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## **Electrokinetic Extraction of Chromate from Unsaturated Soils\***

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### INTRODUCTION

Heavy-metal contamination of soil and groundwater is a widespread problem in industrial nations. Remediation by excavation of such sites may not be cost effective or politically acceptable. Electrokinetic remediation is one possible remediation technique for in situ removal of such contaminants from unsaturated soils. Previous papers discussing the work performed by researchers at Sandia National Laboratories (SNL) and Sat-Unsat, Inc. (SUI) (Lindgren et al., 1991, 1992, 1993) focused on the transport of contaminants and dyes by electrokinetics in unsaturated soils. These experiments were conducted with graphite electrodes with no extraction system. As the contaminants migrated through the soil, they increased in concentration at the electrode creating a diffusion flux in the opposite direction. This paper discusses a technique to remove the contaminants from unsaturated soils once they have reached an electrode.

### BACKGROUND

To conduct electrokinetic remediation, electrodes are implanted into the ground and a direct current is imposed between the electrodes. The application of direct current leads to two effects; ionic species in the soil-water solution will migrate to the oppositely charged electrode (electromigration), and accompanying this migration, a bulk flow of soil-water is induced toward the cathode (electroosmosis) (Hunter, 1981). The combination of these two phenomena leads to a movement of contaminant ions towards one or the other electrodes.

Contaminants arriving at an electrode may potentially be removed from the soil/water by one of several methods; electroplating or adsorption onto an electrode, precipitation or co-precipitation at the electrode (with possible excavation), pumping the water near the electrode, or complexing with ion-exchange resins that are coated on the electrode. Most of the above methods are designed to operate in the saturated zone. Pumping water from a well that contains an electrode appears to be the most common electrokinetic extraction method. However, unlike groundwater in saturated soil, pore water in the vadose zone is held under tension in the soil pores (Hillel, 1980). This tension prevents the pore water in the vadose zone from flowing into extraction wells as it does in the saturated zone. Therefore, effluent extraction techniques at an electrode proposed for saturated methods will not work in the vadose zone.

### ELECTRODE DESIGN

Our proposed electrokinetic extraction method employs the use of a porous ceramic cup similar to that used by Shmakin (1985) for mining exploration. However, unlike the open porous cup design, our technique uses a vacuum applied to the interior of the electrode as is done in a suction lysimeter. A suction lysimeter is a device that uses a porous material that exhibits a high bubbling pressure to extract pore water samples from the vadose zone. To collect a pore water sample, a vacuum is applied to the inside of the lysimeter. Depending on the magnitude of the applied vacuum and the tension of the porewater in the vadose zone

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about the lysimeter, the resultant pressure gradient across the porous material will either cause water to hydraulically flow into the lysimeter or to leave it. Therefore, the use of suction lysimeter technology offers a technique to control the addition and extraction of water in the vadose zone. The lysimeter design can operate at any depth and minimizes the chance of uncontrolled mobilization of contaminants that may occur with surface flooding and vadose zone well infiltration methods.

Combining electrokinetic processes with soil water sampling lysimeter technology is possible by placing an electrode inside the lysimeter. Figure 1 illustrates our design of a vadose zone lysimeter electrode. The bottom portion of the electrode is constructed of porous ceramic whereas the upper portion of the electrode is constructed of an impermeable material. The fluid between the graphite electrode and the ceramic casing is continuously purged to mitigate electrolysis reactions, sweep off gas bubbles from the electrode due to water hydrolysis, remove contaminants that enter the electrode, and to introduce desirable ions and/or surfactants to the unsaturated soil. Solution extracted from the electrode lysimeter can be treated at the ground surface.

One problem to overcome when applying electrokinetic remediation to the vadose zone is the drying of the soil near the anode. When an electric current is applied to the soil between the electrodes, water will flow by electroosmosis in the soil pores, usually towards the cathode. The movement of this water will cause a depletion of soil moisture adjacent to the anode and a collection of moisture near the cathode. In SNL electrokinetic experiments conducted in a closed system (ie. no water addition or extraction) the soil near the anode dried out enough to stop the conduction of electricity (Mattson & Lindgren, unpublished work). Our electrode design allows water to enter the soil at the anode to replenish the electroosmotic water, allowing continuation of the remediation process for an indefinite period. Such electrode systems have been designed for both laboratory and field applications.

A second difficulty of combining an electrode in a lysimeter is the production of hydrogen and hydroxide ions at the electrodes due to electrolysis of the water. These reactions can be neutralized by adding the appropriate acid or base, or left to build up high concentrations of hydrogen and hydroxide ions that will migrate into the soil matrix. Some researchers wish to exploit the production of hydrogen ions at the anode and propagate these ions across the soil media to strip heavy metals from the soil surfaces. Research by Acar et al. (1989) have shown encouraging results, where as other research has illustrated precipitation of metal hydroxide problems occurring near the cathode and complexation changing the net charge on the ion (Runnells and Wahli, 1993).

Due to some of the potential problems associated with pH effects (as discussed above), and the alkaline nature of the soils in the southwestern United States, our approach is to neutralize the electrolysis reactions and replace the hydrogen and hydroxide ions with other ions. Care must be taken in choosing the replacement ions such that precipitates are not formed or the replacement ions do not react with the soil, thus changing its physical properties.

#### EXPERIMENTAL DESIGN

The above described electrode system was tested in the laboratory to demonstrate its ability to transport and remove chromium from unsaturated soils. The experimental setup consisted of rectangular acrylic cells having internal dimensions of 3/4 x 6 x 10 inches. The cell was packed with native soil where particles greater than 16 mesh were removed. The soil was chemically equilibrated with a simulated groundwater solution (0.005 M CaCl<sub>2</sub>) prior to packing.

Two experiments were conducted to test the new electrode design. The first experiment had an approximately 2 cm strip of soil contaminated with a chromate solution placed midway between the electrodes. The second experiment was a fully contaminated experiment, where a chromate solution was added to the soil everywhere between the electrodes.

In the contaminated strip experiment, the electrodes were emplaced at each end of the cell and a vacuum was applied to the electrodes to desaturate the soil. No current was applied to the cell during this portion of the experiment. After the soil moisture came into equilibrium with the applied vacuum, a strip of soil was removed between the electrodes, microwaved dried, and contaminated with 20 ml of 1000 ppm potassium chromate solution to match the microwaved determined moisture content. This contaminated soil (119 ug Cr/g soil) was then repacked into the cell as seen in Figure 2. A constant current of 10 mA was then applied to the electrodes. The electrode reactions were neutralized with a phosphate buffer solution. Effluent from both electrodes was collected for a period of 7.8 days and analyzed for chromium by emission spectrometry. At the end of the experiment, the soil was sectioned and chemically analyzed for water soluble chromium.

The fully contaminated experiment was conducted much like the above described experiment except the soil was totally contaminated with the potassium chromate solution at a concentration of 81 ug/g soil prior to packing, Figure 3. The applied vacuum was adjusted to be in equilibrium with the soil moisture. The electrode reactions in this fully contaminated experiment were neutralized with HCl and NaOH. This experiment was operated for almost 14 days before termination. The soil was sectioned and analyzed by emission spectrometry for both water extractable chromium and acid extractable chromium.

## RESULTS

In the contaminated strip experiment, over 88 percent (17.64 mg) of the initial 20 mg chromium was recovered in the anode effluent, Figure 4. The chromium was in its anionic form as chromate ( $\text{CrO}_4^{=}$ ) and was transported to the anode by electromigration. The chromate migration rate was greater than the electroosmotic flow rate that was in the opposite direction. The electromigration transport hypothesis is supported by no detection of chromium in the cathode.

As seen by the slope of the cumulative collection of the chromium versus time in Figure 4, chromium was not detected in the anode effluent until approximately 20 hours into the test. The bulk of the chromium arrived between 20 and 100 hours. After 100 hours, only a small amount of chromium was detected in the effluent at a fairly constant rate.

Destructive sampling of the soil in the test cell and subsequent water extraction of these soil samples, recovered an additional 2.5% of the applied chromium. This remaining water soluble chromium in the soil was found to be located adjacent to the anode at concentrations less than 0.22 ug Cr/gm soil, Figure 5. It is hypothesized that this remaining chromium would have entered the anode and been extracted if the system continued to be operated for a slightly longer period of time. Little chromium was detected in the initially contaminated soil strip or towards the cathode portion of the cell.

Cumulative extraction of the chromate from the anode versus time is illustrated in Figure 6 for the fully contaminated experiment. There appears to be no apparent delay in the extraction as expected. The shape of the curve indicates a fairly uniform extraction rate for the first 3 days, with decreasing extraction rate for the remainder of the experiment.

The soil in the cell was destructively sampled into 30 sections as seen in Figure 7. The water extractable chromium ( $\text{CrO}_2^{=}$ ) was able to account for an additional 6.1% with the highest concentrations being located near the anode. Acid extracted soil samples that were analyzed for total chromium ( $\text{CrO}_2^{=}$  and  $\text{Cr}^{3+}$ ), Figure 8, exhibit a similar relative concentration profile as the water extracted soils but shown higher concentrations. The acid extracted soils accounted for 15.9% of the applied chromium.

It is inconclusive whether the chromium remaining in the electrokinetic cell is in its trivalent form ( $\text{Cr}^{3+}$ ) or if the chromium is still in its anionic form ( $\text{CrO}_2^{=}$ ). Experimental conditions and electrode extraction results support the anionic form of chromium, but the greater concentrations obtained in the acid extracted soil analyses compared to the water extracted analyses suggest a change of some of the chromium to the trivalent form.

The conditions of the electrokinetic experiment were set so that it was unlikely that the chromium would have been reduced to its trivalent state. Ferguson and Nelson (1986) stated that anionic chromium is stable in oxidizing environments with near neutral to alkaline Ph values. Since the electrode reactions were neutralized and the soil has a high buffering capacity, the Ph in the electrokinetic cell was such that no portion of the cell should have ever gotten below 6. In addition, the soil contains little reducing species such as  $\text{Fe}^{2+}$  or organic matter. The high pH and small reducing potential of this experiment imply that the chromium should be in its anionic state.

If the chromium had changed valences to its trivalent state, it would have migrated towards the cathode and possibly been detected in the cathode effluent. No chromium was detected in the cathode effluent, however trivalent chromium may have sorbed on the soil prior to reaching the cathode. The distribution of chromium in the electrokinetic cell after treatment (Figure 8) was such that near the cathode, less than 5% ( $\{<4\mu\text{g/g}\}/\{81\mu\text{g/g}\}$ ) of the initial concentration remained.

The new electrodes allowed for analysis of the chromium breakthrough curves in both experiments. These analyses were performed to calculate time to extract the center of mass of the chromium. Using these times and the initial location of the center of mass, the linear migration velocity was calculated for both experiments. Surprisingly, the linear migration velocity of the chromium for both experiments was nearly identical ( $7.3 \times 10^{-7}$  m/s for the contaminated strip experiment and  $6.6 \times 10^{-7}$  m/s for the fully contaminated experiment) even though the final moisture contents of the two experiments were 15.7 and 12.8% (by weight) respectively.

#### SUMMARY

Uncontrolled water release to the vadose zone, long term operation, and Ph conditioning of the electrode reactions were the major difficulties to overcome when designing an electrode system to extract contaminants from unsaturated soils. We developed a new unsaturated soil electrokinetic electrode system that incorporates soil physics technology and demonstrated it to be effective for removing chromium at the anode in unsaturated soils.

Laboratory bench scale experiments illustrated that a majority of the chromate can be extracted (88 and 78%) in a relatively short period of time with additional removal of chromium likely if the experiments were conducted for a longer period of time. Subsequent, destructive sampling of the soil in the cell revealed little recovery of water soluble chromium in the cell. The remaining water soluble chromium was at higher concentrations at the anode with lower to zero concentrations located near the cathode. Extraction of soil samples with nitric acid enabled a greater recovery of the remaining chromium, however these results are inconclusive concerning the valence of the remaining chromium.

The new electrode design also allows for analysis of the contaminant breakthrough curve. These analyses can be used to determine the linear electromigration velocity, and assist in determining when the experiment should be terminated.

These results are preliminary, additional tests of the electrode extraction system are being conducted to evaluate the use of different electrode neutralization solutions on the removal efficiency. Moisture content distribution, chromium valence, and electroosmosis rates are also being studied in these tests. Pilot scale electrodes have been build and are currently being tested.

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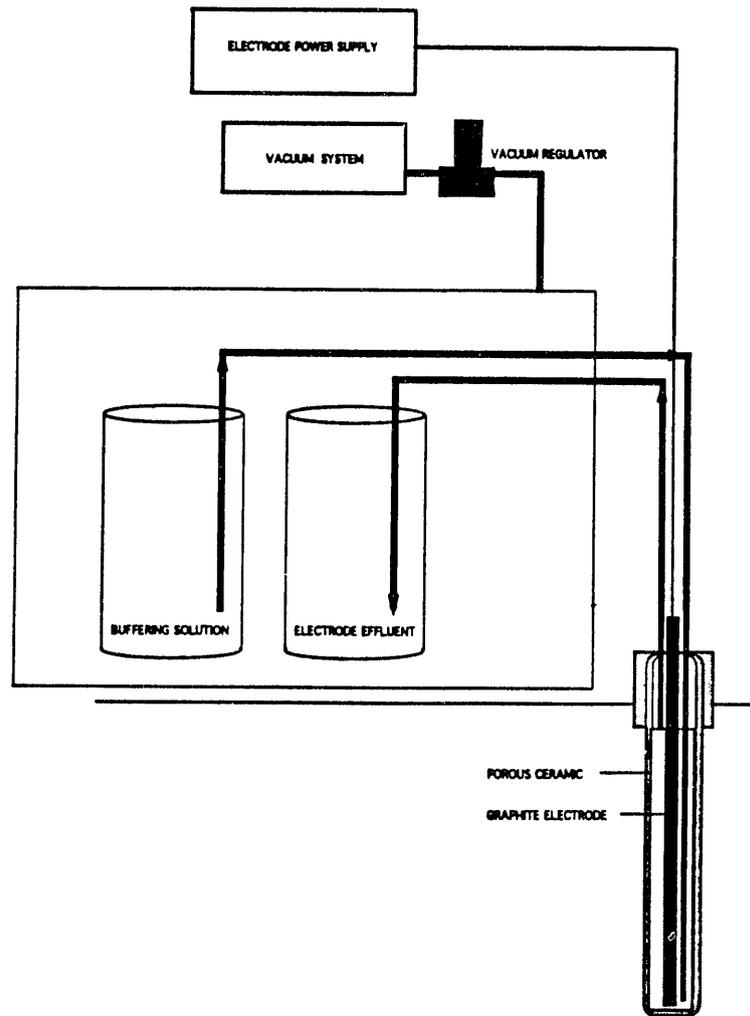


Figure 1. Lysimeter/Electrode Laboratory Design for Unsaturated Soils.

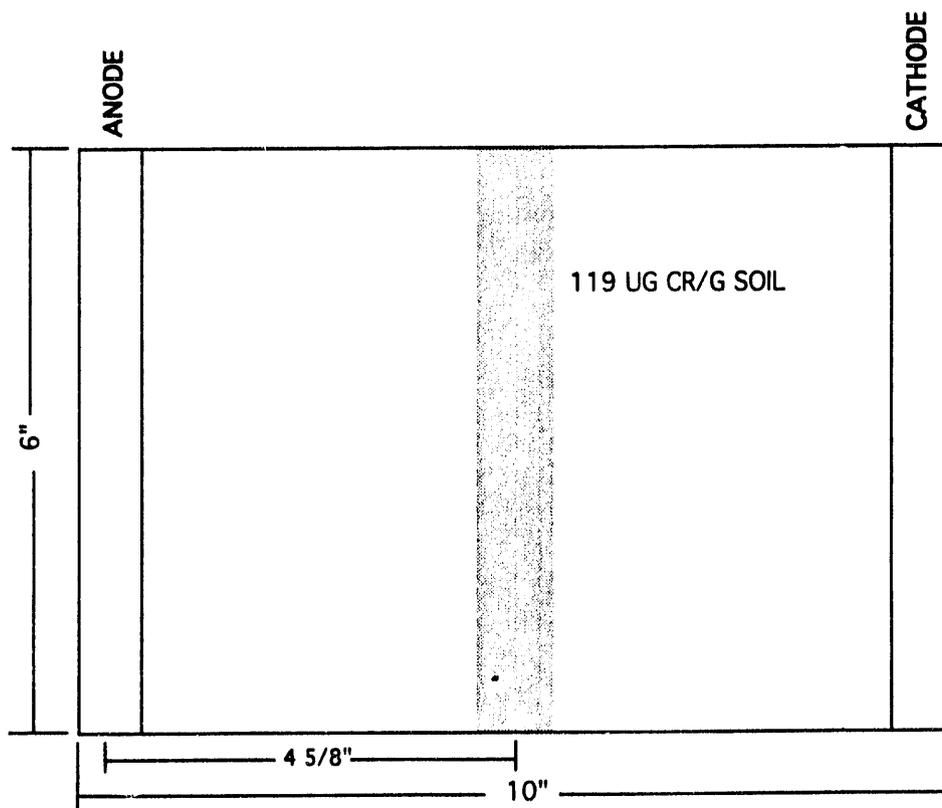


Figure 2. Initial location of chromium in the "Contaminated Strip" experiment.

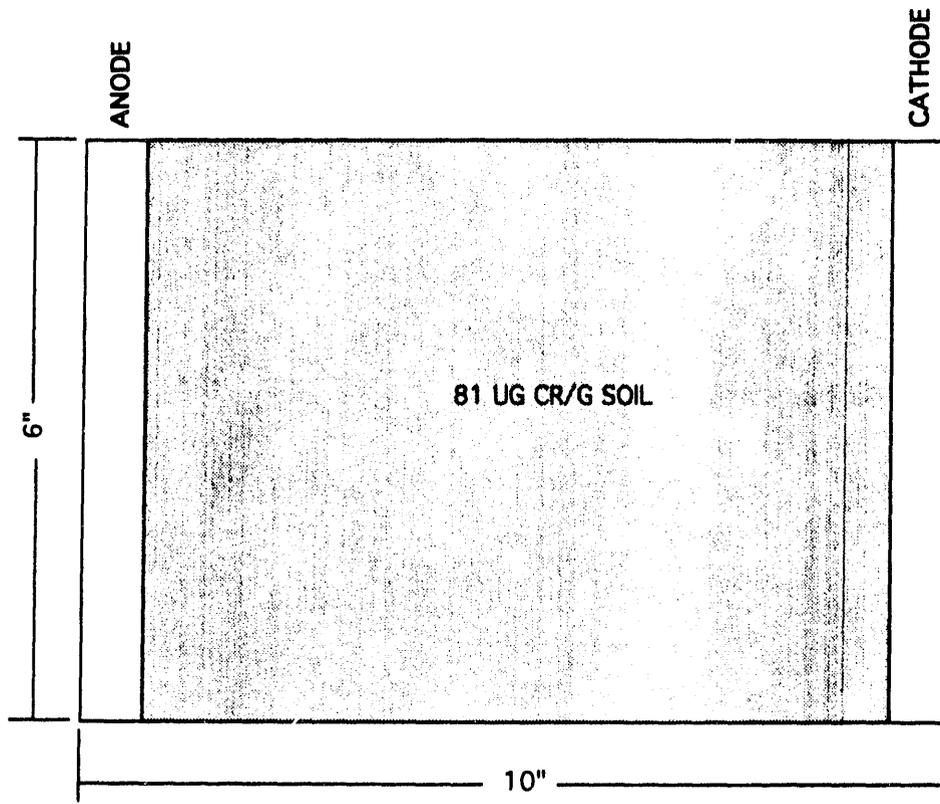


Figure 3. Initial location of chromium in the "Totally Contaminated" experiment.

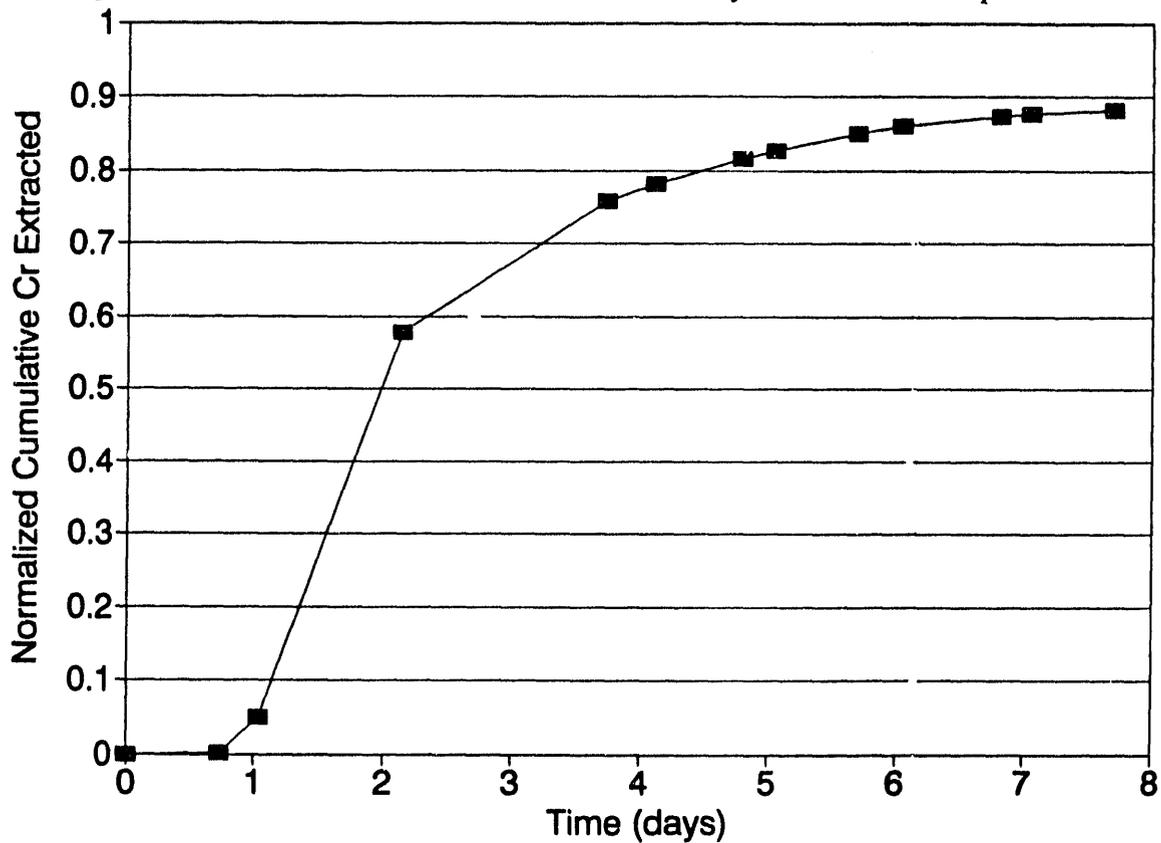


Figure 4. Normalized cumulative extraction of chromium in the "Contaminated Strip" experiment.

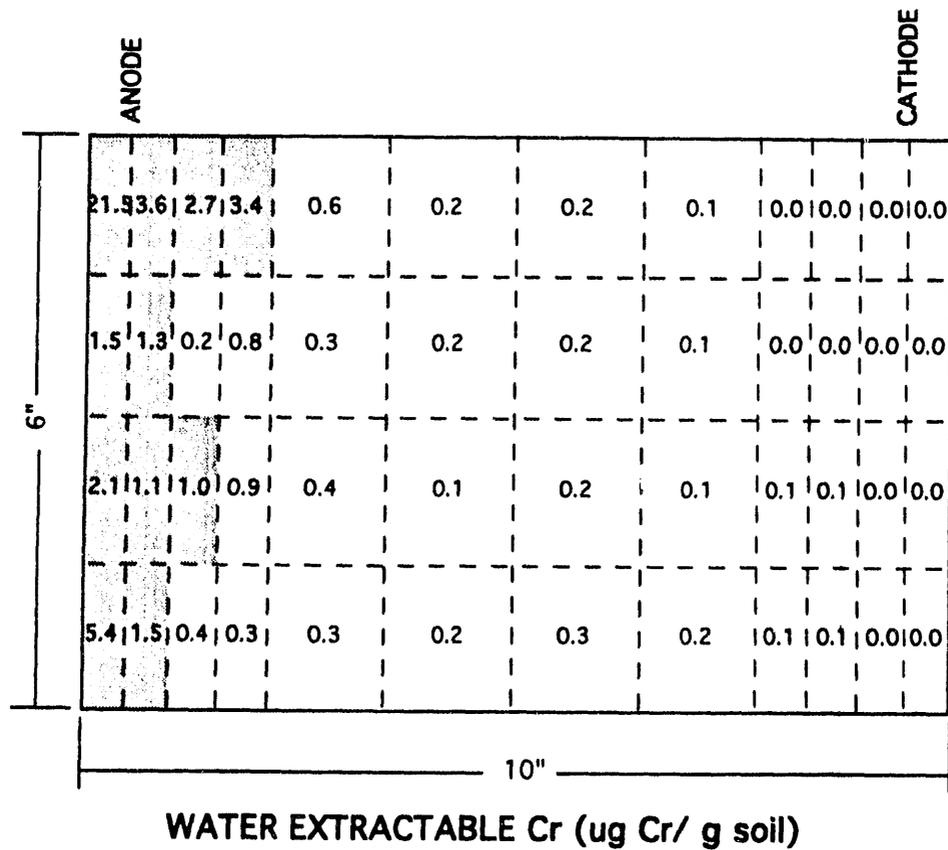


Figure 5. Water extractable chromium remaining in the "Contaminated Strip" experiment.

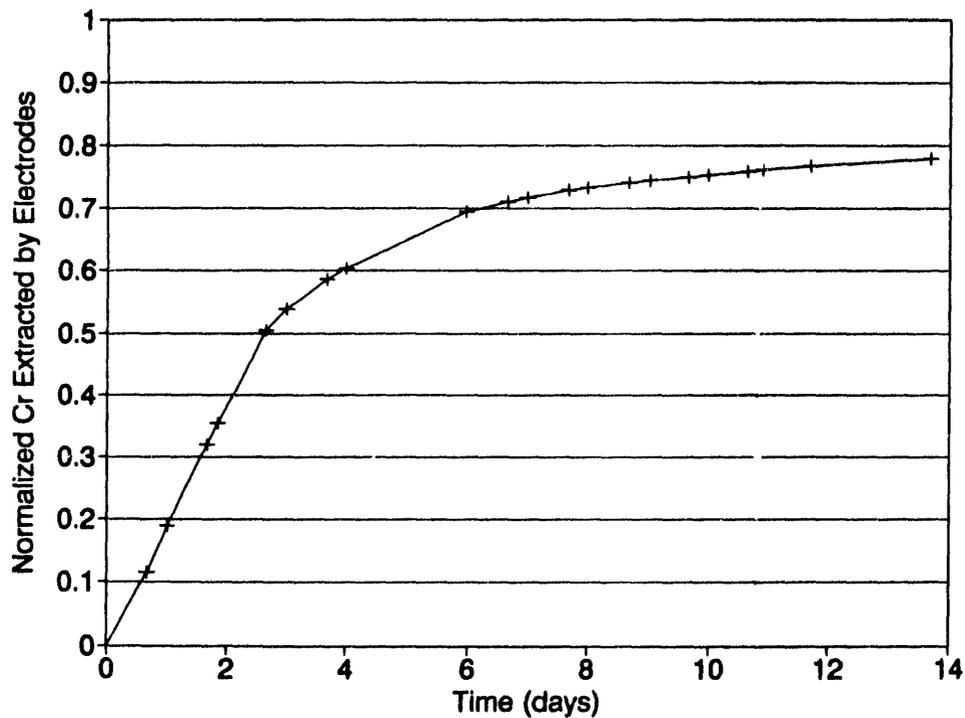


Figure 6. Normalized cumulative extraction of chromium in the "Totally Contaminated" experiment.

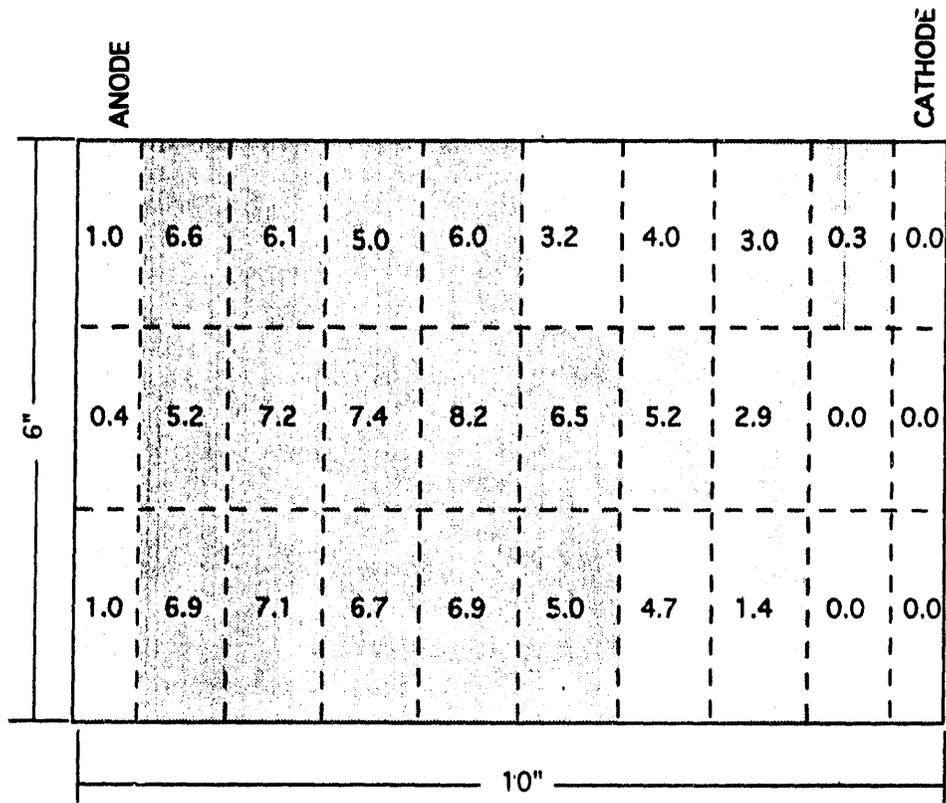


Figure 7. Water extractable chromium remaining in the "Totally Contaminated" experiment.

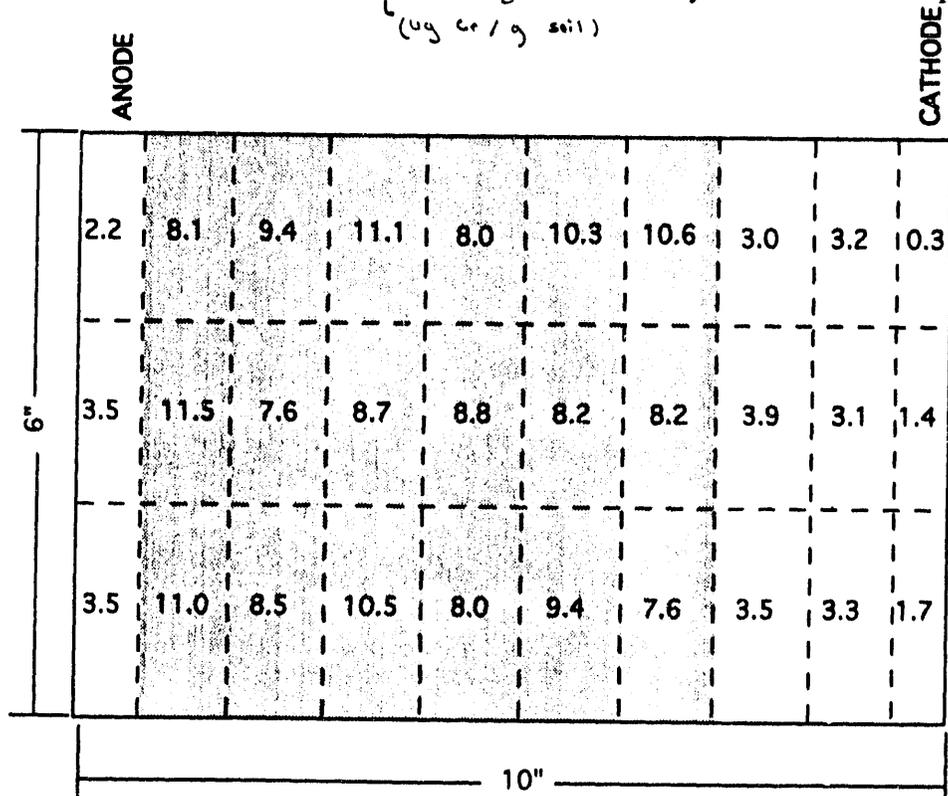


Figure 8. Acid extractable chromium remaining in the "Totally Contaminated" experiment.

( $\mu\text{g Cr/g soil}$ )

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