ENHANCEMENT OF ELECTROKINETIC SOIL CLEANING USING PLATE GRAPHITE ELECTRODES: FIRST RESULTS

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Remediation of soil polluted by heavy metals is an important issue of the environmental engineering, since the wide variation in the characteristics of soil and pollutants requires different methods to remediate contaminated soil. Electrokinetic (EK) remediation is a recent technique for fine-grained soil and/or clayey soil (Acar et al., 1993).

Traditionally EK remediation is based on the application of a fixed voltage between two electrodes inserted vertically in the soil: this technique requires high power levels (some MW), with consequent security and cost problems. In order to prevent these problems, several enhanced processes have been developed, which depend on the class of contaminants and on the characteristics of the surface soil. Some of these enhanced processes are based on the control of pH by addition of acid solution near the cathode (Zhou et al., 2003) or by using IEM (ion exchange membrane) or CSM (cation selective membrane) to prevent penetration of OH- in the soil; other methods are "different" versions of the EK process like EK bioremediation, electrochemical geooxidation,
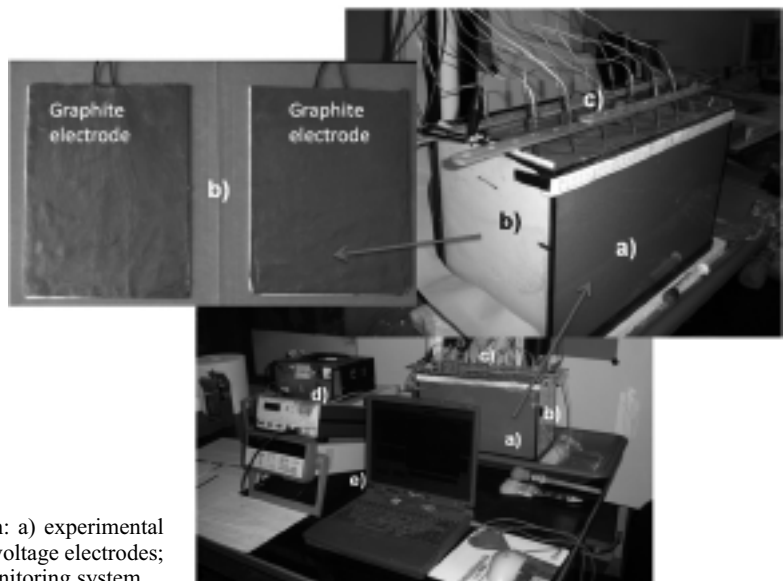

Fig. 1 – Experimental system: a) experimental cell; b) current electrodes; c) voltage electrodes; d) energization system; e) monitoring system.

electrosorb (Reddy et al., 2003; Chang et al., 2006; Mascia et al., 2007; Kim et al., 2009). Starting from 1998 at the Applied Geophysics Laboratory of the University of Florence many experiments have been carried out to enhance the EK remediation: these enhanced processes are based on the requests of lower voltage levels by means the signal optimization (Losito et al., 1995; Cherubini et al., 2002) and on the optimization of the electrode material (Losito et al., 2009). In this work we present the results of the last experiments carried out to study an enhanced electrode configuration (plate electrodes (Fig. 1b) instead of linear or vertical electrodes) and the signal optimization (sinusoidal or ramp up positive signal).

The experimental cell is a glass box (39 x 19 x 24 cm) (Fig. 1a): the carried out experiments can be considered as a medium-scale, that means intermediate level between the soil-sample scale and the field-model scale. The used soil is a very fine silica sand coming from Melfi (Potenza – Italy) with a small content of silt (Ømean = 0.125 – 0.063 mm): we selected this sand because of its high silica content and the very low level of phyllosilicates. We polluted the sand with a solution of $Na_2CrO_4 \cdot 4H_2O$ to have a concentration of 2.5 $mg_{Cr(VI)}/kg_{dry\ soil}$, that is a bit higher than the minimum legal limit (2 $mg_{Cr(VI)}/kg_{dry\ soil}$). We tested two different initial pollutant distributions: concentrate and diffused. We tested and compared two different energization signals: a positive sinusoidal (T_{Sin}=24 h, ΔV_{MaxSin}=1 Vcm^{-1}) and a positive ramp up (T_{Ramp}=24 h, $\Delta V_{MaxRamp}$=1 Vcm^{-1}).

The energization electrodes are two very thin (0.25 mm) ®Sigraflex foil (flexible graphite foil manufactured by SGL Carbon Group from expanded graphite) stuck on a PVC plate (19 x 21 x 0.3 cm) (Fig 1b): since the preliminary test on this materials (electrolysis of salt water) have shown its excellent quality (good conductivity and mechanical strength for at least 170 h) we decided to use this material, although we never test before plate electrodes of this size (Cherubini et al., 2002; Losito et al., 2009) and references are almost absent.

The experiments have been carried out as follow:

a) placement of graphite electrodes; b) filling the glass tank with no-polluted dry sand (about 17 l); c) water saturation of the sand; d) pollution of a sand little volume (0.17 l); e) pause of 60 h; f) start of energization with positive sinusoidal signal; g) energization for 96 h; h) stop of the energization;

i) mix of the sand to obtain a diffused concentration of the pollutant; j) start of energization with the same signal; k) energization for 96 h; l) stop of the energization; m) empty the glass box;

n) start of a new procesess, with the same procedure from step a) to step m) using new no-polluted sand and using a rump up signals as energization function at steps f) and j).

During the processes we sampled the soil for chemical analysis.

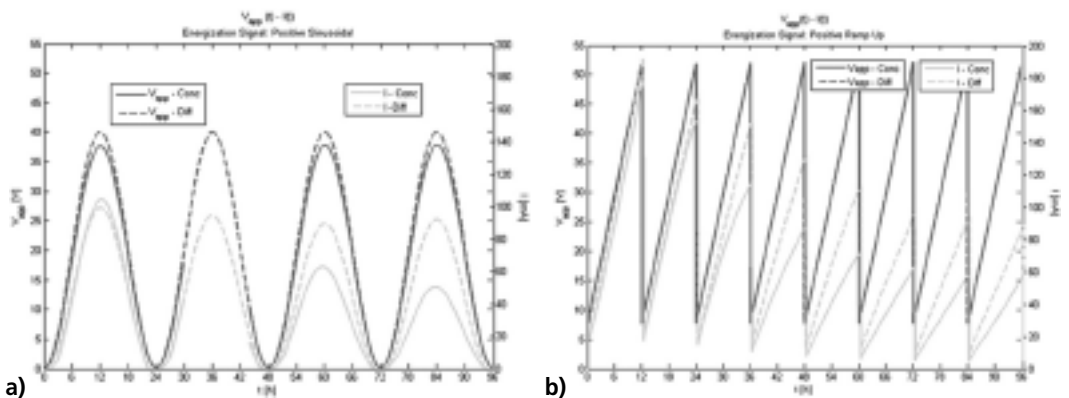The tests carried out in the glass box with ®Sigraflex plate electrodes confirm the excellent

Fig. 2 – Electrical signals: comparison between Sinusoidal energization (a) and Ramp Up energization (b). Black lines are Vapp [V] and grey lines are I [mA] for two different initial pollutant distribution, concentrate (solid lines) and diffused (dashed line).

quality of this material (mechanical strength for at least 385 h), allow to better constrain the electric field and allow to test different operating conditions with no decay until breaking of the electrodes.

The monitored applied voltage (V_{app}) and current (I) (Fig. 2) show that:

i) all the experiments carried out for four days and all data are coherent, although during the first a monitoring interval have been lost;

ii) given the initial concentrate pollutant distribution, the current during the sinusoidal energization ($I_{SinConc}$) is halved after 48 h (Fig. 2a, grey solid line) because the cell resistivity increased of 50% (Fig. 3, black solid line);

iii) given the initial diffused pollutant distribution, the current during the sinusoidal energization ($I_{SinDiff}$) remains almost stationary (Fig. 2a, grey dashed line) and consequently also the resistivity (Fig. 3, blue dashed line);

iv) the current during the ramp up energization decreases both for concentrate and diffused initial pollutant distribution ($I_{RampConc}$ and $I_{RampDiff}$) (Fig. 2b, grey lines) and consequently the cell resistivity increase (Fig. 3, grey lines);

v) the EK process is more effective starting from a non homogeneous distribution of the pollutant and using a positive Ramp Up energization signal (Fig. 3).
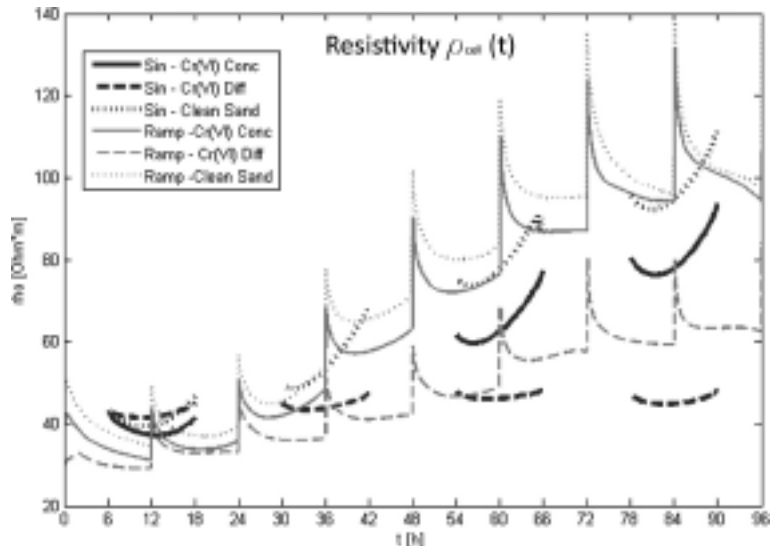

Fig. 3 – Resistivity trends [Ωm] of EK processes. Comparison between during Sinusoidal energization (black lines) and Ramp Up energization (grey lines) for three different initial pollutant distribution: concentrate (solid lines), diffused (dashed lines) and no-polluted (dotted lines).

The increase in resistivity was attributed to the chemical cleaning of the sand, produced by the EK process and clearly enhanced by the plate electrodes.

To verify this hypothesis we:

a) decided to study the electrical behavior of four sand samples (one of natural sand, one of sand polluted with the same concentration of heavy metal tested in the glass box, one made for 1/3 of polluted sand and the remaining 2/3 clean sand and the last made for 2/3 of polluted sand and the remaining clean sand; Ø=3.5 cm, L=10.5 cm) versus frequency (0.001 – 1000 Hz) and voltage amplitude (1.5 V_p, 3 V_p and 5 V_p) using the 4-electrode array technique. The results of these frequency test (Fig. 4) show that the resistivity and the phase displacement of the two non-homogeneous samples is higher than the one of the homogeneous: there is an overvoltage due to sample anisotropy, so that our hypothesis is verified.

b) decided to test the EK process starting from no-polluted sand, using the same glass box and the same energization signals: also for these test we observed a strong increase of resistivity (Fig.
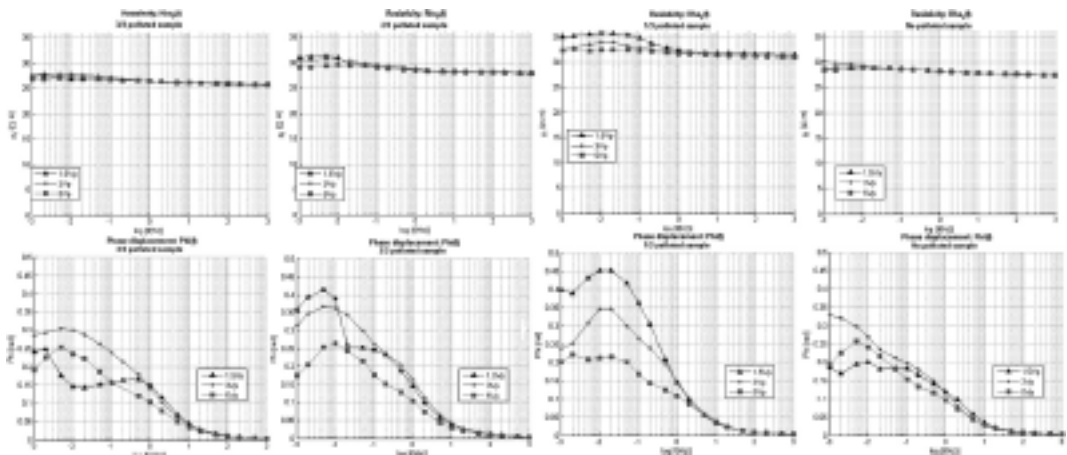
Fig. 4 - Comparison between sample resistivity [Ωm] and sample phase displacement [rad] versus frequency (0.0011-1000 Hz) and voltage amplitude (1.5V_p, 3V_p and 5V_p).

3, dotted lines). The Fig. 3 also shows that the sinusoidal signal is more effective within the first 48 h and that with the ramp up signal, starting from a non homogeneous distribution of the pollutant, we obtain the same result as with the sinusoidal signal, starting from a non-polluted sand.

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