

REMOVAL OF HAZARDOUS AND RADIOACTIVE METALS FROM SOIL USING ELECTROCHEMICAL MIGRATION

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ABSTRACT

Toxic or hazardous elements and ions can be removed from soil by the process of electromigration. Conventional methods also migrate and collect non-hazardous elements and ions, and remove water from the soil. A method has been developed to selectively migrate toxic or hazardous elements and ions without depleting the soil of natural non-hazardous mineral content and moisture. This process uses selective permeable membranes (anion or cation), selected "driver" ions, and control of chemical reactions in the collector electrode compartment. This paper describes the selective electromigration process for the removal of mercury and uranium from contaminated soils.

INTRODUCTION

Contamination of soil with heavy metals (e.g., Hg^{2+}), and ions containing heavy metals (e.g., CrO_4^{2-}) is a major problem within the United States. The problem is especially significant at US Department of Energy and US Department of Defense sites. In many cases, solutions containing heavy metals have been discharged as controlled releases to seepage basins (or cribs) for disposal to the soil column. During the time this discharge practice occurred, it was thought that the soil underlying the seepage basin would capture and confine these heavy metals, preventing migration and contamination of groundwater or aquifer sources. In some cases, heavy metals and/or solutions containing heavy metals were accidentally released in uncontrolled spills.

Recent environmental sampling data has confirmed that heavy metal contaminants in soil have resulted in contamination of groundwater and drinking water supplies. Groundwater and/or aquifer water treatment can reduce the levels of contamination to below US Environmental Protection Agency standards for Drinking Water, thus rendering the water safe for human consumption. However, the continued presence of the contaminant in the soil, provides a source of contamination to the water supply, thus requiring continued treatment. Additionally, should new wells or water removal points be installed, it could be possible for humans to consume untreated water. Even in the event that all water removed for human consumption is treated, the contamination could affect flora and fauna.

A variety of methods have been used to immobilize or remove contamination from soil. These include: chemical precipitation; soil washing; chemical extraction; installation of permeable barriers (e.g., coal, flyash, limestone, or activated carbon) to capture the contaminants that reach the barrier; capping; in-situ vitrification; and electrokinetic treatment. In all of the above examples except soil washing, chemical extraction, and electrokinetic treatment, the contaminant remains in the soil, and if soil conditions change (e.g., pH, moisture, etc.), the contaminant may be released to the groundwater or aquifer. In the case of in-situ vitrification, the contaminant remains in the soil, but the soil is vitrified to a glass product which prevents further contaminant release. The vitrified glass product remains in the soil, and can interfere with future land use.

Previous applications in electrokinetic treatment (i.e., electrochemical migration) used the flow of electric current to migrate positively charged ions to a cathode while simultaneously migrating negatively charged ions to an anode. During this process, water in the soil also migrated to the cathode (electroosmosis). The cations and anions would chemically react with the cathode or anode, respectively, forming a compound which could be collected and removed from the soil.

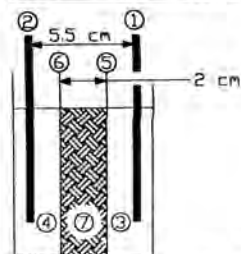
PROCESS DESCRIPTION

In the treatment of soils with the selective electrochemical migration process (patent pending), a cathode and anode are placed in the soil. The collector electrode (cathode for cations, or anode for anions) may be surrounded by a porous material to provide a liquid reservoir that is separated from the soil. The driving electrode (anode for cations, cathode for anions) is surrounded by a permeable membrane which passes only the ions of the same charge as the contaminant ions to be collected. The solution in the driver electrode compartment contains a solution which provides free driver ions (i.e., cations for cation collection, or anions for anion collection). The driver ions migrate through the permeable membrane carrying the electric current. The driver ions are selected such that as they enter the contaminated soil, they will displace the contaminant ions in the soil, with the contaminant ion migration carrying the electrical current. The contaminant ions are either recovered from the collector electrode solution (keeping the concentration low); or interact at the collector electrode to form a precipitate, amalgam, or to plate out on the electrode. The contaminants are then collected by either recirculation of the electrode solution (in the case of a precipitate formation or a dissolved ion) or by periodically removing and replacing the electrode (in the case that an amalgam forms or the contaminant plates out on the electrode).

The process is further described by the following examples.

Recovery of Mercury from Soil

A series of short test runs were performed using soil contaminated with mercury. Figure 1 depicts the test cell geometry for the runs cited in this example. Two of the runs were with hydrogen as the "driver" ion, and one was with



1. ANODE - PLATINUM
 2. CATHODE - COPPER
 3. ANOLYTE - 3M SODIUM FORMATE
 4. CATHOLYTE - WATER
 5. CATION SELECTIVE MEMBRANE
 6. NON SELECTIVE MEMBRANE
 7. SOIL - 85% CLAY
15% SAND
5% GRAVEL
- OVERALL MERCURY BURDEN = 17mg/g

Fig. 1. Schematic diagram of experimental configuration.

sodium as the "driver" ion. For these runs platinum was selected as an "inert" anode, and copper was selected as the cathode. Copper was selected on the basis that it forms an amalgam with mercury, has a relatively high overvoltage for hydrogen gas production, and would be environmentally acceptable.

Mercury saturated soil was produced for these runs, by contacting dry soil with a solution of mercuric chloride for 48 hours. The soil/solution mixture was stirred during the contact period. Following contact, the soil was filtered and washed with water. A sample of the soil was treated with 5N nitric acid and rinsed. This extraction was performed twice to ensure that all of the mercury was recovered from the soil sample. Analysis of the mercury in the washings and acid leaching from the soil sample proved that the mercury was physically or chemically bound to the soil and was not present as solution being interstitially contained.

In the case of the hydrogen runs, considerable effervescence in the soil compartment was observed. This is believed to be due to reactions with carbonates and other bases, resulting in off-gassing and temperature increases. Table I summarizes the operating parameters and test results obtained in each of these runs. These test runs highlighted the importance of catholyte chemistry. Under acidic conditions of the hydrogen "driver" runs, mercury in solution in the catholyte was deposited onto the cathode. At the completion of these runs, all the mercury was either in solution or on the cathode. The alkali conditions brought about by the sodium ions, however, resulted in deposition of the mercury on the cathode, followed by the formation of a dark precipitate.

This run showed the system to be very tolerant of the additional cation burden in the soil. The mercury continued to precipitate at the cathode and represented 30% of the precipitate by weight. This is a significant factor when waste management is considered. Previous experience with electrochemical systems suggests that optimization of the system towards increased current efficiency and selective waste product production is possible. It may, for example, be possible to use dilute sulfuric acid catholyte which will maintain most metal ions in solution, but allow the precipitation of mercury. Due to the concentration gradients produced for non-precipitating cations under these conditions, this technique could lead to increased migration of mercury (i.e., improved current efficiency), as well as increase the percentage of mercury in the precipitate (further reducing waste volume).

Recovery of Uranium from Soil

The selective electrochemical migration approach can be used to recover other contaminants also. Uranium contamination of soil at US Department of Energy sites is a major problem. Uranium is found in the soil primarily as uranium dioxide. Uranium dioxide is known to form carbonate com-

TABLE I

Summary of Mercury Migration Soil Study Results

	H ⁺ Run 1	H ⁺ Run 2	Na ⁺ Run 1
Time, hrs	1	3	5.6
Average Voltage	16	12	28.4
Average Amps	1.2	1.6	1.0
Cath. Plating			
Hg (mg)	1.63	9.23	1.4
Cath. Precipitating			
Hg (mg)	-	-	7
Cath. in Solution			
Hg (mg)	2.95	4.39	25
Migration of Hg to			
Cathode (mg hr ⁻¹)	4.58	4.54	5.96
Cath. Surface Area			
(cm ²)	70	70	200
F hr ⁻¹	0.045	0.0597	0.0359
F Total	0.045	0.179	0.2
Hg left on Soil (mg)	-	-	1289
Total Hg Migrated	-	-	2%
Current Efficiency	0.1%	0.076%	0.15%

An extended run of 72 hours was performed with sodium as the "driver" ion. The operating parameters and test results obtained are as provided in Table II.

TABLE II

Summary of Extended Mercury Migration Soil Test

	Na ⁺ Run 2
Time, hrs	72
Average Voltage	7.5
Average Amps	0.91
Cath. Plating	
Hg (mg)	18.3
Cath. Precipitating	
Hg (mg)	230
Cath. in Solution	
Hg (mg)	80
Migration of Hg to	
Cathode (mg hr ⁻¹)	4.5
Cath. Surface Area	
(cm ²)	76
F hr ⁻¹	0.0339
F Total	2.44
Hg left on Soil (mg)	1535
Total Hg Migrated	19%
Current Efficiency	0.125%

plexes which are anionic. The same selective approach as described above can be used in principle to recover uranium from soil.

In this application, carbonate ions would be migrated from the cathode, through an anion permeable membrane. The carbonate ions would migrate through the soil, carrying

the electric current, until they intercept a uranium dioxide molecule. The uranium dioxide and carbonate ion would combine forming the uranium carbonate complex, $UO_2(CO_3)_3^{4-}$. The uranium carbonate complex would then migrate to the anode, carrying the electrical current. The uranium carbonate complexes would be recovered from the anolyte solution by anion exchange. This would keep the concentration of uranium carbonate low in the anolyte, yet allow other anions to build up in concentration, eventually generating back-diffusion gradient of other anions, leaving only the uranium carbonate ions to migrate and carry the current.

The uranium carbonate complexes are recovered from the anion exchange column by elution in nitric acid. The nitric acid solution can be evaporated and recovered for continued use in resin regeneration, and the uranium recovered in the evaporator concentrates.

FIELD APPLICATION

The electrochemical migration process can be applied in the field by installing anodes and cathodes in the soil in a close pitched hexagonal array. This geometry provides a continuum of treatment "cells." Figure 2 depicts this arrangement.

Figure 3 depicts the anode and cathode configuration for recovering mercury from soils. The depth of electrode installation would be approximately 1 meter below the depth of contamination to be treated. The anodes and cathode compartments would be 10 to 15 cm in diameter, and would be located in a bore hole drilled for specifically for the placement of the electrode. The electrode spacing would vary based on soil chemistry. A nominal spacing would be approximately 3 meter centers. The catholyte solution would be continually recirculated to recover the mercury precipitate by filtration. Since the precipitate sloughs off the cathode, the cathode can continue in service without replacement or removal for long treatment periods.

COSTS

The cost of application will vary with the area to be treated, the depth of treatment, and the specific contaminant

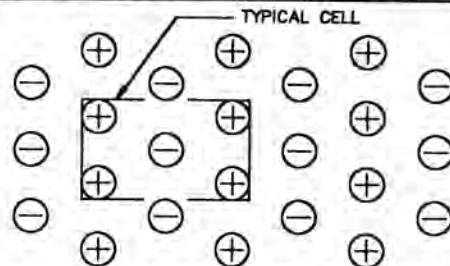


Fig. 2. Plan view - placement of electrodes in contaminated area.

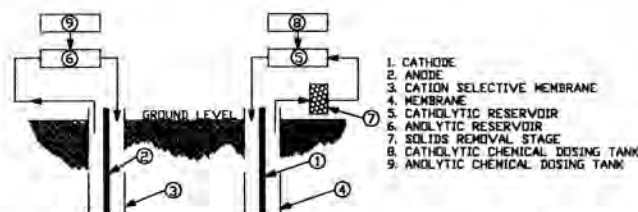


Fig. 3. Schematic diagram of the electrochemical migration removal process.

and concentration to be treated. For example purposes, we have evaluated the cost to treat an area 100 meters by 100 meters, 4 meters deep, contaminated with mercury at a level of 5 mg/kg to a level of < 1 mg/kg. Considering capital costs, operating directs, labor, and site clean-up; the treatment cost for this example would be in the range of \$200 to \$250 per cubic meter of soil.

CONCLUSIONS

Remediation of soils contaminated with heavy metals and radionuclides is a major activity facing the US DOE and the US EPA. In some cases, excavation of soil for ex-situ treatment is not feasible (e.g., under buildings which will not be demolished). Selective electrochemical migration provides a means to recover these contaminants in-situ, in a cost effective manner. The selective nature of the process minimizes wastes, which is also important when considering waste disposal and disposal costs.