Electrokinetic Remediation of Mercury-Contaminated Soils Using Iodine/Iodide Lixiviant

CHRIS D. COX,*
MATTHEW A. SHOESMITH, AND
MRIGANKA M. GHOSH

Department of Civil and Environmental Engineering, Center for Environmental Biotechnology, 223 Perkins Hall, University of Tennessee, Knoxville, Tennessee 37996-2010

In-situ remediation of mercury-contaminated soils, by electrokinetic or other means, is difficult because of the low solubility of mercury and its compounds. In this research, enhanced electrokinetic remediation of HgS-contaminated soils using I_2/I^- lixiviant was investigated using bench-scale electrokinetic cells. The thermodynamic conditions under which the lixiviant could be effective were determined by constructing a pE−pH diagram for the Hg−S−I system. Introduced near the cathode, the lixiviant migrated through the soil to the anode by electromigration. Mercury, released by the oxidation of HgS compounds by I_2, was complexed as HgI_4^{2-}. The negative complex continued to electromigrate toward the anode. Up to 99% of the Hg present in laboratory-contaminated soils could be removed. Electrokinetic treatment of a field-contaminated soil, containing more organic matter than the laboratory-contaminated soil, occurred much slower. The critical issues in determining the efficacy of the process are the oxidation of reduced Hg by I_2 and I_3^- and the transport of the resultant HgI_4^{2-} complex.

Introduction

In recent years, there has been considerable interest in the application of electrokinetic processes for the remediation of contaminated soils and groundwaters. The goal of electrokinetic remediation is to affect the migration of subsurface contaminants in an imposed electric field via electroosmosis, electromigration, and/or electrophoresis processes (*1*). In soils that carry a negative surface charge, electroosmotic flow of pore water is from the anode to the cathode. Electromigration is the transport of ions to the electrode of opposite charge and is typically over an order of magnitude greater than electroosmosis (*1*). Electrophoresis is the transport of particles under the influence of an electric field; contaminants bound to mobile particulate matter can be transported in this manner.
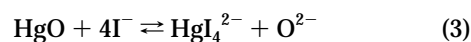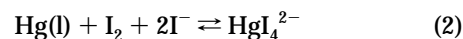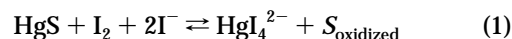
In some laboratory investigations, electrokinetic processes have removed greater than 80% of metal (*1, 2*) and

* To whom correspondence should be addressed; telephone: (423) 974-7729; fax: (423) 974-2669; e-mail address: ccox9@utk.edu.

organic (*3, 4*) contaminants. In other experiments, uniformly high removal of metals from all portions of the test soils was not observed (*1, 5, 6*). During electrokinetic treatment, electrolysis results in the formation of H^+ at the anode and OH^- at the cathode. H^+ and OH^- migrate toward one another by electrokinetic processes. As these two fronts meet, a rapid transition from low to high pH occurs, creating a region of minimum solubility of metals (*6, 7*). In this region, the metals concentration may increase many fold. This can be prevented by flushing the cathode with water or a dilute acid to arrest the migration of the OH^- front into the soil (*1, 6, 7*). Recent studies (*7, 8*) emphasized the importance of both pH and redox potential in electrokinetic mobilization of metals having multiple oxidation states. The purpose of this work is to demonstrate the use of iodine/iodide lixiviant for maintaining proper thermodynamic conditions for effective electrokinetic remediation of Hg-contaminated soils.

Background

Effective electrokinetic remediation depends on both the solubilization and transport of the contaminant. Electrokinetic remediation of Hg-contaminated soils is difficult because of the low solubility of Hg in most natural soils. Hem (*8*) determined the predominant insoluble species of Hg as a function of pE and pH in a solution 0.001 M in Cl and S. For the pE−pH conditions typical of soils (*9*), the predominant species of insoluble Hg are HgS, Hg(l), and Hg_2Cl_2 (*8*). The maximum solubility of these compounds are 10^{-11}, 1.3×10^{-7}, and 5.1×10^{-4} M, respectively. The prospect of effective electrochemical remediation under conditions in which the contaminant is so insoluble is bleak.

Foust (*10*) has recently developed a process which uses an I_2/I^- lixiviant solution to solubilize Hg from contaminated solids. Oxidation of reduced insoluble Hg by I_2 releases Hg(II), which is complexed as HgI_4^{2-}. Reactions describing the solubilization of various insoluble Hg species are given as:

$$HgS + I_2 + 2I^- \rightleftarrows HgI_4^{2-} + S_{oxidized} \qquad (1)$$

$$Hg(l) + I_2 + 2I^- \rightleftarrows HgI_4^{2-} \qquad (2)$$

$$HgO + 4I^- \rightleftarrows HgI_4^{2-} + O^{2-} \qquad (3)$$

A pE−pH diagram of the predominate species of insoluble Hg in equilibrium with a solution 0.1 M in total I and 0.001 M in total S was constructed (Figure 1) using the equilibrium relationships listed in Table 1. For each insoluble species, the solubility of Hg was determined as a function of pE and pH. A region in which Hg solubility was in excess of 0.01 M was identified and indicated in Figure 1; the predominant soluble species in this region is HgI_4^{2-}, owing to the large value of the stability constant for this complex.

Once solubilized, the Hg must migrate through the soil to be removed. The total flux of contaminant though the soil matrix is the sum of the fluxes due to hydraulic transport, diffusion, electromigration, and electroosmosis (*14*). The latter two fluxes are proportional to the electrical potential gradient through the soil and normally dominate in fine-grained soils. The efficiency of the electromigration, the
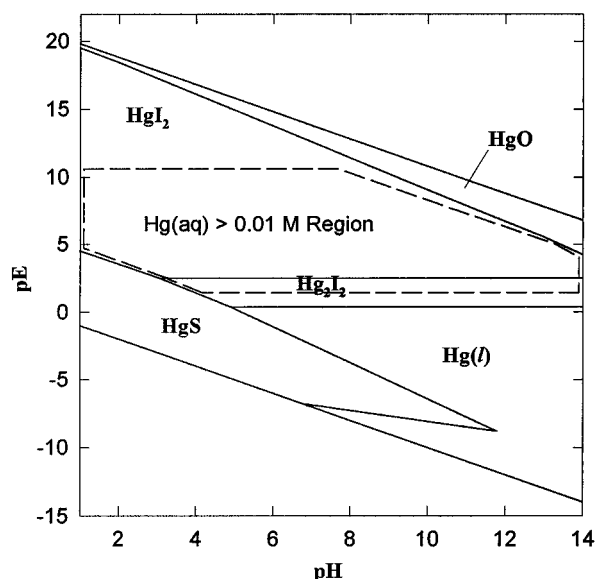
FIGURE 1. Stability diagram for Hg in the presence of 0.1 M total I and 0.001 M total S.

TABLE 1
Equilibrium Thermodynamic Equations Used in Figure 1

equation	log K	ref
$Hg^{2+} + I^- \rightleftharpoons HgI^+$	12.83	11
$Hg^{2+} + 2I^- \rightleftharpoons HgI_2^0$	24.07	11
$Hg^{2+} + 3I^- \rightleftharpoons HgI_3^-$	27.77	11
$Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$	29.79	11
$HS^- \rightleftharpoons S^{2-} + H^+$	−14	12
$H_2S \rightleftharpoons HS^- + H^+$	−7.1	12
$HgO + 2H^+ \rightleftharpoons Hg^{2+} + H_2O$	2.44	11
$HgI_2(c) \rightleftharpoons Hg^{2+} + 2I^-$	−28.62	11
$Hg_2I_2(c) \rightleftharpoons Hg_2^{2+} + 2I^-$	−2.22	11
$HgS \rightleftharpoons Hg^{2+} + S^{2-}$	−52.03	11
$I_2(aq) + 2e^- \rightleftharpoons 2I^-$	20.96	12
$I_3^- + 2e^- \rightleftharpoons 3I^-$	18.24	12
$IO_3^- + 6H^+ + 6e^- \rightleftharpoons I^- + 3H_2O$	−110.0	13
$HIO_3 + 5H^+ + 6e^- \rightleftharpoons I^- + 3H_2O$	−109.2	13
$Hg^{2+} + e^- \rightleftharpoons 1/2Hg_2^{2+}$	15.4	11
$SO_4^{2-} + 8H^+ + 8e^- \rightleftharpoons S^{2-} + 4H_2O$	20.74	11
$1/2Hg_2^{2+} + e^- \rightleftharpoons Hg(l)$	13.46	11

more significant of the two processes, is related to the transference number (t_i), defined as the fraction of the total current carried by ionic species i (1):

$$t_i = \frac{z_i \mu_i^* c_i}{\sum\limits_{1}^{j} z_j \mu_j^*} \qquad (4)$$

where z_i, c_i, and μ_i^* are the valance, concentration, and valence of the ions in solution. Electrokinetic remediation may be inefficient for ions with very low values of t_i, especially when transport by electroosmosis is negligible.

In this research, electrokinetic remediation using the I_2/I^- lixiviant was investigated. Iodide solution and I_2 crystals, introduced near the cathode, react to form I_3^- complex. Reduced forms of insoluble Hg can be oxidized by either I_2 or I_3^-; however, transport of oxidant through the soil is dependent on the electromigration of the I_3^- anion. The HgI_4^{2-} complex, formed via reaction with lixiviant solution, is removed from the soil by electromi-
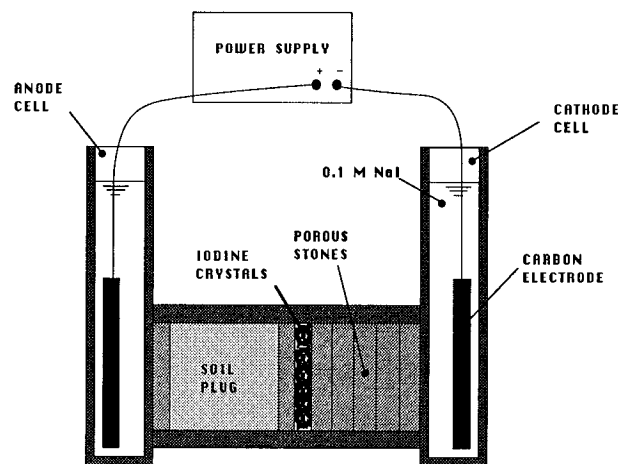

FIGURE 2. Electrokinetic cell.

gration toward the anode. The use of a lixiviant and electromigration of a metal as an anionic complex are unique aspects of this research.

Experimental Section

Most electrokinetic experiments were conducted using a laboratory-contaminated loam (LCL) soil containing about 4% soil organic matter. One experiment was conducted using a field-contaminated sandy-loam soil from East Fork Poplar Creek (EFPC) in Oak Ridge, TN, containing about 11% soil organic matter. The initial total Hg concentration in the EFPC soil was about 250 mg/kg. The presence of *m*-cinnabar and $Hg^0(l)$ were indicated by X-ray diffraction of the soil, but determination of Hg mineralogy by chemical means was inconclusive (15).

The electrokinetic cell used in the experiments is shown in Figure 2. The anode and cathode chambers were bolted together to hold the 6.35 cm i.d. soil tube in place. Carbon electrodes, each 12.7 cm × 12.7 cm, were connected to a dc power supply, capable of either constant-current or constant-voltage operation.

Soil samples were prepared by mixing 250 g of soil with 500 mL of deionized water to create a slurry. Laboratory contaminated soils were amended with 500 mg/kg HgS (cinnabar). The soil slurry was degassed under vacuum and poured into the soil tube of the electrokinetic cell. The bottom of the cell was capped with a porous stone lined with filter paper. After the additional degassing, the other end of the tube was capped using an additional filter paper-lined porous stone. The soil was consolidated using a soil consolidation apparatus over a 2-week period to a final length of 5.1 cm. Additional porous stones were added to the tube to occupy the space vacated by soil during consolidation. The final bulk density of the consolidated laboratory- and field-contaminated soils were 1.23 and 1.17 g cm^{-3}, respectively. After consolidation, the second innermost porous stone was replaced with an equal volume of I_2 crystals. The cathode and anode chambers were filled with 0.1 M NaI solution; in some experiments the anode chamber was filled with deionized water.

Potential gradient, current density, and the pH and pE of the fluid in the electrode chambers were monitored during each experiment. At the end of electrokinetic treatment, usually about 15 days, the soil core was sectioned into eight even increments. Each increment was mixed to ensure homogeneity and then split into separate subsamples A and B. Subsample A was dried for 24 h at 60 °C

TABLE 2

Summary of Electrokinetic Experiments

	experiment no.						
	1	2	3	4	5	6	7
duration (days)	7	29	15	15	15	16	14
total charge transferred (MC/m^2)	0.233	0.949	0.499	1.04	0.524	2.78	2.88
iodine crystals	no	no	yes	yes	yes	yes	yes
cathode solution	0.1 M NaI	0.1 M NaI	0.1 M NaI	0.1 M NaI	0.1 M NaI	0.1 M NaI	0.1 M NaI
anode solution	DI water	DI water	DI water	DI water	0.1 M NaI	0.1 M NaI	0.1 M NaI
constant current (mA/m^2)	380	380	380	760	380	NA	NA
constant voltage (V/cm)	NA	NA	NA	NA	NA	0.39	0.39
cathode drip solution	none	0.1 M NaI at pH 2	none	none	none	none	none
anode drip solution	none	none	none	none	0.1 M NaI	0.1 M NaI	0.1 M NaI
removal of Hg (%)	0	22	74	74	28	99	6
total Hg recovery (%)	109	78	46	43	82	67	96
range of calculated t_i	a	a	0.003−0.07	0.0008−0.05	0.01−0.05	0.0001−0.0002	0.0008−0.009

^{a}Data required for calculating t_i were not available.

and analyzed for total soil Hg. The soil moisture content was determined gravimetrically. Pore water, recovered by centrifugation of subsample B, was analyzed for pE, pH, Hg, I$_2$, and I$^-$. Measurements of pE and pH were made using Pt and glass combination electrodes, respectively.

The concentrations of I$^-$ and I$_2$ in pore water were determined by titration (16). The I$_2$ concentrations determined by the method and reported in the present work include both oxidizing species: I$_2$ and I$_3^-$. Mercury was determined in soil and pore water samples by digestion and subsequent cold-vapor atomic adsorption spectrophotometry (EPA-600 Method 245.5, 1982). The presence of iodine interferes with Hg analysis because of the strong complexes formed. The sensitivity of the cold-vapor technique allowed the samples to be diluted until iodine concentrations were below those that cause interference, about 1×10^{-5} M.

Results and Discussion

Electrokinetic experiments are summarized in Table 2. Two terms in Table 2 require definition. Hg removal is the fraction of the initial Hg measured in the soil after treatment. Hg recovery is the fraction of the initial Hg that could be measured in the soil, electrode chambers, and wash solutions at the end of the experiment. Soluble and insoluble Hg remaining in the soil core were easily recovered: Hg recovery was high when Hg removal was low. Mercury removed from the soil was more difficult to recover; a loss mechanism at the anode was suspected but could not be identified. Improved recovery of removed Hg occurred when a 0.1 M NaI anode-wash solution was used. Hg removal does not appear to be closely correlated with the total charge transferred during the experiment (Table 2), implying that chemical processes in addition to electrokinetic transport must contribute to the removal of Hg from the soil.

In experiments 1 and 2, an attempt was made to mobilize Hg using I$^-$ alone as the lixiviant; little mobilization of Hg was accomplished. The pH and pE distribution in untreated soil was determined by analyzing the pore water from a sacrificed soil core after contamination and consolidation. Values ranged from 6.1 to 7.3 for pH and from 7.5 to 8.9 for pE, well within the domain of high Hg solubility indicated in Figure 1. The poor solubilization of Hg observed may have been caused by slow oxidation kinetics under moderately oxidizing conditions. In experiment 2, an acid
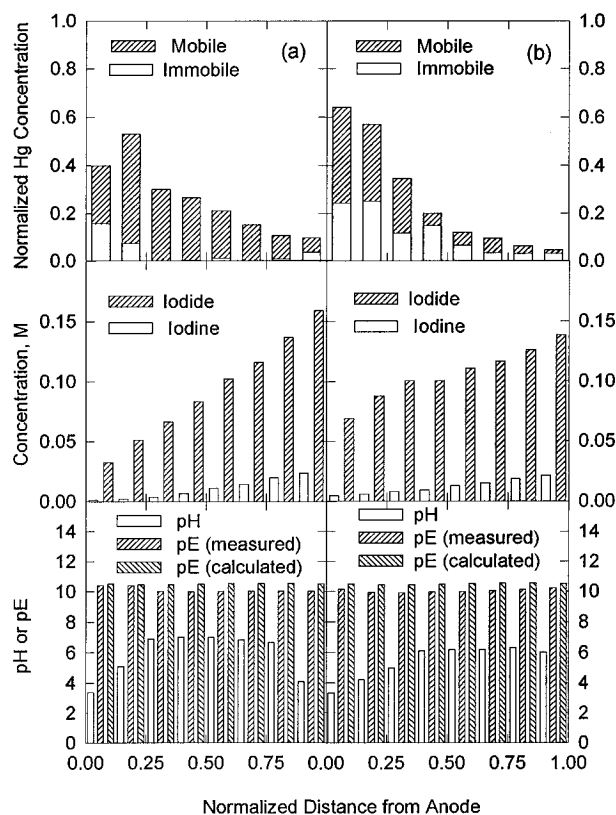

FIGURE 3. Distribution of mercury, iodine, and iodide and pH and pE in the LCL soil at the end of (a) experiment 3 (current density = 380 mA/m^2) and (b) experiment 4 (current density = 760 mA/m^2).

solution was dripped into the cathode in an attempt to complex sulfide released by the dissolution of HgS. Some mobilization of Hg occurred near the anode where oxidizing conditions prevailed, but none occurred in the remainder of the soil.

Experiment 3 represents a typical experiment in which a combination of I$^-$ and I$_2$ were used as the lixiviant. Mercury removal (74%) was dramatically greater than in systems using I$^-$ alone. At the end of the experiment, the distribution of mobile (Hg in pore water) and immobile (total Hg less Hg in pore water) Hg species, I$_2$, I$^-$, pH and pE, were measured (Figure 3). In Figure 3, the mass of Hg remaining in the pore water (mobile) and insoluble (immobile) are normalized to the total mass of Hg initially
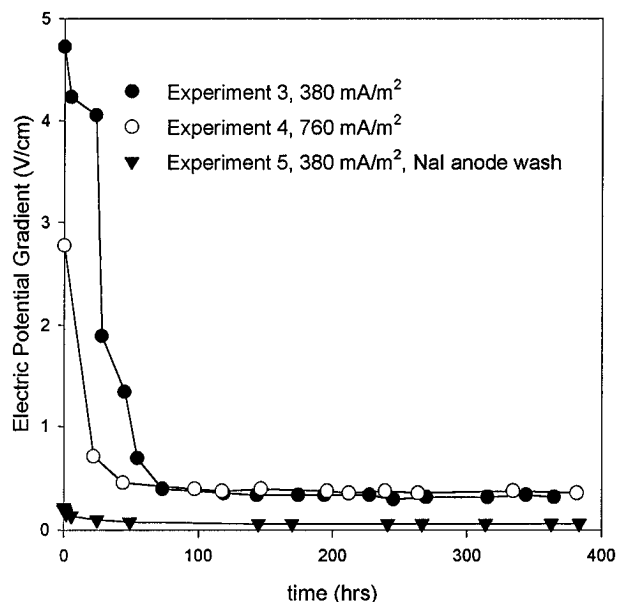
FIGURE 4. Variation of voltage gradient across the cell as a function of treatment duration for constant current density experiments.

present in the soil. Under the conditions of the experiment, it can be calculated that in excess of 90% of the mobile Hg would be speciated as HgI_4^{2-}. The improved performance of the process in the presence of I_2 can be attributed to oxidative dissolution of HgS. Iodine has migrated across the entire soil core (Figure 3); as a result, the pE has been increased to approximately 10, in agreement with that calculated from the I_2/I^- ratio using the Nernst equation (Figure 3). The pE and pH of the soil are within the domain of high Hg solubility in Figure 1. Mercury released by oxidation of HgS is complexed with I^-. The resulting HgI_4^{2-} complex is removed by migration toward the anode. Most of the Hg remaining in the soil core was found in the pore water, indicating that good solubilization of Hg had been achieved (Figure 3). Higher removal efficiencies are dependent upon improving the transport of solubilized Hg in the soil.

In experiment 4, the current was doubled in an attempt to increase the rate of transport through the soil; however, chemical profiles though the soil were remarkably similar to experiment 3 (Figure 3). The higher current enhanced transport of I^- and I_3^- into the soil and resulted in greater concentrations of these ions. As a result, the benefit of increased current was largely offset by a decrease in t_i for HgI_4^{2-} (values of t_i are tabulated in Table 2 assuming equal μ_j^* for I^- and HgI_4^{2-}). The relatively small values of t_i indicate that the process is inefficient with respect to electric current utilization; this is likely to hold true whenever a high ionic strength lixiviant is used. As treatment progresses values of t_i near the cathode will continue to decrease as the concentration of contaminant decreases and the concentration of lixiviant increases. A similar conclusion can be drawn by comparing the potential gradient across the cell as a function of time (Figure 4). In both experiment 3 and 4, the potential gradient decreased to a constant value of about 0.4 V/cm within the first 50−75 h of the experiment as the iodide migrated across the cell. Iodine migration and the concomitant decrease in potential gradient occurred slightly faster in experiment 4 because of the greater current density; however, during most of the two experiments the potential gradient and, hence, the electromigration flux were similar. Despite the low values
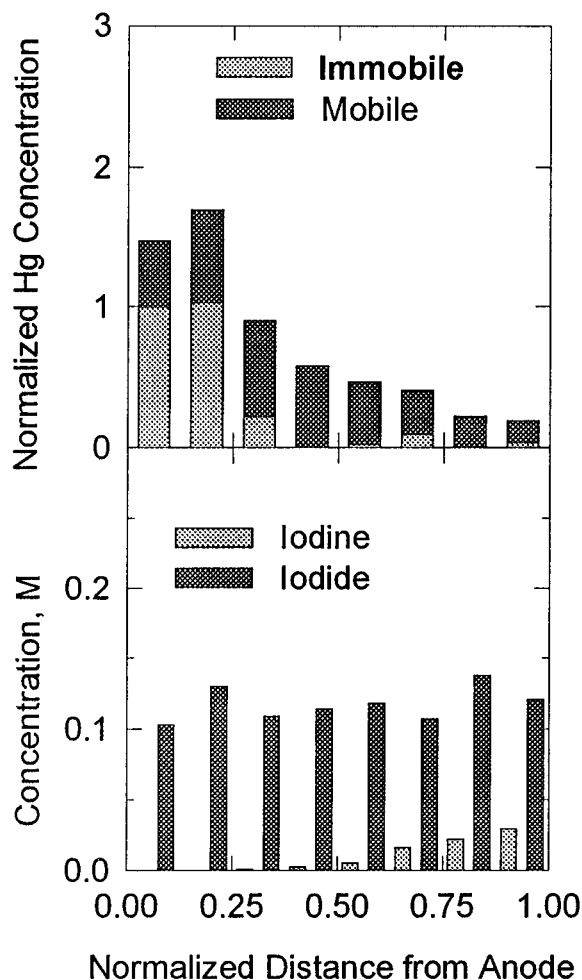

FIGURE 5. Mercury and iodine distributions in LCL soil at end of experiment 5 (current density =380 mA/m², anode washed with 0.1 M NaI solution).

of t_i, additional transport of solubilized Hg removal can be expected given a greater transfer of charge through the soil, as will be demonstrated in experiment 6.

A 0.1 M NaI anode rinse solution was employed in experiments 5−7. The purpose of the rinse was to lower the pE of the anode chamber near 10, via the oxidation of I^- to I_2, with the goal of increasing Hg recovery from the anode solution. Experiment 5 was conducted using the same constant-current density as used in experiments 1−3, 380 mA/m². However, the addition of NaI to the anode chamber significantly increased the conductivity of the cell, reducing the steady-state voltage gradient from about 0.39 V/cm in previous experiments to only 0.059 V/cm (Figure 4). As a result, electromigration of lixiviant into the cell decreased. At the end of the experiment, the lixiviant front had yet to penetrate to the two soil sections closest to the anode (Figure 5). The correspondence between I_2 distribution and HgS solubilization was excellent. Nearly all of the HgS was dissolved in the four soil sections closest to the cathode through which the lixiviant front had passed. In the following soil section at the lixiviant front boundary (third closest to the anode), some but not all of the Hg was dissolved. No dissolution of HgS had occurred in the two soil sections near the anode that the front had not yet reached.

Experiment 6 was identical to experiment 5 except that the cell was operated using a constant-voltage drop of 0.39 V/cm. Iodine fully penetrated the soil core, reaching a
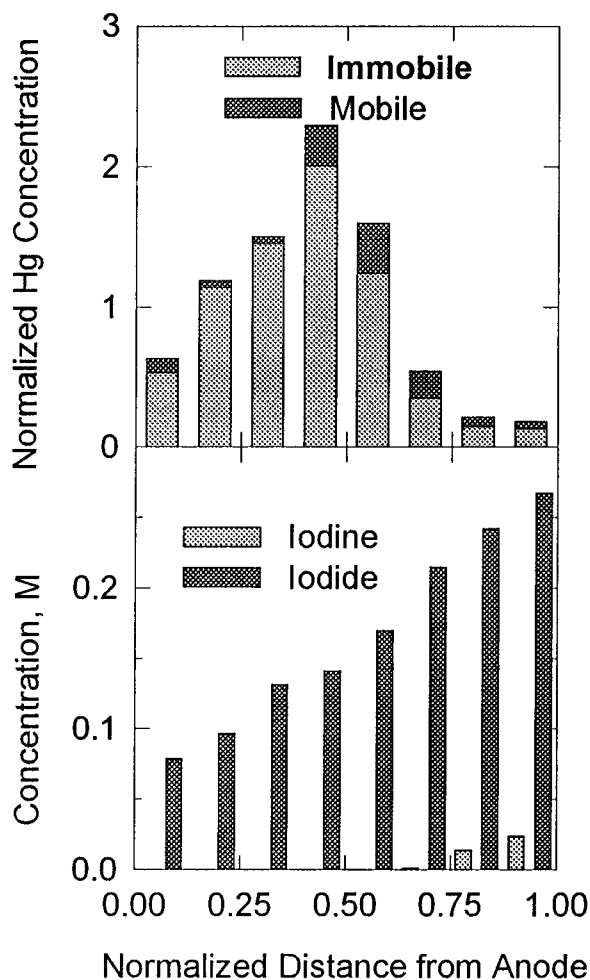
FIGURE 6. Mercury and iodine distributions in EFPC soil at end of experiment 7 (voltage gradient = 0.39 V/cm, anode washed with 0.1 M NaI solution).

FIGURE 7. Insoluble mercury concentration as a function of iodine (I_2) concentration.

concentration of 0.062 M in the section closest to the anode. Almost 99% of the Hg was removed from the soil, to a level of less than 10 mg/kg. About 85% of the remaining Hg was immobile. Of the Hg recovered during the experiment (67%), most was found in the anode-wash solution. In addition to enhancing the recovery of Hg, the NaI wash solution improved the transport of HgI_4^{2-} through the cell. In experiments 3 and 4, much of the voltage drop across the cell occurred in the anode chamber, initially filled with deionized water, instead of the soil. In experiments 5−7, most of the voltage drop can be attributed to the soil because of the high conductivity of the anode solution. As a result, the transfer of charge and hence the transport of solubilized Hg was much greater in experiment 6 than in any previous experiment, even though the potential gradient across the cell was similar. Removal of Hg across the entire soil sample is dependent upon both the effective solubilization of Hg and sufficient transfer of charge to effect the transport of the mobilized contaminant.

In experiment 7, an attempt was made to remove Hg from EFPC soil. Although the experiment was conducted under the same conditions as experiment 6, only 6% of the Hg was removed. The distribution of I^- and I_2 and mobile and immobile Hg are shown in Figure 6. The I_2/I^- lixiviant was observed to penetrate the three soil sections closest to the cathode; significant reductions in total and immobile Hg were achieved in this portion of the cell. Normalized
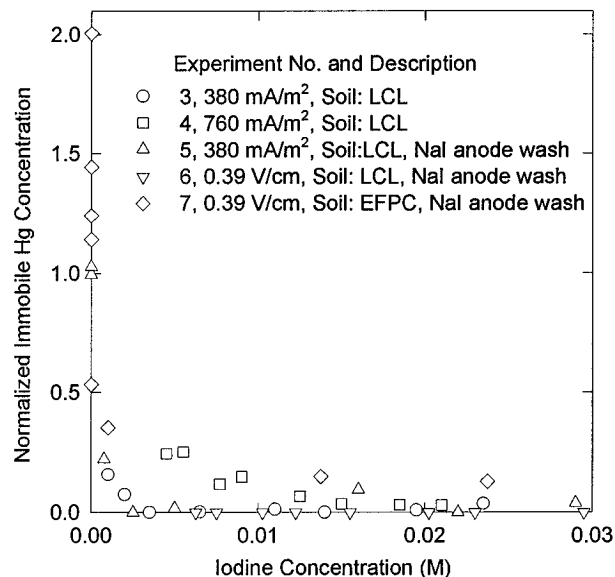
immobile Hg concentrations greater than 1 were observed in some soil sections, indicating that Hg mobilized from soil sections near the cathode became immobilized after migrating into soil sections closer to the anode. According to Figure 1, reprecipitation of Hg is thermodynamically infeasible under the pE and pH conditions measured in the pore water. Instead, the binding of Hg to soil organic matter is hypothesized, consistent with the high organic matter content of the EFPC soil. Hamilton (17) has shown that soil organic matter can effectively bind Hg in the presence of high iodide concentrations. In this case, ultimate removal of Hg may depend on the oxidation of organic matter by I_2 and I_3^-. The greater demand of EFPC soil for I_2 and I_3^- is evidenced by I^- concentrations greater than those observed in experiments with LCL soil. The concentration of I^- is affected by both transport of I^- and reduction of I_2 and I_3^-. The latter will result in greater iodide concentrations in more reduced soils for a given concentration of I_2. Some removal of Hg also occurred in the soil section closest to the anode. This can be attributed to the formation of I_2 at the anode via oxidation of I^-. This phenomena was not observed in experiment 5 because the anode chamber was flushed at a rate about 20 times greater, thereby flushing I_2 from the chamber before it could solubilize Hg. Electrokinetic remediation of EFPC soil may be infeasible because of its high demand for I_2, but may occur at acceptable rates in soils containing lower organic matter content.

The critical role of I_2 in the electrokinetic remediation of Hg is emphasized in Figure 7. In this figure, immobile Hg remaining in the soil is normalized to the total Hg initially present in the soil. Over 90% of Hg was solubilized in all soil sections with greater than 0.01 M I_2. In excess of 70% solubilization could be achieved with I_2 concentrations as low as 0.001 M. Insoluble Hg remaining in EFPC soil (experiment 7) is slightly greater than in laboratory soil (experiments 3−6), possibly due to the presence of auto-genic HgS crystals in grain pores and fissures inaccessible to the lixiviant. Although predominance area diagrams can indicate the thermodynamic conditions necessary to solubilize Hg, conditions resulting in rapid solubilization during remediation appear to be more specific.

Several limitations must be overcome before the process can be used to remediate sites. The soil preparation procedures used in this research result in fairly uniformly contaminated specimens. Field soils would be much more heterogeneous with respect to contaminant concentrations and flow uniformity. Even though the inventory of total Hg in the soil was reduced by 99% in experiment 6, residual pore water Hg was 8×10^{-6} M, far in excess the limit of 1×10^{-8} M allowed in hazardous waste regulations (40 CFR 261.24). Conceivably, soluble Hg in the pore water could be removed or reprecipitated by removing the lixiviant source from the cathode and effecting the removal of residual total iodine by electromigration. During treatment, concentrations of soluble Hg in the range of several hundred milligrams per liter are common and may pose unacceptable risks. From another perspective, this investigation has demonstrated that radical manipulation of the soil chemistry is required to mobilize reduced Hg in soils. It may be hypothesized that these compounds may remain stable for long periods of time even under moderate changes in soil chemistry. If so, mercury from soils contaminated with HgS may pose little risk to humans and the environment via aquatic pathways.

Acknowledgments

Literature Cited

(1) Acar, Y. B.; Alshawabkeh, A. N. *Environ. Sci. Technol.* **1993**, *27*, 2638.
(2) Hamed, J.; Acar, Y. B.; Gale, R. J. *J. Geotech. Eng.* **1991**, *117* (2), 241.
(3) Burell, C. J.; Segall, B. A.; Walsh, M. T. *J. Environ. Eng.* **1992**, *118* (1), 68.
(4) Shapiro, A. P.; Probstein, R. F. *Environ. Sci. Technol.* **1993**, *27*, 283.
(5) Pamukcu, S.; Wittle, J. K. *Environ. Prog.* **1992**, *11* (3), 241.
(6) Probstein, R. F.; Hicks, R. E. *Science* **1993**, *260*, 498.
(7) Hicks, R. E.; Tondorf, S. *Environ. Sci. Technol.* **1994**, *28*, 2203.
(8) Hem J. D. In *Mercury in the Environment*; USGS Paper 713; United States Geological Survey: Denver, CO, 1970; p 19.
(9) Bass-Becking, L. G. M.; Kaplan, I. R. Moore, D. *J. Geol.* **1960**, *68*, 243.
(10) Foust, D. F. U.S. Patent 5,226,545, 1994.
(11) Lindsay, W. L. *Chemical Equilibria in Soil*; Wiley-Interscience: New York, 1979.
(12) Snoeynink, V. L.; Jenkins, D. *Water Chemistry*; Wiley-Interscience: New York, 1980.
(13) Vanleugenhaghe, C.; Valensi, G.; Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*; Pourbaix, M., Ed.; Pergamon Press: New York, 1966; pp 614−626.
(14) Acar, Y. B.; Alshawabkeh, A. N.; Gale, R. J. *J. Waste Manage.* **1993**, *12* (3), 1410.
(15) Barnett, M. O.; Turner, R. R.; Harris, L. A; Henson, T. J.; Melton, R. C.; Stevenson, R. J. *Proceedings from the ACS Symposium Emerging Technologies in Hazardous Waste Management VI*; Atlanta, GA, Sep 19, 1994; American Chemical Society: Washington, DC, 1994; p 1292.
(16) Skoog, D. A.; West, D. M. *Fundamentals of Analytical Chemistry*, 2nd ed.; Holt, Rinehart, and Winston Inc.: New York, 1969.
(17) Hamilton, W. P. M.S. Thesis, University of Tennessee, Knoxville, TN, 1995.