Suitability of electro-remediation for clean-up of PAH-contaminated clays

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Abstract

The removal of PAH from soils, especially clayey soils, is a difficult task. Electro-osmosis is a technique which has been applied for the mobilization and cleanup of contaminants in clayey soils. The present focus is on the laboratory study of electroosmosis in two clayey materials: Wyoming bentonite and a contaminated peaty clay soil from Olst, the Netherlands. The results were quite disparate, but Olst soil experiment achieved a quite promising coefficient of electro-osmotic conductivity and a good base for field applications.

Key words

electro-osmosis, clay, polycyclic aromatic hydrocarbons (PAH), clay weathering, remediation.

Introduction

Clay layers act as semi permeable membranes, where water transport can be induced by a gradient in electrical potential. This flow type, termed electro-osmosis, is significant in materials of very low permeability, i.e. of hydraulic conductivity ≤ $1 \cdot 10^{-9}$ m /s(Mitchell 1993). Fluid flow by hydraulic force is impeded, whereas electro-osmosis is far more effective for creating fluid flow. The electro-osmotic volume flux of a solution (J_v in m/s) is expressed by the following phenomenological equation:

$$J_v = k_e \, \nabla(-E)$$

where E is the electrical potential (V), and k_e is the coefficient of electro-osmotic conductivity (m^2 /V/s). The practical range for k_e of fine-grained soils is between $1 \cdot 10^{-9}$ and $1 \cdot 10^{-8}$ m^2 /V/s.

Electro-osmosis has been applied for the mobilization and cleanup of contaminants in clayey soils (Pamucku and Wittle 1992; McNab and Ruiz 1999; Saichek and Reddy 2005) and may be a promising and cost-effective technology, in particular for the removal of hydrophobic organic contaminants (HOC) from clays. A common group of HOC in soils are the polycyclic aromatic hydrocarbons (PAH). Recent studies (Saichek and Reddy 2005) have focused on electro-remediation of PAH-contaminated clayey soils and emphasize the large enhancement of PAH-mobility by surfactants. Until now successful application of electro-osmosis for cleanup of contaminated sites has been scarce. In part this is due to insufficient knowledge of geochemical processes involved. Electro-osmosis in clay has resulted in unexpected side effects, e.g. acidification and subsequent clay mineral degradation and precipitate formation in the soil. At large voltages electrolysis of water occurs, causing production of H^+ and O_2(g) at the anode and of OH^- and H_2(g) at the cathode (Grundl and Michalski 1996; Chen and Murdoch 1999). In lime-deficient soils the resulting low pH front moves through the clay, meeting the hydroxyl-ions near the cathode. Since at low pH soil-Fe and -Al and contaminant heavy metals become mobile, they may precipitate as salts near the cathode and/or cause changing surface charge of the minerals, leading to declining electro-osmotic and hydraulic conductivities (Cherepy and Wildenschild 2003*)*. We studied these effects of electro-osmosis in contaminated clay soil and clean Wyoming bentonite The soil is contaminated by PAH, which are hard to remove by hydraulic flow. The major objectives of this presentation are to quantify the magnitude of electro-osmosis in the selected clayey materials, to identify geochemical processes and effects of electro-osmosis in the solid and liquid fractions of the clay and to quantify the transport of polycyclic aromatic hydrocarbons from clays by means of electro-osmosis.

Methods

Two soils were studied in the laboratory: a pure Wyoming bentonite clay and a contaminated peaty clay soil, from a former asphalt factory terrain in Olst, the Netherlands. The pH of the bentonite clay and contaminated soil was determined in a standard 1:2.5 KCl suspension, using a glass electrode; cation exchange capacity (CEC) was quantified by the silver–thiourea method, and the exchangeable ions were determined by inductively coupled plasma mass spectrometry (ICP-MS); zeta-potential measurements were performed by

Malvern Zetasizer Nano equipment; PAH were extracted according to Hartmann (1996) and quantified by gas chromatography–mass spectrometry (GC-MS); organic carbon and carbonate content were determined by TGA, using a Metler AT200.

An experimental cell was designed for the study of electro-osmotic flow and geochemical side effects in clayey soils (Figure 1). The current density used to study the electroosmotic flow in bentonite was 0.005 A m^{-2}. For the contaminated soil, current density was increased to 0.1 A m^{-2}. The cylindrical cell, made of PVC, consists of a top and bottom part in between which a layer of dry bentonite or soil is fitted in a circular space of about 6 mm thick and 50 mm diameter. The resulting bulk density of the clay is 0.85 g cm^{-3}. On each side of this clay slab a porous stone is present of about 5 mm thick. On the interface of each porous stone with the clay, a gold wire is placed to function as electrode. By means of tygon tubing through the top and bottom of the cell the clay is in contact with equilibrium reservoirs containing influent and effluent aqueous solutions. Initial equilibrium composition of both reservoirs is 10 mmol/L NaCl in demineralized water. Water saturated clay is placed in the cell and subsequently brought in equilibrium with the reservoir solutions during 5 days. Each reservoir is connected to a capillary standpipe with an internal diameter of 2.93 mm. Thus inflow and outflow rates are monitored. The volumes of anolyte and catholyte reservoirs are approximately 10 ml each. The volume of the water-saturated bentonite is kept constant by means of clamp screws, inserted on the cell, to prevent it from swelling. Throughout the experiments both reservoirs are continuously recirculated.

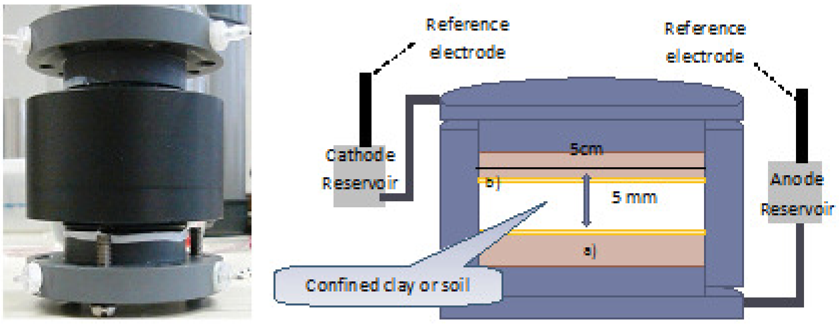

Figure 1. Experimental cell and schematic representation. a) porous stone; b) gold electrodes

During the electro-osmotic experiment the pH is monitored in both the anolyte and catholyte reservoirs. Furthermore the voltage difference between the electrodes is monitored as well as the reservoir voltages. Both electro-osmotic flow and pH are recorded for 34 days. After termination of electro-osmosis both reservoirs are sampled for analysis of PAH by GC-MS and the clay layer is cut in four slices perpendicular to the flow direction. .

Results and discussion

The two clayey materials are strongly different, in terms of contaminant content and composition. Table 1 shows some of the characteristic features of the materials. There is a noticeable difference in pH. Bentonite's higher pH and lime content strongly buffer the acidic front generated by the electric field. Figure 2 exemplifies the pH differences occurring during electroosmosis in Olst soil.

Table 1. Summary of the material characteristics; *CEC occupied by Ca,K, Mg, Na; ** in 0.01M NaCl solution

Parameter	**Olst soil**	**Bentonite**
pH	4.84	7.51
*CEC (cmol·kg)**	10.78 ± 0.263	18.69 ± 0.645
$CaCO_3$ *(%)*	n.d.	10.63
*Zeta potential (mV)***	-42.10	-52.8 ± 4,55
Organic carbon (%)	1.6	0.0064
PAH (mg/kg)	2751.5±113	n.d.

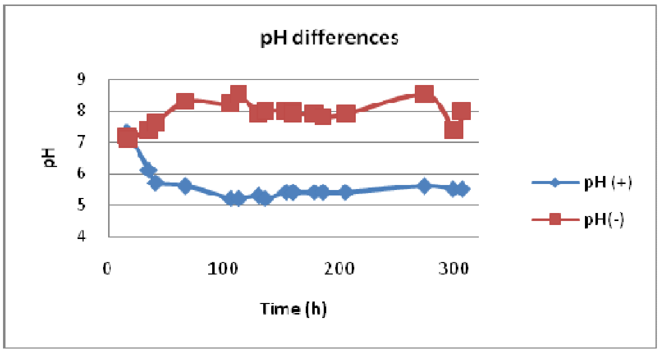

Figure 2. Development of the acidic front (pH +) from the anode, and alkaline front (pH -) from the cathode during electroosmosis in Olst soil.

The achieved electroosmotic flow significantly differed between the bentonite and the contaminated soil. After determining the total quantity of water transported to the cathode (or anode, depending on environmental conditions), the coefficient of electro-osmotic conductivity was determined. The bentonite experiment resulted in a $k_e = 4.2 \cdot 10^{-8}$ m^2/V/s. Figure 3 shows the water flows during the electroosmotic experiment in the Olst soil. This experiment has a $k_e = 2.2 \cdot 10^{-8}$ cm^2/V/s. This increase of electroosmosis is in the optimistic range of literature, which says that k_e for soil should be between $1 \cdot 10^{-8}$ and $1 \cdot 10^{-9}$ m^2/V/s (Mitchell 1993). This value is quite promising for electroosmotic remediation in the field. Almost 300 ml have passed though a 5 mm soil plug during 12 days at a voltage gradient range of 0.58 to 8.0 V/cm.

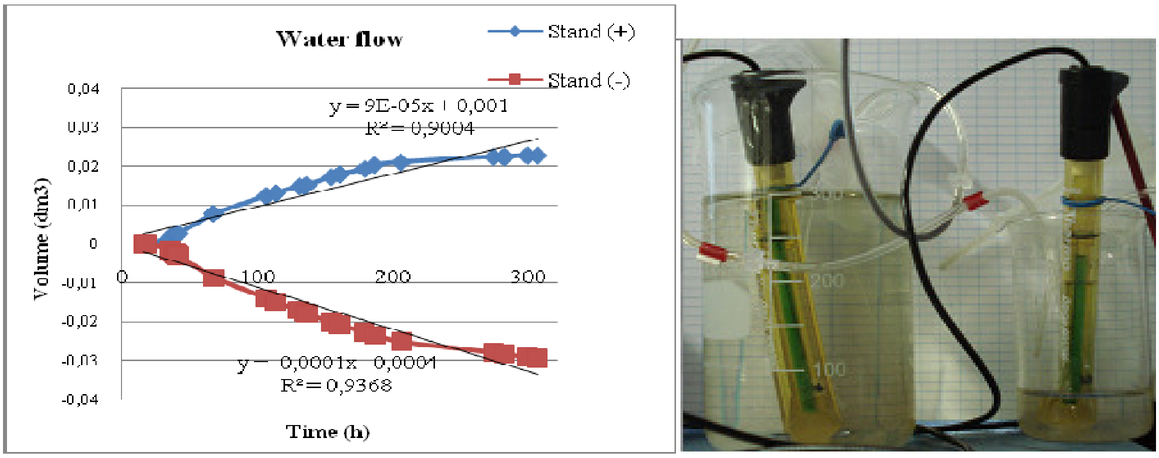

Figure 3. Graph presents the water flow during the experiment from cathode to anode, while the picture on the right shows the difference in water level after 12 days of experimental time

However, the water flow in the Olst soil was the opposite to the expected direction. Migration of water towards the anode is expected in specific cases, e.g. where the pH of the soil is below its zero point of charge. Minerals such as Fe_2O_3, $Fe(OH)_3$ and $Al(OH)_3$ have a positive surface charge in the pH-range below about 7 (e.g. Sposito 2008). FeS_2 was identified by Scanning Electron Microscopy (SEM) as a possible species existing in the Olst soil (Figure 4).

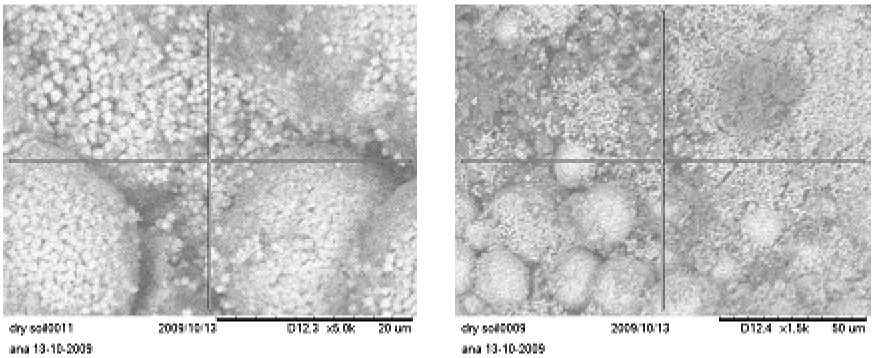

Figure 4. Scanning Electron Microscope images of Olst soil showing possible presence of FeS_2 species.

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