deduce eqn. (4)

$$\mathrm{Q} = \mathrm{Q_h} - \mathrm{Q_e} = \mathrm{A}\left[\left(\mathrm{k_h}\frac{\partial \mathrm{H}}{\partial \mathrm{x}}\right) - \left(\mathrm{k_e}\frac{\partial \mathrm{V}}{\partial \mathrm{x}}\right)\right] \qquad (4)$$

where it was considered that the electroosmotic flow, Q_e, has opposite direction to the hydraulic flow, Q_h, and where Q is the total flow originated by the crossing of these two effects.

The electroosmotic conductivity, k_e, is a fundamental property when considering EKT both in laboratory scale experiments and in field applications. This property is time dependent and is considerably influenced over the period of treatment. It is also dependent on the type pore fluid and on void ratio. The literature on this technique goes back to 1940’s, when authors like Casagrande started experimenting on electrokinetic properties of clays (Gingine, 2017).

The electroosmotic permeability of the sand was measured using the apparatus modified from an oedometer cell, as described by Cardoso and Santos (2013). The EKT box setup, specially designed by Gingine (2017), was used for the EKT test.

The main objective of this work is to study the electroosmosis as a decontamination technique for stratified soils containing layers of sandy soil. To achieve this objective two tests were performed, one in which the sample is only sand, and the other in which the sample was prepared with two soil strata, one of compacted clay and one of sand. In both configurations the soils were saturated with leachate. In all tests, a constant voltage was applied and pH and the correspondent electric current were measured. The determination of the electrical resistivity with these parameters allowed the monitorization of the test, to understand the evolution of the decontamination.

A few field and pilot scale studies have demonstrated the success of EKT on removing heavy metals and organics from contaminated soils, though some have shown limited success. In situ applications have been challenged by the complex and heterogeneous field conditions (Gabrieli, 2010).

Treatment of contaminated clay soils using such methods as soil washing, bacteria and other biochemical treatments are sometimes ineffective and costly due to the low hydraulic permeability of the clayey soils. EKT, also known as *in situ* electrokinetic treatment, has been shown to be suitable for decontamination of contaminated clays.

The application of electrokinetic treatment *in sit*u consists of drilling wells or drains, where electrodes are installed and later an electric potential of very low direct current is applied. In some situations, water pumping systems and electrode conditioning may be required. Fig. 1 shows an in situ soil decontamination system using electrokinetic treatment. Similarly, EKT can be performed *ex situ* using specially designed surface equipment. The *ex situ* decontamination treatment involves removing the contaminated soil to treat it in other site.

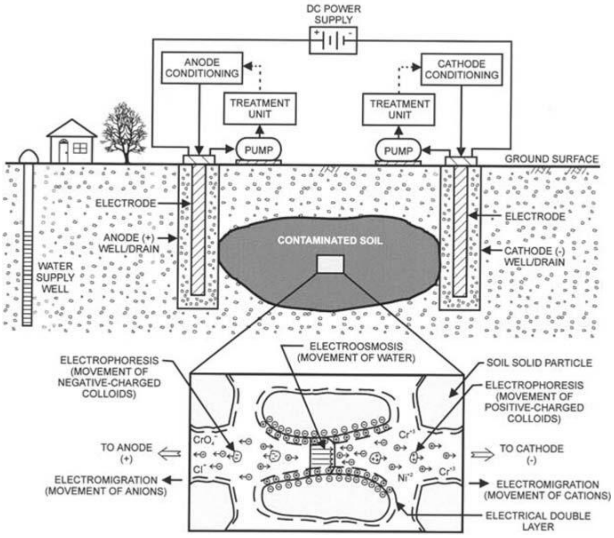

Fig. 1 - EKT in situ (Reddy, 2010)

2. Materials and Methods

2.1. Sand Characterization

APAS 20 sand and white kaolin, both commercially available in Portugal, were used for the experimental research. APAS 20 is classified as a clean sand poorly graded (SP), with specific gravity G_s=2.68. Kaolin is classified as highly plastic silt (MH), having 59% in mass of grains with silt size and 40% with clay size, with specific gravity $G_s = 2.61$, liquid limit $w_L = 52\%$, plastic limit $w_P = 30\%$ and plasticity index $PI = 22\%$.

Sand samples were prepared with a void ratio of 0.723. For this void ratio hydraulic permeability is 2.15×10^{-3} m/s. To guarantee uniformity mass of sand was calculated by eqn. (5) for a certain volume.

$$\gamma_d = \frac{G_s}{1+e}\gamma_w = \frac{W_s}{V} \to m_s(V) = \frac{V}{g} \times \frac{G_s}{1+e}\gamma_w \tag{5}$$

The samples were prepared to have relative density of 50%.

2.2. Clay Characterization

Clay sample was prepared by compaction directly in the cell, following the procedure adopted by Gingine (2017). The soil was prepared with water content of 25% and was compacted in 3 different layers in order to have a relatively uniform void ratio of 0.9. For this void ratio the hydraulic saturated and electroosmotic permeabilities are 1.3×10^{-8} m/s and 9.3×10^{-10} m^2/V/s respectively.

2.3. Sand Electroosmotic Permeability

The electroosmotic permeability of the sand was measured using the apparatus modified from an oedometer cell. This cell has a special provision for the inlet and outlet of the water as well as for the electrical wires attached to the silver electrodes, as described by Santos (2012). Fig. 2 presents a photograph of the cell, showing the silver electrodes placed at the top and bottom porous stones.

Fig. 2 - EKT oedometer (Santos, 2012)

2.4. EKT Box

The experimental setup consists of a bench scale perspex box, electrodes and a power source. The bench scale box consists of 3 detachable compartments: a soil cell in the middle (350 mm long, 100 mm wide and 150 mm high) and two electrode chambers, all made of Perspex material

(Fig. 4). The cell has a provision of 12 holes on each face forming a grid of spacing 100 mm along the length and spacing of 40 mm along the height. These holes will give access for the monitoring electrodes to measure the voltage readings. The chambers are capable to contain 6 litres of the solution along with the electrodes. The electrodes were a graphite (Cathode) and a steel (Anode) plate.

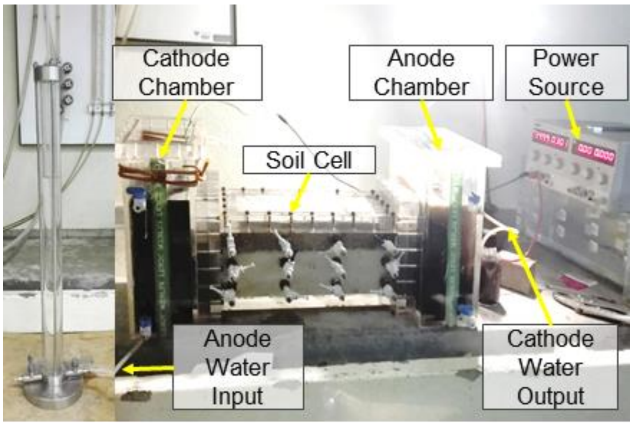

Fig. 3 - EKT box during EKT test

2.5. EKT tests

Two soil configurations were used in the EKT box: one with only sand (Sand, Fig. 5a), and the other with two horizontal layers of soil, one of sand one and of clay (Sand + Clay, Fig. 5b), with a thickness of 6 cm and 8 cm respectively.

Leachate collected from a waste landfill near Lisbon was used as contaminant fluid. This leachate is composed of organic and inorganic matters. Its pH was 8.

To reduce energy consumption and corrosion of electrodes, Current Intermittence (CI) technique was used in this experimental study. CI technique consists of applying voltage at a predetermined on/off intervals instead of continuous DC supply. A scheme of 60 mins ON- 30 mins OFF was used as shown in. The Voltage of 35 V and 70 V was applied for the voltage gradient 1 V/cm and 2 V/cm respectively. Voltage drop was measured between Cathode and zone A, B, C, D and Anode, as explained by scheme (Fig. 5)

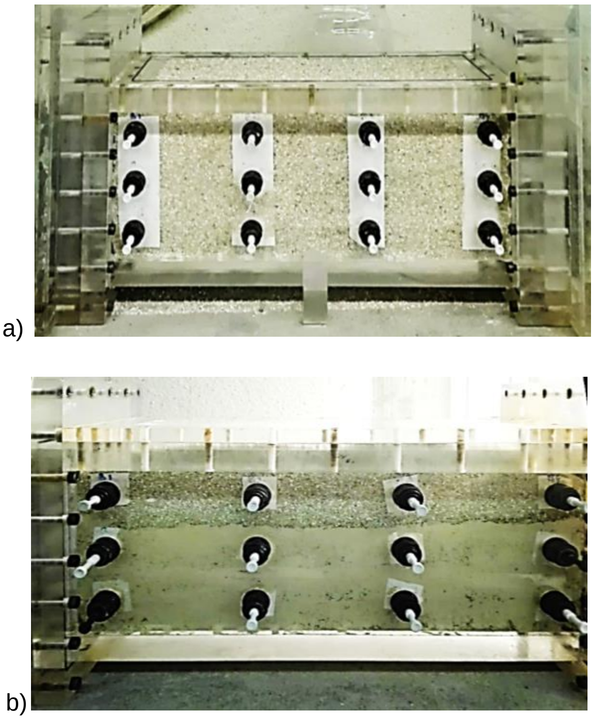

Fig. 4 - Samples tested: a) Sand; b) Sand + Clay

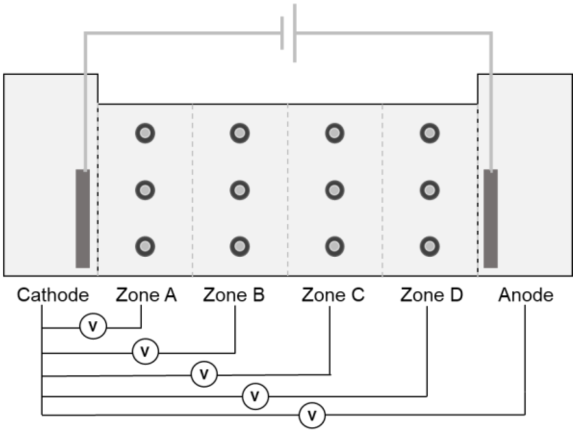

Fig. 5 - Voltage drops measurements

During the EKT, the pH at the anode and cathode chamber decreases and increases due to the oxidation and reduction of water respectively (eqn. (6) and (7)).

$$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- \ (Anode) \qquad (6)$$

$$2H_2O + 4e^- \rightarrow H_2(g) + 2OH^-(Cathode) \qquad (7)$$

In Enhanced treatment (Et), the fluid in the electrode chambers is replaced by normal tap water every 24 hours in order to maintain the pH near the electrodes to 7. EKT tests were then conducted according to the test plan in Tab. 1.

Tab. 1 - EKT test plan

Soil Configuration	Tests	Time (hours)	V/cm	Fluid in Electrode Chambers
Sand	B - I	72 (IC)	1	Tap Water (Et)
	B - II	72 (IC)	2	Tap Water (Et)
	B - III	72 (IC)	2	Tap Water
Sand + Clay	C - I	72 (IC)	1	Tap Water (Et)
	C - II	72 (IC)	2	Tap Water (Et)
	C - III	72 (IC)	2	Tap Water

CI - Current Intermittence; Et - Enhanced treatment

Through the measurements of soil electrical resistivity and pH, it was possible to estimate the evolution of the leachate concentration in the soil cell. This information is important for understand the efficiency of EKT for soil decontamination.

3. Indirect Measurement of Contamination

The relationship between the resistivity of the soil contaminated with increasing percentages of contaminant and the percentage of contaminant was determined in order to monitor the decontamination evolution during EKT.

This is a method which can be easily used in the field through geophysical prospection tests. It was used by others (Mota et al., 2004).

This was done by preparing soil samples and saturated them with fluids with different leachate concentration (0%, 1%, 5%, 10%, 50% and 100%). The concentration was determined by dilution. Three sets were prepared, each for a given pH range: 1-3, 7-8 and 10-13. The relationships are presented in Fig. 6.

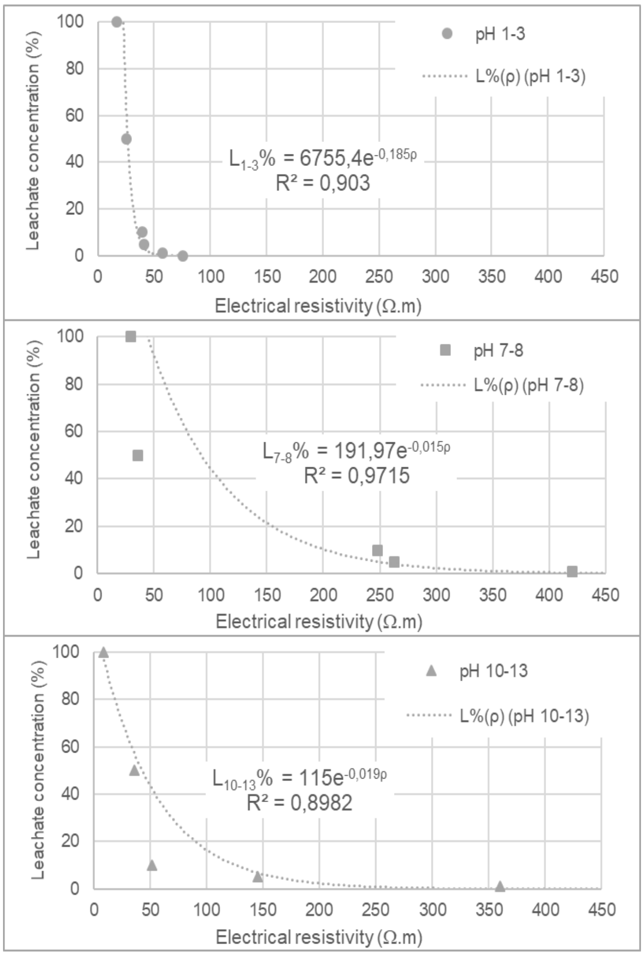

Fig. 6 - Relationships between leachate concentration and sand electrical resistivity for different pH

Similar curves were found for the electrical resistivity of the fluid used to saturate the samples, however this information was not measured because it was difficult to extract the fluid during the test.

4. Results and Discussion

4.1. Electroosmotic Permeability

The electroosmotic permeability coefficient measured for the sand was 8.04×10^{-8} $m^2V^{-1}s^{-1}$. For this material, k_h / k_e = 26500 V/m. This indicates that water percolation driven by water head, transporting the contaminant, may be more efficient than EKT for such soil. For the clay studied, Gingine (2017) had found $k_h=1{,}3\times10^{-8}$m/s e $k_e=9{,}3\times10^{-10}$$m^2$/V/s. This clay is more suitable for EKT than the sand.

When a voltage is imposed on the EKT box the direction of flow would be from anode to cathode. This causes a change in pore pressure in the system, so the flow direction changes. In the sand sample, the water flows from cathode to anode, because k_h/k_e is high and there is water head applied during the test.

4.2. Test B

Evolution of the soil electrical resistivity

The evolution of voltage drop measured in test B is presented in Fig. 7. In general it can be seen that the slope of the curves change along the test, indicating the occurrence of chemical reactions. Electrical resistance decreases due to increasing decontamination. Et in B - II seems to increase decontamination, which appears to slow down in B - III

This voltage drop, current measured and pH allowed estimating the current concentration (percentage) of contaminant in the soil pore fluid. Throughout test B the decrease of the concentration happened quite quickly. At the end of subtest B - I, the percentage of leachate, % L, calculated in all zones of the soil cell presented values lower than 15%. As can be seen in the graph from this subtest, the % L has dropped to values around 0%.

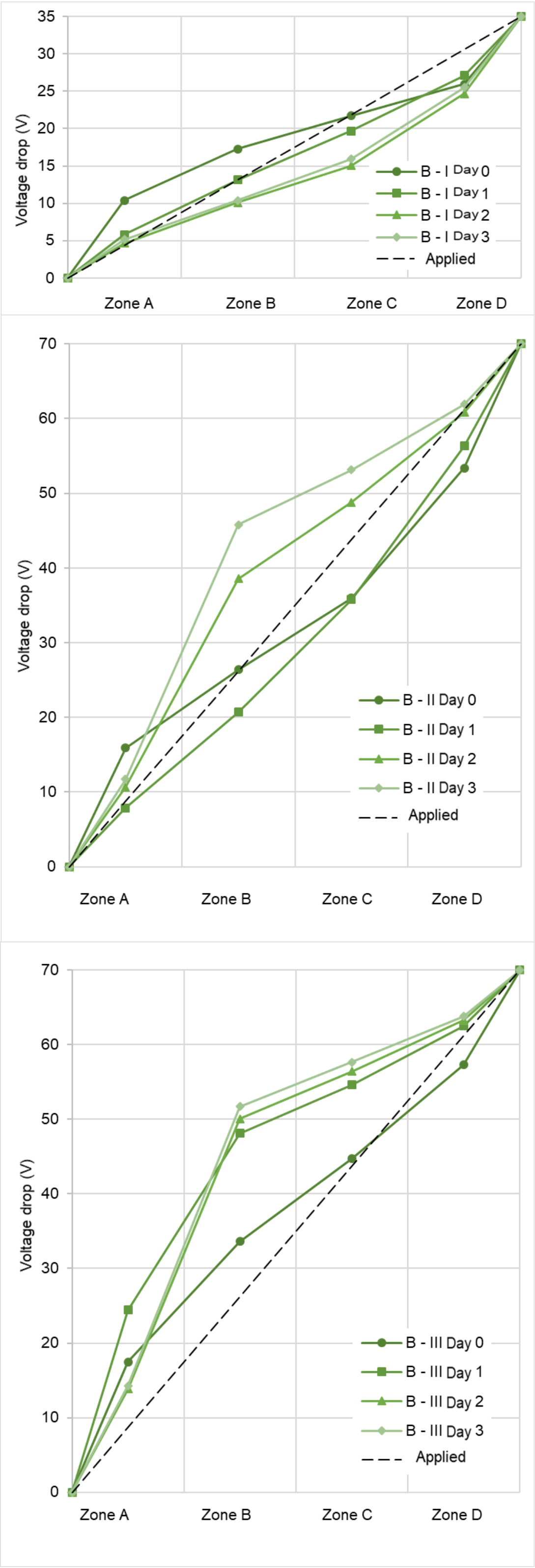

Fig. 7 – Voltage profile for all subtests for test B

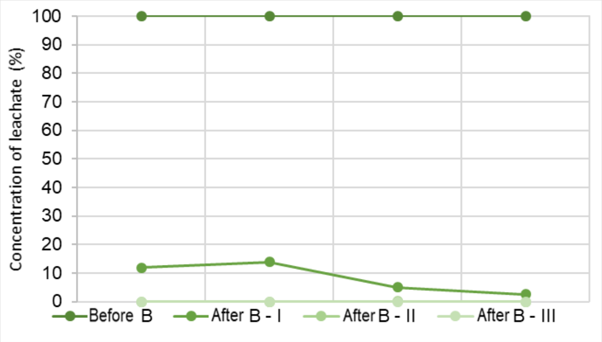

Fig. 8 - Chart of concentration of leachate during time in test B

Visual observation

As it can be seen in Fig. 9, over time the sample to get whiter near cathode. This indicates the oxidation of the organic matter of the leachate due to oxygen formed (Eqn. 6). Nevertheless, because of the high saturated permeability and the existence of a water head, some leachate washing could also have occurred.

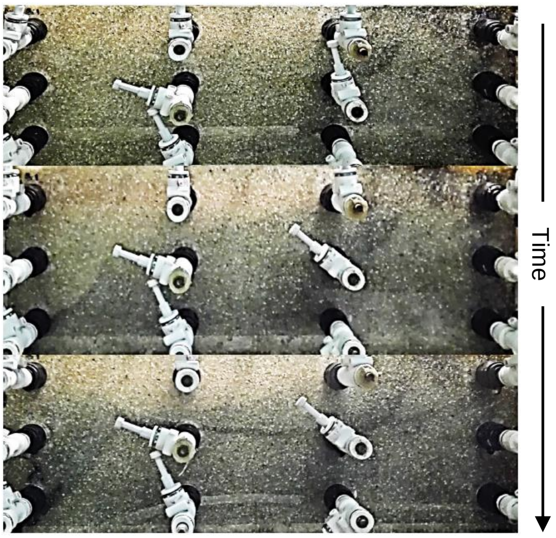

Fig. 9 - Visual observation during time in test B

Discolouration due to washing or oxidation

This method consists of washing the soil at the end of the EKT test with tap water and with oxygen peroxide, respectively (Fig.10). In this case the results are not much visible, however the sample washed with hydrogen peroxide looked cleaner than that washed with water. It was concluded that the EKT decontamination was effective.

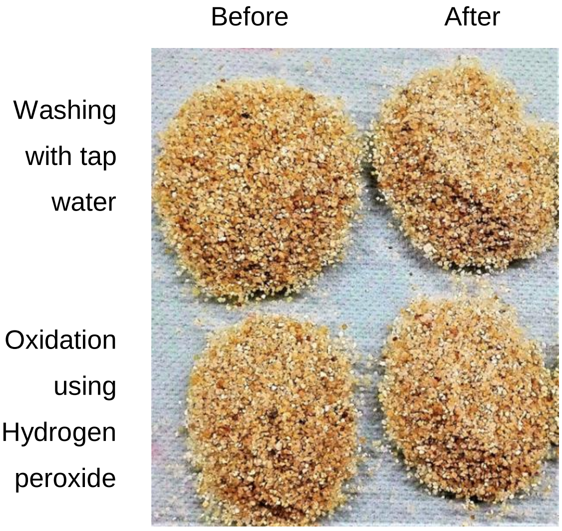

Fig. 10 - Discolouration due to washing or oxidation

4.3. Test C

Evolution of soil electrical resistivity

The evolution of voltage drop measured in test B is presented in Fig. 11. The evolution is similar to that found in test B, however the voltage drop is much higher in test C than in test B. This is due to the presence of the clay layer, more conductive than the sand due to the clay minerals and its ability to adsorb the contaminant ions. Nevertheless. along time and with Et technique the drop is very high, which may be explained by the presence of the sand promoting the percolation of the contaminant.

At the end of the test C both layers show a very low %L. In the clay stratum the concentrations calculated at the end of the test were less than 10% and in the sand stratum less than 5%. These values show that this test is a viable option for decontamination of stratified soils.

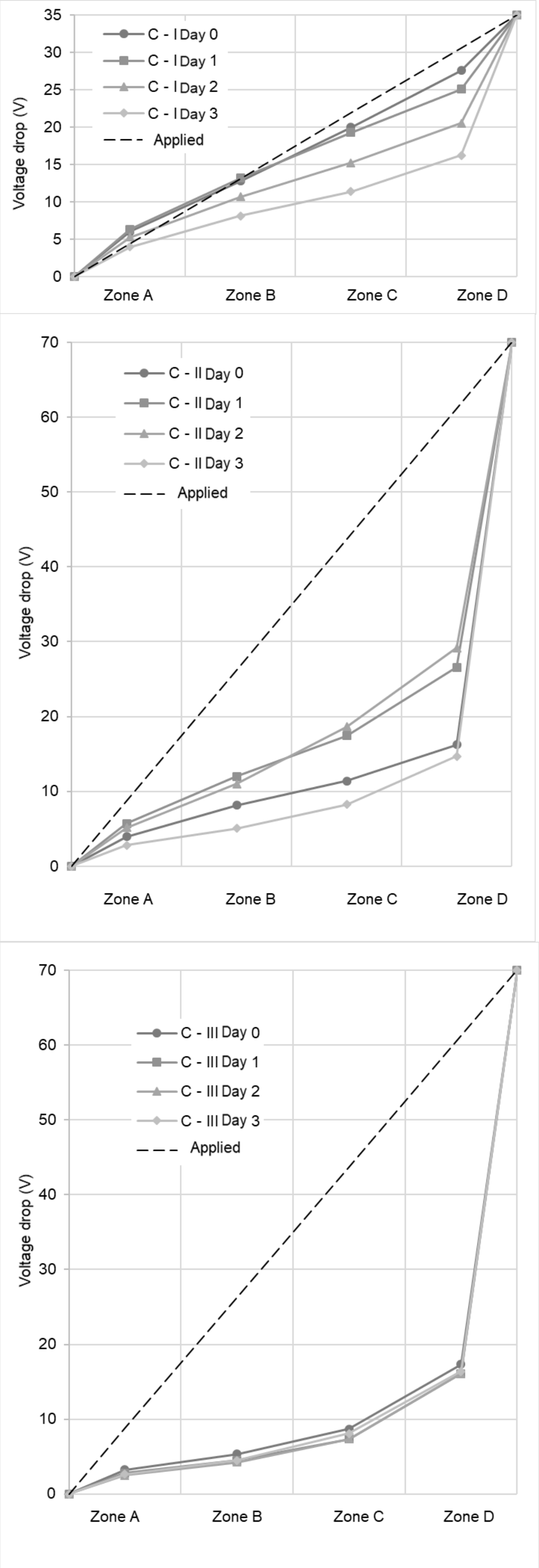

Fig. 11 - Voltage profile for all subtests for test C

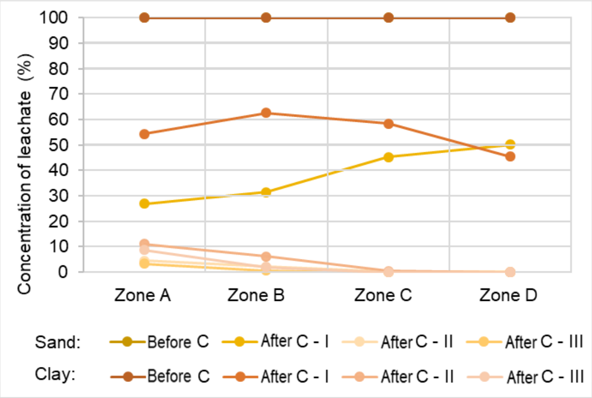

Fig. 12 - Chart of concentration of leachate during time in test C

Visual observation

As it can be seen in Fig. 13, over time the sand sample to get whiter near cathode. The clay sample are getting clean. The clay sample turned whiter in all zones of the soil cell.

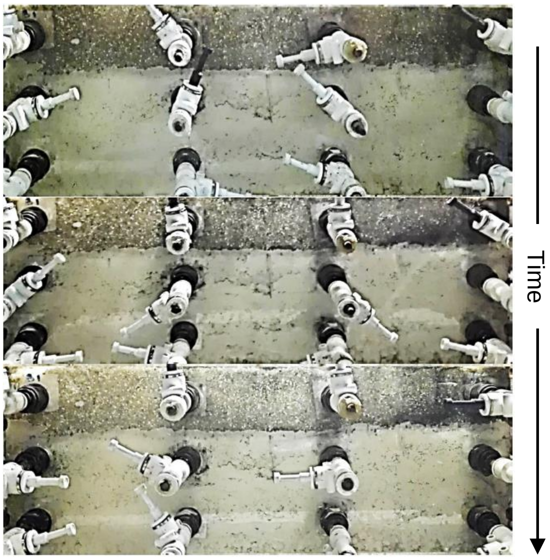

Fig. 13 - Visual observation during time in test C

The explanation of this test is schematically presented in Fig. 14. Due to the presence of the sand there is water percolation washing the soil. Due to EKT there is osmotic flow of ions driven by their electrical charges, and water. There is a contra-flow in the opposite direction due to water accumulation. Due to the fast decontamination of the sand layer there are different ion concentrations and therefore an osmotic flow from the clay to sand will occur.

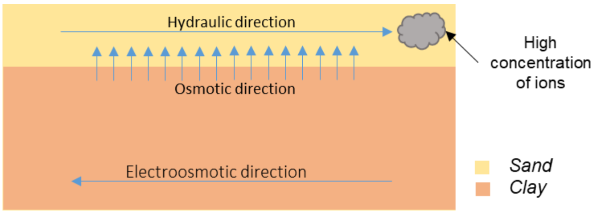

Fig. 14 - Electrochemical and hydraulic phenomena occurring in test C

5. Chemical Analysis

For the direct determination of the amount contaminants in the soil, chemical analysis of the soil after EKT was performed in the Chemistry laboratory of IST. After the EKT, the soil was extracted from different parts of the cell. Representative amounts of soil samples near anode and cathode were sent for the chemical analysis.

Spectroscopy tests were performed to detect the metals, and by acid digestion to the organic matter.

In sand sample the Potassium content was reduced by 84% near cathode and was increased 8119% near anode. Sodium was increased more than 12666% near cathode and near anode. Chromium content was too little to be measured. Iron content was increased by 13% near cathode and 255% near anode. The large increments observed were also explained by the presence of tap water. In the clay sample tested by Gingine (2017), where there was no sand layer, the Potassium content was reduced by 85% near cathode and 33% near anode. Sodium was increased 9400% near cathode and was reduced by 42% near anode. Chromium content was reduced by 57% near cathode and 52% near anode. Iron content was reduced by 58% near cathode and 23% near anode. The reduction was lower than in the presence of the sand, therefore this stratum contributed to increase decontamination.

Chemical Oxygen Demand (COD) indirectly relates to organic content in the medium. In sand sample, COD was reduced by 72% near cathode and 19% near anode. In clay sample, COD was reduced by 13% near cathode and 17% near anode.

It was possible to observe soil decontamination due to EKT, although there is overlap between a hydraulic and electrochemical process due to the high permeability of the sand. The presence of the sand layer therefore operated as a drain, which allowed a more efficient decontamination of the clay layer when compared to the decontamination observed in the clay by Gingine (2017).

6. Conclusions

In this thesis two methods of observation of decontamination were used, indirect and direct methods. The indirect methods of decontamination observation used were by tracking the evolution of the electrical resistivity of the soil and pH, and by visual observation.

Using indirect methods it was possible to estimate the evolution of leachate water concentration in the soil cell. The withish colour observed was caused by the oxydation of the organic matter. The direct method adopted consisted in chemical analysis. By comparing the chemical analyses performed before and after the EKT test, it is possible to quantify the efficacy of EKT.

All methods adopted showed very consistent results and allow concluding that EKT was effective.

Indirect methods can be used *in situ*, after a calibration of the functions that relate the concentration of aqueous solution of leachate and electrical resistivity of the soil. The calibration of the functions is done in the laboratory and for greater accuracy is made for more than one pH value. For *in situ* use, resistivity and pH must be measured locally.

In a general overview it is possible to use EKT for the decontamination of stratified soils, since the results showed a significant decrease in the concentration of leachate.

The efficiency of the electroosmosis is defined by the amount of water moved per unit of electric current, that is, by the electroosmotic permeability coefficient. In clays this treatment is quite effective because of its characteristics. Clays are materials with a high density of surface load and a large specific surface area. With the introduction of stratification, a layer of sand, the complexity increases because the hydraulic phenomena has to be consider. In this case it is necessary to understand what kind of interaction exists between strata, that is, between electrokinetic and hydraulic phenomena.

In order to predict the costs of using the technique, it is necessary to quantify the efficiency increase due to the presence of a sandy strata. With the quantified costs it is possible to compare this technique economically with others, for example to accelerate the drainage through the sand with vacuum.

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