Electrokinetic remediation is based on the application of direct current electric potential to the contaminated soil by one or more series of electrodes adjusted as anodes and cathodes. The difference of electric potential among anodes and cathodes promotes reactions and transport of non-ionic as well as ion species in soil thus resulting in mobilization and transport of contaminants towards electrodes. The main electrokinetic mechanisms are called electro-migration and electro-osmosis. The first creates motion of ionic species towards the electrode of opposite charge in the electric field, hence the electro-osmosis is the motion of liquid induced by an applied potential across a porous material, capillary tube, membrane, microchannel, or any other fluid conduit. The combining effects of the electric field and the electric charge result in electro-osmotic flow towards the cathode (Cameselle and Reddy, 2012). During electrolysis of water at the electrodes, proton (H^+ ) and hydroxyl ion (OH^- ) are generated and then transported towards these electrodes. Acidic front (H^+) is transported from the anode towards the cathode, but an alkaline (OH^-) - from the cathode towards the anode (Acar and Alshawabkeh, 1993). This causes a pH changes inside the treated matrix: low pH close to the anode and high pH in opposite. Some reports suggest that the pH in soil has significant influence in the contaminant retention and electro-osmotic flow (Gomez et al., 2009; Ko et al., 2000).

Electrokinetic remediation works as it is dramatically changing properties of the soil such as pH, conductivity and temperature; it induces electrolysis of water, sorption processes, promotes acid base reactions and creates ionic flow together with the water. This type of remediation initially was used for heavy metal extraction from contaminated soils, but organic contamination can also be destroyed with the help of electrokinetics (ITRC, 1997).
Applicability limitations of electrokinetic technology include low target and high non-target ion concentration and large quantities of iron or iron oxides (U.S. EPA, 2007). Fluid flow occurs due to applied electric field; appropriate placement of electrodes would direct the fluid flow in a controlled manner (Hicks and Tondorf, 1994). Applied electric field creates three interfering processes: electro-osmosis, electro-migration and electrophoresis promoting movement of heavy metal ions in soil, mine tailings or elsewhere (Cameselle and Reddy, 2012).

The aim of the study was to test the efficiency of electrokinetic remediation for copper contaminated clayey soil in laboratory conditions. The tasks of the study were as follows: 1) to spike clayey soil with copper and determine experimental parameters; 2) to perform electrokinetic remediation experiment in batch conditions; 3) to fulfill measurements of electric field and perform analytical studies of soil samples; 4) to model the electrokinetic treatment progress in laboratory scale.

Materials and Methods

Experiments were done using 5 kg of clayey soil with known physical-mechanical properties such as texture and consistency. Soil samples were spiked with known concentration of copper (II) sulphate pentahydrate in order to gain the concentration 350 mg kg⁻¹ of copper in soil. Dried soil was sieved through 2 mm sieve, but fractions finer than 0.05 mm were determined by pipette analysis described by Van Reeuwijk, 1995. According to the USDA soil texture classes, fraction of 0.063-2.0 mm is classified as sand, 0.002-0.063 mm – as silt, but finer than 0.063 mm – as clay (FSCC, 2006). Soil pH₉Cl was measured with a glass electrode in 1 M KCl (1:2.5 mass-to-volume ratio) in triplicates. Cation exchange capacity was determined by methylene blue method (Sarceviča and Actiņš, 2009) and calculated 0.06 mmol g⁻¹ (R²=0.998) Soil pH₉Cl was measured with a glass electrode in 1 M KCl (1:2.5 mass-to-volume ratio) in triplicates. Clay was put in a plastic box 30 × 20 × 20 cm with perforated sides with 18 holes on each side, longitudinal end plane was used. Diameter of holes was 2.6 mm; the distance between holes was kept 3.5 × 1 cm. Holes were covered with 2 layers of filter paper in order to avoid the electro-osmotic flow of the soil from the box to the outer one – the frame box, which was divided in two sides – water supply side (anodic side) and water discharge side (cathodic side) (Fig. 1.).

Graphite electrodes (100 × 70 × 30 mm) were used, connected with non-copper wire to power supply in chain with controlled DC supply and measuring devices for voltage and electrical intensity. Potential difference was kept stable 41 V (2 V cm⁻¹). The initial checking was done in order to define the polarity of electrodes and to check the DC. Reading between the anode and cathode was the same as applied: 41 V, next point was taken 2 cm away from the anode and another point 2 cm from cathode, the voltage measured by the voltammeter showed 32 V, checking was continued, the reading was decreasing, when the distance between anode and cathode measurements was diminished 40V-32V-24V-16V. 

During the first (duration 3 days) and second (40 days) experiment, soil water content was maintained at 65-75% of field soil moisture. It was measured by drying in an oven and calculated. The soil was sampled periodically after application of DC fields (after 1h, 2h, 4h, 8h, 24h, 48h, 72h) during the first cycle of 3 day long experiment and after 10, 20, 30 and 40 days in the second cycle. The electrical currents were recorded constantly after the electrical field was applied. During the experiment soil samples were collected in sections that represent different

Figure 1. Installation for pilot batch electrokinetic experiments: DC power intensity regulators and voltmeter (left); Graphite electrodes in plastic box with wires connected to power supply (right).
spatial zones among anode and cathode (12 samples after each period). The depth sampled was 5 – 10 cm. The samples were kept in a refrigerator at 4 °C for further analysis. Water was collected nearby the anodic part and analyzed with AAS after the 40 days of experiment.

Preparation of soil for analytical procedures was done by wet digestion with the nitric acid (65% analytical grade, Merck) and measurements by atomic absorption spectrometry (AAS) (PerkinElmer A Analyst 200) for liquid samples performed with flame atomization and background correction with applied wavelength 324.8 nm.

X-ray powder diffraction (PXRD) analysis for elements and compounds precipitated on electrodes were performed on a Bruker D8 Advance diffractometer (generator 40 kV, 40 mA) with 0.6 mm divergence slits, 0.2 mm detector slit, CuKα radiation (0.15418 nm), 20 interval from 3-60°, scanspeed 0.5 s/step, step 0.02°; therefore X-Ray spectrometer S8 Tiger was used for determination of oxides.

Results and Discussion

Low voltage DC (170 mA at the beginning of the experiments and 68 mA at the end) was applied to test the efficiency of electrokinetic removal of contaminants from soil. During the experiment intensity was falling as the resistance was growing from initial ~1000 W to > 2000 W at the end after 3 days of DC application.

Electrokinetic treatment is effective in both the saturated and unsaturated zone and applicable in clayey soils, thus the experimental design in a box was constructed for clayey soils just under the saturation consistency. Applicability limitations of electrokinetic technology is low concentration of target ions (ITRC, 1997), therefore the contaminated clayey soil was treated in the pilot experiment by promoting three interfering processes: electro-osmosis, electro-migration and electrophoresis. Water flow with target ions in applied electric field was observed, appropriate placement of electrodes allowed controlled experiment in 3 days of the first experimental cycle and 40 days in the second.

Electrokinetic removal of contaminants from soil by application of low voltage DC was observed from some regions of contaminated soil and re-concentrated in other – close to cathode. Experimental results show that the use of DC power can be the solution for treatment of heavy metal contaminated soils, but the treatment should be applied in longer periods. Fig. 2 shows the curve of change of target ion concentrations in three areas – near anode, cathode and in the middle between. The drop in soil pH was mostly limited to half unit to about 4.5-4.7 from 5.0-5.2 initial and it can be due to large quantities of H+ ions released from anode during the electrokinetic treatment reactions. The difference was observed also between anode and cathode soil distribution areas. Basic front was observed near the cathode (5.5-6.6), but lower (acidic) values closer to the anode (around 4.7) after 3 days of the experiment. After the 40 days, the pH varied in interval of 5.5-6.1 near cathode and 4.0-5.0 near anode.

The concentration of copper in water collected in the pockets (nearby the anode and cathode) after

Figure 2. Change of copper concentration in soil in time after application of DC (each curve point (n=4) is calculated average in distinct areas near anode, cathode and in between them). Time period is shown on horizontal scale.
Electrokinetic remediation of 40 days was 0.05 and 0.085 mg L\(^{-1}\), representing a negligible amount (around 0.02 – 0.03%) of the initial metal amount. This means that electro-osmosis was effective in draining the soils from water but unsuccessful in removing the heavy metals out of the soil.

Experimental results proved that target ions under application of DC are moving towards the cathode. In the anodic side the concentration of Cu in soil is diminishing (Fig. 3). No significant changes are observed in the middle of sample containment box during the 3 days of experiment, but after 40 days diminish and are close to results near the anode. Contamination is still left after 40 days of the experiment, but similar concentrations near the anode and in the middle of the box can be explained with the fact that maximal efficiency of ion removal is reached as the other part of copper ions are strongly bound with clayey and silt particles. This could be examined in the following experiments by analyzing speciation of copper in the electrokinetically treated clayey soil.

General trends are showing patterns of movement of ions by electromigration; the experiments proved that the electrokinetic treatment of soil can significantly diminish the copper concentration in the contaminated soil.

**Conclusions**

Experimental results proved that target ions under application of DC are moving towards the cathode. In the anodic side the concentration of Cu in soil is diminishing. The voltage is dependent on moisture content and performance efficiency is highest when consistency of treated soil is close to liquid limit, however, do not exceed it. XRD analysis has shown that the cathodic area is successfully collecting cations – the electrokinetic effect is proven. Basic front was observed near the cathode, but lower (acidic) values closer to the anode, however, not harmful for potential soil animals if applied on a field scale. Contamination is significantly diminished after 40 days of the experiment, but the concentration level near anode and in the middle of the box can be explained with the fact that maximal efficiency of ion removal is reached as the other part of copper ions are strongly bound with clayey and silt particles.

Electrokinesis can be used for remediation and it is applicable to metal extraction at sites with homogeneous soils that are fine-grained and exhibit both enough high permeability and high moisture contents. Pilot testing results have shown that copper ions are removed slowly by electro-osmotic forces, but electromigration effects are undisputable. This experimental study is the first of such kind research in Latvia and it will be continued to improve methodology towards the field scale research.

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