Journal of Environmental Protection and Ecology 10, No 1, 49–55 (2009)

In situ REMEDIATION OF SOILS POLLUTED WITH HEAVY METALS. PART II. USING OF ELECTROKINETIC TREATMENT

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Abstract. Electrokinetic treatment is used for separation and concentration of heavy metals, radioactive elements, organic compounds, from polluted soils, sediments and sludges. A literature review concerning its principal aspects, is presented. When an electric field is applied between electrodes placed in soil, ions movement takes place due to electromigration, electroosmosis and electrophoresis processes. As a result of water electrolysis, two pH fronts are produced, alkaline – at cathode and acid – at anode. Both fronts are moving towards electrodes with opposite charge, and when they meet each other, there is an pH jump which is placed near cathode zone. Time for electrokinetic remediation depends on transport rate, distance between electrodes, and their configuration. For separation of zinc and manganese from a soil sample placed in a hydraulic flux of about 1 cm^3/min, and 100, 150, 200 V, maximum yield for manganese and zinc extraction was 72 %, at 200 V. By using acetic acid and EDTA for pH control in electrodes chambers, the removal of nickel was 73% and of cadmium 94%.

Keywords: heavy metals, electroremediation, pH gradient, ions migration.

AIMS AND BACKGROUND

Electrokinetic treatment is used for separation and concentration of heavy metals, radioactive elements, organic compounds, from polluted soils, sediments and sludges.

When an electric field is applied between electrodes placed in soil, ions movement takes place, due to electromigration, electroosmosis and electrophoresis processes. Electric field is obtained by application of an electric potential between electrodes which are introduced in soil; polluted soil is placed between electrodes[1–6] .

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Compounds with positive charge will migrate to cathode, and those with negative charge – to anode. Transport processes take place, together with chemical reaction at electrodes, due to water electrolysis. At cathode, water is reduced and hydrogen together with hydroxil ions are formed (reaction (1)). At anode, an oxidation process takes place, and oxygen with hydrogen ions will be formed (reaction (2)):

$$\text{cathode: } 2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (1)$$

$$\text{anode: } 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (2)$$

Due to the above reactions, pH at cathode may reach 11-12, and at anode – acid pH range is between 1.5–2.0. Two pH fronts are formed, and both moved to electrode with opposite charge. When they are meet each other, soil placed between electrodes is divided in two zones: one zone with a small pH, and the other with high pH; between these two zones, there is pH jump which is placed near cathode zone.

One factor that influences the position of pH jump, is relative mobility of hydrogen and hydroxyl ions: mobility of hydrogen ions is twice greater than of hydroxyl ions. pH gradient has a significant effect on pollutant solubility, adsorption, ionic form, and concentration[7–10].

Electrokinetic treatment of soil, known as electrorestoration, electroremediation, was applied for remediation of soils polluted with oil products (gasoline, mineral oils, kerosene), organic compounds (benzene, toluene, ethylbenzene, xylene, phenols, halogenated hydrocarbons), metals (Zn, Hg, Cd, Ni, Pb, Cr, Cu, Fe), radioactive elements[11,12] (Cs-137, Sr-90, Co-60, U, Pl, etc.). When separation process of compounds is finished, pollutants concentrated at electrodes, are removed by precipitation, adsorption, ionic exchange, or concentrated solution accumulated in electrodes chambers are pumped outside for treatment.

Electroremediation is used in combination with other methods, like biological remediation of soils, when organic pollutant has a small solubility, or the ratio electric charge/mass is very high. Bioremediation of soil has some limits, due to difficulties of oxygen and nutrients transport to microorganisms, and necessity of corresponding temperature. The presence of electric current may assure the oxygen, nutrients, and of temperature by thermic effect, necessary to biological processes.

DISCUSSION

Pilot experiments showed an energetic consumptions of about 150-500 kWh/m^3, when distance between electrodes was 1.0-1.5 m. Energetic consumption is proportional with the time necessary for ions movement to electrodes. A typical rate may be considered as 2.5 cm/day.The rate for ions migration is direct proportional

with their mobility, valence, concentration, electric field intensity. Time for electrokinetic remediation depends on transport rate, distance between electrodes, electrodes configuration, and ranged between 800-2400 h (Refs 13-15).

First demonstration of the process for electroremediation of soils polluted with metals was made in Holland, in 1986. Remediation costs are influenced by initial concentration of pollutants, final desired concentration, conductivity of soil and of groundwater. There are different patented processes of specialised companies, for soil electroremediation[16–18].

Electro-clean electrical separation of Electrokinetics Inc., USA, a process that may be applied *in situ* or *ex situ*; the treatment efficiency for heavy metals (Pb, Cr, Cd, U) for an initial concentration of about 2000 mg/kg, is appreciated at 75-95%.

Electrochemical geooxidation (ECGO) of Geotechnologies firm, Germany, is a process applied both for organic and inorganic pollutants removal from soils. The process uses induced electrical currents for producing of oxidation-reduction reactions, to mineralise organic pollutants from soils, placed between electrodes. Soil particles became conductive due to iron, manganese and carbon atoms from soil. Pollutants like heavy metals, may have a catalytic role in redox reactions.

Electrochemical ion exchange, Geokinetics Intern. Inc. USA, uses both electrokinetics and ionic exchange process for extracton of ionic pollutant from polluted soil.

For the treatment of a calcareous soil polluted with Cr, Cu, Ni and Zn, electrodes were placed in chambers where water electrolysis took place (Fig. 1). By using an electric field of 2.2 V/cm, the yields for metals extraction in cathodic chamber were 27-66%.

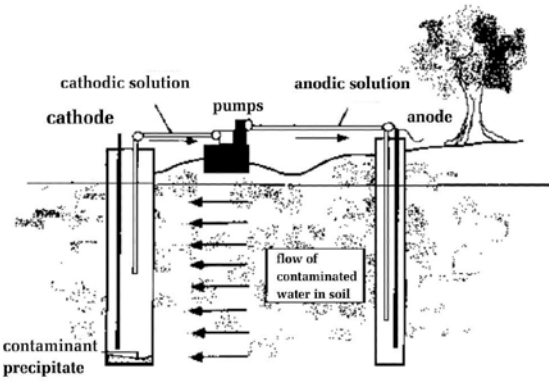

Fig. 1. Scheme of electrokinetc process applied to polluted soils

One polluted soil containing Zn, Mn, Pb, was treated with 0, 100, 150, and 200 V, a solution with low pH was introduced in soil mass, at a hydraulic flux of

about 1 cm^3/min. At 200 V, both Mn and Zn were extracted in proportion of 72%, and Pb removal was 46%.

At Nottingam university, UK, electrokinetic method for remediation was investigated in a project financed by European funds. To realise an electric field, networks of electrodes with their corresponding chambers were placed in polluted soil. When metals concentration at electrodes reached a specific level, electric field was reversed between electrodes. The efficiency of the process may be increased by previously treatment of soil with acidic solutions or biodegradable reagents.

In order to increase yields for metals separation from polluted soils, were developed intensified electroremediation processes, by pH control at electrodes[19–21].

In these processes, electrodes are introduced in specific chambers, like in Fig. 1. Every electrode has a reservoir containing diferent solutions[22].

In an experiment realised both without pH control and with pH control, soil from electrolytic cell contained Ni(II) and Cd(II), with the concentrations of 500 and 250 mg/kg d.s., respectively. Experimental conditions are presented in Table 1. Five experiments were realised, in which solutions from reservoirs were as follows: I – in electrodes chambers was introduced water; II – in cathodic chamber was introduced acetic acid (1 M) in order to avoid a high pH, and in anodic chamber – water; III – in cathodic chamber was introduced EDTA (0.1 M), to investigate heavy metals complexing, and in anodic chamber – water; IV – initial, in chambers was introduced water; then, after 310-710 h, to control pH, acetic acid (1 M) was introduced in cathodic chamber and natrium hydroxide (1 M) – in anodic chamber; thus, precipitation of metals can be avoided; V – initial, in chambers was introduced water; then, after 500-1350 h, acetic acid (1 M) was introduced in cathodic chamber and water was maintained in anodic chamber; after 1310-2250 h, natrium hydroxide (1 M) was introduced in anodic chamber.

Table 1. Experimental conditions for intensified electrokinetic treatment of soil polluted with nickel and cadmium[20]

Anodic solution	Cathodic solution	Time (h)	Initial indicators of soil		
			H_2O (%)	pH	conductivity (mS/cm)
(I) H_2O	H_2O	260	40.6	5.36	1884
(II) H_2O	acetic acid 1 M	120	32.9	5.63	1884
(III) H_2O	0.1 M EDTA	340	36.5	4.51	1371
(IV) t=0-310 h; H_2O; t=310-710 h;1 M NaOH	t=0-310 h; H_2O t=310-710 h; 1 M acetic acid	710	32.6	4.56	1638
(V) t=0-500 h; H_2O t=500-1350 h; H_2O t=1350-2250 h; 1 M NaOH	t=0-500 h; H_2O t=500-1350 h; 1 M acetic acid t=1350-2250 h; 1 M acetic acid	2250	33.3	6.73	2200

During the test with water in electrode chambers (I), current increases from initial value of 3 mA up to 38 mA in 30 h. Next, the current intensity decreased, and finally was stabilised to 2 mA. Due to water electrolysis, the pH nearby anode was about 2, and at cathode up to 12. Nickel and cadmium migrated to cathode where high quantities were determined; but in cathode chamber, the metals were found in small quantities due to their precipitation.

Taking into account concentrations from cathodic reservoirs, nickel removal was negligible in experiment without intensification, 19% when intensification was realised with acetic acid, 10% for intensification with EDTA, 73% for sequential intensification with acetic acid and natrium hydroxide, 310-710 h after treatment with water only, and 71% when sequential intensification was with acetic acid and natrium hydroxide 1350-2250 h after treatment with water. Similar results were recorded for cadmium (Table 2).

Table 2. Yields of accumulation for nickel and cadmium in cathodic chamber, versus experiment type.

Experiment	Yields for accumulation (%)	
	nickel	cadmium
I	5	7
II	19	12
III	10	23
IV	73	87
V	71	94

CONCLUSIONS

1. Electrokinetic treatment is used for separation and concentration of heavy metals, radioactive elements, organic compounds, from polluted soils, sediments and sludges.

When an electric field is applied between electrodes placed in soil, ions movement takes place, due to electromigration, electroosmosis and electrophoresis processes.

2. The efficiency of different electroremediation processes that may be applied *in situ* or *ex situ*, for the treatment of heavy metals (Pb, Cr, Cd, U, etc.) with an initial concentration of about 2000 mg/kg, is appreciated at 75-95%. For separation of zinc and manganese from a soil sample placed in a hydraulic flux of about 1 cm^3/min, and 100, 150, 200 V, maximum yield for manganese and zinc extraction was 72%, at 200 V. By using of intensified processes, nickel and cadmium were concentrated in cathode chamber up to 73 and 94%, respectively.

3. Energetic consumption is correlated with time necessary for ions to reach the electrodes, soil nature, and pollutant concentration, e.g. for a typical application *in situ*, consumption for a tone of polluted soil is between 150-500 kWh.

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Received 26 July 2007
Revised 17 October 2007