The demand for innovative and cost-effective in situ remediation technologies in waste management stimulated the effort to employ conduction phenomena in soils under an electric field to remove chemical species from soils (1-14). This technique, variably called electrokinetic remediation, electroreclamation, electrokinetic soil processing, and electrochemical decontamination, uses low-level direct current on the order of mA/cm² of cross-sectional area between the electrodes or an electric potential difference on the order of a few volts per centimeter across electrodes placed in the ground in an open flow arrangement. A schematic diagram of one configuration used in the field is presented in Figure 1.

The groundwater in the boreholes or an externally supplied fluid (processing fluid) is used as the conductive medium. Open flow arrangement at the electrodes allows the processing or pore fluid to flow into or out of the porous medium. The low-level direct current results in physicochemical and hydrological changes in the soil mass, leading to species transport by coupled and un-coupled conduction phenomena in the porous media. Electrolysis reactions prevail at the electrodes. The species input into the system at the electrodes (either by the electrolysis reactions or through the cycling processing fluid) and the species in the pore fluid will be transported across the porous media by conduction phenomena in soils under electric fields. This transport and sorption, precipitation, and dissolution reactions are the fundamental mechanisms affecting the electrokinetic remediation process. Extraction and removal are accomplished by electrodeposition, precipitation, or ion exchange either at the electrodes or in an external extraction system placed in a unit cycling the processing fluid (15-17).

Electrokinetic remediation technology has recently made significant strides. Electrolysis reactions dominate the chemistry at the boundaries. When the chemistry of the process fluid is not controlled externally (unenhanced electrokinetic remediation), application of direct electric current via electrodes immersed in water results in oxidation at the anode, generating an acid front, while reduction at the cathode produces a base front by:

\[ 2H_2O - 4e^- \Rightarrow O_2 \uparrow + 4H^+ \]
\[ E_a = -1.229 \text{ (anode)} \quad (1a) \]
\[ 2H_2O + 2e^- \Rightarrow H_2 \uparrow + 2OH^- \]
\[ E_a = -0.828 \text{ (cathode)} \quad (1b) \]

where \( E_a \) is the standard reduction electrochemical potential, which is a measure of the tendency of the reactants in their standard states to proceed to products in their standard states. Secondary reactions may exist depending upon the concentration of available species, for example:

\[ H^+ + e^- \Rightarrow (1/2) H_2 \uparrow \quad (2) \]
\[ M_n^{n+} + ne^- \Rightarrow M_n \quad (3) \]
\[ M_n (OH)_m (s) + n e^- \Rightarrow M_n + n OH^- \quad (4) \]
FIGURE 1
A diagram of a field-processing configuration depicting transport of the process fluid and ionic species under an electric field

$M_e$ refers to metals. The type of electrolysis reactions ongoing at the electrodes depends on the availability of the chemical species and the electrochemical potential of these reactions. Although some other secondary reactions might be favored at the cathode because of their lower electrochemical potentials, the water reduction half reaction (H$_2$O/H$_2$) is dominant at early stages of the process.

In unenhanced electrokinetic remediation and at the early stages of the process, electrolysis reactions described by Equation 1 will generate an acidic medium at the anode and an alkaline medium at the cathode. The pH will drop at the anode to below 2 and it will increase at the cathode to above 12 depending on the total current applied ($I$, 18–20). The acid front will advance toward the cathode by transport mechanisms including migration caused by electrical gradients; pore fluid advection caused by prevailing electroosmotic flow or any externally applied or internally generated hydraulic potential differences; and diffusion caused by generated chemical gradient ($\text{H}^+$/$\text{H}_2$) or [$M_{e^{+}}$/Me(s)] are expected to dominate at this stage. Unless the transport of this acid front is retarded by the buffering capacity of the soil, the chemistry across the specimen will be dominated by the transport of the hydrogen ion. Cation exchange capacity of the mineral and availability of organic species and salts (such as CaCO$_3$) that may react with the acid would increase the buffering capacity of the soil (22). Kaolinitic clays show much lower buffering capacity because of lower cation exchange capacity (ceq) compared with other clay minerals, such as montmorillonite or illite.

Figure 2 demonstrates that in Georgia kaolinite the alkaline medium developed at the cathode will first advance toward the anode by ionic migration and diffusion; however, the mass transport of H$^+$ will neutralize this base front, veiling its transport toward the anode. In this mineral, the acid generated at the anode advances across the specimen without significant retardation and neutralizes the base generated at the cathode, lowering the effluent pH as shown in Figure 3a. In an illitic soil, however, this decrease in the effluent pH is not encountered because of higher buffering capacity (Figure 3b).

Transport of species under an electric field

Significant species transport processes in soils under electric fields consist of mass fluxes generated by diffusion, electromigration (or migration), electroosmotic advection, and electrophoresis. Several compositional and environmental variables affect the contribution of each
FIGURE 2
Numerical simulation of pH distribution across a cylindrical Georgia kaolinite specimen

Normalized distance from anode, x/L

Initial pH
Experimental values at the end of 500 h

Time in the numerical model (h)
Transport direction

Ten cm long and 10 cm in diameter, processed for 500 h at a current density of 50 μA/cm² (21).

TABLE 1
The constitutive relationships between the significant fluxes and potential gradients associated with species transport in soils under an electrical field

<table>
<thead>
<tr>
<th>Flux and the associated parameters</th>
<th>Constitutive relationships and associated formalisms proposed for the constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusive mass flux, Jf</td>
<td>Jf = Df ( \nabla (c_j) )</td>
</tr>
<tr>
<td>Effective diffusion coefficient, Df</td>
<td>Df = D j * n</td>
</tr>
<tr>
<td>Molar concentration, c_j</td>
<td>c_j = k_j / ( \sigma^* )</td>
</tr>
<tr>
<td>Tortuosity factor, τ; porosity, n</td>
<td>τ = ζ = A - B log c_j</td>
</tr>
<tr>
<td>Diffusion coefficient in free solution at infinite dilution, D j</td>
<td>D j = k_j/ n</td>
</tr>
</tbody>
</table>

Migrational flux, Jf1

| Effective ionic mobility, u_j* | Jf1 = \( u_j^* \ n \) |
| Electrical potential, E | \( u_j^* = F \/ \epsilon \) |
| Valence, z_j; Faraday’s constant, F | \( u_j^* = \epsilon \ / \ n \) |
| Universal gas constant, R | \( u_j^* = F \ / \ n \) |
| Absolute temperature, T | \( u_j^* = \epsilon \ / \ n \) |

Electroosmotic mass flux, Jf

| Molar concentration of water (= 1), c_w | \( q_w = k_w \ / \ (\sigma^*) \) |
| Electroosmotic permeability, k_w | k_w = \( \epsilon \ / \ n \) |
| Coefficient of electroosmotic water transport efficiency, k_e | k_e = \( \epsilon \ / \ n \) |
| Effective bulk electrical conductivity, \( \sigma^* \) | \( \sigma^* = A - B \log c_j \) |
| Permittivity of the medium, \( \epsilon \) | \( \epsilon = A - B \log c_j \) |
| Zeta potential, \( \zeta \); viscosity, \( \eta \) | \( \zeta = A - B \log c_j \) |
| A, B constants | \( A = B \log c_j \) |
| Total concentration of the electrolyte, c_j | \( c_j = k_j / \( \sigma^* \) \) |

Flux to the total mass flux: soil mineralogy; pore fluid composition and conductivity; electrochemical properties of the present, generated, and introduced species in the pore fluid; and porosity and tortuosity of the porous medium. A sense of the magnitude of the contribution of each requires scrutiny of how each flux is related to the prevailing electrical field, concentration of species, and the compositional/environmental variables. Table 1 presents the constitutive relationships for each flux and defines the associated parameters affecting transport.

The diffusive mass flux of the jth chemical species, Jf, under a chemical concentration gradient is expressed by Fick’s first law. The effective diffusion coefficient in the porous medium is related to the diffusion coefficient in free solution at infinite dilution, D j, by a factor that contains the soil porosity, n, varying over a range of 0.1 to 0.7 for fine-grained soils, and a tortuosity factor, τ, which includes all other factors as well as the tortuosity of the flow path (7, 23). The tortuosity factors reported in different studies are as low as 0.01 and as high as 0.84, mostly ranging between 0.20 to 0.30 (24). Shackelford and Daniel (23) demonstrate that the change in clay fabric (distribution of pores and pore sizes) has little effect on the effective diffusion coefficient of different inorganic chemicals.

There is no sound method yet devised to measure the effective ionic mobility in estimating the migrational mass flux (23); however, it can be theoretically estimated by assuming that the Nernst–Townsend–Einstein relation between the molecular diffusion coefficient D j* and ionic mobility u_j* given in Table 1 holds true for ions in the soil pore fluid (24). Consequently, the effective ionic mobility of a specific ion is a function of its molecular diffusion coefficient, soil porosity, tortuosity factor, and charge.

A comparison of the diffusion coefficients, D j, and ionic mobilities, u_j, for some ionic species are presented in Table 2. The effective ionic mobilities, u_j*, of these species in a soil with a typical porosity of 0.6 and an average tortuosity factor of 0.35 are also presented. Although the ionic mobility of a charged species is at least 1 order of magnitude higher than the diffusion coefficient of the same, the ratio of the effective ionic mobility of a charged species under a unit electrical gradient to the effective diffu-
The Helmholtz–Smoluchowski theory for electroosmosis has been widely used as a theoretical description of pore fluid transport through soils under an electrical potential difference (25). This theory introduces the coefficient of electroosmotic permeability, $k_e$, as the volume rate of water flowing through a unit cross-sectional area due to a unit electrical potential difference (cm$^2$/Vs). $k_e$ is a function of the effective bulk electrical conductivity of the soil (siemens per centimeter) as depicted in Table 1. Extensive research has been carried out on the zeta potential of the glass–water interface. Hunter (25) displays the effect of pH and ion concentration in the pore fluid on zeta potential. Zeta potential is reported to decrease linearly with the logarithm of the pH of the soil medium (25, 26).

Electrophoresis is the transport of charged particles under an electrical field (27). Electrophoresis becomes significant in electrokinetic remediation only when surfactants are introduced in the processing fluid to form micelles (charged particles) with other species or when the technique is employed in remediating slurries. The micelles would be transported across the soil under the electrical field. The efficiency of this technique in remediating nonpolar organics is currently under investigation (10). Electrophoretic transport of negatively charged clay particles is significant only when a slurry is processed.

**Migration versus electroosmosis**

Although fluid flow under hydraulic gradients is significantly affected by the soil fabric and macrostructure (28), electroosmotic flow under electric potential differences depends mainly on the porosity and the zeta potential and is independent of the pore size distribution or the presence of macropores. Therefore, electroosmosis is an efficient method to generate a uniform fluid and mass transport in fine-grained deposits. The relative contribution of electroosmosis and ion migration to the total mass transport varies for different soil types, water content, types of species, pore fluid concentration, and processing conditions. Maximum electroosmotic flow is often obtained in silts and in low-activity clays having high water content (28). Peclet number in solute transport is a measure of the rel-
The time rate of change of the transport number, $\lambda_e$, in experiments conducted with lead-, chromium-, and cadmium-spiked Georgia kaolinite.

**FIGURE 4**

$\lambda = \frac{u}{k_e}$

where $\lambda_e$ defines the relative contribution of the migrational mass flux with respect to the electroosmotic mass flux under equal electrical potential differences.

Ballou (30) reports $k_e$ values of up to $1.1 \times 10^{-4}$ cm$^2$/Vs for a sodium-kaolinite sample at 92% water content. Experiments at Louisiana State University rendered maximum $k_e$ values of $10^{-5}$ cm$^2$/Vs in lead-, chromium-, or cadmium-spiked Georgia kaolinite specimens (5, 14, 20, 31). Figure 4 presents the change in transport number, $\lambda_e$, in these experiments. $\lambda_e$ values are calculated using the effective ionic mobilities reported in Table 2 and the $k_e$ values recorded in these experiments. Mass transport by ionic migration will be at least 10 times higher than the mass transport by electroosmotic advection, and it may reach values as high as 300 in later stages of the process. The fall and the rise in $\lambda_e$ is a direct consequence of the time-dependent dynamic chemistry across the specimen under the electric field.

When the chemistry of the pore fluid at the electrodes is not controlled or the process fluid is not conditioned (unenhanced electrokinetic remediation), the acid front advancing from the anode to the cathode causes a decrease in $k_e$ associated with the increase in conductivity in the anode compartment and a corresponding drop in zeta potential (5, 14). Hence, electroosmotic flow toward the cathode decreases in time both by the decrease in $k_e$ and the decrease in electrical potential gradient (5), making the mass flux by migration 1–2 orders of magnitude greater than the electroosmotic mass flux toward this electrode.

Experiments at LSU further demonstrate that when the initial ionic conductivity of the pore fluid is low (2 to 3), very little electroosmotic transport occurs while the ionic species are transported efficiently (14). Eykholt (32) shows that there may even be a reverse electroosmotic flow when the pH of the pore fluid in the cathode compartment is decreased substantially. At low pH values, the isoelectric point of the clay mineral is reached and the zeta potential changes sign by the relation given in Table 1, reversing the sign of $k_e$. Although the pH value at which this phenomenon may be encountered in soils is not well established, this finding has been replicated in experiments at LSU, and an electroosmotic advective transport is recorded from the cathode compartment to the anode compartment in some experiments when the cathode reaction is depolarized using an acid.

**Transference number**

Ionic migration is demonstrated to be the major transport mechanism for species under electrical fields. The question then is how the current would be distributed among a mixture of species in the pore fluid, because this would relate to the efficiency of transport. When we assume the current to be in transport number, $\lambda_e$, through Faraday’s law for equivalence of mass flux and charge flux,

$$I = \sum_i j_i = \sum_i \frac{z_i u_i c_i}{n_i} I$$

where $j_i$ is the transport (or transference) number of the ion $i$, identifying the contribution of the $i$th ion to the total effective electric conductivity. The summation of transport numbers of all ions in the soil pore fluid should be equal to one. Equation 6 formalizes the dependence of the transference number of an individual ion on its ionic mobility, concentration, and the total electrolyte concentration (or the electrolyte ionic strength) in the pore fluid. The transference number of a species will increase as the ionic concentration of that specific species increases. This implies that as the concentration of a species decreases relative to the total electrolyte concentration in the pore fluid, its transport and removal under electrical currents will be less efficient. Therefore, it is reasonable to assume that the efficiency of removal of a specific species will decrease in time as its concentration with respect to other species in the pore fluid decreases.
Sorption

Heavy metals and other positively charged species are highly attracted and sorbed on the negatively charged clay surfaces. Metals have different sorption characteristics and mechanisms that also depend on the type of adsorbents. Sorption mechanisms include surface complexation (adsorption) or ion exchange. Although the selectivity sequence is generally a function of size and valence of the cation, the type of clay mineral is also a contributing factor (33).

Desorption of cationic species from clay surfaces is essential in extraction of species from fine-grained deposits with high cation exchange capacities. Electrolytic generation of H\(^+\) at the anode and its transport into the soil mass by migration (secondarily by electroosmotic advection and diffusion) will assist in desorption of these species. The sorption mechanism depends on the surface charge density of the clay mineral, characteristics and concentration of the cationic species, and existence of organic matter and carbonates in the soil. The mechanism is also significantly dependent on the pore fluid pH. An increase in H\(^+\) concentration results in desorption of cations by an amount controlled by the soil type (14, 34, 35).

In lead, cadmium, and chromium removal experiments at LSU, when the technique was used without any enhancement (31), it was necessary for the acid front to sweep across the soil mass to remove the lead loaded at a concentration of about a sixth of the cation exchange capacity of Georgia kaolinite, which is 1.06 meq/100 g (5). The species, at this concentration, were associated with the diffuse double layer of the mineral, and their removal required desorption followed by transport under an electric field. In this case, the acid was not significantly buffered by the kaolinite or any salts present in the soil, thus promoting the desorption of lead and its subsequent transport across the specimens.

Dissolution and precipitation

Dramatic changes in the soil electrochemistry throughout electrokinetic soil remediation result in different chemical reactions, including precipitation and dissolution of salts and soil minerals. Species transport in soil pore fluid is highly influenced by the dissolution of any precipitates and formation of new ones.

Unless neutralized by the incoming acid front as depicted in Figure 4, the base front generated by electrolysis at the cathode will cause precipitation of most heavy metals and radionuclides at their hydroxide solubility value. The amount of precipitation will differ from one species to another and it will be highly dependent on the resulting soil and pore fluid pH and the concentration of the species. We also note that the high pH conditions at the cathode and very low concentrations of heavy metals may result in formation of a negatively charged complex. Migration of the negatively charged complex from the anode to the cathode and the transport of positively charged species toward the cathode may focus and accumulate the species to the narrow zone of extreme pH change.

The advance of the acid front generated at the anode is expected to result in dissolution of most of the commonly encountered precipitates. Figure 5 presents tests conducted to determine the buffering capacity of soil samples retrieved from a site contaminated with up to 11% lead. Shell was spread in the area, leading to calcium concentrations of up to 13% in the same samples. The calcium carbonate and the lead in these samples rendered an excessive buffering capacity to the soil. Approximately 2–6 mL of 0.1 M HCl was needed per gram of soil (or 2 to 6 x 1 moles of HCl per gram) to bring down the pH to a value of 3. In the spiked Georgia kaolinite specimens (5, 14), the cation exchange capacity of the mineral (1.06 meq/100 g) was the predominant contributor to the buffering capacity exhibited by this mineral. In this site specimen, however, the buffering capacity is 20 to 60 times that of the Georgia kaolinite. This implies that it will be necessary to produce and introduce 20 to 60 times more acid in the specimens from the site than the lead-spiked kaolinite specimens. Unenhanced electrokinetic remediation tests using this soil did not result in significant removal. Calcium and lead were partially removed in the section close to the anode, but they were precipitated in others. The specimens were observed to be cemented at the cathode and subsequent to electrokinetic remediation. The calcium precipitation close to the cathode clogged the soil pores, hindering further transport of lead and other species. Enhancement schemes are necessary to prevent such premature precipitation of species and
Avoid the precipitates in the cathode compartment. Any envisioned interference of one in transport of another.

Enhancements and conditioning

Acar et al. (10, 36, 37) have recommended the use of different enhancement techniques to remove or avoid the precipitates in the cathode compartment. Any envisioned scheme is expected to have the following characteristics:

- the precipitate should be solubilized and/or precipitation should be avoided,
- preferably, ionic conductivity across the specimen should not increase excessively in a short period of time both to avoid a premature decrease in the electroosmotic transport and to allow transference of species of interest,
- the cathode reaction should possibly be depolarized to avoid generation of the hydroxide and its transport into the specimen,
- in case constant current conditions are used, such depolarization will also assist in decreasing the electrical potential difference across the electrodes, resulting in lower energy consumption,
- if any chemical is used, the precipitate of the metal with this new chemical should be perfectly soluble within the pH ranges attained,
- any special chemicals introduced should not result in any increase in toxic residue in the soil mass, and
- the cost efficiency of the process should be maintained when the cost of enhancement is included.

One technique proposed is depolarization of the cathode reaction by using an acid that forms a soluble salt with the species in transport and to allow transference of its transport with another positively charged species. In such soils, it may be necessary to enhance the process by complementing the anodic acid with another introduced in the processing fluid.

Figure 7 shows that the use of 0.05 M acetic acid, just enough to depolarize the cathode reaction, has overcome uranium precipitation close to the cathode compartment. All uranyl ion was found precipitated at the cathode; more was in the catholyte in the acetic acid enhanced experiments (37). Complete depolarization of the cathode reaction may require addition of 1 to 2 moles per day of acid for every cubic meter of processed soil, which may result in substantial, additional processing costs over several months of processing time. The efficiency and feasibility of using acid depolarization and other techniques are currently under investigation (37).

The migration of the acid generated at the anode would generally aid in desorption of the species from the clay surface and dissolution of precipitates. However, when the increase in the hydrogen ion concentration is considered in conjunction with migration of a species of interest, the substantial increase in hydrogen ion transference number may hinder transport of other species. It is possible to control the acid production and introduction into the soil mass, often by exchanging its transport with another positively charged species.

One other reason for depolarizing the anode reaction is concentration of the dissolution and release of silica, alumina, and heavy metals associated with the clay mineral sheets over long exposure to the proton. Wieberen (15) proposed the use of calcium hydroxide for depolarization of the anode reaction and hydrochloric acid for depolarization of the cathode reaction. Calcium ions in highly active clayey soils may enhance advective transport characteristics of the porous medium through changes in clay fabric, and the calcium ions would not attack the mineral sheet. Otherwise, calcium hydroxide depolarization of the anode reaction would not have any additional advantage over introduction of the proton. It is an added cost to the process, and such depolarization would sacrifice the benefits of desorption and precipi-
state dissolution achieved by the proton. In an attempt to fully exploit the different conduction phenomena, transport processes, and aqueous-phase reactions in field implementation of the electrokinetic remediation technique and to improve efficiency under specific site conditions, it is necessary to optimize the process.

Contaminant transport, capture, and removal

The positively charged species may be electrodeposited or precipitated at the cathode (6, 38) or they may remain in the catholyte as ionic species. Ion exchange columns, chemical precipitation, or electrochemical techniques may be used to remove the excess ions. Wieberen (15) suggests the use of calcium hydroxide to precipitate the metals in a container outside the processing medium circulating the process fluid. This is one option that can be employed in extracting the species from the catholyte fluid. Electrochemical deposition techniques, ion exchange resins, and membrane separation techniques are others.

Summary and conclusions

Electric fields applied across a saturated soil mass result in electrolysis, transport of species by ionic migration, electroosmosis, and diffusion. These transport processes are accompanied by sorption processes in the soil, precipitation and dissolution, and other aqueous-phase reactions in the pore fluid.

The principles of species transport under an electric field demonstrate ionic migration to be the most significant component of mass transport in electrokinetic remediation in most soils. The magnitude of the mass transport by electroosmosis in soils is often at least 1 order of magnitude less than that induced by electrical migration. In unenhanced electrokinetic remediation, the transport of the electrolysis products such as H+ and OH" ions produced at the boundaries significantly affects the chemistry across the soil mass. The hydrogen ion movement toward the cathode assists in desorption of species from clay surfaces and dissolution of the salts in the soil. The back migration and diffusion of the hydroxide ion generated at the cathode may lead to premature precipitation of cations transported to this region. Enhancement techniques are necessary to prevent this premature precipitation. Depolarization of the cathode reaction using low concentrations of acetic acid effectively overcomes uranyl ion precipitation.

The efficiency of transport of a species is directly related to its transference number, which is related to its ionic mobility and concentration. As the concentration of the species decreases by transport across the soil mass, the increase in hydrogen ion concentration in the pore fluid would decrease the transference numbers of other species, thus decreasing their removal efficiency. Anode and cathode depolarization schemes and process fluid conditioning may be employed to enhance transport and avoid shortcomings of the technique. Successful implementation and commercialization of the technology require
development of process optimization schemes, pertinent design and analysis of construction guidelines through critical assessment of carefully conducted pilot-scale field studies, and complementary analysis of the results of theoretical models.

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