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*Journal of* Hazardous Materials

Journal of Hazardous Materials 143 (2007) 682-689

www.elsevier.com/locate/jhazmat

# Electroosmotic flow behaviour of metal contaminated expansive soil

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Available online 9 January 2007

#### Abstract

It is important to study the flow behaviour through soil during electrokinetic extraction of contaminants to understand their removal mechanism. The flow through the expansive soil containing montmorillonite is monitored during laboratory electrokinetic extraction of heavy metal contaminants. The permeability of soil, which increases due to the presence of contaminants, is further enhanced during electrokinetic extraction of contaminants due to osmotic permeability. The variations in flow rates through the soil while the extracting fluid is changed to dilute acetic acid (used to control the increase of pH) and EDTA solution (used to desorb the metal ions from soil) are studied. The trends of removal of contaminants vis-a-vis the changes in the flow through the soil during different phases of electrokinetic extraction are established. Chromium ions are removed by flushing of water through the soil and increased osmotic flow is beneficial. Removal of iron ions is enhanced by induced osmotic flow and desorption of ions by electrokinetic processes.

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Keywords: Adsorption; Acetic acid; EDTA; Osmotic flow; Voltage

# 1. Introduction

Contamination of subsurface and groundwater subsequently occurs due to leachate migration from landfills, industrial activities and other sources. Soils often get contaminated with heavy metals due to improper disposal of sludges and waste water, from rinsing operations at electro plating and metal finishing plants. Decontamination of fine-grained soils from ionic pollutants by conventional methods is not only costly but also mostly ineffective because of their low hydraulic conductivity, low biodiversity and strong adsorption on their surface. The demand for innovative and cost effective in situ remediation stimulated the effort to employ conduction phenomena in soils under an electrical field to remove chemical species from soils. In the electrokinetic remediation process a direct current electric field is passed through a polluted soil, acting as a cleaning agent [1]. When the electric potential is applied across a wet soil mass, cations in the double layer of soil would be attracted to the cathode and anions to the anode. The migrating cations drag water with them increasing flow through soils.

In electrokinetic extraction, the flow is driven by both hydraulic gradient and electric gradient occurs [2]. Electroos-

0304-3894/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2007.01.015 motic fluid volume flow rate is described by an equation analogous to Darcy's law [3,4], which introduces, electroosmotic permeability,  $k_e$  as the volume rate of water flowing through a unit cross-sectional area due to a unit electrical potential difference (cm<sup>2</sup>/V s):

$$Q = k_{\rm e} I_{\rm e} A \tag{1}$$

where Q is the increased fluid volume rate on application of voltage (m<sup>3</sup>/s),  $I_e$  the electric field strength (V/m) and A is the total cross-sectional area perpendicular to the direction of fluid flow.

The electroosmotic flow rate is calculated by subtracting the flow rate due to application of hydraulic gradient from the total flow rate. Electroosmotic flow varies with time during electrokinetic processes. During different stages of the experiment, the peak value of  $k_e$  has been computed to get an idea of the extent of changes.

During electro remediation ions are desorbed from soil surfaces. The cations present in the soil move toward the cathode by the combined actions of electroosmotic advection and ion migration. Ionic migration is a major transport mechanism for ionic contaminant under electrical field. However, Yeung et al. [5] observed that electroosmotic advection is the dominant mechanism for the removal of lead and cadmium from kaolinitic soil. The basic equation [6] to describe electromigration of ions

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through a capillary is given by:

$$U_{\rm m} = \nu E \tag{2}$$

where  $U_{\rm m}$  is the velocity of an ion and  $\nu$  is the ionic mobility.

Shapiro and Probstein [7] modified the above equation for soils to incorporate a tortuosity term. The major factors that influence electroremediation are described by Page and Page [1].

#### 1.1. Catholytic neutralisation

The increase in pH at the cathode due to electrolysis of water precipitates the metallic cationic contaminant at cathode leading to reduction in flow and removal of contaminants from the soil. Weak acids, such as acetic acid, may be introduced at the cathode to neutralize the hydroxyl ions generated by electrolytic reduction of water. However, improper use of some acids in the process poses a health hazard. For example, the use of hydrochloric acid may pose a health hazard. Acetic acid is a weak acid that undergoes partial dissociation in water:

$$CH_3COOH = CH_3COO^- + H^+$$
(3)

There are several advantages in using acetic acid to depolarize the hydroxyl ions generated by cathode electrolytic reduction processes: (1) most metal acetates are highly soluble, (2) the concentration of ions generated by dissociation of the acid is very low due to the high  $pK_a$  value of acetic acid, and thus the electrical conductivity of the soil will not increase drastically, (3) it is environmentally safe and biodegradable, and (4) acetate ions will prevent the formation of other insoluble salts in the vicinity of the cathode, thus preventing the development of a low electrical conductivity zone and dissipation of excessive energy in the soil near the cathode. It was found that 0.03 M acetic acid, just enough to depolarize the cathode reaction, has overcome uranium precipitation close to the cathode compartment. One another reason for depolarizing the anode reaction is concern about the dissolution and release of silica, alumina, and heavy metals associated with the clay mineral sheets over long exposure to the proton. Calcium hydroxide can be used for depolarization of anode reaction and hydrochloric acid cathode reaction. Calcium ions in highly active clayey soils may enhance advective transport characteristics of the porous medium through changes in clay fabric, and calcium ions would not attack the mineral sheet. The rate of neutralisation of alkalinity also depends on the rate of passing neutralising acetic acid solution. Rodsand et al. [8] demonstrated the use of acetic acid to depolarize the cathode reaction. Depolarization of cathode reaction by acetic acid can enhance electrokinetic extraction of lead. Alshawabkeh et al. [3] showed acetic acid enhanced electrokinetic remediation from soil from a site.

#### 1.2. Chelating or complexing agents

In some cases, an acid front may not be able to develop by electrokinetic processes because of the high acid/base buffer capacity of the soil and/or reverse electroosmosis flow. Moreover, the advance of an acid front in the subsurface may cause too much dissolution of soil minerals resulting in an excessive release of some of their constituents, such as Al and Si. Under these circumstances, it is necessary to use enhancement agents to solubilize the contaminants. Chelating or complexing agents, such as citric acid and EDTA, have been demonstrated to be feasible for the extraction of different types of metal contaminants from fine-grained soils [9,5].

Several studies with electrokinetic remediation of soils contaminated with cationic metallic contaminants, such as lead, copper, cadmium, etc., have been reported. The technique has found success in the laboratory to remove:

- more than 90% of heavy metals (arsenic, cadmium, cobalt, chromium, copper, mercury, nickel, manganese, molybdenum, lead, antimony, and zinc) from clay, peat and argillaceous sand [10];
- (2) spiked lead from kaolinite [11,3,12];
- (3) 85–95% of the original concentrations of cadmium, cobalt, nickel, and strontium from laboratory samples prepared from Georgia Kaolinite, Na-montmorillonite, and sand–montmorillonite mixture [13];
- (4) cadmium from saturated kaolinite [14];
- (5) Cr(VI), Ni(II) and Cd(II) from contaminated soil under reducing conditions [15];
- (6) chromium, nickel and cadmium from kaolin and glacial till [16].

The degree of success depends on several factors such as CEC of soil, adsorption capacity of contaminant ion, etc. The ions, which are sorbed strongly on the clay particles, are not removed by enhanced flow alone but by the capacity of applied voltage to desorb and make them mobile. Also the ions, which form stable hydroxides, are not removed unless the pH is efficiently controlled.

Mechanism by which water and solutes are transported through soils under applied electrical fields may involve several processes whose relative importance varies from one system to another. Knowing the factors that inhibit the removal helps to formulate a strategy for the enhanced removal. Immobilisation of contaminants in soils, when their removal is not feasible, can also be achieved electrokinetically. Most of the laboratory studies on electrokinetic extraction are on kaolinitic or commercially pure clays. No information is available on the efficiency of the method for expansive soils. Expansive soils are more difficult to decontaminate because of low permeability, high cation exchange capacity and high adsorption of heavy metal ions on clay surfaces. These soils exhibit acid/base buffer capacity and require excessive acid and/or enhancement agents to desorb and solubilize contaminants. It is proposed to examine the importance of (i) enhanced flow of water by electrolysis of water, (ii) desorption of metal ions from the surface of the clay particles by ionic migration, (iii) acetic acid to control pH and (iv) EDTA solution to desorb ions, etc., in the removal of heavy metals viz., chromium and iron from expansive soil.

Table 1 Properties of soil used

Property	BC soil	
	BC SOII	
Specific gravity	2.74	
Liquid limit (%)	56	
Plastic limit (%)	23	
Shrinkage limit (%)	10.34	
Clay content (%)	35	
Max dry density (kN/m <sup>3</sup> )	15.1	
Optimum moisture content (%)	27.76	
Cation exchange capacity (mequiv./100 g)	29	

# 2. Experimental investigations

#### 2.1. Black cotton soil (BC soil)

The soil was obtained from Davanagere, Karnataka, India. The soil was collected by open excavation from a depth of 1 m from the natural ground level. The soil was dried and passed through the IS sieve size of  $425 \,\mu\text{m}$ . Properties of the soil are summarized in Table 1. The clay content consisted predominantly of montmorillonite mineral. Compaction characteristics required for remolding soil are also determined as per ASTM D 689-91 [17].

### 2.2. Chemicals used

0.05 M acetic acid solution and 0.03 M EDTA (ethylene diamine tetra acetic acid) extracting solution are prepared using the pure chemicals obtained. The chemicals, potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), ferric chloride (FeCl<sub>3</sub>) were used to prepare contaminated soils with chromium, and ferric ions of about 1000 mg/kg of soil. All the chemicals obtained from standard suppliers.

#### 3. Laboratory electrokinetic apparatus

An apparatus designed, fabricated and assembled for carrying out the studies. The electrokinetic cell was fabricated using nylon material for the body, which is a non-conductor of electricity, corrosive resistant, not affected by acid or alkali and can withstand a pressure of 100 kPa. The electrokinetic cell consists of two end caps and a specimen cylinder made up of nylon. The test sample was 80 mm in diameter and 300 mm long. Ten electrical measurement nodes have been installed on the specimen cylinder at 25 mm intervals so that the electrical voltage distribution along the sample can be monitored continuously during the test. The end caps house the graphite plate electrodes, inflow and outflow tubes. As porous graphite is extremely expensive and fabrication of porous graphite electrodes is very labor intensive, normal grade graphite plates were used in this study. Holes of 1 mm diameter were drilled through the graphite plate electrode to facilitate water transport during electroosmosis. Details of electrokinetic cell are shown in Fig. 1. The required electrical circuit has been designed, connected and assembled. Provision has been made to pass fluids through the compacted soil in the cell at desired hydraulic pressure through the inlet using self compensating mercury control device.

#### 3.1. Sample preparation

The oven-dried soil was mixed with water containing specific known amount of chemical contaminants thoroughly to ensure homogeneous distribution of contaminants and kept in a polythene bag and placed in a humid desiccator overnight to achieve uniform moisture content. The soil is then compacted in the cylinder to bring it to 90% of maximum dry density on dry of optimum on the compaction curve. The soil is divided into three equal parts by weight and then each part is emplaced into the specimen cylinder and compacted one by one using a screw jack to ensure uniform compaction for the entire specimen. After compaction, the perforated electrodes were covered with filter papers and the end caps were closed. Fluid inlet and outlet tubes were connected to the cell. The cell was subjected to a specific constant hydraulic head of 40 m using the self-compensating mercury control device and saturated.



Fig. 1. Schematic setup of electrokinetic cell used.

#### 3.2. Sequential extraction of contaminants

#### 3.2.1. Removal by flushing with water

When water flows under hydraulic gradient, soluble contaminant is removed along with hydraulic flow. Since hydraulic gradient is applied from anode to cathode leachate containing soluble contaminant is collected at the cathode.

# 3.2.2. Removal by enhanced flow due to electroosmosis and ion migration

To enhance the flow of water and to make the contaminant desorb from the surface of clay, dc voltage is applied across the soil. The cumulative volume of flow and the concentration of contaminants in the leachate are monitored. The increase in pH due to electrolysis of water is also monitored and plotted.

#### 3.2.3. Removal by catholytic neutralisation

0.05 M acetic acid is passed along with water, introducing acetic acid from anode. The advance of the acid front from the anode is expected to result in dissolution of the most commonly encountered precipitates [14] and enhance or continue the removal of contaminant after passing acetic acid.

#### 3.2.4. Removal by increased electrical potential

To further enhance the extraction of the contaminant electrical potential has been applied across the specimen while passing acetic acid under 1 and 2 V/cm.

#### 3.2.5. Removal by the use of complexing agent

0.03 M solution of EDTA solution was passed to desorb ions from clay surface by its ability to form complexes and carry along with hydraulic flow. It is desirable that EDTA should be introduced at the cathode. EDTA is introduced at the anode, as in the case of passing acetic acid, to complex with metal ions after they are desorbed from soil and migrate to the cathode.

# 3.2.6. Removal by passing of EDTA solution under the application of electric potential

To further enhance the extraction of the contaminant, electrical potential of 1 and 2 V/cm is applied across the specimen while passing EDTA solution.

#### 4. Results and discussion

#### 4.1. Variation of flow rate through the soil

The importance of rate of flow of flow by electrokinetic extraction has been very well understood. The flow through soil varies considerably depending on many factors like the clay mineral present, particle size distribution, porosity, soil fabric and the nature of pore fluid, etc. The variation of flow rate through soil as affected by the presence of contaminant, application of electrical potential and change of pore fluid during electrokinetic extraction has been studied. The rate of flow to any specific fluid can vary depending on the type of contaminant present. For comparing the effect of passing fluids it is necessary to know the rate of flow rate to water not only for soil without contaminants



Fig. 2. Variation of cumulative volume of fluid with time for soil without any contaminant in sequential extraction.

but also for soil with different contaminants. The variations in flow through other fluids employed apart from water acetic acid and EDTA solutions and the effect of applied voltage on the rate of flow has been studied. The flow rates vary with time and for comparison only the values corresponding to peak flow are mentioned. The studies are conducted on black cotton soil with chromium, and iron as individual contaminating metal ions.

#### 4.1.1. Flow through soil without any contaminant

The rate of flow of water through soil without any contaminant is about 0.7 ml/h. Considerable increase in the rate of flow occurs in on application of voltage of 30 V. The rate of flow through soil is tripled to 2.1 ml/h. The increased flow is predominantly due to osmotic flow induced by ion migration. For the soil with high cation exchange capacity the effect of ion migration is considerable and hence the increased flow. Increasing the voltage to 60 V, however, decreases the rate of flow (Fig. 2) to 0.9 ml/h. The decrease in flow is due to increased pH as seen in Fig. 3. To reduce the alkalinity at the cathode and accelerate the flow, acetic acid is passed through the soil. As seen from Fig. 2, flow through the soil to acetic acid, which is almost stopped slowly, observed at rate of about 0.8 ml/h on application of 30 V. With application of voltage (60 V) the rate of flow decreases to 0.5 ml/h. To enhance the removal of contaminants EDTA solution is passed through the soil. Even though passing of EDTA



Fig. 3. Variation of pH with number of pore volumes of fluid for soil without any contaminant during sequential extraction.

solution is not expected to remove any contaminants with soil alone, to enable comparisons later while conducting experiments with the soil containing contaminants EDTA is passed with and without application of voltage. The rate of flow, which reduces to 0.2 ml/h to EDTA solution, increases on application of voltage of 30 V to 1.2 ml/h. However, increasing the voltage has not further improved the flow rate.

#### 4.1.2. Flow through soil with chromium ions

To maintain uniformity, hydraulic flow is maintained only towards the cathode in the soil containing Cr ions. But ion migration under the influence of voltage may also be towards the anode. Though not very efficiently, Cr may move along with water in the direction of cathode. This can only be confirmed by measuring the zeta potential. However, this may not affect the removal of chromium. The variation in the flow through soil due to hydraulic head and osmotic flow has been studied. The effect of applied voltage and pore extraction fluid on osmotic permeability is studied.

The rate of flow of water through soil containing chromium is higher at 1.5 ml/h. under application of constant hydraulic pressure. It is well known that in the presence of higher valency ions, cation exchange takes place leading to suppression of diffused double layer of clay particles. This in turn increases the rate of flow through the soil. Application of voltage (30 V) decreases the flow rate. This can be attributed to opposite directions of flow of water due to the influences of water hydraulic head and chromium ion migration. It has been earlier brought that chromium ions in oxidation state VI are stable as anion and hence move towards the anode. The decrease in flow on application of voltage indicates that the ion still carries hydrated water with it. Increase in voltage (60 V) increases the rate of flow considerably, as seen from Fig. 4. This possibly is the counteraction of other ions (present in the soil as exchangeable ions) over that of chromium. The increase in pH as seen in Fig. 5, after applying 60 V cannot precipitate chromium(VI) and hence cannot decrease the flow. For the sake of uniformity acetic acid is passed through the soil to reduce the pH at the cathode. It is to be observed from Fig. 4 that passing of acetic acid without voltage the flow rate is considerably reduced to about 2 ml/h. This might due to precipitation of metal ion due to increase in the pH and slow restoration of pH on passing acetic acid. Application



Fig. 4. Variation of cumulative volume of fluid with time for soil containing chromium during sequential extraction.



Fig. 5. Variation of pH with number of pore volumes of fluid for soil containing chromium during sequential extraction.

of voltage decreases the rate of flow. The rate of flow to EDTA solution without application of voltage is less at about 0.3 ml/h, which increases on application of voltage.

#### 4.1.3. Flow through soil with ferric iron ions

Presence of iron ions has increased the rate of flow in the soil to about 2 ml/h, as seen in Table 4. Application of voltage of 30 V increases the rate of flow considerably to 13 ml/h (Fig. 6) inspite of increase in pH (Fig. 7). Thus for black cotton soil, application of voltage is more effective to enhance the flow than replacement of exchangeable ions. However with increase in voltage (60 V) there is a reduction in the flow rate though pH is



Fig. 6. Variation of cumulative volume of fluid with time for soil containing ferric iron during sequential extraction.



Fig. 7. Variation of pH with number of pore volumes of fluid for soil containing ferric iron during sequential extraction.

Variation of rate of flow, hydraulic permeability and electroosmotic permeability of soil with water during sequential extraction by electrokinetic method Hydraulic conductivity,  $k_{\rm h}$  (cm/s) Electroosmotic permeability,  $K_0$  (cm<sup>2</sup>/V s) Contaminant 30 V 60 V Uncontaminated soil 1.24E-07 7.69E-06 2.18E-06

almost unaffected as seen from this might be due to delayed and continued precipitation. Passing of acetic acid solution increases the rate of flow to 12.7 ml/h. This indicates that possible dissolution of iron precipitated as hydroxide during application of voltage earlier. As will be seen later iron is removed by passing acetic acid. Application of voltage of 30 V reduces the rate of flow probably due to precipitation of iron. With increase in voltage there is significant increase in flow to 33.5 ml/h. Passing EDTA solution reduces the rate of flow without or with voltage without changing the pH as seen from Figs. 6 and 7.

2.41E-07

3.3E-07

# 4.2. Variation of hydraulic permeability and electroosmotic permeability

### 4.2.1. In the soil without contaminant

The hydraulic conductivity of soil without contaminant is in the range of  $1.2 \times 10^{-7}$  cm/s to water, and  $3.8 \times 10^{-8}$  cm/s to EDTA solution (Table 2). No flow through the soil could be observed for long time while acetic acid solution was allowed to enter from the reservoir under a pressure 100 kPa after stopping passing of water under 60 V. Thus, the hydraulic conductivity of soil to both acetic acid solution and EDTA solution is significantly lower than to water. As explained earlier, the initial condition of the soil while passing water, acetic acid and EDTA solutions is not the same. Acetic acid solution is passed after applying voltage and possible precipitation of hydroxides. EDTA solution is passed after passing of acetic acid without and with application of voltage across the soil. Thus before passing EDTA solution, the hydroxide formed must have precipitated. But as seen from pH of the effluent, often the pH is high some times due to electrolysis during application of voltage even while passing acetic acid. While considering the effects on hydraulic conductivity due to the nature of the fluid, one has to bear in mind these differences in initial soil condition.

On application of voltage, the flow through the soil under the same hydraulic head has increased while passing any fluid. The electroosmotic permeability of black cotton soil at (30 V) is about  $7.7 \times 10^{-6} \text{ cm}^2/\text{V} \text{ s}$  to water,  $4.6 \times 10^{-6} \text{ cm}^2/\text{V} \text{ s}$  to acetic acid solution and  $5.2 \times 10^{-6} \text{ cm}^2/\text{V} \text{ s}$  to EDTA solution (Tables 2 and 4) and the osmotic flow rates are 1.3, 0.8 and 0.9 ml/h, respectively (Fig. 2). Thus, the osmotic flow in black cotton soil is much higher than hydraulic flow. The hydraulic flow rates as seen earlier were 0.7, 0 and 0.2 ml/h to water, acetic acid and EDTA solutions. The osmotic permeability of soil under application 60 V was  $2.2 \times 10^{-6}$  cm<sup>2</sup>/V s to water,  $5.2 \times 10^{-6} \text{ cm}^2/\text{V} \text{ s}$  to acetic acid solution and  $1.1 \times 10^{-5}$  cm<sup>2</sup>/V s to EDTA solution (Tables 2 and 4). Thus, application of higher voltage is increases flow to all fluids. While the increase in flow is not proportional to increase in voltage for water it is almost proportional to acetic acid and is more than proportional to EDTA solution.

5.08E-05 2.30E-04

-4.60E - 06

-2.50E-05

# 4.2.2. Variation of hydraulic permeability and osmotic permeability of soil with chromium ions

The hydraulic conductivity of soil with chromium as contaminant to water is  $2.4 \times 10^{-7}$  cm/s,  $3.3 \times 10^{-7}$  cm/s to acetic acid solution and  $5.2 \times 10^{-8}$  cm/s to EDTA solution (Table 3). Thus, the hydraulic conductivity of the soil to water and acetic acid is higher than to EDTA solution. It has been observed earlier for soil without contaminants that the flow to water is higher than to acetic acid and EDTA solutions. The effect of reduced amount of chromium by the time fluid is changed might have a predominant effect. It will be observed later that a large percent of chromium is removed with passing of water and acetic acid solution and hence the amount of chromium present while passing EDTA solution is less.

The flow through the soil on application of voltage while passing water and acetic acid solution has actually reduced. Consequently, the electroosmotic permeability has become negative. This may be due to migration of water along with Cr(VI) towards anode rather than cathode. With increased voltage to 60 V, the osmotic flow to water was  $5.1 \times 10^{-5}$  cm<sup>2</sup>/V s. With increased voltage to 60 V, the osmotic flow to acetic has become negative. Thus, the flow which is less at 30 V in water has increased on increasing voltage but unable to increase in acetic acid solution on increasing voltage. Application of voltage of 30 V while

Table 3

Table 2

Chromium

Ferric iron

Variation of hydraulic permeability and electroosmotic permeability of soil with acetic acid during sequential extraction by electrokinetic method

Contaminant	Hydraulic conductivity, $k_h$ (cm/s)	Electroosmotic perme	Electroosmotic permeability, $K_0$ (cm <sup>2</sup> /V s)	
		30 V	60 V	
Uncontaminated soil	0	4.61E-06	5.20E-06	
Chromium	3.25E-07	-2.30E-06	-1.70E-05	
Ferric iron	2.11E-07	-2.50E-05	82.30E-04	

Table 4

 Variation of hydraulic permeability and electroosmotic permeability of soil with EDTA solution during sequential extraction by electrokinetic method

 Contaminant
 Hydraulic conductivity,  $k_h$  (cm/s)
 Electroosmotic permeability,  $K_0$  (cm<sup>2</sup>/V s)

Contaminant	Hydraulic conductivity, $k_{\rm h}$ (cm/s)	Electroosmotic permeability, $K_0$ (cm <sup>2</sup> /V s)		
		30 V	60 V	
Uncontaminated soil	3.77E-08	5.24E-06	1.05E-05	
Chromium	5.22E-08	2.08E-06	1.42E - 05	
Ferric iron	1.12E-06	-1.20E-05	-2.20E-05	

passing of EDTA solution has increased the rate of flow and the osmotic permeability is  $2.1 \times 10^{-6} \text{ cm}^2/\text{V} \text{ s}$ . Though osmotic flow is observed at 60 V, it is not proportional to applied voltage.

# 4.2.3. Variation of hydraulic permeability and osmotic permeability of soil with ferric iron ions

The hydraulic conductivity of soil with iron as contaminant is in about  $3.3 \times 10^{-7}$  cm/s with water,  $2.1 \times 10^{-6}$  cm/s with acetic acid solution and  $1.1 \times 10^{-6}$  cm/s with EDTA solution (Table 4). Thus, the hydraulic conductivity of soil has increased with the acetic acid and EDTA solutions.

Application of voltage (30 or 60 V) increases the flow of water through the soil. The osmotic permeability values are  $6 \times 10^{-5}$  cm<sup>2</sup>/V s with 30 V and  $8.2 \times 10^{-5}$  cm<sup>2</sup>/V s with 60 V. Thus, the osmotic permeability increases with increase in voltage. The osmotic permeability in the soil with iron to acetic acid solution is observed only with the application of 60 V only, which is about  $2.3 \times 10^{-4}$  cm<sup>2</sup>/V s, which is very high. This may be due to dissolution of iron hydroxide while passing acetic acid. As will be seen in next section iron is removed from the soil by passing acetic acid. However with EDTA solution there is no osmotic permeability.

#### 4.3. Extraction of metal ions from soil

It has been shown that the efficiency of removal of ions from soil by electrokinetic extraction method makes use of:

- (i) enhanced rate of flow of water due to electro osmosis,
- (ii) desorption of metal ions from the surface of the clay particles by ionic migration, and
- (iii) use of enhancing agents such as EDTA to complex with contaminating ion and remove them,

varies greatly depending on contaminant ions and applied voltage, etc. The effects of ion migration and osmosis on the rate of flow through black cotton soil with different contaminants have already been presented. The effect of precipitation of ions as hydroxide and the role of acetic acid to neutralize the alkalinity on the flow rate have been brought out. To efficiently apply this method to remove ions from soils, it is necessary to know the trends of removal by passing water with application of voltage under a given hydraulic head and the role of other fluids to enhance the rate of removal.

#### 4.3.1. Electrokinetic extraction of chromium ions

The removal trends of chromium under different conditions are shown in Fig. 8. It can be seen from the figure that about 18%

of chromium(VI) present in soil is removed by passing 0.15 pore volumes of water. The rate of removal has not enhanced on application of 30 V of dc current. About 12% of chromium is removed by passing another 0.15 pore volumes of water. It has been noted earlier that the rate of flow in black cotton soil containing chromium has enhanced on application of voltage. Thus, the rate of removal with respect to time is enhanced. At higher voltage the removal of chromium is not observed. Passing acetic acid solution without or with voltage is not able to revive the removal of chromium. Passing EDTA solution without or with voltage is also unable to remove chromium even at a slower rate. The removal trends of chromium from soil shows that it is best by soil flushing. Application of lower voltage can remove chromium at a faster rate.

#### 4.3.2. Electrokinetic extraction of ferric iron ions

Removal of ferric iron with cumulative pore volume of water after continuous washing with water passed under a constant hydraulic head is shown in the initial portion of Fig. 9. Only a small amount of iron of about 5% is flushed out without application of voltage by passing about 0.5 pore volumes of water. Passing about 0.5 pore volume water under 30 V could not remove any iron. But about 20% of iron could be extracted by passing of about 0.5 pore volume of water under 60 V. This indicates that the ionic mobility of iron is less. By passing 0.5 pore volume of acetic acid another 8% of iron could be removed. Thus, the rate of removal of iron is not high with acetic acid. With 0.5 pore volume of acetic acid solution another 5% of iron is removed under application of 30 V. Thus again the rate of removal is not good. Increased voltage has not further effected any removal. Passing EDTA solution is able to remove iron from black cotton soil even without application of voltage. Appli-



Fig. 8. Removal of chromium from soil during sequential extraction by electrokinetic method.



Fig. 9. Removal of ferric iron from soil during sequential extraction by electrokinetic method.

cation of voltage has not enhanced the rate of removal while passing EDTA solution as seen from Fig. 9.

### 5. Conclusions

Based on the results presented in this paper, the following conclusions are drawn:

- (1) The conductivity in any contaminated soil is higher than uncontaminated soil. The increase in the hydraulic conductivity is higher with the Fe than with Cr as contaminant.
- (2) Osmotic permeability of soil to water observed on application of voltage with iron and has not been observed with chromium.
- (3) Removal of chromium is essentially by flushing the soil with water and electrokinetics assists the removal by enhanced flow through the soil.
- (4) Electrokinetics removal of iron is by both enhanced flow through the soil as well as by desorption.

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