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ORIGINAL PAPER

Electrokinetic remediation of soils contaminated with heavy metals

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Abstract This paper describes the results obtained from an electrokinetic treatment of a real soil polluted by lead acetate. Powdered soil samples were pressed with a consolidometer till 100 kPa to obtain cylindrical specimens with the same characteristics as a subsoil. Tests were carried out in a Perspex electrochemical cell where soil specimens were introduced with a hollow punch. A low intensity direct current was applied in order to remove contaminants, due to electrophoresis and electroosmosis phenomena. The water flow, conductivity, apparent electroosmotic coefficient, as well as other characteristic parameters, were measured throughout the test. The water content and degree of pore saturation were estimated at the beginning and end of the test. The soil slab was divided into four slices and the Pb concentration profile determined. The main factor governing the extraction of contaminant was found to be the pH in the acidic range. Indeed, under these conditions high removal efficiencies could be reached. These results could lead to the design of a new electrochemical treatment cell equipped with a cationic membrane to expand the region of favourable pH within the soil.

Keywords Electrokinetic soil remediation · Heavy metals · Electrokinetic phenomena · Soil characterizations

Nomenclature

a	Generic ionic species
c_a	*a* species molar concentration, [mol m^{-3}]
D	Relative electrical permeativity, dimensionless
D_a	*a* species diffusion coefficient, [m^2 s^{-1}]
D*	Effective molecular diffusion coefficient, [m^2 s^{-1}]
F	Faraday constant, [C mol^{-1}]
H	Hydraulic head, [m]
j_{a1}	Electromigrative flux, [mol m^{-2} s^{-1}]
j_{a2}	Electroosmotic flux, [mol m^{-2} s^{-1}]
j_{a3}	Diffusive flux, [mol m^{-2} s^{-1}]
j_{a4}	Hydraulic flux, [mol m^{-2} s^{-1}]
K_{eo}	Electroosmotic coefficient, [m^2 s^{-1} V^{-1}]
K_h	Hydraulic permeability, [m s^{-1}]
M	Generic metal
M^{n+}	Generic metal ion
n	Volumetric porosity, dimensionless
R	Gas universal constant, [8.314 J mol^{-1} K^{-1}]
T	Absolute temperature, [K]
T*	Tortuosity tensor (scalar in isotropic conditions), dimensionless
u_a	Ionic mobility of *a* species, [m^2 V^{-1} s^{-1}]
V	Potential value, [V]
z_a	Ionic valence, dimensionless
ε_o	Void dielectric constant, [C V^{-1} m^{-1}]
ζ	Zeta potential, [V]
η	Dynamic viscosity of the fluid phase, [N s m^{-2}]
τ	Tortuosity factor, dimensionless

1 Introduction

Remediation of polluted sites has become increasingly more important in recent years in most developed countries. Sites that were contaminated by heavy metals, organic compounds and other pollutants can be sources of contamination for groundwater and can be potentially harmful to the inhabitants in the area. In the last few years

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many researchers have studied new techniques to remove contaminants from soils.

Heavy metal contamination is generally recognized as the most difficult to remove. In this context, several remediation techniques have been devised [1]:

- soil vapour extraction and soil flushing with suitable solutions: this only reduces the volume of contaminated soil without reducing the overall toxicity level;
- soil washing: this is an efficient technique to treat heavy metals with high-permeability in the soil matrix;
- electrokinetic soil remediation: this ensures good results for saturated and unsaturated fine-grain soils.

Electrokinetic treatment removes contaminants by imposing a low direct current between two electrodes, either inserted in the soil or placed into an electrolyte solution that permeates the soil [2]. Electrodes must be of inert material and cheap: graphite, stainless steel, titanium, or conductive plastics are suitable materials.

The electrokinetic method was specifically devised for contaminated soil characterized by low permeability and therefore hard to be remediated with other techniques. The soil/groundwater/sediment system together with the electrodes can be considered as an electrochemical cell [3]. Moreover, when it is crossed by an electrical current the ground undergoes a polarization phenomenon, developing properties similar to those of an electrolytic capacitor. The electric energy accumulated by the particles may even promote redox reactions. The applied potential difference enables metal electrodeposition at the cathode, while the organic contaminants are driven to the anode where they react to produce carbon dioxide and water (in the ideal case, total oxidation takes place).

The aim of this study was to investigate the performance of the electrokinetic treatment of real soils suitably contaminated with a heavy metal and to determine the effect of the interstitial water acidification induced by water electrolysis and how the efficiency changes with time.

2 Theory

The two primary transport mechanisms of contaminants through a soil towards electrodes are electromigration and electroosmosis. However, many reactions/interactions between the soil and contaminants can occur, and generally do, e.g.: electrode reactions, adsorption–desorption, electrophoresis and particle soil lattice modifications [4–7].

The overall efficiency of the process can be affected by the reactions that occur at the electrodes. For instance, the reactions of water electrolysis can significantly modify the pH of the specimen:

$$\text{Anode } (+) \qquad 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

$$\text{Cathode}(-) \qquad 4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \tag{2}$$

Apart from electrolysis, secondary reactions can also take place at the cathode (such as redox reactions), involving either ions (with gas phase release) or metals undergoing electro-depositions:

$$2Cl^- + 2e^- \rightarrow Cl_2 \tag{3}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{4}$$

$$M^{n+} + ne^- \rightarrow M \tag{5}$$

$$M(OH)_n + ne^- \rightarrow M + nOH^- \tag{6}$$

The electrokinetic remediation process is highly dependant upon electrode reactions because it is affected by variations in pH.

These reactions create an acid front and a basic front, at the anode and the cathode, respectively. The acid front moves towards the cathode by electrical migration, diffusion and advection, thereby producing acidification of the soil close to the anode. Conversely, the basic front moves towards the anode causing basification near the cathode. When the soil becomes acidic, the different ionic species adsorbed onto it are progressively replaced by the readily available hydrogen ions located in the interstitial water. Cationic metals, which were adsorbed or precipitated into the soil particles, are substituted by hydrogen ions and the metallic ions are then transported by the water flux from the anode towards the cathode. This is advantageous because the contaminants are more easily driven to the cathode. Hence, the removal efficiency of the electrokinetic treatment is improved.

Furthermore, carbonates are converted in acidic conditions as follows:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_{2(g)} + H_2O \tag{7}$$

whereas, in basic conditions, the following reaction is favoured:

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_{3(s)} + H^+ \tag{8}$$

Consequently, CO_2 and water are released close to the anode into the solution phase, thereby increasing the void volume and the quantity of water, respectively. The latter should favour the electroosmotic flux (higher electric conductivity of the soil) and electromigrative flux (increased concentration of the dissolved ions).

Unfortunately, the reduction of water with the production of hydroxyl ions creates a basic front, which may cause precipitation of heavy metals as hydroxides, oxyhydroxides or could enhance adsorption on soil particles [8].

3 Experimental set-up

A fully automated experimental apparatus was set-up. The core of the plant (the electrochemical cell) was made of Perspex to provide the necessary electrical isolation. An automated system allowed the electrolyte solution, stored in a tank, to be flushed through the treated soil sample.

The electrokinetic tests were carried out under constant direct current using a cell divided into three parts:

- *the inner core*, with a diameter of 80 mm and a length of 120 mm where soil specimens were placed. A hollow punch was placed on top to introduce the material inside the core. The two sides of the samples were then covered with a Whatman glass microfiber filter (GF/F, with particle retention 0.7 μm), to retain the soil and to prevent electrophoretic transport towards the anode and electroosmotic erosion of the cathode.
- *two reservoirs* (anodic and cathodic) that constituted the two end sections. Each reservoir was a cylindrical body, with at the top a vertical cylinder of smaller diameter. The reservoirs were connected on one side to the inner part of the cell, where the specimen was placed. The opposite side is closed and sealed by the electrode that supplied the current. The anode was made of graphite, whereas the cathode was stainless steel.

Control systems, connected to the bottom of the reservoirs, were required for process automation in order to both feed enough water during the whole test and to measure the volume of the filtrated solution. The electrolytic solution in the reservoirs was 0,01 M KCl (a small chloride concentration was necessary when measuring with silver electrodes).

On the cathode side, a high precision differential pressure transducer monitored the static pressure increase inside the reservoir created by the water level rise from a start set value. Data were transformed into voltage values and recorded by a data logger. Due to the reservoir geometry, particularly the upper vertical small diameter cylinder, it was easy to convert the pressure readings into water level values (Fig. 1), and then to estimate the volume of water filtered through the sample. This was possible after a rigorous calibration of the transducer (Druck LPM 9481) connected with an indicator/interceptor (Druck DPI 280). The latter received a continuous signal by the transducer as a function of the water level in the vertical cylinder. Once the reservoir top level was reached, specific electro-valves drained the permeate water out of the cathode reservoir and fed fresh anolyte into the anode reservoir.

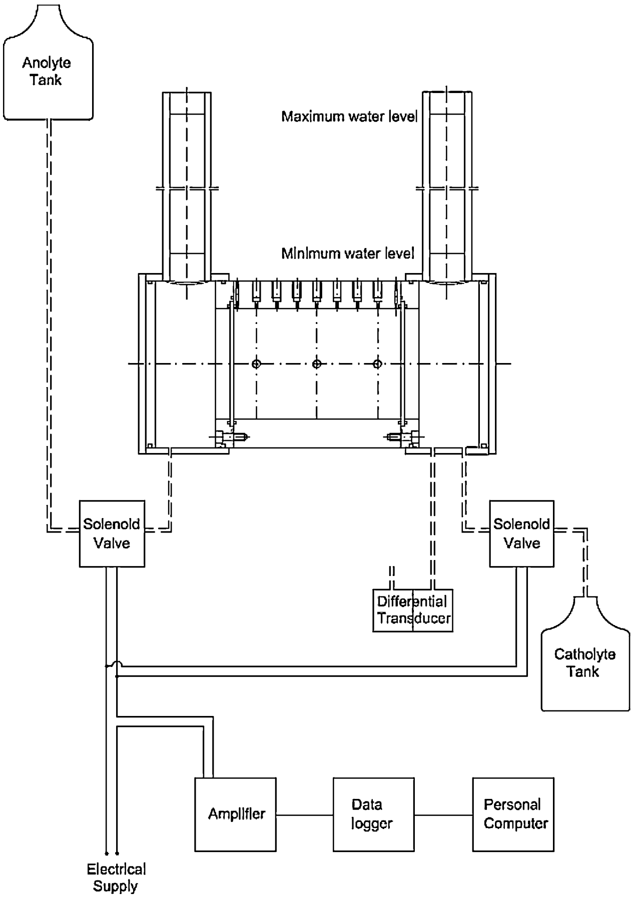

Fig. 1 Scheme of the electrochemical cells with automated feed system

Nine electrodes were inserted into the inner core to determine the loss of potential along the specimen. The cell was provided with three thermocouples to measure the temperature variation along the specimen axis during the experiments. A magnetic stirrer was placed under each reservoir to encourage the release of the gases produced by the electrode reactions.

4 Soil characterization

The choice of the most appropriate technique and operating conditions depends on the nature of the contaminant and the soil characteristics. Only soil with low hydraulic permeability (high clay content) can effectively be treated by electrokinetic remediation. Therefore, specific tests of mineralogical, physical and chemical characterization on actual ground samples are needed. The main characteristics to be analyzed are:

- *Granulometry*: this establishes the grain size and % in weight of all fractions using a molecular sieve (grain size $> 0{,}074$ mm) and aerometer (grain size $<0{,}074$ mm).

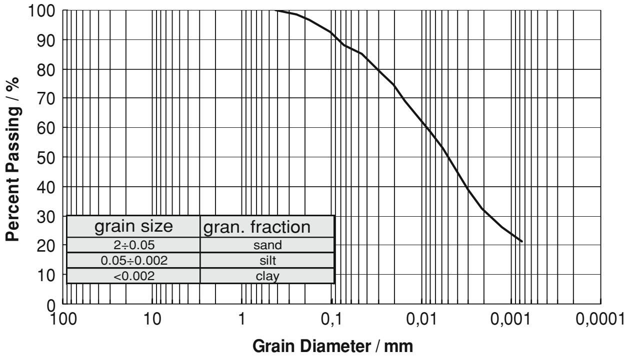

Fig. 2 Grain size distribution curve in the real soil used in the present investigation

The sample used in the present research was a silt-clay soil (Fig. 2) with about 10–15% sand, 30–35% clay and 50–55% silt (see Fig. 2).

- *Atterberg limits* (liquid and plastic limit): the limits are related to the moisture content of cohesive soils and correspond to empirically defined boundaries between the consistency states (liquid, plastic, solid) of the soil fraction passing through the 425 micron sieve. The cohesive state of the soil depends on the superficial negative charge that attracts cations. For the tested soil, the material liquid limit was $w_L = 44.6\%$ and the plastic limit was $w_P = 27.8\%$ (both expressed as percent water over soil mass ratio, but obtained with different testing techniques), with the following plastic index (as difference P.I. $= w_L - w_p$), i.e., P.I. $= 16.8\%$.
- *Cation Exchange Capacity* (C.E.C.): this defines the maximum quantity of cations that can be exchanged by the soil particles. The C.E.C. depends mostly on the clay content and is a function of the quantity of superficial electric charge. A Ba-soil complex is formed from the reaction between $BaCl_2$ and 2 g of soil, after which the complex reacts with $MgSO_4$, where Mg ions replace Ba ions. The excess of Mg ions is determined via EDTA titration. The difference between the initial concentration of Mg and the previous concentration determined through EDTA produces the value of C.E.C. The obtained C.E.C. value was 3.9 milli-equivalent per 100 g of soil.
- *Activity index* (I_a): the determination of the adsorption capacity of surface soil. This parameter is determined with adsorption of a 0.01 g L^{-1} solution of methylene blue: 5 mL doses of methylene blue solution are added step by step to 45 g of soil dispersed in a stirred beacker to form a slurry. After each addition, a small quantity of the soil suspension is collected with a rod and a small drop is then poured onto standard filter paper thereby producing a dark blue stain. The test is prolonged until a dark blue stain surrounded by a light blue halo is formed [9]. With the present investigation I_a values between 10 and 14 were found, which is equivalent to the class 5–6 (according to the activity diagram proposed by Lautrin [10], 5 means soil with active fraction, 6 is normally related to a soil with very active fraction).

5 Sample preparation procedures

A sample of the silt-clay soil was crushed and sieved to select grains smaller than 0.25 mm. The grains were then polluted with a solution of lead acetate (2.5 g L^{-1}) under continuous mixing to get isotropic conditions; a Pb concentration in the soil of about 1000 ppm by weight, referred to dry soil. Usually, the pollutant selection can be done between lead and cadmium due to their interaction with soil pH being stronger than other heavy metals. Pb was selected with confidence because preliminary experiments showed that the soil under study could absorb more Pb than Cd. Moreover, for the Pb treatment, less current density is needed relative to that required by Cd. Furthermore, due to the very high toxicity, Pb is commonly used as a test for polluted soil.

The specimen was then pressed inside a consolidometer until a 100 kPa pressure was reached (Fig. 3). The soil was subsequently inserted into the electrochemical cell and testing was started. Tests were carried out with a constant direct current of 40 mA until 100 V potential drop over the cell was achieved.

Same tests were performed with HCl solutions (0.02 M) as well as with a CH_3COOH/CH_3COONa buffer solution (0.2 M) which permeated from the anode to the cathode by electrokinetic phenomena. HCl and buffer solutions were tentatively used, unfortunately with poor results, in an attempt to hinder soil basification during the treatment.

6 Results

The water volume permeated through the specimen versus run time was calculated from continuous readings of the

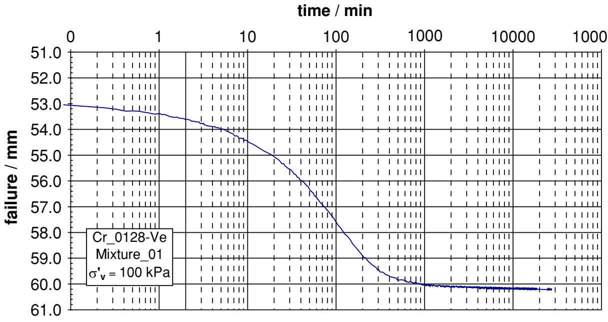

Fig. 3 Consolidation curve (i.e. partitioning of soil vs. time) for the silt-clay employed in the experiments

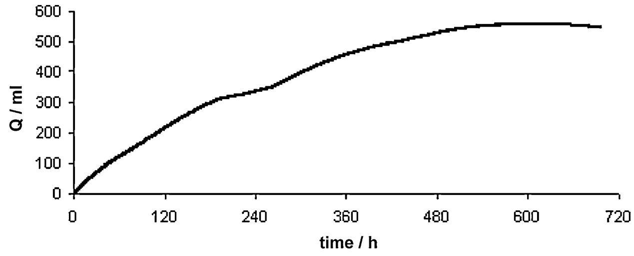

Fig. 4 Water volume permeated through the specimen as a function of treatment time

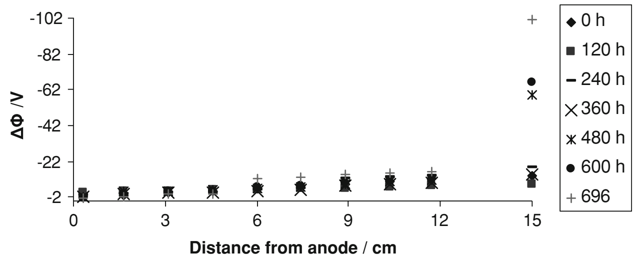

Fig. 5 Potential drop between electrodes vs. time. Legend: 0 h (◆); 240 h (■); 480 h (×); 600 h (●) 696 h (+)

transducer output signals and using the transducer calibration curve. The experimental curve in Fig. 4 reaches a horizontal asymptote after 600 h. From this time on, the water flow was obstructed due to the occlusion of pores by precipitate and several hydroxides.

The overall potential evolution versus time was estimated using nine Ag electrodes inserted inside the specimen (Fig. 5). During the first ten days, the potential drop between the anode and the cathode was almost constant, but in the following days the cathode side potential drop increased. This trend also reflected the occlusion of some pores due to desaturation phenomena in the proximity of the cathode associated with the consequent increase of the potential drop [11].

The evolution of the apparent electrical conductivity coefficients σ_a was determined from the ratio between the current density and the electric field. The electrical conductivity of the liquid phase was directly measured within the interstitial pore liquid. The trend of the electrical conductivity emphasized results already analysed in terms of global potential drop. The measured electrical conductivity coefficients are shown in Figs. 6 and 7.

The apparent electrical conductivity decrease was also confirmed by the increase of the temperature difference between cathode and anode during each test; for all the tests, this temperature difference was about 6 °C at the end of each run. The resistivity increase associated with the decrease in conductivity dissipates, a large amount of heat during the passage of constant electrical current.

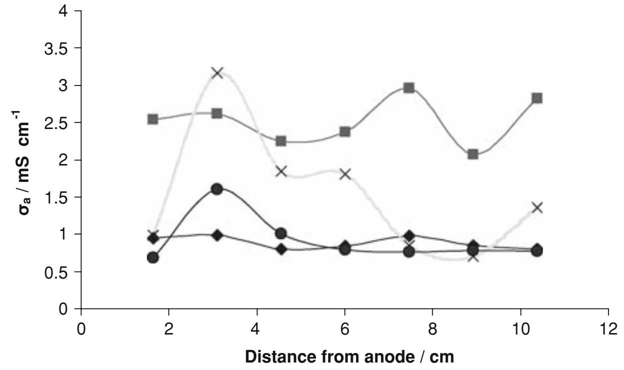

Fig. 6 Evolution of the apparent electrical conductivity coefficient $\boldsymbol{\sigma_a}$ in the specimen at: 0 h (◆); 120 h (■); 360 h (×); 600 h (●) of treatment

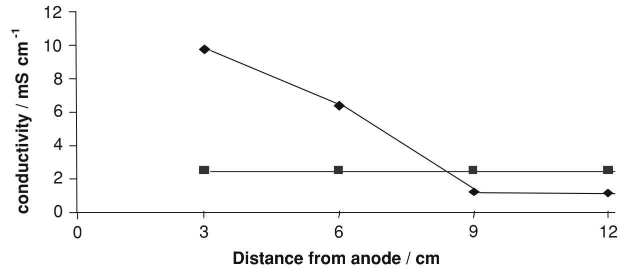

Fig. 7 Electrical conductivity of the interstitial water between the electrodes at the beginning (■) and end (◆) of the test

The anomalous peaks shown in Fig. 6 were due to dissolution of precipitates (e.g. hydroxides, carbonates), which increased the void fraction of the soil.

As with electrical conductivity, the pH was measured within the interstitial electrolyte at the start and the end of the test. The pore solution cannot be obtained from soil samples using chemical extraction methods because this method would alter the composition of the solution. Therefore, a method known as squeezing was chosen. The squeezer is a modified version of an oedometer. The soil was placed into a rigid stainless steel cell mechanically loaded from above, while the interstitial pore electrolyte was drained at both ends through porous stones. Each stone was then connected to a drainage tube for the collection of the squeezed water. The specimen was divided into four slices and for every slice the pH and carbonate/bicarbonate concentration of the interstitial pore solution were measured. The pH and total carbonate concentration values are shown in Figs. 8 and 9, respectively.

Using a small hollow punch (diameter 2.5 cm and height 1 cm) to sample a fixed volume of soil from each specimen slice, it was also possible to determine the saturation, the amount of water and the void volume. Table 1 shows that the void fraction *n* (void volume/total volume) and *w* (interstitial water/dry soil mass ratio) increased near

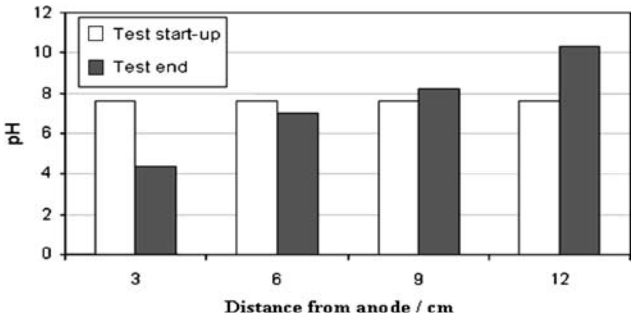

Fig. 8 Pore solution pH along the soil specimen at the beginning and end of the test

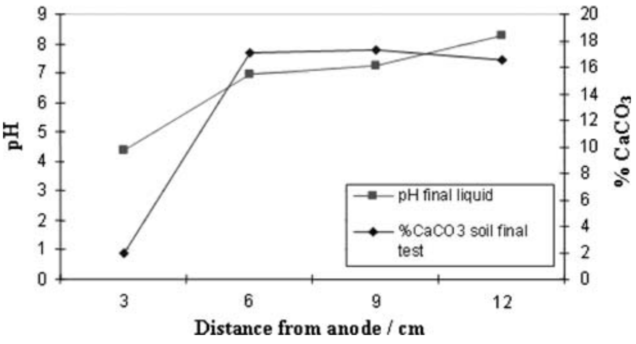

Fig. 9 Pore solution carbonate concentration and pH along the soil matrix at the test end; effect of pH on the carbonate concentration

the anode due to dissolution of the carbonate and several precipitates for the anode acid conditions. In the region of higher pH, close to the cathode, the precipitation of heavy metals hydroxides and carbonates may cause sediment formation, causing pore occlusion and thereby reducing *n* and *w* (Table 1).

The pH variations and the presence of electric field changes in the soil texture can be seen with X-ray diffraction (Fig. 10): not only did the carbonate peak near the anode disappear but other small differences in the spectra were noticeable [12, 13].

A loss of electroosmotic conductivity may be attributed to the zone where the acidic and basic fronts overlap [14]. This phenomenon is due to the low electrical conductivity of the soil, which is the main parameter affecting the electroosmotic flow rate.

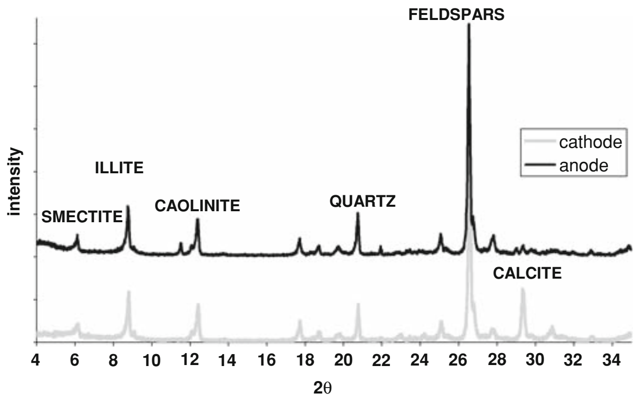

Fig. 10 Comparison of X-ray diffraction spectra at the two extremes of the treated soil

An apparent electro-osmotic coefficient is defined as:

$$K_{eoA} = \frac{q_w/A}{E(x)} \left[\frac{\mathrm{cm}^2}{\mathrm{Vs}}\right] \qquad (9)$$

where $E(x)$ is the electric field calculated between two consecutive Ag electrodes placed in the specimen; $E(x)$ depends on the axial position along the soil sample in the test cell ($x = 0$ and $x = 120$ mm are the end sections of soil specimen near the anode and cathode, respectively).

During the tests two apparent electroosmotic coefficients were derived, one at the anode (inlet flow and acidic conditions, $E(x)_{16.5}$ determined between Ag electrodes 1 and 3) and the other at the cathode (outlet flow and basic conditions, $E(x)_{103.5}$ determined between Ag electrodes 7 and 9). The two coefficients were initially comparable (Fig. 11), but after some time while the anode coefficient remained stable, the cathode one decreased due to the lower pore volume, which induced a higher tortuosity coefficient.

At the end of the tests, for each of the four slices, the Pb concentration was evaluated. The dissolution of Pb from the soil into a liquid matrix was achieved by aqua regia. The samples were analyzed by atomic absorption (Perkin Elmer 1100 B).

Figure 12 shows a considerable reduction of Pb at the anode side, while on the cathode side only a small improvement was perceivable. As described above, the

Table 1 Values of soil characteristic parameters determined with a hollow punch

	Initial specimen	Slice 1 near anode	Slice 2	Slice 3	Slice 4 near cathode
Distance from anode/cm		3	6	9	12
w = solution/dry soil mass	36.4	40.3	34.5	34.8	26.9
n = void fraction	0.48	0.56	0.46	0.48	0.47
e = void volume/dry soil volume	0.91	1.26	0.85	0.93	0.89
S = void volume/water volume/%	92.3	86.1	92.8	84.9	69.0

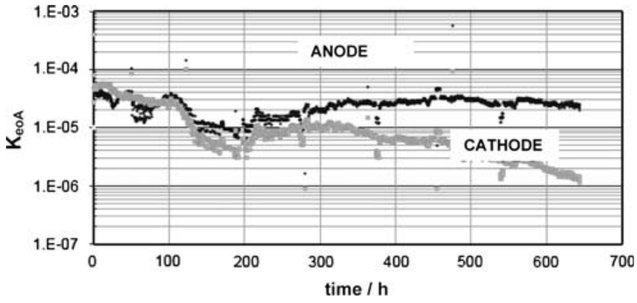

Fig. 11 Apparent electroosmotic coefficient variation during the test

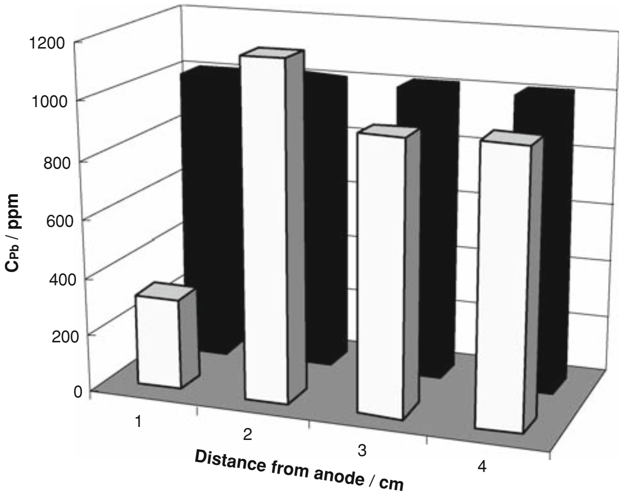

Fig. 12 Pb distribution across the specimen at the start-up (■) and end (□) of the experiment

high quantity of hydrogen ions on the anode side led to the replacement of some metal ions by adsorption onto soil particles. At this point the soluble ions in the pore interstitial liquid could move towards the cathode and be confined in the cationic reservoir basin. Here they could either be electrodeposited on the electrode surface or accumulate in the interstitial liquid. Unfortunately, the pH increase at the cathode side led to the precipitation of metal hydroxides, carbonates and other solids plugging the matrix pores. The plugged pores cause a reduction in the electroosmotic and electromigration flux so the electrokinetic technique becomes progressively ineffective.

7 Conclusions

The following conclusions can be drawn:

- Similar modifications of pH, total carbonate concentration, electrical conductivity and electroosmotic coefficients were monitored during each performed test in four slices of the soil specimen.
- A high fraction of lead was removed in the region near the anode (around 70% of that initially present in this confined basin) because the release of the metal ions into the solution phase was favoured in this region. However, when the metal ions met the region of high pH, near the cathode, they may get adsorbed into the soil or precipitated, therefore only 7% of the pollutant is effectively removed from the soil.
- The removal efficiency of the process is significantly reduced if the soil has either a high pH or a large carbonate fraction because these parameters provoke the pores occlusion due to precipitation phenomena. As a consequence, a decrease in the electroosmotic coefficient of electrical conductivity and consequently of liquid fluxes takes place.
- High heavy-metal removal efficiencies could be obtained only when the specimen was characterized by an acidic pH. The soil matrix acidification is, unfortunately, both expensive and not safe from the environmental viewpoint.
- The selection of the electrokinetic process depends not only on removal efficiencies but also on cost evaluation. Many aspects must be taken into account: labour and electrical power (the latter is a function of the clean-up time) costs, electrodes and membranes costs as well as the soil properties and depth of contamination.

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