COST AND PERFORMANCE REPORT

Electrokinetic Extraction at the Unlined Chromic Acid Pit
Sandia National Laboratories, New Mexico

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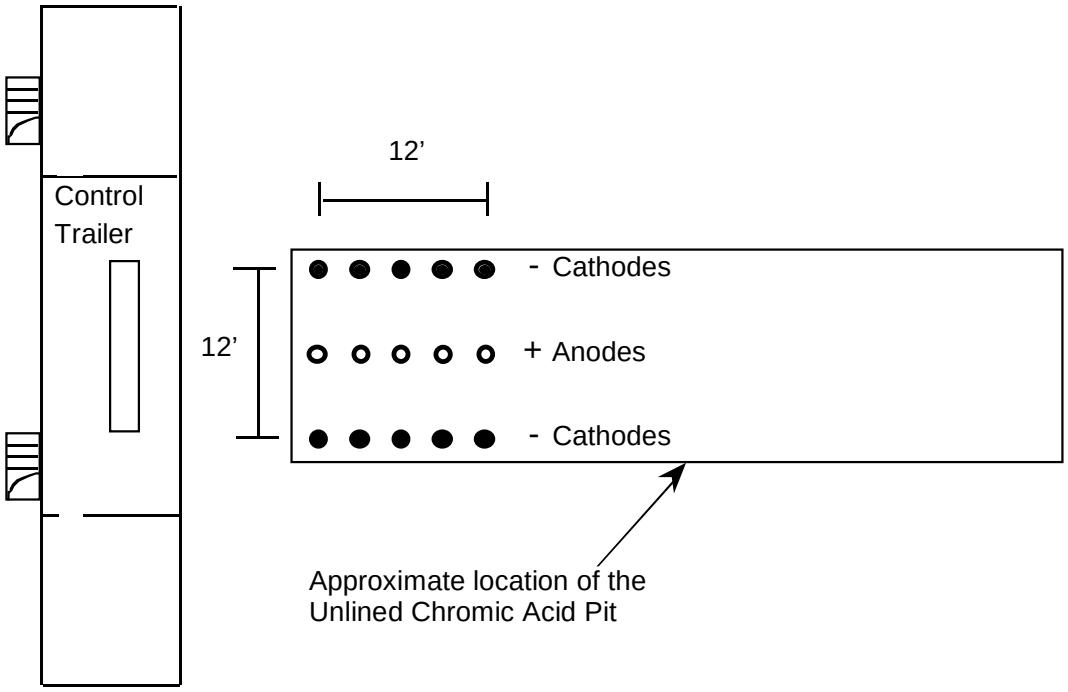
Background Information

SNL is located southeast of Albuquerque, New Mexico, in Bernalillo County within the boundaries of Kirtland Air Force Base. The Unlined Chromic Acid Pit is located in the Chemical Waste Landfill, which is located in Technical Area III. The chromium disposed of in the Unlined Chromic Acid Pit was in the form of chromic sulfuric acids. A chromium plume resides in the vadose (unsaturated) zone beneath the pit (Lingren, 1998). The most contaminated horizon beneath the pit contained chromium concentrations above 200 ppm (Figure 1), up to 10,000 ppm (U.S. EPA, 1995). Water soluble, anionic hexavalent chromium was targeted for *in situ* electrokinetic extraction.

A field demonstration of the *in situ* electrokinetic extraction technology was conducted at the Unlined Chromic Acid Pit from May 15 to November 24, 1996 (Lindgren et. al., 1998). The purpose of the field demonstration was to show that chromate could be extracted from unsaturated soils on a field scale without the addition of significant amounts of water (Lindgren, 1999b). The demonstration was funded by the U.S. Department of Energy's Office of Science and Technology through the Subsurface Contamination Focus Area. The *in situ* electrokinetic extraction technology was independently evaluated under the U.S. EPA's SITE Program. (A description of the SITE demonstration and results are contained in U.S. EPA's Superfund Innovative Technology Evaluation Demonstration Bulletin, "In situ Electrokinetic Extraction System, Sandia National Laboratories," EPA/540/MR-97/509, November 1997 (U.S. EPA, 1997). Two versions of this demonstration bulletin can be found on the web at http://www.epa.gov/ordntrnt/ORD/SITE/reports/ 509.html and http://www.epa.gov:80/ordntrnt/ORD/ SITE/reports/540_MR-97_509.pdf. The demonstration at SNL was the first electrokinetic extraction demonstration to successfully remove contaminant ions from arid soil at the field scale (Lindgren et. al., 1998).

The near surface geology at the Chemical Waste Landfill consists of alluvial fan deposits with some eolian deposits. Boring logs of soil beneath the Unlined Chromic Acid Pit indicates that the sediments consist of intercalated fine-to-coarse grained, well-sorted to poorly-sorted sands, gravels, and cobbles (Lindgren et. al., 1998). At the Chemical Waste Landfill, the water table is located approximately 485 feet below the land surface and, therefore, did not play a role in the *in situ*

(a) Plan View



(b) Cross Sectional View

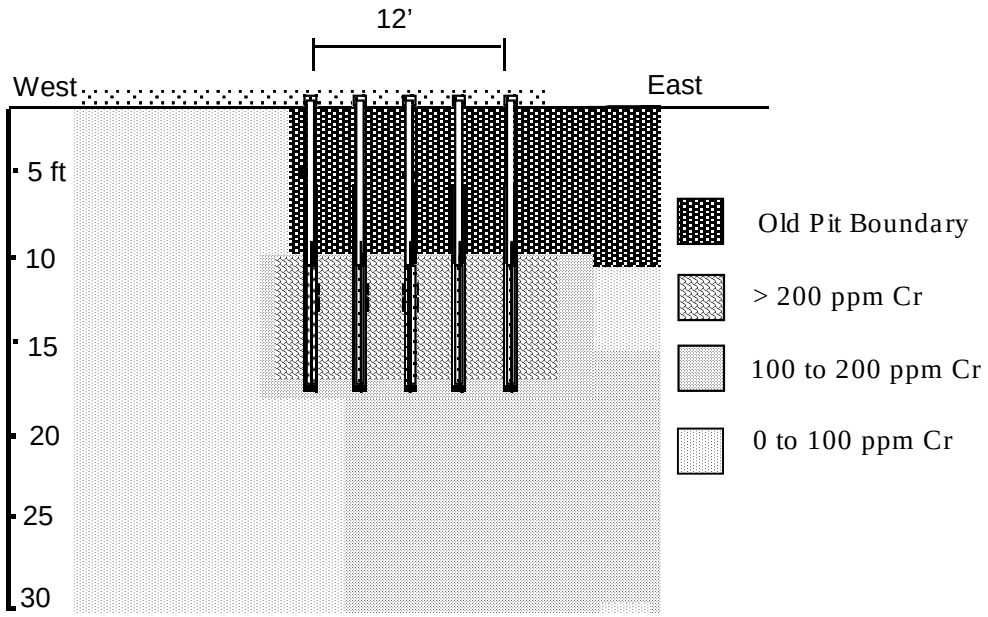


Figure 1. Layout of the Sandia National Laboratories field demonstration at the Unlined Chromic Acid Pit (modified from Lindgren, 1999b)

electrokinetic extraction demonstration. The vadose soils had a moisture content of about 10 weight percent (varied from 2 to 12 weight percent) (Lindgren et. al., 1998).

During late 1995 and 1996, investigations were conducted to determine the subsurface electrical conductivity, and soil samples were collected for chemicals and physical analyses. A high density, surface geophysical survey was conducted over the site to determine if any significant buried metal was located within the Unlined Chromic Acid Pit. The survey consisted of a magnetometer survey, an electromagnetic metal detection survey, and an electromagnetic ground conductivity survey. No metallic objects were detected in the area of interest (Lindgren et. al., 1998). A summary of the soil matrix characteristics beneath the Unlined Chromic Acid Pit are presented in Table 1.

Table 1. Characteristics of the Soil Matrix Beneath the Unlined Chromic Acid Pit

Parameter	Value
Soil type	Fine to medium-grained sands with a few pebbles
Soil conductivity	<10 mS/m
Extract conductivity	0.3 - 11 mS/cm
pH of extract	7.6 - 9.2
Moisture content	2 to 12wt%
Contaminant concentrations	25 (background) to 10,000 ppm chromium

Source: Lindgren et. al., 1998 and U.S. EPA, 1997

Technology Description and System Design

The electrokinetic extraction remediation system used at SNL is the only electrokinetic approach specifically designed to operate continuously in unsaturated soils. Pore water in the unsaturated zone is held under tension in the soil pores, which prevents the pore water from entering simple groundwater extraction wells as it does in the saturated zone.

SNL's patented electrode design (Lindgren and Mattson, 1995) removes contaminants from the soil without requiring the addition of significant amounts of water that could spread the contamination. The electrode system is constructed of a porous, ceramic outer casing and an inner, iridium-coated titanium electrode. The electrode system extracts contaminants by moving them into water held under

tension (i.e., under partial vacuum) inside the outer casing that surrounds the electrode, in effect, a large suction lysimeter. The lysimeter technology is used to create a continuum between the anode effluent (anolyte) and the pore water both hydraulically and electrically. The electrode fluid is held under tension inside the electrode by an applied vacuum to keep the fluid from saturating the adjacent soil. (U.S. EPA, 1997)

The layout of the field demonstration is shown in Figure 1 (see plan view). The demonstration targeted the most contaminated soils immediately below the floor of the former pit at a horizon 8 to 14 feet below the surface (see Figure 1, cross-sectional view). Three rows of electrodes were placed in a 12-foot by 12-foot area. The center row was five anodes and the outer two rows were each five cathodes. The electrodes were spaced at approximately 3 foot increments within a row, and the rows were spaced approximately 6 feet apart (Lindgren et. al., 1998). Additional electrodes were deployed across the site to be used either as active "bare" electrodes to increase the voltage gradient or as "cold fingers" to function as heat sinks to remove excessive heat from the soil. (Lindgren et. al., 1998)

The system used in the field demonstration included an extraction system and four main operational units — a liquid control system, a vacuum control system, a power application system, and a monitoring system — as well as ancillary equipment.

The patented electrokinetic extraction electrodes allowed the transfer of contaminant ions from water contained in the soil pores to liquid contained in the electrode casing. The fluid between the inner drive electrode and the ceramic casing was continuously circulated out of the electrode casing (U.S. EPA, 1997). The pH of the anode electrode solution was maintained at about 8.8 using a sodium hydroxide solution, and the pH of the cathode electrode solution was maintained at about 5.5 using acetic acid (Lindgren et. al., 1998). In order to maintain a constant temperature in the electrodes, a heat exchanger, cooled by chilled water, was used to extract heat from the recirculating fluid of each electrode (Lindgren et al., 1998).

A vacuum applied to the interior of the anode electrode casing created the pressure gradient necessary to hydraulically control water movement between the anode casing and the soil. Hydrogen gas, produced by electrolysis reactions of applying direct current, was purged from the cathode casings to mitigate the explosion hazard (Lindgren et al., 1998).

A voltage potential was applied between electrodes, and the current applied to each electrode was monitored and limited to 15 amperes (U.S. EPA, 1997). Over time, the contaminant concentration built up in the electrode casing liquid, and a small amount of solution was periodically diverted to a waste barrel (Lindgren, 1999b).

The monitoring system recorded water control system information such as anode casing water level, recycle flow rate, influent and effluent rates, recycle flow temperature, conductivity, and pH. The monitoring systems also recorded air purge rates, vacuum in the anodes, and ancillary equipment information such as soil temperature and voltage profiles of subsurface soil. Anolyte samples were collected daily during the system's operation (U.S. EPA, 1997).

A summary of the design and operating parameters used during the demonstration are shown in Table 2.

Table 2. Design and Operating Parameters for SNL's Field Demonstration

Parameter	Value
Total treatment area	144 ft^2
Treatment depth	Soil zone 8 to 14 ft below ground surface
Distance between central row of anodes and either row of cathodes	6 ft
Total treatment period	2700 hours
Total energy applied	1572 kW/hrs
pH of solution at anode	8.8 (maintained using sodium hydroxide solution)
pH of solution at cathode	5.5 (maintained using acetic acid)
Electricity applied to each electrode	$\leq$ 15 amperes

Source: Lindgren et. al., 1998 and U.S. EPA, 1997

Technology Performance

During the demonstration, 13 tests were performed. The first 12 tests examined different operating parameters and energized electrode geometrics to determine the system's preferred operating conditions and to facilitate the migration of hexavalent chromium toward the central portion of the test area. Test 13 consisted of system performance testing (U.S. EPA, 1997).

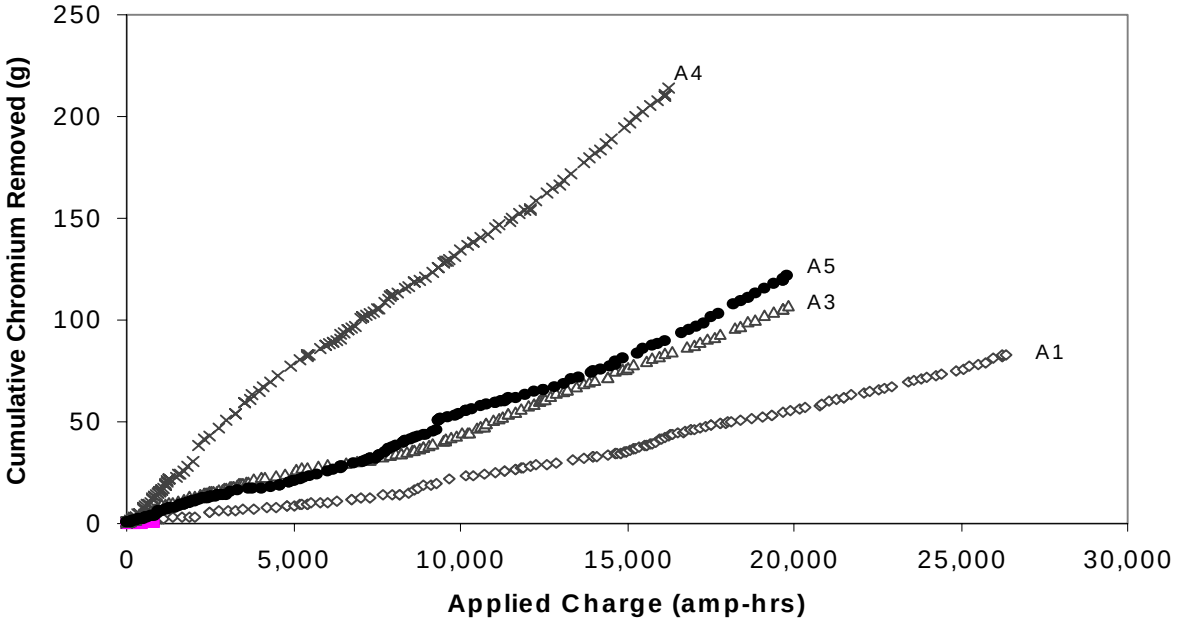


Figure 2. Cumulative chromium removal as a function of applied charge per anode (modified from Lindgren, 1999b)

The demonstration was operated for 6 1/2 months (from May 15 to November 24, 1996) (Lindgren et. al., 1998). After the 13 tests had been completed, a total of approximately 600 grams of hexavalent chromium were removed from the soil after 2700 hours of operation (i.e., 0.22 g per hour). At the system's preferred operating conditions during Test 13, approximately 200 grams of hexavalent chromium were removed during 700 hours of operation (0.29 g per hour), and the overall removal efficiency for the system was approximately 0.13 g of hexavalent chromium per kilowatt hour (Lindgren et. al., 1998). During the demonstration, chromium extraction efficiencies (grams of hexavalent chromium removed per ampere hour) at the anodes did not deteriorate, indicating that the electrokinetic process is stable over long periods of time (see Figure 2). (The operation of anode A2 was terminated early in the demonstration because of low extraction efficiency.) (Lindgren, 1999b)

Prior to conducting the demonstration, soil samples taken in the area of the cathodes had toxicity characteristic leaching procedure (TCLP) extract chromium concentrations as high as 28 mg/L. Soil samples collected in the remediation zone after the demonstration indicated that chromate had migrated

from the cathodes to the anodes. Soil samples adjacent to the cathodes had TCLP chromium concentrations of less than 5 mg/L, indicating that if the soil was excavated, it would not be considered hazardous waste. No significant changes in chromium concentrations were noted outside of the remediation zone. By design, the demonstration was terminated prior to complete cleanup of the soil. It is expected that all of the soil in the remediation area could have passed TCLP criteria if the remediation had run to completion (Lindgren, 1999b). The performance of SNL's system is summarized in Table 3.

Table 3. Summary of Performance for SNL's Field Demonstration

Parameter	Value
Total mass of contaminant removed	600 g hexavalent chromium
Rate of contaminant removal	0.22 g hexavalent chromium removed per hour
Pre-demonstration contaminant concentrations in soil at cathodes	402 ppm; maximum of 28 mg/L chromium (TCLP extract)
Post-demonstration contaminant concentrations in soil at cathodes	72 ppm; < 5 mg/L chromium (TCLP extract)

Source: Lindgren et. al, 1998

The SNL electrokinetic remediation demonstration successfully removed chromate contamination from unsaturated soil without the need to increase the soil moisture content. Prior to being placed in the ground, the anode casings were treated with a coating that mitigated the water loss to the soil through electro-osmosis. Water mass-balance calculations indicated that only a net of approximately 21 gallons (79 liters) of water was added to the soil during the electrokinetic demonstration. However, three times that amount of water was transported in the soil-water system from the anodes to the cathodes due to electro-osmosis. No significant changes in the soil moisture content profiles were noted when compared to the pre-demonstration values. In addition, no significant changes in electrical conductivity and only minor changes in soil pH were noted during the demonstration (Lindgren et. al, 1998).

According to SNL, this method could also be used for extracting other important soluble anionic heavy metals such as chromate ($Cr_4O^{=}$), molybdenate ($MoO_4^{=}$), selenate ($SeO_4^{=}$), perchlorate (ClO_4^{-}), and radionuclides such as iodide ($^{129}I^{-}$), and pertechnetate ($^{99}TcO_4^{-}$). (Lindgren, 1999b)

Technology Cost

The total amount of energy applied during the demonstration was 7253 kW-hrs (Lindgren et. al, 1998). No cost information was presented in the literature or was provided by SNL.

Summary of Observations and Lessons Learned

During the field demonstration at SNL's Unlined Chromic Acid Pit, application of increased power resulted in higher Cr removal rates; however, the electrical cost per mass of chromium removed increased (Lindgren et. al, 1998). Also, attempts to speed the chromate extraction by increasing the power density led to soil heating problems, even when the electrode solution was actively cooled. During the demontration, soil temperatures ranged from 15°C to 48°C (Lindgren et. al, 1998). Excess soil heating can cause several negative effects on the electrokinetic extraction process:

- Electrical currents could concentrate in certain areas of the soil profile, bypassing other contaminated soil zones.
- Soil pore water could be either diminished by thermally-induced gradients or evaporated from the soil zone, which would effectively stop the electrokinetic process.
- Indigenous biological organisms could be killed.
- An increase in organic vapor pressures could significantly increase concentrations of VOCs in the soil gas.

While not all of these effects were observed during the electrokinetic extraction demonstration at SNL, it is reasonable to assume that they were taking place to some extent. When the system was operated at lower power densities, soil-heating problems were alleviated. (Lindgren, 1999b)

Soil gas concentrations in the electrokinetic remediation area increased slightly likely due to an increase of the soil temperature. However, no significant concentrations of VOCs were noted in the cathode effluent or in the cathode vacuum exhaust. (Lindgren et. al, 1998)

The copper cold fingers installed as backup electrodes were thought to be safe from electrical oxidation due to their small diameter and the fact that they were placed parallel to the voltage gradient.

However, high copper concentrations were detected in the cathodes during the first phase of testing. The source of copper was confirmed to be the cold fingers attached to the cathode casings; they corroded due to the high voltage gradient near the cathodes. (Lindgren et. al, 1998)

While SNL's electrokinetic extraction system was successful in removing an anionic contaminant (i.e., chromate) from unsaturated sandy soil, SNL noted that the electrode system was a research prototype and was not specifically engineered for commercialization. The system developers (Dr. Eric Lindgren and Earl Mattson, SNL) suggest that the system be re-designed before large-scale use (Lindgren, 1999b).

After the 1996 field demonstration, SNL began developing a passive system, where the system is operated at a lower power, thereby avoiding the expense of actively cooling the electrokinetic electrode system. The new system uses a solid matrix capture system, eliminating the need for the liquid control and vacuum systems.

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References

Lindgren, E.R., and E.D. Mattson, 1995. "Electrokinetic System for Extraction of Soil Contaminants from Unsaturated Soils," United States Patent # 5,435,895, July 25.

Lindgren, Eric R., 1999b. E-mail from Eric Lindgren, Sandia National Laboratories, to Kate Mikaulka, Science Applications International Corporation, Case History of Demonstration at Unlined Chromic Acid Pit, August 16.

Lindgren, Eric R., 1999a. E-mail from Eric Lindgren, Sandia National Laboratories, to Kate Mikaulka, Science Appliations International Corporation, Description of New Passive Electrode System, August 16.

Lindgren, Dr. Eric R., Matthew G. Hankins, Earl D. Mattson, and Patricia M. Duda, 1998. *Electrokinetic Demonstration at the Unlined Chromic Acid Pit*, Sandia Report SAND97–2592, January.

U.S. Environmental Protection Agency (EPA), Superfund Demonstration Bulletin, 1997. "In situ Electrokinetic Extraction System, Sandia National Laboratories," EPA/540/MR-97/509, November (as contained in http://www.epa.gov/ordntrnt/ORD/SITE/reports/509.html or http://www.epa.gov:80/ordntrnt/ORD/SITE/reports/540_MR-97_509.pdf.).