Spectral induced polarization for monitoring electrokinetic remediation processes

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Electrokinetic remediation (EKR) is an emerging technology employed to extract heavy metals, radionuclides and organic compounds from saturated or unsaturated soils, sludge and sediments.

This technique relies on the application of a low-intensity electric field across electrode pairs placed on each side of the contaminated mass. The applied electric field induces the mobilisation of contaminants and water through the medium toward the electrodes due to three main transport mechanisms: electromigration, electroosmosis and electrophoresis. Electromigration is the transport of charged species trough the pore solution towards the oppositely charged electrode, electroosmosis is the movement of pore fluid and electrophoresis is the transport of charged particles and colloids. Moreover, during the electrokinetic process, electrolysis reactions occur at the electrodes, producing oxygen gas and H^+ ions at the anode and hydrogen gas and OH^- ions at the cathode. Water oxidation at the anode generates an acid front that migrates toward the cathode; conversely, water reduction at the cathode produces a base front migrating toward the anode. The pH profile across the porous medium significantly affects the efficiency of the remediation process. The advance of the acid front generally results into desorption and dissolution of metallic species, promoting their mobility. On the contrary, the advance of the base front typically has several negative effects such as adsorption and precipitation reactions that result in a decrease in the process efficiency. In some cases, the acid front may not be able to develop because of the high buffering capacity of the medium. Under this condition, it is necessary to use chemical reagents such as acids or chelants to control the pH to a desired level and achieve the solubilisation of contaminants.

Monitoring of electrokinetic processes both in laboratory and in field is usually conducted by means of point measurements and collecting samples from discrete locations. Geophysical methods can be very effective in obtaining high space and time resolution mapping for an adequate control of the electrokinetic processes. This study investigates the possibility of using geophysical methods to monitor electrokinetic remediation processes. Among the geophysical methods, the spectral induced polarization (SIP) technique has been selected because of its capability to provide qualitative and quantitative information about the physico-chemical characteristics of the porous medium.

Laboratory-scale electrokinetic remediation experiments were carried out on marine sediments contaminated by heavy metals, under different operating conditions. Four experiments (EXP1, EXP2, EXP3 and EXP4) were performed by changing the intensity of the applied electric field and the type of conditioning agent circulated within the system to enhance the extraction process. The experiments were conducted in a prismatic acrylic cell, consisting of four principal parts (Fig. 1): the sediment compartment, the electrode compartments, the electrolyte solution reservoirs and the power supply. Tap water was used as processing fluid in EXP1 and EXP2. To promote metal removal a 0.1 M solution of citric acid and 0.1M EDTA solution were used in EXP3 and EXP4, respectively. The applied voltage gradients were 50 $V\,m^{-1}$ (EXP1 and EXP3) and 80 $V\,m^{-1}$ (EXP2 and EXP4). The treatment duration was 10 days. At the end of each experiment, the material was sampled from five locations (S1 to S5) and analysed for pH and total metal content.

SIP measurements were performed on the sediments before and after the EKR treatments. Sediment samples were collected directly from the sampling locations S1 to S5 of the EKR cell. The measurements were performed on cylindrical sample holders, having a length of 200 mm and an inner diameter of 36 mm. They were made of acrylic, which produces no spurious phase response. The current electrodes were stainless steel plates. The potential electrodes were circular silver wires placed inside grooves to keep them outside the current path, in order to reduce erroneous phase shifts due to their polarization. The samples were manually prepared and compacted, resulting in slight differences in porosity and water saturation which influenced the SIP response. Three repeated measurements were taken on each sample in the frequency range 10^{-3}-10^{3} Hz, each time by performing a new sample preparation. The mean resistivity and phase spectra were calculated. To quantitatively compare the SIP responses of the sediment samples, the Debye decomposition method was used to fit the data. Three parameters were determined for each spectrum: DC resistivity (ρ_0), total chargeability (m) and mean relaxation time (τ). By analysing the data, a linear relationship between the sample total chargeability (m) and pH was found (Fig. 2). This relation can be explained taking into account the electrical double layer (EDL) polarization mechanism. According to the EDL theory, a pH variation is responsible for a change in the zeta potential of the sediment, which is proportional to the amount of electric charge at the EDL. A variation of chargeability is thus directly associated with an alteration of electric charge at the EDL. Such a relationship has potential value for the interpretation of SIP data, encouraging the field-scale engineering implementation of the SIP method for monitoring EKR processes.

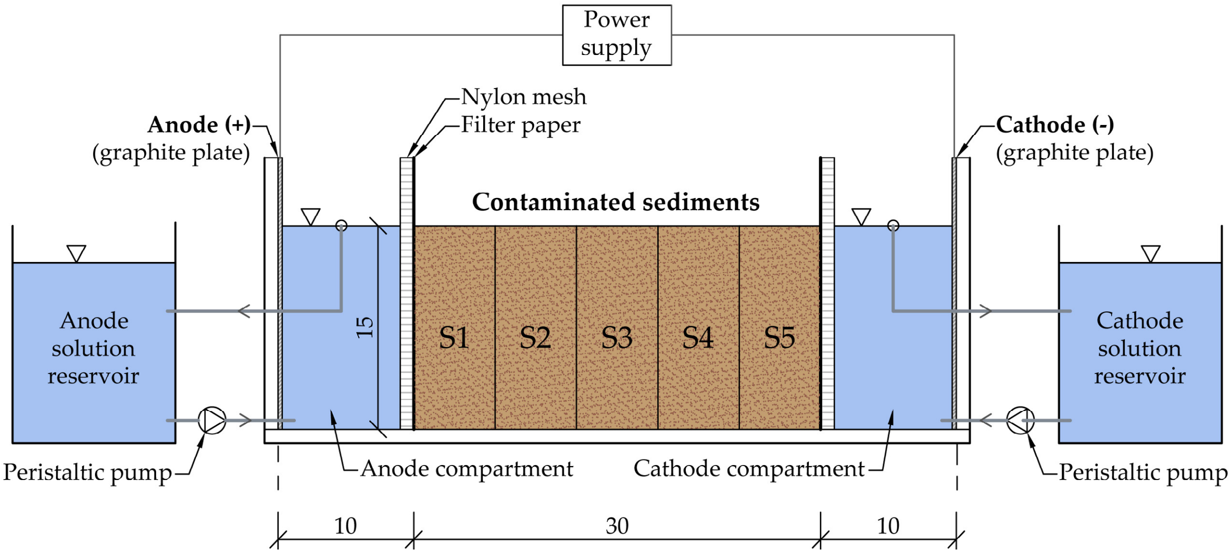

Fig. 1: Schematic diagram of the experimental electrokinetic cell. The material is divided into five equal sections (sampling locations) from S1 to S5. (Dimensions are in cm).

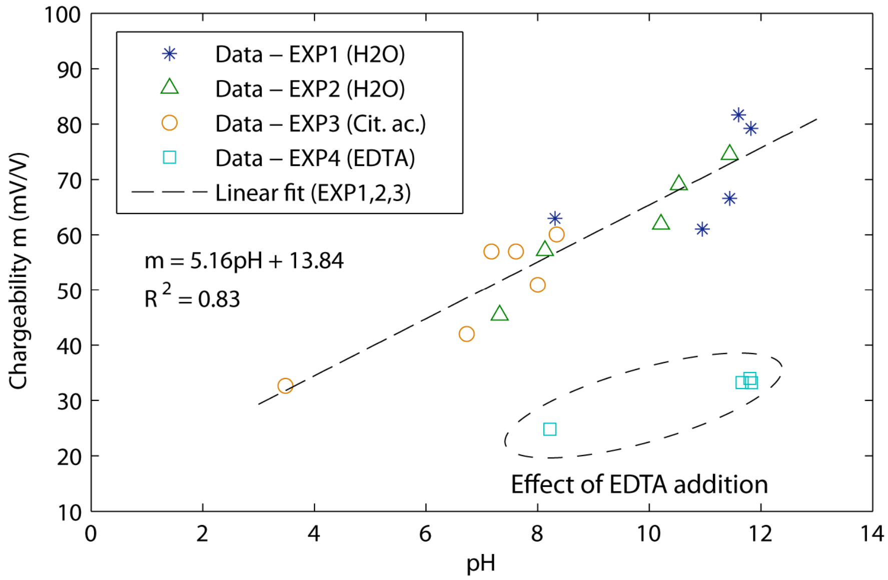

Fig. 2: Variation of chargeability with pH. Symbols show measured data. The line is determined by linear regression. The quality of fitting is indicated by the coefficient of determination R^2.