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Milestone developments, myths, and future directions of electrokinetic remediation

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ABSTRACT

This is the 9th Symposium on Electrokinetic Remediation. In Chinese, "9" is pronounced as "久" which means longevity. As the first symposium of the series to be held on Chinese soil, it may be appropriate to follow the Chinese tradition so as to set the stage for the longevity of the symposium series. Therefore, it is time for us to recognize the milestone developments of past researchers, to clarify some of the myths, and to establish future research directions of electrokinetic remediation.

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1. Introduction

As a result of our ever-improving living quality and lack of environmental awareness in the past, soil contamination is a worldwide problem nowadays. Many remediation technologies have been developed to restore the damaged environment and ecology so as to protect the public health of this and future generations. The varying degree of success of soil remediation depends heavily on the nature of contaminated soil, contaminant type, contaminant concentration in the subsurface, and the environmental conditions [1]. However, remediation of contaminated fine-grained soil is particularly difficult due to its extremely low hydraulic conductivity and very large specific area. The extremely low hydraulic conductivity of the fine-grained soil makes it very difficult for an adequate volume of fluid to permeate the soil within a reasonable remediation period, rendering the technology of pump-and-treat, soil flushing, etc. ineffective. When the hydraulic gradient applied is too low, the duration required for remediation is unacceptably long. When the hydraulic gradient applied is too high, the seepage force induced may trigger hydraulic fracturing of the contaminated soil, generating random migration paths for the contaminant to further spread in the subsurface and thus aggravating the already undesirable situation. The very large specific area of the fine-grained soil provides numerous reaction sites between the contaminant and soil particle surfaces. These soil–contaminant interactions are soil specific, contaminant specific, pH-dependent, and reversible, thus increasing the variability, complexity, and difficulty of remediation technologies. Sorption of the contaminant on soil particle surfaces and/or precipitation of the contaminant in the soil pores may make the contaminant immobile temporarily, rendering the contaminant difficult to be removed. If the contaminant can be stabilized or solidified permanently, the hazards of the contaminant to the environment and living organisms are greatly reduced. Unfortunately, the contaminant may only be temporarily immobilized. When the environmental conditions change, these chemical reactions are reversed and the contaminant becomes mobile and hazardous again. The key factor controlling the success of most remediation technologies is to maintain the solubilization and mobility of the contaminant, so that it can be removed effectively and efficiently from soil. Electrokinetic remediation is no exception [2].

Researchers have been conducting considerable volume of research on different aspects of electrokinetic remediation of fine-grained soils for a few decades worldwide. In fact, this is already the 9th Symposium on Electrokinetic Remediation focusing on this important and specialized remediation technique for contaminated soil. After eight successful symposia held in: (1) Albi, France (1997); (2) Lyngby, Denmark (1999); (3) Karlsruhe, Germany (2001); (4) Mol, Belgium (2003); (5) Ferrara, Italy (2005); (6) Vigo, Spain (2007); (7) Seoul, Korea (2008); and (8) Lisbon, Portugal (2009). Most papers presented in the later Symposia were published collectively in special issues of different journals. The 10th Symposium will be held in Utrecht, the Netherlands in July 2011 and the 11th Symposium has been scheduled in 2012 to be held in Hokkaido, Japan. The growing interest in the remediation technique is evidenced by the increasing frequency of the Symposia, the considerable extension of the geographical distribution of economies and institutions hosting the Symposia, the significant increase in the number of participants of these Symposia, and the increasing number of publications in the specific research area.

Many important lessons have been learnt, different techniques have been developed, and the applications of electrokinetic remediation have been widely extended throughout the years. It may be an appropriate time for us to recognize and record the mile-
stone developments of past researchers, and to clarify some of the myths so that researchers can have a better understanding why and how some of these past research decisions were correctly or incorrectly made, before the collective memory is lost. On the solid foundation of these past achievements, future research directions of electrokinetic remediation are proposed.

2. Historical developments

The observation of electroosmosis dates back to 1802. It was first studied in detail by Reuss [3] in his classic experiment shown in Fig. 1 which he prepared to repeat the experiments performed in April 1800 by Nicholson and Carlisle on electrolytically decomposition of water. Quartz powder was placed at the bottom of the U-tube of approximately a quarter of an inch in diameter and 8 in. long with two platinum wires fused at the bottom. The U-tube was filled with water and connected to S-shaped capillary tubes. The platinum wires were then connected to a voltaic pile of ninety-two silver rubles and an equal number of zinc plates to impose a direct-current electrical gradient across the quartz powder. He observed that water rose about 23 cm in the arm containing the cathode. Water is thus pumped uphill effectively against gravity without any electrical or mechanical moving parts.

The results of further experiments indicate that if the water levels on both sides were the same initially, the level on the cathode side rose gradually and produced an excess hydraulic pressure until the electroosmotic flow induced by the electrical gradient was balanced by the hydraulic flow generated by the excess hydraulic pressure. If the water levels on both sides were kept at the same level by an overflow device, water flowed continuously while the electrical gradient was maintained. The electroosmotic volume flow rate can be described by

\[ Q_e = k_e \lambda e A \]  

where \( Q_e \) is the electroosmotic volume flow (m³/s); \( k_e \) the coefficient of electroosmotic conductivity (m²/(V·s)); \( \lambda \) the direct-current electrical field applied (V/m); and \( A \) the total cross-sectional area perpendicular to the direction of flow. The equation is analogous to that of Darcy’s law describing the hydraulic flow driven by a hydraulic gradient. Different theories including: (1) the Helmholtz–Smoluchowski theory; (2) the Schmid theory; (3) the Spiegler friction model; (4) the ion hydration model; and (5) the Gray–Mitchell approach; have been proposed to quantify the coefficient of electroosmotic conductivity on the basis of different assumptions of ion distribution in the pore fluid. The derivations of these theories are summarized by Yeung [4]. The most widely accepted theory for electroosmotic flow in soil is the Helmholtz–Smoluchowski theory. Nonetheless, values of the coefficient of electroosmotic conductivity of most soils are in the range of \( 1 \times 10^{-9} \) to \( 1 \times 10^{-8} \) m²/(V·s) [4–6]. The observation of the electroosmosis phenomenon in soils has led to the idea of using a direct-current electrical field to drive the flows of fluid and chemicals in fine-grained soils effectively. In fact, many applications of electroosmosis have been developed in geotechnical engineering.

Electroosmosis was first applied to reverse the seepage flow direction and to decrease the water content of soil in 1939, so as to stabilize a long railroad cut at Salzgitter, Germany [7,8]. Since then, the process has been applied successfully to stabilize slopes, embankments, and dams [5.7–14], and to render large excavations stable for constructions [5,7,8,10,15–17]. The technique has also been applied to strengthen subgrades and sub-bases under pavement [10,18,19], to dewater and consolidate fine-grained soils effectively [20–30], to increase the undrained shear strength of very soft quick clay [31], and to improve cyclic deformation characteristics of soft sensitive silty clay [32]. The effect of electroosmosis on the soils in these applications is primarily consolidation of the soil, resulting in an increase in shear strength of the soil. In most cases, the sensitivity of the soil is also greatly reduced and the plasticity index is slightly increased. However, the increase in shear strength always exceeds the value predicted from the results of consolidation of the soil, indicating electroosmosis may change the physicochemical properties of the soil. The shaft resistance of a metallic friction pile driven into a clay stratum can be changed dramatically by electroosmosis [8]. Using the metallic piles as anodes, Soderman and Milligan [33] observed in a series of tests on long H-piles that the shaft resistance increased by a factor of at least 2.5. Using the metallic piles as cathodes, it has also been observed in a series of model pile tests performed at the University of Southampton that the shaft resistance could be reduced almost instantaneously by the same factor. Thus, electroosmosis may be a good technique to reduce the negative skin friction on piles [8,34] or to facilitate pullout of sheet piles installed for temporary lateral support for excavation. These changes in shaft resistance are attributed to the excess negative or positive pore water pressure in the clay near the piles developed by electroosmosis. Long-term increases in load-carrying capacity of piles after electrical treatment regardless of polarity were observed by Butterfield and Johnston [35] in their model pile tests. Electroosmosis thus must have changed the soil properties while it develops excess negative or positive pore water pressure near the piles. Electroosmosis was also investigated as a potential measure to improve the stability of the Leaning Tower of Pisa in Italy by controlled consolidation of the clay on north side of the Tower to reduce the angle of tilt and thus loading eccentricity [6].

In 1930s, electrokinetics was suggested to remove excess salts from alkali soils in India. The results of laboratory and field studies of several investigations indicated that sodium ions were leached from alkali soils in India. The results of laboratory and field studies of several investigations indicated that sodium ions were leached from alkali soils in India. The results of laboratory and field studies of several investigations indicated that sodium ions were leached from alkali soils in India.
[41–46], different techniques to improve the efficiency of electrokinetic remediation have been developed [2,47–53], and many new applications have been pioneered [54–62]. Therefore, it is time for us to recognize the milestone developments by past researchers, to clarify some of the myths, and to establish future directions of electrokinetic remediation in this invited paper of the 9th Symposium on Electrokinetic Remediation.

3. Relevant questions

The answers to the following questions, among many others, will be presented in this invited paper to recognize the milestone developments by past researchers and to clarify some of the myths in electrokinetic remediation:

(1) When and where were the first applications of electrokinetic remediation?
(2) When and where was modern research on electrokinetic remediation started?
(3) Who’s who in electrokinetic remediation?
(4) Who were present in the very first “Workshop on Electrokinetic Treatment and Its Applications in Environmental Geotechnical Engineering for Hazardous Waste Site Remediation” organized by the U.S. EPA in Seattle, WA, U.S.A. in 1986?
(5) Where is the origin of the application of 1 V/cm electrical gradient in laboratory experimental work and what are the rationales behind it?
(6) Who did recognize the importance of soil pH in electrokinetic remediation?
(7) When were enhancement agents first used in electrokinetic remediation, who were the researchers, and what were these agents?
(8) What are the milestone developments in numerical modeling of electrokinetic remediation?
(9) What were the first developments in the installation of in situ electrodes?
(10) When was the Nernst–Einstein equation first applied to relate the effective ionic mobility to the effective diffusion coefficient in soil and how was its validity established?
(11) …

4. Answers to some of these questions

Partial answers to some of these questions are given briefly in this invited paper to facilitate further discussion.

4.1. First applications of electrokinetic remediation

Electrokinetics was suggested to remove excess salts from alkali soils in India as early as 1930s [63]. The purpose of the study was to investigate the possibility of removing sodium from alkali soils so as to restore alkali soils to arable land. Their results of laboratory and field studies indicate that sodium ions were leached from a soil by imposing a direct-current electric field across it. Puri and Anand [63] is probably the first documented real-life application of electrokinetics to migrate chemicals in soil. Similar results were obtained by Gibbs [64] of the Bureau of Reclamation of the U.S. in large-scale model tests. The results of studies performed at Moscow University also demonstrated experimentally that the application of a direct-current electric field during leaching accelerated desalinization of alkaline and saline soils. The salt removal rate measured was proportional to the electric current density [65]. Although sodium is not necessarily a hazardous contaminant from the environmental engineering standpoint, its excessive presence in soil is detrimental to crop production. Nonetheless, the results of these early studies establish the viability of using electrokinetics to migrate contaminants in soil and its potential as a remediation technology for hazardous waste sites. Some factors affecting the effectiveness of electrokinetics in contaminant removal were specifically studied in England in late 1970s at the University of Manchester [66,67].

4.2. Workshop on electro-kinetic treatment and its applications in environmental geotechnical engineering for hazardous waste site remediation

Many subsurface contamination problems were unveiled in the U.S. during early 1980s. The complexities and difficulties of effective and economical hazardous waste site remediation urged the U.S. Environmental Protection Agency to develop innovative solutions to these worsening public health problems. Electrokinetics was one of the emerging remediation technologies and candidate solutions for the government agency to consider. The Workshop on Electrokinetic Treatment and Its Applications in Environmental Geotechnical Engineering for Hazardous Waste Site Remediation held in Seattle, WA, U.S.A. in 1986 was thus sponsored by the Hazardous Waste Engineering Laboratory of the U.S. Environmental Protection Agency and hosted by the Department of Civil Engineering of the University of Washington to investigate the potential of electrokinetics in hazardous waste site remediation.

Five position papers covering different fundamental aspects of electrokinetic remediation of hazardous waste sites were presented at the Workshop. These position papers were: (1) "Potential uses of electro-kinetics for hazardous waste site remediation" by Professor James K. Mitchell of the University of California at Berkeley [36]; (2) "Physics and chemistry of electrokinetic processes" by Professor Donald H. Gray of the University of Michigan at Ann Arbor and Dr. Harold W. Olsen of the U.S. Geological Survey [37]; (3) "Quantification of fluid and chemical flow in electrokinetics" by Professor Ronald F. Probststein and Dr. Patricia C. Renaud of the Massachusetts Institute of Technology [38]; (4) "Migration of inorganic contaminants in groundwater under the influence of an electric field" by Professor John F. Ferguson of the University of Washington [39]; and (5) "Practical considerations in the use of electro-kinetics" by Professor Burton A. Segall of the University of Massachusetts at Lowell [40].

The state-of-understanding of the fundamentals and mechanisms of electrokinetics in migrating fluid and chemicals in soil and potential applications of electrokinetics for remediation of hazardous waste sites are summarized in these important position papers. In addition to those identified at the Workshop, potential applications of electrokinetics in hazardous waste site remediation may include the following individual applications or a combination of these applications [43,46]:

(1) Concentration, dewatering, and consolidation of wastewa-ter sludges, slimes, coal washeries, mine tailings, or dredged materials [30];
(2) Injection of grouts to control groundwater flow.
(3) Injection of cleansing agents to decontaminate contaminated soils [68–70].
(4) Injection of vital nutrients for the growth of microorganisms to support biodegradation of specific wastes [71–73].
(5) Passive electrokinetic barriers to contaminant transport through compacted clay landfill liners or slurry encapsulation walls [74–77].
(6) Generation and/or enhancement of reactive barriers [78–82].
(7) Electrokinetic extraction of contaminants from contaminated soils.
It has been overlooked that the electrical current density passing through the soil specimen was too high and a large volume of air bubbles was generated by electrolytic decomposition of water at the ends of the specimen, impeding the electroosmotic flow. Some bubbles may migrate into the soil specimen to decrease the degree of saturation of the specimen, thus affecting all the flow parameters of fluid and chemicals, such as coefficient of electroosmotic conductivity of soil, hydraulic conductivity of soil, effective diffusion coefficients of contaminants, and effective ionic mobilities of contaminants. Of the specimen, the situation is worse during electrokinetic remediation of soil contaminated by inorganic contaminants. The conductivity of the soil is increased by the presence of the contaminants, resulting in an even higher electrical current density. Moreover, a high electrical current density passing through the soil promotes electrochemical changes in the soil, thus rendering the interpretation of laboratory results very difficult.

4.5. The importance of soil pH in electrokinetic remediation of soil

The importance of pH in the electrokinetic remediation of soils was first recognized by Professor Yalcin B. Acar and his research team at Louisiana State University in mid-1980s [95]. Their findings were supported by results of Beddies et al. [96]. A low pH environment promotes the solubilization of inorganic contaminants, thus facilitating their removal by electroosmosis and electromigration. However, a low pH environment may change the zeta potential of soil particle surfaces [97,98], producing a negative electroosmotic flow, i.e., from the cathode towards the anode [99]. The two effects may diminish each other depending on the chemical state and polarity of charges of the inorganic contaminant. As a result, there are many complexities of the electrochemical processes for researchers to untangle. Nonetheless, many enhancement techniques on electrokinetic remediation of soils were developed on the basis of pH control [2,99–105].

4.6. Use of enhancement agents in electrokinetic remediation

In view of the complexities of pH control, enhancement agents have been used in the electrokinetic remediation process to keep the contaminants in a mobile state without excessive lowering of the pH of the environment. In general, enhancement agents should have these important characteristics [2]: (1) they should not form insoluble salts with the contaminant within the range of variation of pH values during the process; (2) they should form soluble complexes with the contaminant that can be efficiently migrated by a direct-current electric field; (3) they and their contaminant complexes should be chemically stable over a wide range of pH values; (4) they should have a higher affinity for the contaminant than soil particle surfaces; (5) they and their contaminant complexes should not have a strong affinity for soil particle surfaces; (6) they should not generate toxic residues in the treated soil; (7) they should not generate an excessive quantity of wastewater, and the end products of the treatment process should be amenable to concentration, precipitation, recovery, treatment, and/or recycling; (8) they should be cost-effective including reagent costs, handling costs, and treatment costs for the resulting waste collected and/or wastewater generated; (9) they should not induce excessive solubilization of soil minerals or increase the concentrations of any harmful species generated; (9) they should not inducing excessive solubilization of contaminants.

Many experimental parameters were selected on the basis of limited understanding of the processes involved during the early research. In the laboratory experiments performed for the establishment of the viability of passive electrokinetic barriers designed by Yeung [74], an electrical gradient of 1 V/cm was selected for the following reasons: (1) the power required for the laboratory experiment can be adequately provided by a laboratory direct-current power supply; and (2) if the laboratory results are favorable, an electrical gradient of 100 V/m is practically applicable on site.
4.7. Development in numerical modeling of electrokinetic remediation

The electrokinetic remediation process is a very complex process involving transport of contaminants under the influence of combined hydraulic and electrical gradients, electrochemical reactions, and soil–contaminant interactions. The flows of fluid and contaminants are coupled flows as flow of one type is driven by a driving force of another type [6]. It should be noted that all these processes are occurring simultaneously, rendering the solving of the related equations very difficult and computing resources very intensive.

Many numerical models have been developed to simulate various aspects of electrokinetic extraction including transport and fate of contaminants, pore pressure distribution, electrical voltage distribution, electric current density, migration of acid front, electrochemical reactions, and soil–contaminant interactions. These models are developed on the basis of different assumptions on the electrochemical processes during electrokinetic remediation, different numerical schemes, etc. They can predict specific bench-scale laboratory experimental results with varying degrees of success. These numerical models include those developed by Yeung [74], Narasimhan and Ranjan [76], Eykholt and Daniel [107], Aalshawabkehe and Acar [121,122], Eykholt [123], Hicks and Tondorf [124], Jacobst et al. [125], Choi and Liu [126], Yeung and Datla [127], Denisov et al. [128], Yu and Neretnieks [129,130], Haran et al. [131], Liu and Lui [132], Ribeiro and Mexia [133], Jennings and Mansharamani [134], Shiba et al. [135], Mattson et al. [136,137], Rahner et al. [138], Röhrs et al. [139], Kim et al. [140], Musso [141], Oyaf不知whatet al. [142], Vereda-Alonso et al. [143], among many others. However, none of these models can fully describe all the simultaneous processes occurring during electrokinetic remediation.

4.8. Development in electrodes

For in situ electrokinetic remediation, chemically inert and electrically conducting materials such as graphite, coated titanium, or platinum can be used as an anode to prevent electrode dissolution and the generation of undesirable corrosion products in an acidic environment. If necessary, sacrificial electrodes can also be used as the anode. Any conductive materials that do not corrode in a basic environment can be used as the cathode [144].

The design, development, and testing of an innovative electrode system, i.e., the NEOCHIM electrode, are detailed in Leinz et al. [145,146]. The technology obviates the H⁺ and OH⁻ problems by using an electrode made of two compartments linked by a salt bridge. The conducting electrode is immersed in a conducting fluid in the inner compartment where H⁺ and OH⁻ produced by electrolysis are retained and prevented from reaching the outer compartment by the salt bridge. The salt bridge is retained by a semi-permeable parchment membrane at the base of the inner compartment. A further conducting fluid is retained by the outer compartment as shown in Fig. 2.

4.9. The Nernst–Einstein equation

The Nernst–Einstein equation was first applied to relate the effective ionic mobility to the effective diffusion coefficient in soil by Yeung [74] in his formulation of the coupled flow theory describing the flows of fluid, electricity, and contaminants under the combined influences of hydraulic, electrical, and chemical gradients, on the basis of the formalism of irreversible thermodynamics [147]. The Nernst–Einstein equation, i.e.,

\[
\frac{D_i}{u_i} = \frac{RT}{z_i F}
\]

\[
(2)
\]

where \(D_i\) the diffusion coefficient of species \(i\) in free solution; \(u_i\) the ionic mobility of species \(i\) in free solution; \(z_i\) the charges of species \(i\); \(R\) the universal gas constant; \(T\) the absolute temperature; and \(F\) Faraday’s constant; relates the ionic mobility and the diffusion coefficient of an ion in a dilute solution [148,149]. Although the validity of the equation has been well established in free solution, its validity in porous media, such as soil, has not been proven experimentally, as the flow paths are much more tortuous than those in free solution.

5. Way forward

Throughout the past few decades, we have made strides in the development of electrokinetic remediation technologies. Therefore, it is important to document and consolidate the thoughts and findings of past researchers so as to set the stage for present and future researchers. We can only charter our future directions on the basis of a better understanding of the past. After the milestone developments have been recognized, and myths have been clarified, some of the thoughts on future research directions of electrokinetic remediation are proposed in this invited paper. It is hoped that this paper will become a useful document recording the history of electrokinetic remediation with a forward-looking view on future research directions.

5.1. Fundamental phenomena of electrokinetic remediation

Many physicochemical processes are occurring simultaneously during electrokinetic remediation. Many of these processes are pH dependent. However, electrokinetic remediation changes the soil pH as a function of time and space, thus complicating these processes. When the pH changes, some of these processes are reversible but some are irreversible. The results of many experimental studies reveal that it is very difficult to extract contaminants such as cadmium or lead from soil although they can be moved and concentrated in a localized region [99], an observation that cannot be fully explained by the theoretical developments to date. Probably there are still soil–contaminant interactions that are not fully understood. The issues are further complicated when enhancement agents are used to facilitate the remediation process [44].

Is there a theoretical explanation on the variation of electroosmotic volume flow rate as a function of time? It has been attempted by Eykholt [123] and Hsu [150] to include the effect of soil pH on the zeta potential of soil to predict the electroosmotic volume flow rate by averaging the values of the coefficient of electroosmotic conductivity determined from the soil pH along the flow path [151]. However, the results are not very satisfactory. Therefore, the interactions of the hydraulic flow driven by the excessive pore pressure generated during electrokinetic remediation and the electroosmotic flow have to be fully understood. The interactions are complicated as the electroosmotic volume flow rate is governed by the coefficient of electroosmotic conductivity. The coefficient of electroosmotic conductivity is a function of the zeta potential of soil particle surfaces, which is a function of soil pH, and soil pH is a function of time and space during electrokinetic remediation.

Is the soil-fluid-chemical system an electrochemical system? Yeung [152] provides experimental evidence to indicate that the soil-fluid-chemical system is an electrochemical system on the basis of Faraday's laws of electrolysis. It is recommended that future experiments on electrokinetic remediation should measure the electric current passing through the soil and the volumetric gas generation rates at the electrodes simultaneously as a function of time to provide more experimental evidence of the phenomenon. In fact, such an apparatus has been designed by Yeung et al. [153]. How does electric current pass through soil? Why is it a function of time during electrokinetic remediation? Experimental observations indicate the variation of electric current with time resembles that of a Leclanché battery [152] and the apparent electrical properties of soil can be determined from curve-fitting. However, there is no theoretical explanation on the phenomena observed and the physical meanings of the electrical properties so obtained. A better understanding of the phenomena will give a deeper insight on the influence of electrical treatment on soil.

The characterization of soil–contaminant interactions as a function of pH is another important fundamental area to be developed in the electrokinetic remediation. The zeta potential of soil particle surfaces is a function of soil pH and pore fluid chemistry [44]. The electroosmotic flow direction of pore fluid is controlled by the zeta potential [99,153]. The sorption and desorption characteristics of contaminants onto and from soil particle surfaces are also controlled by soil pH, which are key factors controlling the mobility of contaminants during electrokinetic remediation. The use of enhancement agents changes the sorption and desorption characteristics of contaminants. Unlike many other remediation technologies, the effects of enhancement agents as a function of soil pH have to be evaluated thoroughly before their applications, as the soil pH changes as a function of time and space during electrokinetic remediation.

5.2. The validity of the effective Nernst–Einstein equation

The diffusion coefficients of ions in soil are related to the corresponding coefficients in free solution by taking the tortuosity of migration paths in soil into account. If the effects of tortuosity of migration paths on ionic mobilities of ions are similar, the effective Nernst–Einstein equation should be valid, i.e.,

\[
\frac{D_i^*}{D_i} = \frac{RT}{z_i^2} F
\]

where \(D_i^*\) is the effective diffusion coefficient of species \(i\) in soil; \(D_i\) is the effective ionic mobility of species \(i\) in soil. However, there is no experimental evidence to support the validity of the equation. If the validity of the equation can be established, it is not only useful in the understanding of electrokinetic remediation but also that of contaminant transport and fate in soil, as it is considerably easier to measure the effective ionic mobility of a species than its effective diffusion coefficient in soil. The effective diffusion coefficient is an important parameter to quantify contaminant transport in soil, in particular in fine-grained soil [154].

5.3. Numerical simulation

Numerical simulation of electrokinetic remediation is not an easy task to accomplish as many processes are occurring simultaneously. These processes include: (1) contaminant transport processes; (2) electrochemical reactions; and (3) soil–contaminant interactions. The contaminant transport can be described by the coupled flow theory developed by Yeung and Mitchell [147] or the modified advection-dispersion equation. The electrochemical reactions can be described by: (i) the mass balance equations of chemical species; (ii) the mass action equations of chemical reactions; (iii) the hydrogen balance equation; (iv) the solubility product equations of precipitates; and (v) the electrolysis equations of water. Soil–contaminant interactions can be described by: (i) sorption–desorption characteristics of chemical species; (ii) acid/base buffer capacity of soil; (iii) soil chemistry; and (iv) pH-dependent soil–contaminant interactions. These processes are dependent on soil pH, contaminant concentration, and physicochemical properties of soil. More importantly, they are inter-dependent. As a result, solving all these governing equations simultaneously is difficult and computer resources demanding, not to mention the applicability of some of these governing equations in electrokinetic remediation has yet to be established experimentally.

A practical approach being adopted is a two-step go-and-stop approach within each time step of simulation. The contaminant transport is simulated for a time step. All the electrochemical reactions and soil–contaminant interactions occur instantaneously at the end of the time step on the basis of the contaminant concentration and environmental conditions at the instant. The approach has separated the transport and reaction processes numerically. The contaminants do not react when they are migrating and vice versa. It yields reasonable results if the rates of reactions are considerably faster than the rates of transport and the time step is reasonably small. However, it is well known that the rates of some of the reactions are slow. Therefore, the need for a better simulation algorithm is evident.

5.4. Unification of nomenclature, notations, and sign conventions

The background of researchers in electrokinetic remediation is much diversified, including chemical engineering, civil engineering, environmental science and engineering, geotechnical engineering, materials science and engineering, petroleum engineering, and soil science. There is a need to develop unified nomenclature, notations, and sign conventions to facilitate effective communication among researchers in electrokinetic remediation of different disciplines, and to avoid unnecessary confusion and misunderstanding. For example, the symbol of zeta or electrokinetic potential of the soil particle surface is the sixth letter of the Greek alphabet \(\zeta\). It is the electrical potential of the shearing plane within the diffuse double layer relative to that of the pore fluid, i.e., the potential of the pore fluid is taken as the reference or zero potential. If the charge of mobile ions in the diffuse double layer is positive, the zeta potential is negative, and positive electroosmotic flow is in the direction of anode towards the cathode. The change in zeta potential should be described in mathematical terms, i.e., an increase in zeta potential means it is becoming less negative or more positive.
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