Removal of Contaminants from Soils by Electric Fields

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Application of a direct-current electric field in soils that contain contaminated liquids is expected to produce an important in situ means of environmental restoration. The electric field induces a motion of the liquid and dissolved ions that transports the contaminants to wells for removal. Electrode chemistry plays an important role, and reagents can be introduced at the electrodes to enhance contaminant removal rates. Experiments and modeling demonstrate high degrees of contaminant removal, propagation of sharp acid and base wave fronts from the electrodes, and a "focusing" effect by which metals accumulate in regions of the soil.

Economical restoration of contaminated soils to an environmentally acceptable condition is an important challenge facing the scientific and technical community. A relatively new and potentially important in situ technique has emerged in which a dc electric field is applied across electrode pairs placed in the ground. The contaminants in a liquid phase in the soil are moved under the action of the field to wells where they are then pumped out (*1*). The method is still in the early stages of development, with most efforts restricted to the laboratory. Limited field tests have been carried out, the most extensive of which have been in the Netherlands (*2*), where the potential for removal of some types of ionic contaminants has been demonstrated.

The principal mechanisms by which contaminant transport takes place under the action of an electric field are electromigration, electroosmosis, and electrophoresis. Electromigration is simply the transport of a charged ion in solution. In electroosmosis, a liquid containing ions moves relative to a stationary charged surface, as in a capillary pore. Electrophoresis is the mirror image of this process, in that a charged particle moves relative to a stationary liquid (*3*). Colloidal particle transport by electrophoresis is of limited importance in compacted soil systems.

Electroosmosis in a pore occurs because of the drag interaction between the bulk of the liquid in the pore and a thin layer of charged fluid next to the pore wall that, like a single ion, is moved under the action of the electric field in a direction parallel to it. The thin layer of charged fluid, or double layer, has a typical thickness between 1 and 10 nm. It arises because charge neutrality must be maintained by balancing the surface charge with an opposite charge in the fluid.

The convective liquid velocity from electroosmosis is proportional to the so-called zeta potential ζ of the surface and to the applied electric field strength $\mathbf{E}$, defined as minus the gradient of the electrical potential. For a thin double layer in comparison to the pore size, this velocity is given by the Helmholtz-Smoluchowski relation (*3*)

$$\mathbf{u}_{eo} = \epsilon\zeta\mathbf{E}/\mu \qquad (1)$$

where ϵ is the permittivity of the solution and μ is its viscosity. In electromigration the ion velocity is proportional to the electric field strength and the ionic charge number z or

$$\mathbf{u}_{em} = vzF\mathbf{E} \qquad (2)$$

where v is the ion mobility and F is Faraday's constant.

The transport as described leads to one of the most important advantages of contaminant removal by electric fields: the high degree of control of flow direction that can be achieved because the material moves along electric field lines that are defined by the electrode placement. Soils are typically heterogeneous, and pressure-driven flushing processes invariably channel the fluid through the largest size pores, leaving the smaller ones untouched. Electroosmosis is only effective in fine-grained soils with micrometer-size or smaller pores. In such low-permeability soils, the electroosmotically driven flow is insensitive to pore size (*4*). Electromigration is not dependent on pore size and so is applicable equally to coarse and fine-grained soils.

Charge on the soil is fundamental to the transport of pore liquid by electroosmosis, although the movement of charged ions by electromigration does not depend on the soil charge. The origin of the charge on the soil when in contact with an aqueous solution results from a number of effects, including chemical and physical adsorption and lattice imperfections. In any case, the saturating liquid composition and its pH are critical to the surface charge (*5*). For water-saturated silts and clays, the zeta potential is typically negative, with values measured in the 10- to 100-mV range.

Convection of the saturating liquid through the soil by electroosmosis and transport of dissolved species within the liquid by electromigration are by themselves usually insufficient to characterize the contaminant motion. Integral to the process are the desorption, dissolution, and chemical interactions with the soil. In addition, there are chemical reactions at the electrodes and in the bulk fluid. At the electrodes, electrolysis of water produces H^+ ions at the anode and OH^- ions at the cathode

$$\begin{aligned} H_2O &\rightarrow 2H^+ + \tfrac{1}{2}O_2(g) + 2e^- \\ 2H_2O + 2e^- &\rightarrow 2OH^- + H_2(g) \qquad (3) \end{aligned}$$

If the ions produced are not removed or neutralized, these reactions lower the pH at the anode and raise it at the cathode, accompanied by the propagation of an acid front into the soil pores from the anode and

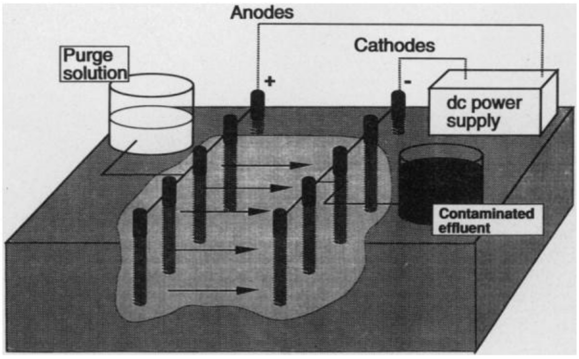

Fig. 1. Schematic of soil decontamination by electroosmotic purging. The dc electric field moves the contaminating fluid to the cathode wells for removal and draws in a nontoxic reagent that helps drive out the contaminated liquid, washes and treats the soil, and prevents crack formation by maintaining soil saturation.

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a base front from the cathode. This process can have a significant effect on the soil zeta potential, as well as solubility, ionic state and charge, and level of adsorption of the contaminants.

A schematic of a field installation of in situ electroosmotic purging (6) is shown in Fig. 1 in which anode and cathode electrode pairs are positioned in wells drilled into the waste site. The parameter ranges are illustrated in Table 1.

Electroosmosis and Removal of Organic Compounds

Soils contaminated by organics may be distinguished by whether the organic compounds are soluble or insoluble in water. Insoluble organics, such as heavy hydrocarbons, are essentially not ionized, and the soils in contact with them are not charged. The removal of insoluble organics by electric fields is limited to their movement out of the soil by electroosmotic purging of the liquid either with water and surfactant to solubilize the compounds or by pushing the compounds ahead of a water front (6). These procedures probably have limited applicability. However, there exists a wide range of organics that are relatively soluble in water and in a weakly ionized state that may be classified as ubiquitous ground-water contaminants (*7*). These organics include aromatic compounds such as benzene, toluene, xylene, and phenolic compounds, as well as chlorinated solvents. The aqueous solutions formed with soluble organic compounds when in contact with soils such as clays can be expected to give rise to soil zeta potentials for which electroosmotic convection will take place under the action of an applied electric field.

The ability to remove soluble organics from clays by electric fields has been demonstrated in a number of laboratory experiments (*7–10*). In Fig. 2A are results for the cumulative volume of effluent as a function of time for the removal of aqueous phenol and acetic acid solutions from saturated and compacted kaolin clay samples (8). The fraction of initial contaminant removed as a function of the pore volume of effluent collected is shown in Fig. 2B. Because the soil was maintained at saturation, the effluent volume corresponds to the volume of purge solution drawn in. The correlation in Fig. 2B of the contaminant removal with pore volume shows that the primary mechanism of contaminant removal is electroosmosis; the removal results essentially from the convection of the fluid out of the soil. Moreover, $\sim$95% of the organic contaminants are removed by passage of only 1.5 pore volumes of purge solution. Experiments at higher voltages show the actual rate of removal to be roughly linear in the applied voltage, which is consistent with an electroosmotic flow. However, the energy dissipation losses increase correspondingly (*10*).

Table 1. Parameter ranges for electroosmotic purging.

Parameter	Range
Applied potential	40 to 200 V
Applied electric field	20 to 200 V m^{-1}
Electrode spacing	2 to 10 m
Electrode depth	2 to 20 m
Current density	0.5 to 5 A m^{-2}
Electroosmotic velocity	10^{-7} to 10^{-5} m s^{-1}
Hydraulic permeability	10^{-16} to 10^{-13} m^{2}

Other laboratory experiments for the removal of organic contaminants from clay samples have been carried out in an apparatus similar in size to that for the experiments in Fig. 2, with the contaminants at their solubility limits and the clay initially at $\sim$80% saturation (*7*). Contaminants included in the experiments were benzene, trichloroethylene, toluene, and *m*-xylene, whose solubilities range, respectively, from $\sim$1730 to 150 mg liter^{-1}. Although the experiments were run for periods of only 2 to 5 days with removal rates in the range of 15 to 25%, extrapolation of the data to longer times indicates that relatively high degrees of removal could be attained.

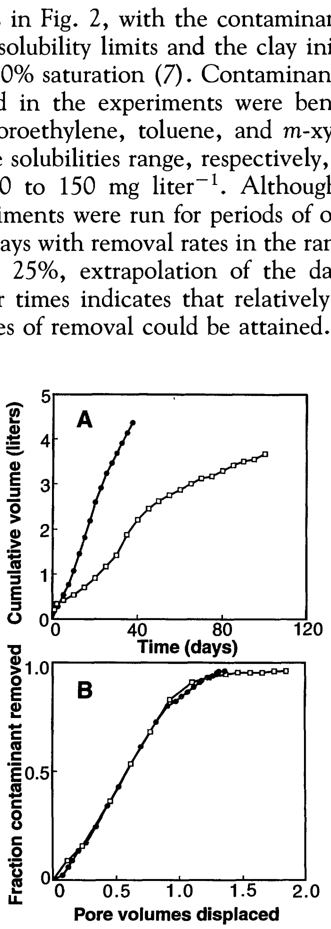

Fig. 2. (**A**) Cumulative volume of effluent versus time and (**B**) fraction of contaminant removed versus pore volumes displaced. Results in both are from the electroosmotic purging of phenol and acetic acid solutions from kaolin clay samples that were compacted in an acrylic cylinder 0.5 m in length and 0.1 m in diameter with porous carbon fiberboard electrodes at each end across which a constant voltage of 25 V (E = 50 V m^{-1}) was applied. Filled circles, phenol (450 mg liter^{-1}) with a tap-water purge; open squares, acetic acid (0.5 M) with a NaCl (0.1 M) purge. Pore volume: phenol, 2.4 liters; acetic acid, 2.7 liters. [Modeled after (*8*)]

An important problem facing electroosmotic procedures can be seen in Fig. 2A where the curve for the removal of acetic acid deviates from linearity. This deviation indicates a time-dependent convection velocity that can be attributed to a transient behavior in the zeta potential, electric-field distribution, or both in the clay. Such variations can be expected because of the dependence of both the zeta potential and the electric field on ionic concentration and pH. The lower pH of the acetic acid compared with that of the phenol causes the clay to have a lower zeta potential mostly because of the increase in adsorbed hydrogen ions, which neutralize the negative charge on the soil. This situation leads to a lower electroosmotic velocity for the acetic acid than for the phenol solution.

Different results, which at first seemed surprising, were obtained when the same experiments were repeated with the initial phenol concentration one-tenth and the acetic acid concentration one-fifth of that indicated in Fig. 2. The removal of acetic acid leveled off at $\sim$40% of the acid that was initially in the clay after a displacement of 1.5 pore volumes, and the phenol reached a plateau at $\sim$75% after 1 pore volume was extracted, with the flow actually stopping at $\sim$1.1 pore volumes.

The reason for the lower acetate removal for the 0.1 M solution could be traced to the increase in effluent pH to a high value (>12) because of the generation of hydroxyl ions at the cathode. At the high pH, all of the acetate is negatively charged and actually migrates back toward the anode. The removal that does take place results from transport by diffusion across the steep concentration gradient formed near the cathode. On the other hand, in the 0.5 M case the acetate concentration is high enough to keep the pH relatively low so that most of the acetate is undissociated and convected out with the effluent. Thus, the ability of the acid to buffer the electrode reactions plays a key role in the removal process (*10*).

The lower degree of phenol removal with lower concentration is not traceable to the electrochemical reactions because the pH change was not large between the cases. The limited removal is likely a consequence of phenol adsorption on the clay, where at the lower concentration the amount adsorbed represents a higher fraction of the total mass.

The observations of the effects on contaminant removal of the electrode reactions, adsorption on the soil, and reduction of zeta potential led to the concept of the introduction of nontoxic purge solutions at the electrodes. These solutions, typically used at the anode, serve as enhancing agents for contaminant removal where the purge solutions are moved into the soil electroosmotically (6). Such reagents might include buffering compounds to control pH or enhance the zeta potential, as well as solutions to enhance desorption, increase solubility, or aid in flushing out the contaminants. Moreover, products of the electrode reactions that have a deleterious effect, such as the hydroxyl ions at the cathode, might be removed directly at the electrodes by flushing or chemical conditioning.

Figure 3 illustrates the effect of purge solutions of the same ionic strength but different pH on phenol removal. Nearly all soils become more negatively charged with increasing pH, and this effect on the clay zeta potential is evident. When an alkaline purge solution was used, the flow rate was nearly double that with an acid purge. In addition, the flow rate was steady with the alkaline solution, whereas the flow stopped with the acidic solution (*10*).

Electromigration and Removal of Metals

The application of an electric field appears to have an even greater potential for the removal of solubilized metals than for the removal of organics. This method shows promise because the metal ions are positively charged and the electroosmotic flow is enhanced by the electromigration of these cations to the cathode, at least when the soil is negatively charged. A number of studies (*11–13*) have been reported on metals removal by electric fields. Some of the results are ambiguous because of the greater reactivity of many inorganic contaminants and, in the case of heavy metals, the sensitivity of their reaction equilibria to the pH of the saturating liquid. For the metals to be affected by the electric field, they must be present in solution in the saturating liquid. It has been suggested (*14*) that the production of hydrogen ions at the anode, which leads to a low pH condition and an acid front that migrates to the cathode, would aid metal solubilization from the soil.

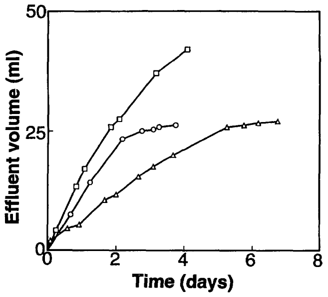

Fig. 3. Effect of purge solutions of same ionic strength but different pH on electroosmotic purging of phenol from kaolin clay plugs (3 to 4 cm in length and 3 cm in diameter) at a constant applied current density of 0.2 A m^{-2}. Open squares, 0.01 M NaOH (pH 12); open circles, 0.01 M NaCl (pH 7); and open triangles, 0.01 M HCl (pH 2). [Modeled after (*10*)]

A seemingly undesirable consequence of the promotion of acidic conditions is that the zeta potential, and hence the electroosmotic flow, would be suppressed by the large concentration of hydrogen ions in the acid. However, because the metals are present as charged ions, they can be removed by electromigration. In our studies, electromigration transport occurred at rates about three times the electroosmotic flow rates that are typical of organics removal; this result may not be general.

Diffusion can also play a significant role in the transport of metals through the soil. The diffusional velocity is given by

$$\mathbf{u}_{\text{diff}} = (D/c)\nabla c \qquad (4)$$

where c is the molar concentration. The diffusion coefficient D is related to the mobility v by the Nernst-Einstein relation $D = vRT$ (*3*), in which R is the gas constant and T is temperature. This diffusion should become increasingly important as the treatment progresses as a result of the steepening of the concentration gradients and the decrease in the amount of metals remaining in the pores.

As the metal enters the region of high pH near the cathode, it may adsorb onto the soil, precipitate, or form hydroxo complexes. Typically, an intermediate pH of minimum solubility exists at which virtually all of the metal will be precipitated. At higher pH values, the solubility increases because of the increasing stability of soluble hydroxo complexes. Although redissolution of the metal as a hydroxo complex is then favored, the dissolution kinetics may be slow. Hydroxo complexes that are formed may be negatively or positively charged or neutral. Negatively charged complexes migrate back toward the anode and precipitate near the region of minimum solubility.

The effect of the high pH on the transport of metal is demonstrated in Fig. 4, which shows the removal of zinc from a clay sample with flushed and unflushed electrodes (*15*). The dominant transport processes were electromigration and diffusion; electroosmotic flow was negligible. Figure 4A shows the focusing of the zinc that occurs where the acid and base fronts meet. The pH distribution developed within a few hours and then remained relatively stationary for the remaining 9 days of the test. The positive zinc ions near the anode and the hydroxo complexes near the cathode migrate toward the region where the pH jumps. They then accumulate at the position where the pH corresponds with the isoelectric point, that is, the pH at which the concentrations of negative ions and positive ions are equal. The phenomenon is analogous to that of isoelectric focusing that is used in electrophoretic separations (*16*). In our case, the focusing is reinforced by precipitation of the metal because the pH of minimum solubility generally also occurs at the isoelectric point. In fact, virtually all of the metal found at the peak shown in Fig. 4A was in the precipitated form.

The zinc reaching the electrode wells, mainly by diffusion, is <5% of the total. Accumulation of metal at the anode has been observed, although the dominant species in this region, the cation, migrates toward the cathode. It appears that the steep concentration gradients, combined with the greater solubility in the acid in the anode well, result in a significant contribution by diffusional transport in this region (*13*).

The position of the pH jump was in agreement with the relative ion mobilities of hydrogen ions to hydroxyl ions of nearly 2:1 (*17*). The addition of pH indicators to the soil showed the acid front to move at a speed almost exactly double that of the base front moving from the cathode (Fig. 5).

Although these tests showed that a metal pollutant can be concentrated at some intermediate region between the electrodes and so can subsequently be removed by excavation of a relatively small amount of soil, true in situ removal at the electrodes is the desired objective. To accomplish this removal, the formation of a focusing region must be eliminated by flushing of the cathode with tap water to remove the hydroxyl

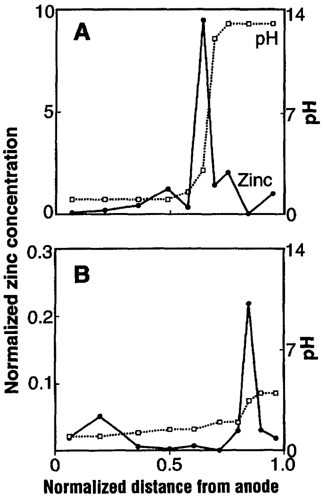

Fig. 4. Distributions of normalized zinc concentration and pH along an acrylic cylinder 200 mm in length and 32 mm in diameter that was packed with kaolin clay after 9 days of zinc removal by electromigration and diffusion. The clay was initially saturated with a zinc solution (500 mg liter^{-1}, pH ~6), and a constant voltage of 20 V was applied across porous carbon electrodes at the ends of the cell (E = 100 V m^{-1}). (**A**) Unflushed cathode that shows focusing of zinc where acid and base fronts meet and (**B**) cathode flushed with tap water (*15*).

ions generated there. As shown in Fig. 4B, this simple procedure virtually eliminated the pH jump, and 98% of the zinc was removed at the cathode in the 9-day test period.

In tests with lead in a 98% kaolinite soil under conditions of a constant current (*11*), an electroosmotic flow was obtained after ~10 to 20 hours that increased to a maximum within ~2 days and then declined. During the period of high flow, the pH of the effluent at the cathode was alkaline, but after ~0.8 to 0.9 of a pore volume had been discharged the pH dropped and the flow rate decreased. In tests in which the pH of the effluent dropped below 7, most of the lead was transported to the cathode and was electroplated onto the graphite cathode. However, in a test that was stopped when the effluent pH was still >8, most of the lead remained in the soil and was concentrated a short distance from the cathode, although the profile was not as sharply peaked as in Fig. 4A.

An important difference between the zinc tests and those with lead is the attainment of a significant electroosmotic flow rate in the latter. Electroosmotic flows with metal-contaminated clays have been reported by others. For example, an initial but rapidly declining flow rate of 0.5 of a pore volume per day was obtained in the identical equipment and clay as used for the zinc test described above but with copper as pollutant (*18*). The delay in the onset of the electroosmotic flow is also not unusual. In tests with a highly contaminated fly ash, an electroosmotic flow increased abruptly from 0.1 to 0.6 of a pore volume per day on the fifth day of testing (*15*). The electroosmotic flow rate increased even further to 0.9 of a pore volume per day after an alkaline purge was allowed to diffuse into the fly ash for 10 days.

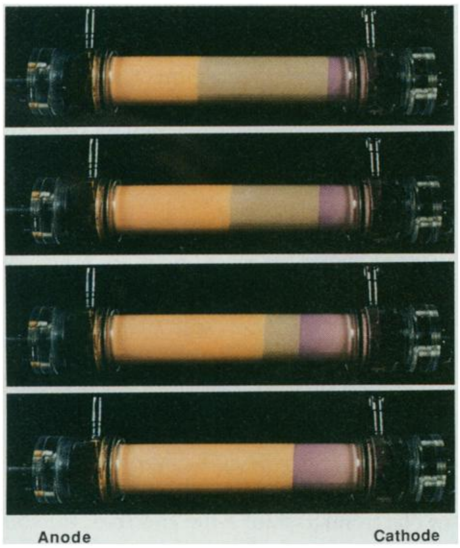

Fig. 5. Motion of acid front from the anode and base front from the cathode for zinc removal tests shown in Fig. 4 with 8 V applied across a clay sample ($E = 40$ V m^{-1}). Indicators of pH are bromphenol blue and phenol red. The front speeds are constant, and the final position of the pH jump is about two-thirds of the cylinder length from the anode. The frame times from top to bottom are 6, 8, 10, and 11.3 hours, respectively (*15*).

Modeling

The phenomena and processes described can be modeled by convective diffusion equations with chemical reactions. These equations characterize the transient behavior of concentration fields for a set of chemical species in solution that are transported by convection, migration, and diffusion in an electric field. The most general models apply these equations in a cylindrical capillary and by means of a capillary model to a porous medium. Dilute solutions, rapid dissociation-association chemical reactions, and small double-layer thickness are assumed (*8, 10, 14*).

Time-dependent boundary conditions must be imposed at the electrodes that correspond to the heterogeneous electrochemical reactions that take place there to permit the passage of current through the pore solution. These reactions, whose rates are proportional to the current, are incorporated into the fluxes of the species produced and are applied as boundary conditions at the capillary ends, such as those shown in Eq. 3.

The boundary conditions at the soil surface can be specified in a relatively straightforward way, although the parameters are not always as easily defined because of the complexity of the solution-soil chemical interactions. Some measure of the uncertainties is removed because the convective electroosmotic velocity that enters into the convective diffusion equations is the volume-averaged value of the Helmholtz-Smoluchowski velocity given by Eq. 1 (*19*). Therefore, what is important are not the local values of the zeta potential and the electric field but the volume average of the scalar product of these two values. Although the transient and nonuniform behavior of the electric field can be readily accommodated in any calculations, constant average values have generally been used because of the system specificity of the zeta potential and the complications in its determination.

Another modeling problem is the definition of the surface boundary condition that describes the physical adsorption at the soil surface for any given solute-solvent-soil system. An equilibrium adsorption isotherm that gives the dependence of the solute adsorbed on the concentration in the bulk solution can be measured experimentally. However, the application of an equilibrium criterion requires that the time scale of the adsorption process be small compared with the time scales of flow and of diffusion, a relation that generally means that the adsorption equilibrium must be attained in a couple of hours (*20*).

Finite-element numerical calculations for one-dimensional geometries have been carried out on the basis of the modeling described, and the solutions are in agreement with the observed physical and chemical behaviors. The potential for the characterization of quite complex phenomena can be seen in Fig. 6, A and B, where comparisons are given between calculations and experimental results for removal of acetic acid from a clay sample. The only parameter chosen is a volume-averaged zeta potential that is matched to give the mean experimental flow rate. In this instance, the deeper penetration of the acid front from the anode results primarily from the electroosmotic flow (*8, 10*).

As shown in Fig. 1, electrode pairs in an actual field operation will be deployed in an array, although not necessarily rectangular, in which the spacing and orientation as well as the magnitude of the applied electric field will strongly affect the degree, costs, and rate of contaminant removal. Therefore, an understanding of the effect of geometry is required. To this end, experiments have been carried out with a single electrode pair and grids of electrode pairs in rectangular box cells (*21, 22*). For a contaminant-soil system homogeneous with depth and with electrode depths that are relatively comparable to or deeper than their horizontal spacing, the field may be

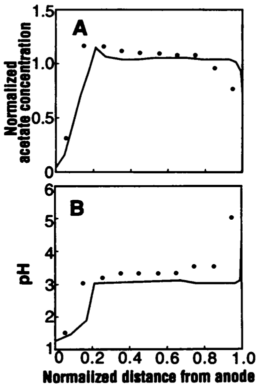

Fig. 6. Comparisons between finite-element calculations (solid traces) and an experiment after 0.12 of a pore volume of liquid had been removed (solid points). The clay is initially saturated with a 0.1 M acetic acid solution. The geometry and test conditions are the same as for Fig. 2. (**A**) Normalized acetate concentration profile along sample and (**B**) pH profile that clearly shows penetration of electrode effects into the soil. [Modeled after (*10*)]

treated as independent of depth and two-dimensional.

Experiments together with modeling calculations in two dimensions (*22*) have graphically illustrated how contaminant removal is affected by electrode placement. In those cases where electroosmosis is the dominant transport mechanism, a knowledge of the electroosmotic velocity distribution is critical to the determination of the shape and extent of the effective area cleaned by an electrode pair. Figure 7A shows the electroosmotic velocity distribution in the purging of phenol from a clay sample in a rectangular box cell. The velocities are calculated from smoothed spatial measurements of the electric-potential distribution as a function of time and from Eq. 1. The most highly purged area appears along a line that connects the electrodes where the electric-field strength is highest. The purging decays in magnitude in a manner roughly similar to that of a dipole, where the anode is the source and the cathode is the sink. Other three-dimensional experiments on the removal of organics show a similar behavior (*21*).

Figure 7B shows the calculated electroosmotic velocity distribution for the same geometry and conditions as in the experiment. For these calculations adsorption was considered, but neutral species and a constant zeta potential have been assumed. Although qualitative agreement with experimental results is seen, quantitative agreement cannot be expected without inclusion of the pH and ionic concentration changes that result from the dissociation-association reactions in the bulk and at the electrodes. Moreover, the model is designed on the assumption of an initially uniform pore-liquid distribution giving rise to the symmetric solution, in contrast to the asymmetry of the measured data in Fig. 7A.

Process Considerations

Although the idea that electric fields might be used to clean up contaminated soils in situ is relatively recent, its origins most certainly lie in the work of Casagrande (*23*), who in mid-1930s Germany was the first to use electroosmosis for dewatering and stabilizing soils. Subsequently, electroosmosis has been used in a variety of other practical field situations, including dewatering coal mine tailings and mineral sediments (*24*). Of greatest relevance to soil decontamination is that, despite the heterogeneous character of most soils, economic application of an in situ electrical technique under actual field conditions can modify soil characteristics.

Any use of electric fields in the restoration of waste sites will require the identification of the dominant mechanism for moving the contaminant (*25*). Soil characteristics are most critical, and important properties include the permeability, adsorption capacity, buffering capacity, and degree of saturation. Spatial variation in permeability can nullify the decontamination process if electroosmotic flow in the fine soils induces a pressure gradient that causes a return flow through the coarser region (*26, 27*).

Interaction of the pollutant with the soil can also significantly affect performance. In laboratory tests of field samples containing seven heavy metals (*2*), the individual metal removal rate was sensitive to the type of metal and the soil permeability. Although soil properties generally cannot be altered, careful selection of operating conditions and the introduction of appropriate reagents by electroosmotic purging can result in successful waste treatment at a variety of sites. Because of the many variables and their complex interaction, the optimum conditions are best explored by mathematical modeling.

The mobility of the pollutants is also determined by the level of saturation of the soil. Waste sites, some of which occur in semiarid regions, may not be completely saturated. There is laboratory evidence that effective removal by electromigration can be achieved in partially saturated soils (*27*). Moreover, the soil may be saturated by introduction of a purge solution by electroosmosis. The purge solution can also be used to increase the solubility, to complex, to chelate, or to enhance the electromigration characteristics of specific contaminants. Environmental regulations, which in some instances even prohibit the introduction of pure water into the ground, will ultimately have to be modified to accommodate the introduction of nontoxic substances that enhance contaminant removal.

In cases where the electroosmotic flow rate is small, it may be necessary to flush the electrodes (for example, to flush out hydroxyl ions at the cathode or to introduce a chemical to alter the electrode reaction). Membranes surrounding the electrodes may be used to prevent any chemicals that are introduced from entering the soil. Alternatively, the electrode may be surrounded by ion-exchange material to trap the contaminant and prevent its precipitation (*28*). Of course, all materials in aqueous streams, whether reagents or contaminants, that are brought out from the soil will require recovery by standard processes such as ion exchange, adsorption, or precipitation.

The ease with which the pH can be altered, either by electrolysis or by purge solutions, depends on the buffering capacity of the liquid and the soil. Many ground waters contain high concentrations of bicarbonates that consume added hydrogen ions to form carbonic acid or hydroxyl ions to form carbonate ions. Possibly more important in work with metal wastes is the limited solubility of many metal carbonates. The effect of other chemicals such as sulfide, sulfate, chloride, and ammonia, which might be introduced into the soil along with the metal, should also be evaluated if present. As in the case of hydroxyl and carbonate ions, these species might form charged or neutral soluble complexes or might limit the solubility.

Many waste sites will contain mixed organic and inorganic compounds, each of which may interact differently with the soil. Thus, the presence of heavy metals in a mixture can lead to a negligible zeta potential so that the decontamination proceeds in stages, the first of which is metal removal by electromigration. After this step, the soil may acquire a significant potential and the organics removal would then proceed by electroosmosis.

The electrode spacing and orientation, as with the optimum voltage for a given waste site, are not readily determined. However, the general ranges for electroosmosis are given in Table 1, where the record of dewatering technologies has been used as a guide (*23*). Modeling tech-

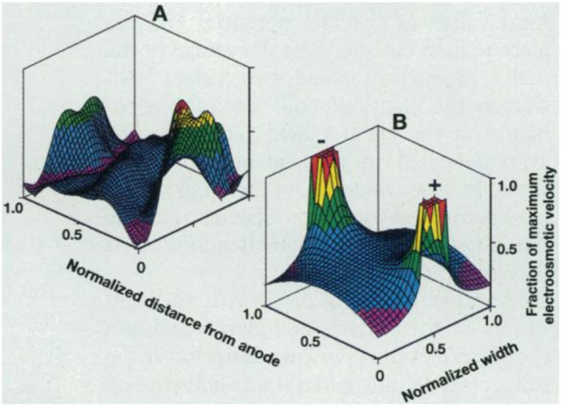

Fig. 7. Electroosmotic velocity distribution after removal of 1 pore volume of liquid from a rectangular clay sample 28 cm long, 14 cm wide, and 7 cm deep that was initially saturated with a phenol solution (450 mg liter^{-1}). Carbon rods are placed symmetrically in porous cylindrical wells 13 cm apart, across which 35 V is applied. The anode purge is an NaOH (pH 10) solution. (**A**) Velocity distribution from measured potentials at a depth of 3 cm, calculated with Eq. 1. (**B**) Model calculations for same geometry and conditions, on the assumption of neutral species. Fraction of maximum velocity: red, yellow, and green, 100 to 50%; blue, 50 to 30%; and purple, <30%. [Modeled after (*22*)]

niques that have and are being developed can aid greatly in this definition. With respect to the dc source, photovoltaics may prove ideal because they produce a dc current, the voltages from individual photovoltaic panels are in the range of interest, and storage requirements are likely not needed.

Ultimately the cost of the process will define its utility. Estimates of the energy cost have been made and depend on whether the principal removal mechanism is electroosmosis or electromigration. In electromigration the energy cost per mole of contaminant removed will be proportional to the resistivity and current (that is, the voltage). On the other hand, in electroosmosis it will be proportional to the strength of the electric field and inversely proportional to the contaminant concentration in the pore solution. In other words, the cost to move the pore fluid is proportional to the electroosmotic flux (Eq. 1), independent of the contaminant concentration.

Laboratory experiments on organics removal by electroosmotic purging (*10, 21*) at moderate voltages, so that heating losses are not excessive, show energy costs averaging about 20 kWh per cubic meter of effluent. With 2 pore volumes of purging, a soil of 50% porosity and dry specific gravity of 3, and an energy price of 10 cents per kilowatt-hour, the power would cost $1 per ton of soil treated—a modest cost. Comparable electromigration costs are more difficult to estimate because they are concentration- and voltage-specific. However, laboratory experiments on lead (*11*) and zinc (*15*) at concentrations and applied voltages similar to those in the tests with organics have yielded average energy costs of ~40 kWh per cubic meter of soil, which corresponds to a cost of $2 per ton of soil treated. The estimated energy costs for contaminant removal by electric fields are probably somewhat optimistic, so that total treatment costs, which may be as much as ten times the cost of power, could approximate $20 to $30 per ton. These values seem promising when compared with total costs of ~$150 per ton by conventional methods (*29*).

Conclusions

Laboratory experiments applying dc electric fields to soils containing aqueous solutions of soluble contaminants show much promise for an effective in situ means for cleaning waste sites. Limited field tests and computer modeling support this projection, although the ability to make quantitative predictions of expected contaminant removal and costs at an actual hazardous waste site is at an early stage. Several developmental steps are needed to assess this method's potential: the results of well-characterized field tests together with additional laboratory data, particularly on the removal of heavy metals and their interactions with different soils of varying degrees of saturation; reagents for enhancing the desorption and solubilization of both organic and inorganic contaminants; and improved predictive models that enable optimization of the process variables.

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