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Electrochemical extraction and stabilization of selected inorganic species in porous media

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Abstract

There are metal and alkaline earth species which tend to remain ionic under a large range of pH and redox potential values. Those substances are expected to electromigrate and separate even under high pH and variable redox conditions unless they become adsorbed onto soil surfaces and clay interstices. In this study, first near complete separation of Na and Cl was accomplished in samples of drilling mud sludge recovered from a settling pond. Na recovery was invariable with the quantity of water flow through the sludge specimens of various initial degrees of water saturation. High recovery of Na and Cl was demonstrated with less than 0.5 pore volume of electroosmotic water flow. In most field situations, the contaminants are often found adsorbed onto soil surfaces. Natural buffering capacity of soil may hinder desorption and dissolution or high pH generated at the cathode site may cause insoluble hydroxide precipitates of some metal contaminants. Under such circumstances, electrochemistry may still be useful to stabilize and contain certain groups of contaminants in the ground. In this study, use of electrochemical process to deliver Fe(II) to reduce soluble species Cr(IV) to a less toxic and less soluble species Cr(III) was demonstrated in the laboratory. © 1997 Elsevier Science B.V.

Keywords: Electrochemical extraction; Hydroxide precipitates; Stabilization; Containment

1. Introduction

The electrochemical restoration of soils involves applying a low direct current or a low potential gradient to electrodes that are inserted in the subsurface. As a result, the contaminants are transported to the anode or cathode compartments where they are removed by one of several different methods: electroplating; adsorption onto the

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electrode; precipitation or co-precipitation at the electrode; pumping near the electrode; complexing with ion exchange resins; capturing in reactive permeable barriers. Electromigration is the primary mechanism of electrochemical treatment when the contaminants are ionic or surface charged. Speciation and precipitation are major factors in transport of heavy metal constituents by ion-migration. The speciation and precipitation are dependent upon a number of fairly well understood parameters including pH, redox potential, and ion concentration ([1]). Transport by electroosmotic advection is best achieved when the physical state of the contaminant is suitable for the flowing water to carry it through the tight pores of soil without causing an immovable plug of concentrated material to accumulate at some distance from an electrode.

Electrochemical treatment in soil-water systems cause transient migration of an acid front from the anode to the cathode ([2]). The reduced pH is beneficial in desorption of metals from soil, as well as dissolution of most metal precipitates. Natural soils with high buffering capacity and carbonate content, or those under the groundwater table would tend to neutralize the acid front and maintain a high pH environment. The base front generated at the cathode electrode penetrates the soil a narrow distance creating a zone of high pH promoting retention of inorganic species on the clay surfaces, and precipitation of some inorganic species into hydroxide salts. In field situations, the contaminants are often found adsorbed onto soil surfaces, iron-oxide coatings, soil colloids and natural organic matter (humic substances), or retained in clay interstices as hydroxycarbonate complexes, or in the form of immobile precipitates in soil pore throats and pore pockets ([3,4]). As a remedy, properly selected solubilizing fluids, complexing agents or ligands that render mobility of the contaminants may be used. Selection of these substances is critical since they may require secondary treatment once injected into the soil. It may also be difficult to separate the contaminants from these arresting agents, that often form a colloidal sludge, at the collection wells.

Past experience with electrochemical treatment of contaminated porous media has shown that the process is most effective when the transported substances are ionic, surface charged or in the form of small micelles with little drag resistance. ([2,5–15]). This is analogous to soil washing whereby the contaminant is *extracted* from the soil and subsequently collected in aqueous phase in a collection well or deposited at the electrode site. The alkali metals and alkali earth metals such as Na, K, Cs and Sr, Ca are expected to electromigrate and be extracted from soil matrix readily unless they become preferentially sorbed onto solid surfaces and clay interstices. Under ideal conditions, the predominant cation and its accompanying anion may be caused to separate efficiently by electromigration only, for which little or no electroosmotic water advection may be necessary.

When extraction becomes ineffective or infeasible, electrochemistry may still be useful to *stabilize* and/or *contain* certain groups of metals and some organic compounds in the ground. In conjunction with electro-remediation, *stabilization* may be defined as fixing the substance in place thereby rendering it less likely to move elsewhere under ambient hydrogeological conditions ([16,17]). *Containment* may be defined as causing a controlled accumulation of the substance by sorption in a small volume of a substrate. Electrochemical stabilization can be accomplished by delivering an appropriate oxidizing or reducing agent to the contaminant in the soil that subse-

quently will: (i) degrade the contaminant; or (ii) change it to a non-toxic or immobile species; or (iii) enhance stable adsorption and incorporation of the contaminant into the soil structure. Electrochemical containment may be accomplished by causing the electro-migration or electroosmotic transport of the contaminants to reactive permeable barriers strategically situated between the electrodes, where they are attenuated and the filtered water is allowed to pass through. In actual field applications, such permeable structures could be installed at various positions throughout a contaminated site serving as primary and secondary treatment locations.

In this paper the two methods of using electrochemical treatment: extraction and stabilization was demonstrated with appropriately quantified laboratory experiments. Field specimens of a high salt content sludge recovered from a settling pond were used to evaluate the efficiency of electrochemical extraction of Na and Cl. The results compared well with previously obtained data for Sr of a similar salt, SrCl_2 ([18]). Electrochemical stabilization was tested using the well documented process of reducing a fairly soluble form of Cr(IV) to its less toxic and less mobile form of Cr(III) in the soil by delivering iron (Fe(0), Fe(II), or Fe(III) with co-reagents) ([19–21,17]). Cr(III) is readily sorbed by soil clay, and the interaction with iron may also results in chromium-iron hydroxide solid solutions with lower equilibrium solution activities than pure solid phases ([20]).

It should be noted in here that, electrochemical stabilization and containment, ought to be regarded as interim or pre-treatment processes to permanent treatment technologies, since these would require either further or ex situ treatment of the contaminant at a later time. For example, Cr may still be required to be taken out from the stabilized site owing to changing hydrogeological conditions that may render it mobile again. Likewise, the saturated bed of sorbent material with contaminants would be either regenerated or taken out for disposal.

2. Methodology

2.1. Equipment and test protocols

Laboratory experiments of electrochemical treatment of contaminated soil samples were conducted using the electrokinetic cells, (E-K), developed at Lehigh University. A schematic representation of this equipment is given in Fig. 1. The sample tube has an ID of 2.7 cm and a length of 10.2 cm and is made of clear glass tube with threaded ends. The tube accommodates *three auxiliary graphite electrodes* (1 mm diameter), separated at equal distance along one side. These electrodes are used to measure voltage in soil during experiments. The tube is assembled to the electrode chambers with O-rings placed inside the housings cut on the inner walls (facing the sample tube) of the chambers. Porous dividers made of glass frit are placed at each end of the sample tube to hold the soil sample in place during the experiments. These dividers have a hydraulic conductivity coefficient of 10^{-3} cm/sec, which is high compared to the typical clay soils tested with coefficients ranging from 10^{-5} to 10^{-8} cm/sec.

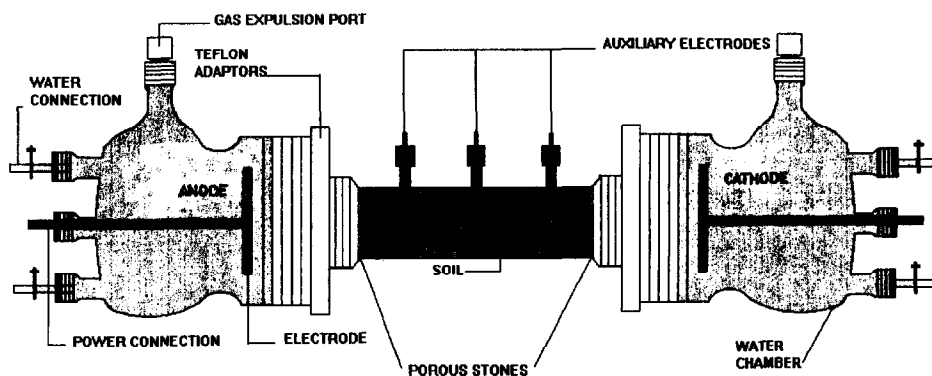


Fig. 1. Schematic details of the Lehigh electrokinetic (E-K) test cell.

The electrode chambers are approximately 175 cm³ in volume. They house the electrodes at each end of the soil sample tube. These chambers are removable for filling and emptying of fluid and also facilitate cleaning after each test run. Teflon couplers are used to attach the soil sample tube to the electrode chambers at each end. Electrode assemblies with a surface area of 22.6 cm² facing the soil specimen were constructed of graphite rods with a 0.635-cm diameter held together with conductive adhesive. The assembly's connecting rod extends towards the back wall of the chamber through a port and is connected to a variable DC power source via an electric socket and wiring. Dedicated electrical equipment for each electrokinetic cell consist of a variable direct current (DC) power supply capable of applying either constant voltage (0 to 120 V), or constant current (0 to 1500 mA). These units also contain analog meters for measuring voltage and current. Teflon or stainless steel quick-connections are provided on the back wall of the electrode chambers. These outlets or inlets are then connected to volume measuring tubes via Teflon tubing. Gas expulsion or liquid extraction/injection ports are provided on top of each electrode chamber. These valves have metal surfaces that are coated to control any deterioration by electrochemical reactions or metal ion deposition on them. Sample extractions or fluid injections are accomplished using a volumetric syringe that allows for accurate control of quantities of fluids. Glass burettes with a capacity of 25 cm³ are used to measure inflow, normally at the anode (positive electrode) chamber, and outflow, normally at the cathode (negative electrode) chamber to an accuracy of 0.1 cm³. The specific techniques used to operate these equipment have been adequately discussed elsewhere ([9,22]).

All chemical extractions and analysis procedures were performed in accordance with EPA Method 3010 (Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA and ICP Spectroscopy) and Method 3050 (Acid Digestion of Sediments, Sludges, and Soils), respectively. Flame Atomic Adsorption Apparatus (AA) was used to analyze the concentrations of Fe, Cr and Na, while Ion Chromatography was used to analyze Cl.

Table 1
Index properties of retrieved drilling mud soil specimens

Sample ID*	Water content $\omega\%$	Degree of saturation $S, \%$	Void ratio, e	Bulk unit weight, kN/m^3	Measured initial concentration, (ppm)	
					Na	Cl
S1	23.3	81	0.62	16.10	3409	1936
S2	19.1	53	0.77	14.22	5845	5515
S3	19.1	65	0.63	15.44	5845	5515
KSSr	41.0	99	1.10	17.77	718	–

2.2. Sample and materials preparation

2.2.1. Electrochemical extraction tests

Electrochemical extraction tests were conducted on retrieved specimens of drilling mud sludge recovered from three separate locations of a settling pond located in Southern Louisiana. The index properties of these samples are given in Table 1. Properties of a laboratory prepared soil sample, designated as KSSr is also given in Table 1. KSSr was a kaolinite specimen containing SrCl_2 salt. It was tested for Sr extraction in a previous study ([18]). The physical properties of this sample are also given here to aid in data comparison presented in the results section.

The core samples, retrieved by split spoon, were cut in appropriate lengths, trimmed and hand packed into the E-K soil sample holder. Deionized water was used in the electrode chambers and the flow tubes.

2.2.2. Electrochemical stabilization tests

The electrochemical stabilization test was conducted by impregnating a nearly saturated, homogeneous kaolinite clay soil sample with solutions of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$ from the anode and the cathode side, respectively. The soil sample was prepared by mixing 254 g of kaolinite clay with 154 ml of distilled water and normally consolidated at 100 kPa for 41 h. After consolidating, a specimen of the cylindrical sample weighing approximately 103 g was placed into the E-K soil chamber. The initial water content of the soil sample was 41.7%. The anode and the cathode solutions were prepared by mixing pentahydrate iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) with distilled water slightly below their solubility limits, respectively. The concentration of the FeSO_4 solution used was 140,800 ml/l (ppm). After mixing the FeSO_4 solution, a volume of approximately 171 ml was added to the anode chamber of the electrokinetic cell. The concentration of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution used was 220,000 ml/l (ppm). After mixing the $\text{K}_2\text{Cr}_2\text{O}_7$ solution a volume of approximately 164 ml was added to the cathode chamber.

The main reason for selection of high concentration solutions of the reacting agents and using them as tracers solutions was to be able to detect any color change in the soil matrix as insoluble Cr and Fe complexes form. A visual observation of contrast color products forming on tan colored kaolinite clay was expected to confirm the anticipated

reactions thereby help to locate the appropriate zones of soil for analysis. It was also intended to minimize the possibility of formation of chromic hydroxide precipitates such as $\text{Cr}(\text{OH})_3$ by maintaining low pH. The high concentrations of these salts of strong acids resulted in initial pH of 2.95 and 4.05 for the anode and cathode chamber solutions of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$, respectively.

2.3. Testing

The extraction tests were performed on the drilling mud samples as outlined above in the methodology section. These tests were conducted to a maximum of 10 days at constant 30 V DC applied across the electrodes. During the E-K test, inflow, outflow, voltage, current, and pH data were measured. The cathode chamber served as the inflow source, while the anode chamber was the outflow. Water samples were collected from the anode and cathode chamber periodically during each test. Soil was destructively sampled at the completion of each test and analyzed for Na and Cl.

In electrochemical stabilization application, the Fe(II) and Cr(VI) were introduced to the kaolinite sample as tracer solutions. The experiment was performed for approximately 4.5 days (105 h) under constant 15 V DC across the electrodes. During this experiment, data was obtained for flow, pH, voltage, and current. A light brown band of reaction products became visible at around 1/4 sample length distance from the cathode side after about 24 h of treatment. As treatment continued, brown colored reaction products appeared to spread from the cathode side towards the anode side of the sample and ceased spreading slightly passed the mid-section of the sample at about 80 h of treatment. Upon completion of the E-K test, the soil sample was divided into four equal parts. Each portion weighed approximately 27.75 g. A representative sample, weighing 10.0 g, was obtained from these sections. Each 10.0 g sample was divided into two 5.0-g samples for acid and water extractions. Water and acid extractions were performed according to the standard protocols given above to obtain the water soluble and insoluble fractions of total iron and chromium, respectively. Speciation analysis was not warranted since the objective was to demonstrate the retention of Cr in soil as a water insoluble product at the low soil pH.

3. Results and discussion

3.1. Electrochemical extraction

Fig. 2 shows the inflow (anode side measurement) and current variation with time for the two retrieved samples of drilling mud. Table 1 lists the physical and chemical properties of these samples designated as S1, S2 and S3. The mud specimen with higher degree of saturation S1 ($S = 81\%$) exhibited larger volume of cumulative flow than that of S2 with lower degree of saturation ($S = 53\%$). This was expected since steady state flow should occur earlier in the higher degree saturated specimen. The interesting observation was the variation of current over time, which remained similar for the first 75 h of treatment of the two specimens. Current dropped well below 1 mA for S1, while

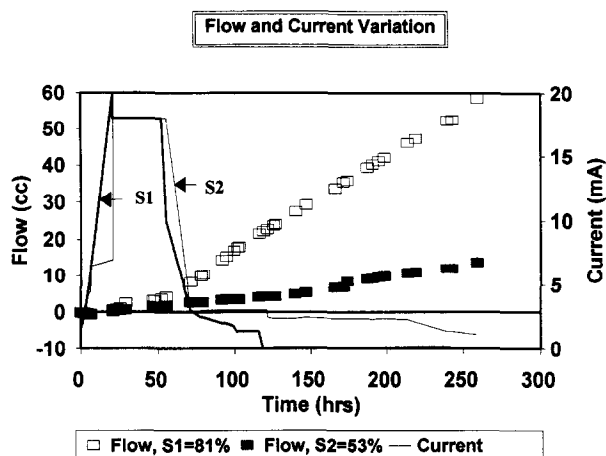
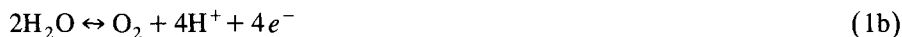


Fig. 2. Variation of flow and current in NaCl separation experiment using E-K cell (S1, S2: sample designations given in Table 1).

ion migration continued for S2 after 100 h of treatment. The next set of figures shed light on this occurrence.

Fig. 3a and b show the separation of Na and Cl and the final pH profiles in three samples of the drilling mud sludge. As observed in Fig. 3a, close to 100% recovery of the Na is accomplished in the 81% saturated specimen (S1) at the termination of the test, while about 70% of Na is recovered for the 53% saturated specimen (S2). The ionic migration appears to continue in S2 as indicated by the higher current it carried in Fig. 2. The specimen designated as S1 shows a substantial recovery of Cl in the anode chamber (Fig. 3b), although not as high a recovery as Na. The analysis showed little or no presence of Cl in the soil, which suggested inability to account for all the Cl transported to the anode chamber. This result was attributed to perhaps formation of gaseous chlorine which would have been ventilated from the anode chamber periodically. In sufficiently acid solutions having high Cl^- concentrations (pH below approximately 4), oxidation of chlorides will lead to formation of gaseous chlorine ([23]). This oxidation can be brought about chemically or electrolytically, as would be the case in the anode chamber of the E-K cell. The pertinent reactions involving chloride may then be written as follows:



The Fig. 4 shows the variation of Na and Cl concentration in the cathode and the anode chambers respectively after the initial 48 h of treatment. As observed the concentration of Na increases steadily, while the concentration of Cl shows little or no change. There is a small decrease of the Cl concentration with respect to its initial level, by the end of the 10-day (260 h) treatment. This observation strengthens the supposition that the excess Cl is oxidized to gaseous chlorine in low pH environment and

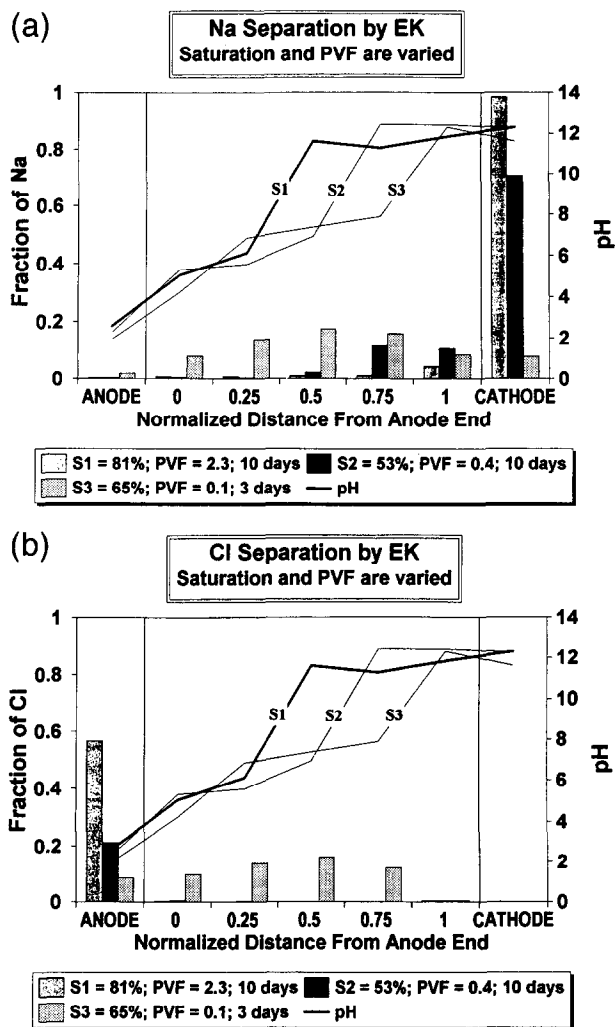


Fig. 3. a) Separation of Na by electrochemical treatment of a retrieved field soil sample of different initial water saturation (S1, S2, S3: sample designations given in Table 1; PVF = pore volume of flow). b) Separation of Cl by electrochemical treatment of a retrieved field soil sample of different initial water saturation (S1, S2, S3: sample designations given in Table 1; PVF = pore volume of flow).

subsequently was lost to the atmosphere with ventilation. Observing the data in Fig. 4, it appears that neither initial degree of water saturation, nor the quantity of electroosmotic flow have appreciable effect on the variation of concentration of Na or Cl in the cathode and the anode chambers, respectively. This clearly shows that the process is predominantly controlled by the electromigration of the ions.

The Fig. 5 shows the variation of recovery of mass fraction of total Na in the cathode chamber with pore fluid of water flow. Data pertaining to two specimens of different initial degree of water saturation values, S1 and S2 are given in this figure. Superim-

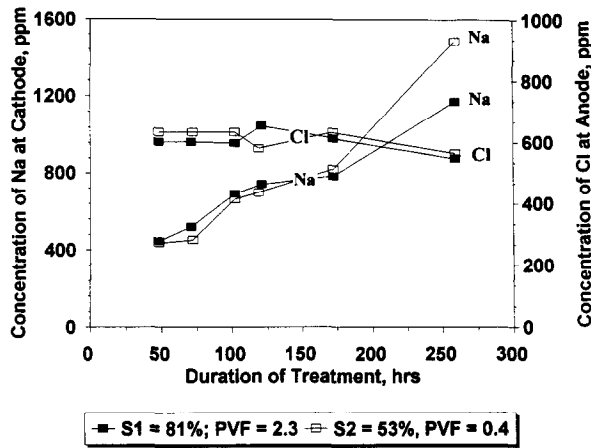


Fig. 4. Variations of Cl and Na concentrations in the anode and cathode chambers with duration of treatment.

posed on the data is recovery of Sr from close to 99% saturated kaolinite clay. As observed, again water flow has little affect on the separation of the Na and Cl, nor Sr which tend to electromigrate under the applied potential. Yet, water advection is important as it increases the water saturation of the pores thereby helping desorption of the surface held ions. This can be observed by the non-linear trend of the removal curves shown in Fig. 5. The flatter portion of the curve for the specimen with initial water saturation of 81% shows the contribution of electroosmotic advection at low remaining concentration of Na in the soil. As observed, approximately 60% of the total mass of Na in the soil is caused to electromigrate initially for which the pore volume of flow is measured only around 0.1. A similar observation is made for the second specimen with lower degree of water saturation (53%), for which 50% of the total Na is removed upon about 0.1 pore volume of flow. The flat portion of the removal curve represents a

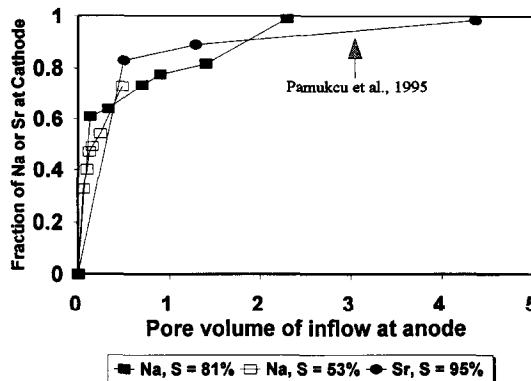


Fig. 5. Pore volume of flow versus Na and Sr accumulation in cathode chamber. (S designates degree of saturation).

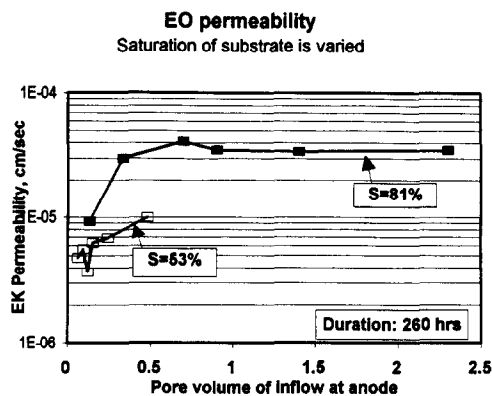


Fig. 6. Variation of computed electroosmotic permeability of two specimens different initial saturation values versus pore volume of flow.

time-dependent flow of Na into the cathode chamber caused by a combination of electromigration and electroosmosis. Electroosmosis is a significantly longer process than the initial migration of the Na ions in the pore fluid. Similar results were obtained in an earlier study ([18]) where more than 80% of the total Sr was recovered in cathode chamber after about 0.5 pore volume of flow (Fig. 5).

The contribution of electroosmotic advection is perhaps most accountable once a steady state flow is achieved with constant electroosmotic permeability. This phenomenon is observed in Fig. 6 where the computed electroosmotic permeability in cm/sec is plotted against the pore volume of flow. The specimen with higher degree of saturation attains a constant coefficient of electroosmotic permeability (approximately 3.5×10^{-5} cm/sec or 1.2×10^{-6} cm/sec V) after about 0.5 pore volume of flow. Therefore the contribution of electroosmotic flow to the removal of Na may be quantified accurately only for the 30% of the mass fraction removed after 0.5 pore volume of flow, as observed in Fig. 5.

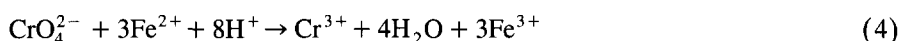
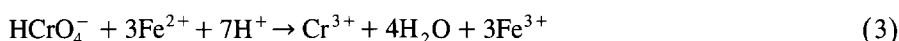
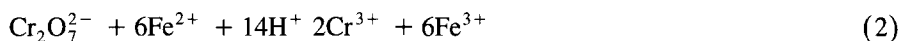
3.2. Electrochemical stabilization

Chromium exists in two possible oxidation states in soils: the trivalent Cr(III) and the hexavalent Cr(VI) chromium. The hexavalent chromium is more toxic than trivalent chromium. Hexavalent chromium exist in soil as water soluble anions, HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. Due to their negative charge they are not readily adsorbed or exchanged at clay surfaces, therefore remain in soil pore water and be readily transported. This was observed in an earlier study by electromigration of chromate towards anode in the opposite direction of water flow ([11]). However, acid solutions of dichromate get reduced easily ([24]). Therefore, sufficiently low pH (below 2.5) condition at the anode end of the soil promotes formation of Cr(III). Trivalent chromium ion which occur at lower pH is readily adsorbed by soils ([25,26]).

Cr(III) forms hydroxide complexes in presence of OH^- . These species precipitate at pH 4.5 and complete precipitation occurs at 5.5. At high concentrations of Cr(IV), the hydrolysis of the produced Fe(III) and Cr(III) depresses the pH to 3 to 4 ([21]). These

products are soluble hydrolyzed species of Fe(III) and Cr(III). Hexavalent chromium can also be reduced to Cr(III) under normal soil and pH conditions, for which soil organic matter has been identified as the electron donor ([26]). Bartlett [27] reported that in natural soils, this reduction may be extremely slow, requiring years. In subsurface soils where there is less organic matter, the Fe(II) containing minerals reduce Cr(VI) at pH less than 5 ([19]). Electrochemically injected Fe(II) into a matrix of soil containing hexavalent chromium should facilitate the reduction of Cr(VI). The delivery of Fe(II) has also been shown to enhance formation of chromium-iron hydroxide solid solution $[(Cr_xFe_{1-x})(OH)_3(ss)]$ which has a very low equilibrium solution activity ([20]), thereby relatively immobile than other species of chromium.

The half reactions used to define Cr(IV) and Fe(II) interaction are shown below:



Based on the equilibrium constants of these reactions, the reduction of Cr(VI) to Cr(III) is expected to occur instantaneously. Yet, it has been reported that a pH less than 3 is required for reasonably rapid reduction ([28]).

Fig. 7 shows the flow-current and electrode site pH variations with time. The current measurements appear to be affected by the redox reactions as it varies between 1 to 4 mA throughout the test. The flow is not substantial and the electrode chamber pH values change only slightly. Fig. 8 shows the distribution of total and non-aqueous Cr and Fe and the final pH in the soil and liquid compartments of the electrokinetic cell. Table 2 presents the mass balance computation results for the total iron and chromium distribution in the soil sample. According to the mass balance data about 30% of the iron remains unaccounted for and there is about 17% excess Cr. Such discrepancies in mass balance computations are warranted considering the large sectioning of the soil sampled for analysis.

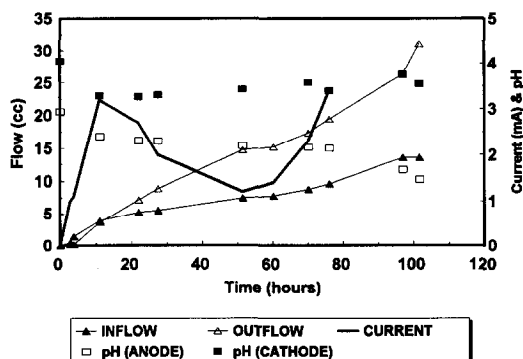


Fig. 7. Variation of flow-current and electrode chamber pH in Fe promoted reduction of Cr experiment using E-K.

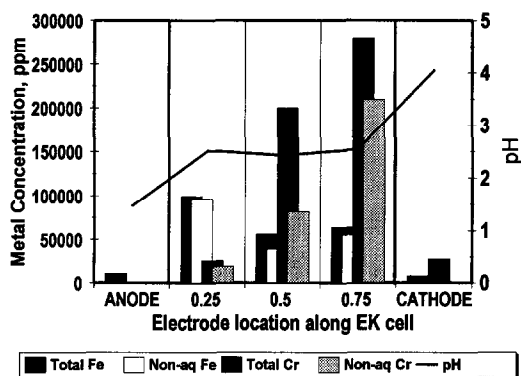


Fig. 8. Post E-K test concentration distribution of total and non-aqueous Cr and Fe.

As observed in Fig. 8, the soil pH is fairly uniform below 3, which is favorable for rapid reduction of Cr(IV). The depression of soil pH is probably due to formation of hydrolyzed species of Fe(III) and Cr(III) as was discussed by Lin and Vesilind [21]. These species are readily soluble as indicated by the aqueous concentrations of Cr and Fe in Fig. 8. Most of the non-aqueous Cr appears to have accumulated in the center and cathode side, and little has migrated towards the anode. Since hydroxide complexes and chromic hydroxide occur at higher pH levels than 3, the non-aqueous form of the Cr and Fe is likely due to formation of chromium-iron hydroxide solid solution $(Cr_xFe_{1-x})(OH)_3$ (ss), which has low equilibrium solution activity than pure solid phases at low pH ([20]). It should also be noted that, part of the non-aqueous Cr concentration mass may be due to sorption of Cr(III) by the clay substrate ([26]). These results compare favorably with those reported previously ([17]) where the researchers showed migration of chromate and iron from the cathode and anode ends of sand

Table 2

Average post E-K concentrations of total Cr and Fe and subsequent mass balance computation

Sample sections (normalized distance from) anode	Pre E-k		Post E-K			
	Total Fe (mg)	Total Cr (mg)	Total Fe	Total Cr	Total Fe	Total Cr
			Conc. (mg/kg) ppm	Mass fraction %	Conc. (mg/kg) ppm	Mass fraction %
Anode chamber	14142.3	—	10800	14.20	1300	1.71
0.25 (1/4 section)	—	—	99000	18.03	26000	3.44
0.50 (1/2 section)	—	—	55600	20.25	199800	52.92
0.75 (1/4 section)	—	—	63600	11.58	279600	37.03
Cathode chamber	—	19442.7	7400	5.86	28000	22.18
Total				69.92		117.28

substrate, respectively. Their results showed subsequent retention of Cr(III) in soil pores as chromic hydroxide precipitate under high pH conditions on the cathode side of the soil samples.

4. Conclusions

Within the scope of the chemical analysis results for the Na–Cl separation and Fe(II) promoted reduction of Cr(VI), electrochemical treatment was shown to be effective for extraction or containment of selected inorganic elements. The selection of the type of treatment is highly dependent on the in situ soil-contaminant characterization. Electrochemical treatment may be engineered to extract and collect soluble species of cations and anions by electromigration without the need of water flushing and secondary treatments. Whenever, the targeted substance possess complex aqueous chemistry and electrochemistry, it may be feasible to use electrochemistry to stabilize the substance in situ and render it immobile.

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