

Physicochemical soil–contaminant interactions during electrokinetic extraction

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Abstract

The feasibility of using electrokinetics to extract contaminants from soils has been established by bench-scale laboratory experiments and small-scale field tests. However, the physics and chemistry associated with the innovative remediation technology are not yet fully understood. Many physicochemical reactions occur simultaneously during the process. These reactions may enhance or reduce the cleanup efficiency of the process. They are particularly important in fine-grained soils because the large specific surface area of the soil provides numerous active sites for these reactions. In this paper, several prominent physicochemical soil–contaminant interactions during electrokinetic extraction and their influences on the cleanup efficiency of the technology are discussed. These interactions include: (1) change of zeta potential at the soil particle/pore fluid interface; (2) resistance of the soil–fluid–contaminant system to pH change; and (3) sorption/desorption of reactive contaminants onto or from the soil particle surface and precipitation/dissolution of metallic contaminants in the pore fluid. The effects on these interactions of injecting an enhancement fluid into the contaminated soil are also discussed. In addition, a brief review on the state-of-development of the technology is presented. © 1997 Elsevier Science B.V.

Keywords: Electrokinetic extraction; Physicochemical reactions; Soil-fluid-contaminant

1. Introduction

Electrokinetic extraction is a feasible technology for efficient and economical remediation of contaminated soils under certain circumstances. The technology is particularly useful for fine-grained soil when pump-and-treat technology is impractical, if not impossible. The fundamental contaminant removal mechanisms of electrokinetic extraction are electroosmosis and ionic migration [1,2]. When a direct-current (dc) electric

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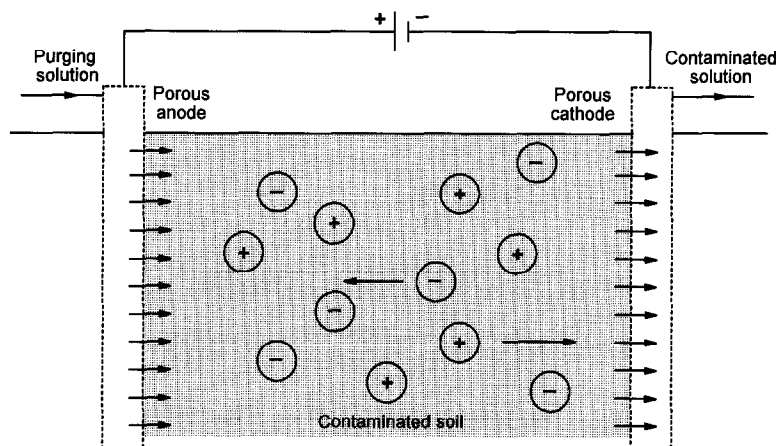


Fig. 1. Concept of in-situ electrokinetic extraction of contaminants.

field is imposed on a wet mass of soil, pore fluid is moved from one electrode toward the other by electroosmosis due to the interaction between the diffuse double layer existing at the soil particle/fluid interface and the pore fluid [1,3–5]. Derivations of the governing equations describing the diffuse double layer in SI units are given by Hunter [3] and Yeung [6]. The impact of pore fluid chemistry on the thickness of the diffuse double layer can be estimated explicitly from these equations. Contaminants are thus moved with the motion of the pore fluid by advection [7]. If the contaminant species carry charges, they are also moved by ionic migration. The direction of ionic migration is dictated by the polarity of the contaminant, and the migration velocity is controlled by the effective ionic mobility of the species in soil [8–10]; anionic and cationic contaminants migrate toward the anode and the cathode, respectively, relative to the motion of the pore fluid. Effective ionic mobility of chemical species in a porous medium such as soil is considerably lower than that in free solution due to tortuosity of the flow path [9] and possibly to interactions between the contaminant and the soil particle surface. Combining these two contaminant removal mechanisms results in the possibility of electrokinetic extraction as depicted in Fig. 1.

Although the fundamental concept of electrokinetic extraction can be easily understood, many electrochemical reactions and physicochemical soil–contaminant interactions that occur simultaneously are yet to be investigated. If these reactions and interactions are not properly taken into consideration, erroneous interpretation of results obtained from laboratory experiments and pilot field-scale tests may ensue. In many cases, the applicability of the technology has not been thoroughly assessed and the potential cleanup efficiency has been overestimated [11]. The situation is particularly complex in fine-grained soils because of their large specific surface areas. The large specific surface area provides numerous active sites for soil–contaminant interactions. Moreover, these dynamic interactions are dependent on pH and concentration of contaminant in the pore fluid. As pH and contaminant concentration in the soil are a

function of time and space during electrokinetic extraction, these interactions are also a function of time and space.

The injection of an enhancement fluid into the contaminated soil during the process makes the situation even more complex. In this paper, several prominent physico-chemical soil–contaminant interactions during electrokinetic extraction and their influences on the cleanup efficiency of the technology are discussed. These interactions include: (1) change of zeta potential at the soil particle/pore fluid interface; (2) resistance of the soil–fluid–contaminant system to pH change; and (3) sorption/desorption of reactive contaminants onto or from the soil particle surface and precipitation/dissolution of metallic contaminants in the pore fluid. The effects on these interactions of injecting an enhancement fluid into the contaminated soil by electrokinetics are also discussed. In addition, a brief review of the state-of-development of the technology is presented.

2. State-of-development of the technology

The technique has been used successfully 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 [12]; to remove spiked lead from kaolinite [13,14]; to remove 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 [15]; to remove cadmium from saturated kaolinite [16]; and to remove sulfate, metals and other contaminants from high-purity fine quartz sand [17]. Eykholt [18] and Eykholt and Daniel [19] gave similar supporting experimental results on removal of copper from kaolinite, and identified other complicating features of the technology. Rødsand et al. [20] pioneered the use of acetic acid to depolarize the cathode reaction and an ion-selective membrane to halt hydroxyl ion migrating from the cathode into the soil. Their experimental results indicate that depolarization of the cathode reaction by acetic acid can enhance electrokinetic extraction of lead, whereas the membrane extraction technique does not enhance the technology as expected. Results on removal of zinc from Georgia kaolinite presented by Hicks and Tondorf [11] indicate that problems related to isoelectric focusing can be prevented simply by rinsing away the hydroxyl ions generated at the cathode, and that 95% zinc removal can be achieved. Yeung et al. [21] demonstrated the possibility of using disodium ethylenediaminetetraacetate solution as an enhancement fluid for the removal of lead from a natural kaolinite. The extracted anionic and cationic contaminant ions accumulate at or in the vicinity of the anode and the cathode, respectively. Depending on their concentration and the electrode potential of the metal relative to that of electrolysis of water, metallic ions may deposit on the cathode as metal [17]. The method is also effective for the removal of organic pollutants such as acetic acid, phenol, gasoline hydrocarbons and TCE from contaminated soils [22–29]. Although the technology has been proven to be feasible in laboratory bench-scale experiments and small-scale field tests, a thorough understanding of the complex transport phenomena and electrochemistry involved has yet to be developed.

A two-dimensional steady-state numerical model has been developed to simulate the fluid flow patterns and electrical potential distributions in and around a simulated waste site for coupled electroosmotic and hydraulic flows for different site geometries, electrode configurations and values of the physicochemical parameters [30,31]. However, migration of contaminants is not included in these early works.

Shapiro and Probstein [28] model the one-dimensional migration of contaminants using the advection–dispersion equation. Contaminant migrations induced by electroosmosis and ionic migrations are treated as advective transport. Not all coupling effects between driving forces and flows are considered. A set of one-dimensional governing equations describing the simultaneous transport of water, a chemical, and electric current in a compressible porous medium has been developed on the basis of macroscopic conservation of mass and electric charge [32]. However, the coefficients used in the formulation cannot be readily measured. Jin and Sharma [33], using non-equilibrium thermodynamics, extended the theoretical formulation of coupled flows induced by hydraulic and electrical gradients to a heterogeneous porous medium by using a two-dimensional network model consisting of a regular square lattice arrangement of nodes interconnected by cylindrical tubes. The heterogeneity of the medium is modeled by varying the surface potentials and radii of these interconnecting tubes at different positions within the medium. However, electrochemical reactions that occur during the flow processes are not included in any of these formulations. Datla and Yeung [2,34,35] extended the work of Yeung and Mitchell [8,10] to simulate the transport of contaminants under the combined influences of hydraulic, electrical, and chemical gradients. The coupling effects of driving forces are properly taken into account. The importance of the coupling effects between hydraulic and electrical gradients on fluid flow quantity in fine-grained soils is depicted by Yeung [36]. The electrochemical reactions between contaminants in the pore fluid, such as acid–base reactions, dissociation of water, aqueous complexation and precipitation of metal oxides and hydroxides, are modeled by applying: (1) mass balance equations of different chemical components; (2) mass action equations of different chemical reactions; (3) the charge balance equation; and (4) solubility equilibrium equations of different hydroxide precipitates. However, no physicochemical soil–contaminant interactions except instantaneous sorption/desorption reactions are included in the model. A mathematical model was developed by Alshwabkeh and Acar [37] to simulate transport of multicomponent species in soils under simultaneously imposed hydraulic, electrical and chemical gradients. Mass balance of chemical species and fluid, and charge balance are used in the formulation. Instantaneous sorption/desorption and precipitation are also included. However, acid/base buffer capacity of the soil and pH-dependent physicochemical soil–contaminant interactions are not explicitly considered.

Electrochemical reactions occur simultaneously during electrokinetic treatment of contaminated soil in addition to electroosmosis and ionic migration. The most pronounced effect identified may be the generation of pH gradient during the process [18,19,38,39]. Theoretical formulation of the migration of acid front during the process has been attempted [27,37–40]. These researchers assumed 100% Faraday efficiency for the electrolytic decomposition of water at the electrodes to estimate the quantities of hydrogen ions and hydroxyl ions generated at the anode and the cathode, respectively,

during the process. They used these concentrations as boundary conditions to model the migration of these ions into the soil by their modified advection–dispersion equation. The ionic migration was included by adding an ionic migration term to the advection component of the advection–dispersion equation. The pH in the soil was calculated from the concentrations of hydrogen and hydroxyl ions as a function of time and space. The assumption of 100% Faraday efficiency for the electrolytic decomposition of water in a soil–water–contaminant system may not be realistic. Eykholt [18] improved the approach by adding an efficiency term to the reactions to estimate the pH of the fluid in the reservoirs of his experiments. He then used these computed pHs as boundary conditions to solve the same modified advection–dispersion equation. The acid fronts computed by these models should eventually flush the sample, resulting in a uniform acidic pH in the pore fluid throughout the sample. Such a phenomenon has never been observed experimentally [18,29,41]. Therefore, the migration of hydrogen and hydroxyl ions must be controlled by other mechanisms in addition to advection and dispersion. Hicks and Tondorf [11], Jacobs et al. [42] and Yeung and Datla [2,43] used electrical neutrality as a controlling condition to determine pH as a function of time and space.

3. Physicochemical soil–contaminant interactions

When a dc electric field is imposed on a wet soil mass, many reactions in addition to electroosmosis and ionic migration occur simultaneously. These reactions may include: ion diffusion, ion exchange, development of osmotic and pH gradients, desiccation due to heat generation at electrodes, gas generation at electrodes due to electrolysis of water, mineral decomposition, precipitation of salts or secondary minerals, hydrolysis, oxidation, reduction, physical and chemical sorption, and fabric change [5]. Some of these reactions may be beneficial as they may increase the mobility of contaminants during electrokinetic extraction. However, others, such as heat and gas generation at electrodes, sorption of contaminants onto the soil particle surface, and precipitation of contaminants, may impair the removal efficiency of electrokinetic extraction. Some others, such as development of pH gradient, hydrolysis, oxidation and reduction, may enhance or reduce the cleanup efficiency of electrokinetic extraction, depending on the type and physicochemical properties of the contaminants and the soil. Therefore, a thorough understanding of the physicochemical soil–contaminant interactions during electrokinetic extraction is crucial before the potential of the technology can be fully utilized.

3.1. Change of zeta potential at the soil particle / pore fluid interface

Most soil particle surfaces are negatively charged as a result of isomorphous substitution and presence of broken bonds [44]. The zeta potential at the soil particle/pore fluid interface is thus negative. The mobile ions in the pore fluid balancing the charge deficit have to be positively charged. In most clays, the range of values for zeta potential is between 0 and -50 mV, depending on the chemistry of the soil system [1,5]. When a

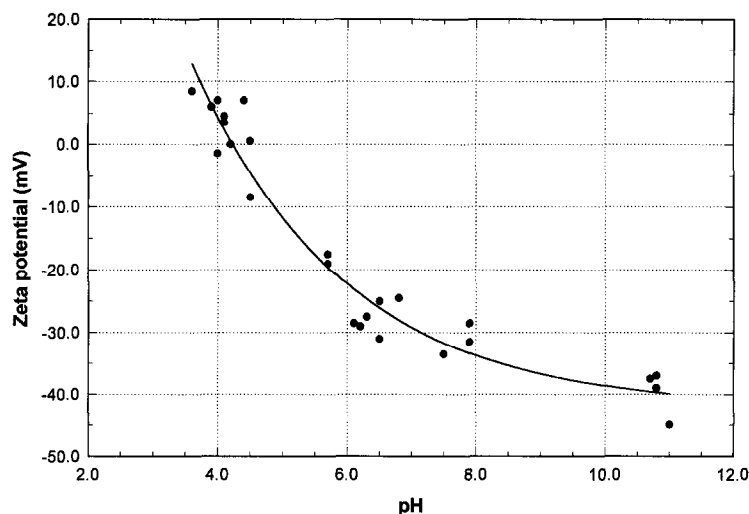


Fig. 2. pH-dependent zeta potential of kaolinite beds (data from Lorenz [47]).

dc electric field is imposed on the system, the mobile positive ions exert more momentum than the fixed negative ions on the pore fluid. Pore fluid is thus driven from the anode toward the cathode by electroosmosis. Therefore, electroosmosis is conventionally taken to be the hydraulic flow induced by an externally applied electrical gradient from the anode toward the cathode. The phenomenon has also been observed in many short duration experiments on electroosmotic flow [1].

However, when the chemistry of the soil–fluid–contaminant system is changed by a prolonged application of a dc electric field or the existence of contaminants in the pore fluid, the direction of electroosmotic flow may be reversed, i.e., from the cathode toward the anode. The phenomenon can be due to the development of a pH gradient in the soil resulting from electrolytic decomposition of water. Typically, the pH in the vicinity of the anode can fall to 2 and that of the cathode can rise to 12 [45,46]. The low pH in the soil can reverse the polarity of zeta potential of kaolinite, as depicted in Fig. 2 [47]. When the polarity of zeta potential is reversed, the direction of electroosmotic flow may consequently be reversed [19,48]. The pH at which polarity reversal of zeta potential takes place depends on the physicochemical properties of the soil and pore fluid [49]. Moreover, sorption of hydrolysable metal ions such as Co^{2+} , Cd^{2+} , Cu^{2+} and Pb^{2+} onto the clay particle surface can also change the charge of kaolinite [48,50,51]. Depending on the initial metal concentration and sorption capacity of the soil, the initially negative surface becomes less negative, approaches zero, and may become positive at a pH around the original point of zero charge. Similarly, chemisorption of anions makes the surface more negative [52]. The relative importance of these two factors remains unknown. Experimental results on removal of copper from Georgia kaolinite by Eykholt and Daniel [19] indicate that the low pH in the soil resulting from electrokinetic treatment may be a significant contributing factor. However, the low soil pH observed by Hamed et al. [13] during removal of lead from Georgia kaolinite did not

generate a reverse electroosmotic flow. Moreover, experimental results on removal of lead from Milwhite kaolinite by Yeung et al. [21] indicate the contrary. They observed reverse electroosmotic flow at a soil pH much higher than the pH at which polarity reversal of zeta potential occurs. West and Stewart [48] also observed reverse electroosmotic flows in their experiments on extraction of lead from kaolinite. Thus, the sorption of Pb(II) ions on the soil particle surface may also be a contributing factor.

Since the direction of ionic migration of species is dictated by the polarity of the charges carried by the contaminant species, electroosmotic flow may enhance or diminish the removal of some of the contaminant species in the soil. When electroosmotic flow is driven from the anode toward the cathode, the removal of cationic species is enhanced as cationic migration is accelerated by electroosmotic flow. The removal of anionic species is diminished as anionic migration is retarded by electroosmotic flow. More importantly, a forward electroosmotic flow, i.e. from the anode toward the cathode, promotes the development of a low pH environment in the soil. As a low pH environment inhibits most metallic contaminants from being sorbed onto the soil particle surface and precipitating as a separate solid phase, a forward electroosmotic flow resulting from the existence of a negative zeta potential enhances the removal of metallic contaminants by electrokinetic extraction. On the other hand, a reverse electroosmotic flow may enhance the removal of anionic species. However, it may raise the pH in the soil and impair the removal of metallic contaminants.

The polarity of the zeta potential may be reversed when the soil pH becomes too low, as shown in Fig. 2, and the direction of electroosmotic flow is reversed. Therefore, the ideal pH of the environment should be low enough to keep all metallic contaminants in the dissolved phase while high enough to maintain a negative zeta potential and thus a forward electroosmotic flow. However, these ideal conditions can seldom, if ever, be satisfied in reality. For example, a pH environment as low as 2 is required to keep all the lead in a contaminated soil in the dissolved phase. However, the polarity of zeta potential of most kaolinitic soils has already been reversed at a higher pH. Nonetheless, the condition is even more difficult to satisfy during electrokinetic treatment of contaminated soil as the pH gradient in the soil is generated by the process. To maintain a negative zeta potential at the soil particle/pore fluid interface and simultaneously to keep metallic contaminants in the dissolved phase remain an obstacle to be overcome in full-scale implementation of electrokinetic extraction of metallic contaminants. Moreover, sorption of hydrolysable metal ions onto the clay particle surface may cause charge reversal [51]. The use of enhancement fluid to keep metals in the dissolved phase at a higher pH may provide a solution to the problem.

3.2. Resistance of the soil–fluid–contaminant system to pH change

A low pH is generated at the anode while a high pH is generated at the cathode during electrokinetic extraction. Although the controlling mechanism of the development of pH gradient in the contaminated soil during electrokinetic treatment is still a subject of debate, an acid front is generally observed migrating from the anode toward the cathode when forward electroosmotic flow occurs. If the acid/base buffer capacity of a soil is low, i.e., its resistance to pH change is low, a low pH environment can be

developed across the contaminated soil during electrokinetic extraction except possibly in the close vicinity of the cathode. Buffer capacity or buffer intensity of a system is defined as the amount of strong base (strong acid) which when added to the system causes a unit increase (decrease) in pH [53]. As discussed earlier, a low pH environment can promote the removal of metallic contaminants from fine-grained soils. The low acid/base buffer capacity of Georgia kaolinite may contribute significantly to the removal of a very high proportion of metallic contaminant initially spiked to it, as observed in many laboratory bench-scale experiments [11,13,21,54]. However, the degree of lead removal from a natural kaolinite of much higher acid/base buffer capacity is negligible [21]. Results of acid/base buffer capacity measurements on: (1) Georgia kaolinite and (2) Milwhite kaolinite are presented to illustrate the importance of this physicochemical effect.

Georgia kaolinite is a white, high purity and well characterized kaolinitic soil from Georgia. Its properties are readily available in the literature [55]. Milwhite kaolinite is a commercially refined product from Bryant, Arkansas. It is reddish-brown in color and contains about 4.3% iron oxides as Fe_2O_3 and other impurities such as SiO_2 and TiO_2 . X-ray diffraction indicates that the clay is predominantly composed of kaolinite mineral with a trace of chlorite. The cation exchange capacity of the soil is measured to be 29 mmol kg^{-1} . 94% of the material passes the No. 200 sieve (opening size $75 \mu\text{m}$). The liquid limit, plastic limit and plasticity index are determined to be 46.4%, 25.4% and 21.0%, respectively. The specific gravity of the solid particles is measured to be 2.74. The clay is classified as CL in accordance with the Unified Soil Classification System.

Dry kaolinite samples of 1.5 g each were placed in centrifuge tubes and 30 ml of deionized water was added to each sample. The soil mixtures were thoroughly mixed for 24 h using a wrist action shaker. An accurately measured quantity of 1 M HNO_3 (aq.) or 1 M NaOH (aq.) was added to each soil–deionized water mixture. The amount of strong

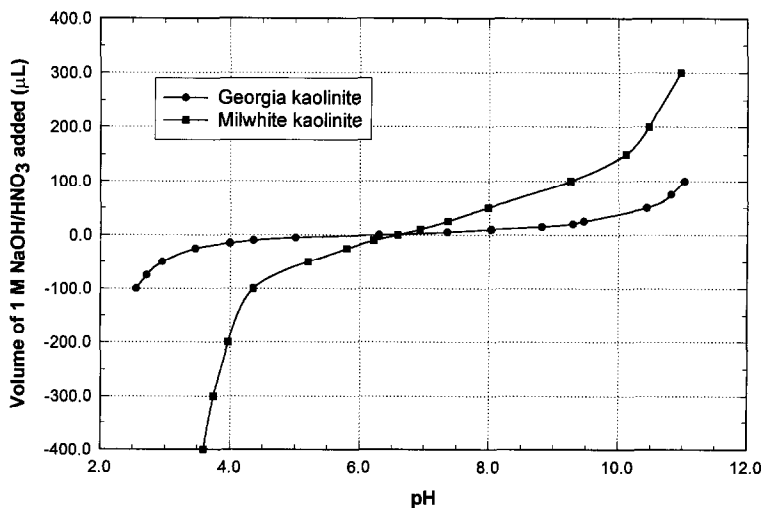


Fig. 3. Acid/base capacity curves of Georgia and Milwhite kaolinite.

acid or base added ranged from 0 to 100 μl for Georgia kaolinite and from 0 to 400 μl for Milwhite kaolinite. The samples were mixed again for another 24 h and the pH of each soil mixture was measured. The pHs of the two kaolinites as a function of volume of strong acid or base added are presented in Fig. 3. The volume of 1 M HNO_3 (aq.) added to the soil is taken to be negative to be consistent with the definition of buffer capacity. The slopes of the curves shown in Fig. 3 give the buffer capacities of the two kaolinites at different pHs. It can be observed in Fig. 3 that Milwhite kaolinite has a much higher acid/base buffer capacity than Georgia kaolinite at all pHs. In the pH range of 4 to 9, addition of 25 μl of 1 M HNO_3/NaOH (25 μmol of H^+/OH^-) can change the pH of Georgia kaolinite by approximately 3 units and that of Milwhite kaolinite by only 1 unit under identical conditions. When the pH is lower than 4 or higher than 9, the buffer capacities of both kaolinites increase. However, the increases in Milwhite kaolinite are much higher than those of Georgia kaolinite. The strong buffer capacity of Milwhite kaolinite at low pH is probably due to the presence of Al oxides and Fe oxides [56]. It can be observed in Fig. 3 that it is very difficult to adjust the pH of Milwhite kaolinite to any value lower than 3.5, which renders removal of metallic contaminants very difficult. A possible solution is to inject enhancement fluid into the contaminated soil to solubilize metallic contaminants in the dissolved phase at a higher pH.

3.3. Sorption / desorption of reactive contaminants onto / from the soil particle surface and precipitation of metallic contaminants in the pore fluid

Most in-situ cleanup techniques such as electrokinetic extraction are only effective in removing mobile contaminants from contaminated soils. Contaminants in soil are considered to be mobile when they exist as a solute in the pore fluid, an immiscible liquid in soil pores, or in various phases attached to mobile colloids in the pore fluid. Thus, they are not permanently fixed on the solid phase of the porous medium and they can be removed by any type of external force that can effectively drive a fluid flow and/or a contaminant flow through the medium. However, the contaminants may become immobile when they are sorbed on the soil particle surface or precipitated as a separate solid phase. The adverse effect of sorption on contaminant removal is very significant in fine-grained soils because of the very large and active specific surface area provided by the soil. Precipitates do not carry charge and their mobility in the pore fluid by advection is very low. Thus, it is very unlikely that electrokinetic extraction can remove precipitates.

Both sorption/desorption and precipitation/dissolution depend on type of contaminant, concentration of contaminant, type of soil, surface characteristics of soil, chemistry of pore fluid, and soil pH [53,57]. The reactions are dynamic, time dependent, non-linear, reaction path dependent, and partially reversible. The situation is particularly complex during electrokinetic extraction as the concentrations of contaminant and pH are a function of time and space. Contaminants may become immobile under specific environmental conditions. However, the temporary immobilization of contaminants cannot be taken as permanent solidification and stabilization of the contaminants. When the environmental conditions change during the electrokinetic process, they may become mobile again.

Equilibrium isotherms are commonly used to model sorption/desorption [7,58]. These models assume that the contaminant sorbed on the soil particle surface and that in the dissolved phase reach instantaneous dynamic chemical equilibrium at all times. The assumption may be adequate when the flow velocity of groundwater is low. However, as the migration velocity of contaminant during electrokinetic extraction is relatively high, the validity of using these equilibrium isotherms to model sorption/desorption may not be adequate. Injection of enhancement solution may further complicate the situation as the chemistry of the pore fluid and the pH-dependent behavior of the soil and the contaminant may change drastically.

Results on the experimental evaluation of the sorption and precipitation characteristics of lead in Georgia and Milwhite kaolinite at different pHs are presented as an illustration. It is practically very difficult to differentiate the effects of sorption and precipitation in batch experiments unless a separate solid phase can be observed. Thus, the proportions of lead in the dissolved phase at different soil pHs were measured in these experiments to determine the sorption and precipitation characteristics of lead in Georgia and Milwhite kaolinite. 25 ppm Pb(II) solution was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ powder in deionized water. Kaolinite samples each of mass 0.5 g were placed in test tubes and 10 ml of the Pb(II) solution was added to each sample. Experiments were designed to ensure complete interaction between soil and contaminant, and to ensure the total amount of Pb(II) in the mixture was less than the sorption capacity of the soil. The soil mixtures were mixed thoroughly by shaking with a wrist action shaker. The pHs of the samples were monitored every 6–8 h and adjusted to predetermined target values by the addition of 1 M HNO_3 (aq.) or 1 M NaOH (aq.). The samples were shaken for another 24 h after the final pH adjustments had been made. The soil mixtures were then centrifuged and the lead concentrations of the supernatant were measured by atomic absorption spectroscopy.

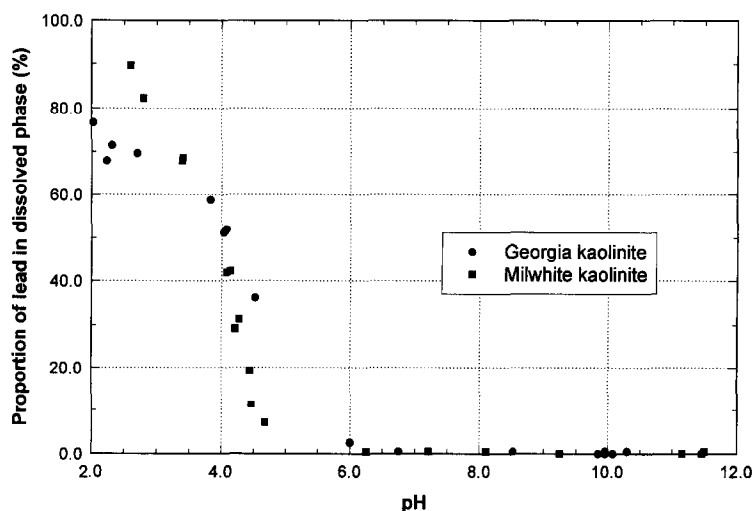


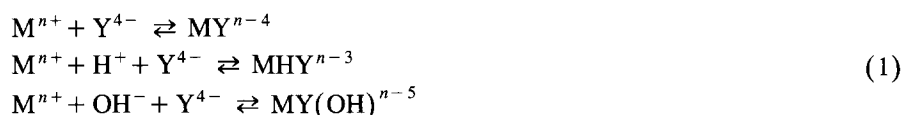
Fig. 4. pH-dependent sorption and precipitation characteristics of lead in Georgia and Milwhite kaolinite.

The pH-dependent sorption and precipitation characteristics of Georgia kaolinite and Milwhite kaolinite are presented in Fig. 4. In the pH range of 2–3, a lower proportion of lead was found in the dissolved phase in Georgia kaolinite. When the pH is higher than 4, the sorption and precipitation characteristics of lead in both kaolinites are almost identical. When the pH is higher than 5, there is almost no lead in the dissolved phase. The results reveal that both kaolinites have similar sorption potential in a practical range of pHs. More important, the experimental results reveal that electrokinetic extraction is very inefficient in removing lead from these kaolinites when the soil pH is higher than 5.

4. Effects of injecting enhancement fluid

Many potential problems associated with sorption and precipitation at a relatively high pH may be solved by injection of an enhancement fluid into the contaminated soil. The primary purpose of injecting an enhancement fluid is to solubilize the contaminant in the dissolved phase at a legally acceptable and practically attainable soil pH. Proper selection of enhancement fluid is soil and contaminant specific. Potential candidates for metallic contaminants are those that are able to form strong water-soluble chelates with metals. The effects of injecting ethylenediaminetetraacetate (EDTA) into lead-contaminated soil on the physicochemical soil–contaminant interactions during electrokinetic extraction is discussed in this paper as an illustration.

Ethylenediaminetetraacetic acid is a tetraprotic acid abbreviated as H_4Y , where Y denotes the ethylenediaminetetraacetate ion $EDTA^{4-}$. It is slightly soluble in water and dissociates into H_3Y^- , H_2Y^{2-} , HY^{3-} and Y^{4-} ions with pK_a values of 2, 2.76, 6.16 and 10.26, respectively, at 20°C and in the presence of 0.1 M KNO_3 [59]. Each $EDTA^{4-}$ ion can attach to a metal ion at six different sites since each of the four acetate groups and the two nitrogen atoms have free electron pairs available for coordinate bond formation, as shown in Fig. 5. In fact, this is the reason for the high stability of metal–EDTA complexes [53]. With a metal ion M, it can form a complex MY, a protonated complex MHY, a hydroxo complex $MY(OH)_n$, and a mixed complex MYX where X is a unidentate ligand. Complexes of the form MY_2 or higher have not been observed [59]. The complexation reactions involved are:



and the stability constants of these reactions are defined by:

$$\begin{aligned} K_{MY} &= \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]} \\ K_{MHY} &= \frac{[MHY^{n-3}]}{[M^{n+}][H^+][Y^{4-}]} \\ K_{MY(OH)} &= \frac{[MY(OH)^{n-5}]}{[M^{n+}][OH^-][Y^{4-}]} \end{aligned} \quad (2)$$

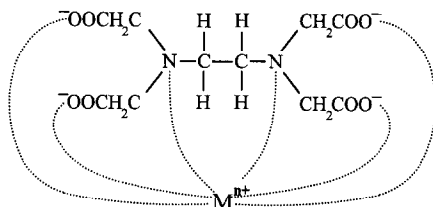


Fig. 5. Configuration of metal–EDTA complexes.

where the unit of concentration, as indicated by [], is mol l^{-1} . The $\log K_{MY}$, $\log K_{MHY}$ and $\log K_{MY(OH)}$ for various metals are tabulated in Table 1 [60]. The relatively high values of the stability constants of its metal complexes signify the stability of these water-soluble complexes and indicate the high potential of EDTA in enhancing the removal of metals from contaminated soils.

Due to its ability to form strong water-soluble chelates with most metals, EDTA has recently been used to extract heavy metals from contaminated soil as an enhancement to the pump-and-treat technology [61]. Results of their batch and column tests show that EDTA is able to remove more than 90% and 60% of the lead and cadmium, respectively, from the contaminated soil collected from a Superfund site. Moreover, the product of the treatment, Pb–EDTA, can be recovered and reused so that no secondary contaminant will be generated [62].

The sorption and precipitation characteristics of lead in Milwhite kaolinite in the presence of EDTA were evaluated first. Solutions of 25 ppm Pb(II) and various concentrations of EDTA were prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ powder and disodium ethylenediaminetetraacetate in deionized water simultaneously. The concentrations of EDTA were 4, 10 and 50 mol m^{-3} . Kaolinite samples each of mass 0.5 g were placed into test tubes and 10 ml of the solution was added to each sample. The soil mixtures were thoroughly mixed by shaking with a wrist action shaker. The pHs of the samples were monitored every 6–8 h and adjusted to predetermined target values by the addition

Table 1
Stability constants for the formation of metal–EDTA complexes [60]

Metal ion (1)	$\log K_{MY}$ (2)	$\log K_{MHY}$ (3)	$\log K_{MY(OH)}$ (4)
Al^{3+}	16.13	18.7	24.2
Ca^{2+}	10.7	13.8	—
Cd^{2+}	16.46	19.4	—
Co^{2+}	16.31	19.5	—
Cr^{3+}	23.0	25.3	29.6
Fe^{2+}	14.33	17.2	—
Mn^{2+}	14.04	17.2	—
Pb^{2+}	18.0	20.9	—
Zn^{2+}	16.5	20.9	19.5
Zr^{4+}	29.9	—	37.7

Note: K_{MY} , K_{MHY} , and $K_{MY(OH)}$ are defined in Eq. (2).

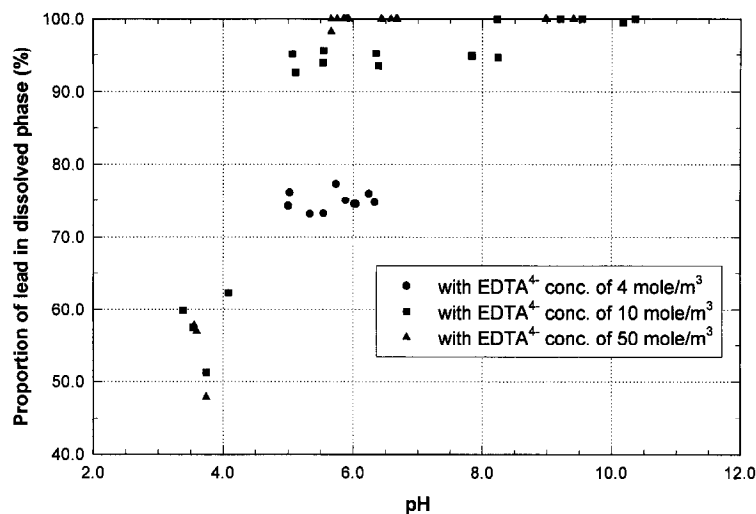


Fig. 6. Effects of EDTA on sorption and precipitation characteristics of lead in Milwhite kaolinite.

of 1 M HNO_3 (aq.) or 1 M NaOH (aq.). The samples were shaken for another 24 h after the final pH adjustments had been made. The soil mixtures were then centrifuged and the lead concentrations of the supernatant were measured by atomic absorption spectroscopy.

The effects of EDTA on the sorption and precipitation characteristics of lead in Milwhite kaolinite are presented in Fig. 6. It can be observed from Figs. 4 and 6 that the addition of EDTA changes these physicochemical characteristics completely. When the pH is lower than approximately 4.5, the addition of EDTA reduces the proportion of lead in the dissolved phase. The reduction may be due to sorption of metal–EDTA complexes on the soil particle surface [63]. When the pH is higher than 5, EDTA is very effective in keeping the lead in the dissolved phase. Moreover, the proportion of lead in the dissolved phase increases with increase in concentration of EDTA as the concentrations of water-soluble complexes increase. The experimental results also show that, under the given experimental conditions, an EDTA concentration of 50 mol m^{-3} is able to keep all the lead in the dissolved phase when the pH is higher than 5. However, more EDTA will be needed when the lead or soil concentration increases. Otherwise, more lead will exist in the sorbed phase when the concentrations of different phases are in equilibrium with EDTA and soil. Moreover, the results reveal that an enhancement fluid may worsen the situation under some environmental conditions. As in this case, the addition of EDTA promotes sorption and precipitation of lead in Milwhite kaolinite in a low pH environment.

During the electrokinetic extraction experiments on Milwhite kaolinite, reverse electroosmotic flows occurred. Therefore, disodium ethylenediaminetetraacetate solution was injected into the soil from the cathode reservoir and the dissociated Y^{4-} ions were transported toward the anode. These ions competed with soil particle surfaces for Pb^{2+} ions. Since most metal–EDTA chelates are negatively charged, they are moved toward

the anode by both electroosmotic flow and ionic migration. Results indicate that EDTA can enhance the removal efficiency of lead from Milwhite kaolinite. Approximately 90% of the lead spiked uniformly into the soil was moved toward the anode and accumulated in the soil within 25 mm from the anode. Details of the experimental study are given by Yeung et al. [21].

Although the limited amount of experimental data obtained to date are encouraging, the use of an enhancement fluid during electrokinetic extraction should be exercised with extreme care to prevent: (1) introduction of a secondary contaminant into the subsurface; (2) generation of waste products or by-products as a result of electrochemical reactions; and (3) injection of an inappropriate enhancement fluid that will aggravate the existing contamination problem.

5. Conclusions

The basic principles of electrokinetic extraction of contaminants from fine-grained soil have been proven experimentally to be feasible. However, there are still many electrochemical reactions and physicochemical soil–contaminant interactions that need to be understood before the technology can be utilized at its full potential. Several prominent physicochemical soil–contaminant interactions during electrokinetic extraction and their influences on the performance of the process have been discussed. Bench-scale experimental results are presented as illustrations. These interactions include: (1) change of zeta potential at the soil particle/pore fluid interface; (2) resistance of the soil–fluid–contaminant system to pH change; and (3) sorption/desorption of reactive contaminants onto or from the soil particle surface, and precipitation/dissolution of metallic contaminants in the pore fluid. The possibility of injecting an enhancement fluid into the contaminated soil has also been discussed. Encouraging results of using EDTA as an enhancement fluid to increase the removal efficiency of lead from Milwhite kaolinite are presented. However, extreme care must be exercised to select the appropriate enhancement fluid for the type and concentration of contaminant in the subsurface and the given environmental conditions.

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