

ELECTROKINETIC REMEDIATION OF CONTAMINATED SOILS: AN UPDATE*

E. R. Lindgren and M. W. Kozak
Sandia National Laboratories
Waste Management Systems Division 6416
Albuquerque, NM 87185

E. D. Mattson
SAT-UNSAT Inc.
12004 Del Rey NE
Albuquerque, NM 87122.

ABSTRACT

Electrokinetic remediation of chromium contaminated soil has been demonstrated for unsaturated 50 - 100 mesh sand with 10% moisture by weight. The initial region of sand contaminated with 100 ppm_w chromate ions was completely cleansed of contamination. After 22 hours of treatment, chromate was found near the anode and apparently migrated at a rate of at least 0.40 cm/hr with a pore water current density of 2.26 mA/cm².

An analogous run was made using the same sand and FD&C Red No. 40 as the contaminant at a molar concentration equivalent to the 100 ppm_w Cr run. The position of the migrating dye was monitored photographically. After similar treatment conditions, the visual dye concentration profile exhibited characteristics similar to the chromate. The migration rate of the dye was slower than the chromate but the qualitative similarity of behavior in an electric field suggests the dye is an analog for chromate ions. The slower migration rate of the dye is not unexpected because the dye molecule is larger than chromate. The use of dye as an analog for chromate greatly accelerates the experimentation process in unsaturated soil because destructive sampling is not required to monitor the contaminant location.

Experiments were also conducted to determine the effect of soil heterogeneities on the electrokinetic processes. Unsaturated sands in size fractions of 50 - 100 mesh (medium) and 100 - 200 mesh (fine) were studied both individually and in layers. The dye migration rate was accelerated in the fine sand and slowed in the medium sand of the layered experiment when compared with the corresponding individual experiments. This discrepancy was explained by estimating the current density in each layer which was proportionally higher in the fine layer and lower in the medium layer. These preliminary experiments illustrate the significant dependence of electromigration rates on current density.

INTRODUCTION

Heavy-metal contamination of soil and groundwater is a widespread problem in the DOE weapons complex, and for the nation as a whole. For example, soil beneath the old chemical waste landfill (CWL) located at Sandia National Laboratories (SNL), Albuquerque, is contaminated with chromate ions from past chromic acid disposal. One possible technique for *in situ* removal of such contaminants from soil is the use of electrokinetics.

In electrokinetic remediation, electrodes are implanted in the soil, and a direct current is imposed between the electrodes. The application of direct current leads to a number of effects: ionic species and charged particles in the soil-water solution will migrate to the oppositely charged electrode (electromigration and electrophoresis), and concomitant with this migration, a bulk flow of water is induced toward the cathode (electroosmosis).⁽¹⁾ These phenomena are illustrated in Fig. 1. The combination of these phenomena leads to a movement of contaminants toward the electrodes. The direction of contaminant movement will be determined by a number of factors, among which are type and concentration of contaminant, soil type and structure, interfacial chemistry of the soil-water system, and the current density in the

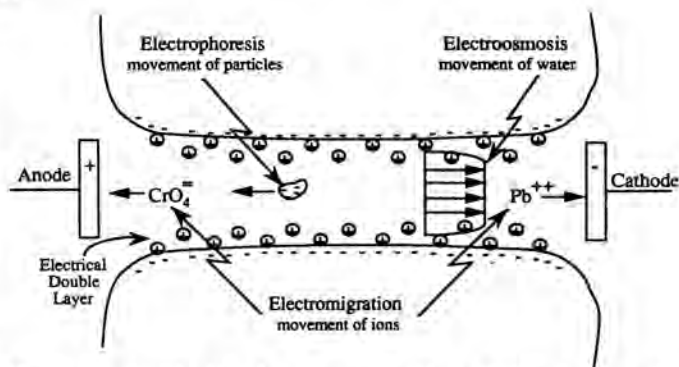


Fig. 1. Electrokinetic phenomena pertinent to *in situ* remediation.

soil pore water. Contaminants arriving at the electrodes may potentially be removed from the soil by one of several methods, such as electroplating at the electrode, precipitation or co-precipitation at the electrode, pumping of water near the electrode, or complexing with ion-exchange resins.

An experimental program is underway at SNL to determine the feasibility of using electrokinetic processes to remediate the chromium plume located at the CWL. Past disposal practices have resulted in a chromium plume which was

* This work funded by the Environmental Impact and Restoration Division 7723, and performed at Sandia National Laboratories which is operated for the U. S. Department of Energy under Contract No. DE-AC04-76DP00789

detected at a depth of 75 feet in 1987. Figure 2 shows a cross section of the plume. Most of the plume is less than 200 ppm_w with a small lens of higher concentration just below the old pit boundary. The plume is entirely in the vadose zone and groundwater is located 480 feet below the surface. Moisture contents of the soil range from 3 to 10 wt%.

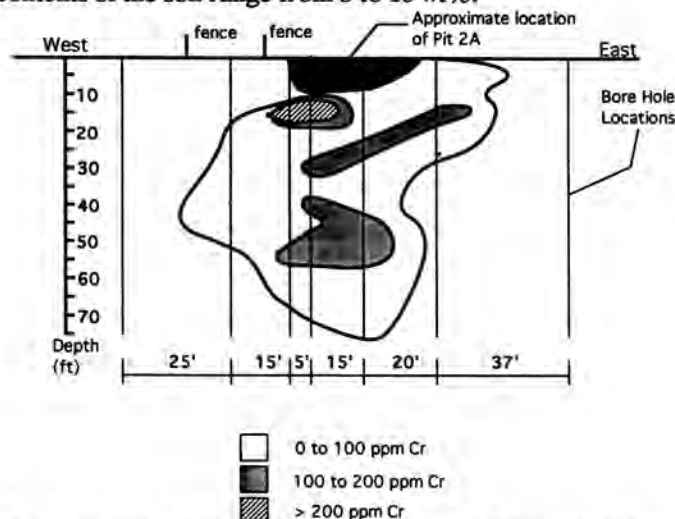


Fig. 2. Approximate extent of chromium plume migration based on a 1987 borehole study.

Initial experiments demonstrated the electromigration of large anionic dye molecules in unsaturated sand with moisture contents typical of native soils at the CWL. These preliminary results were presented at Environmental Remediation '91.(2) In the present paper we compare the electromigration rate of chromate ions with a dye analog and investigate the effect of layered unsaturated soils.

EXPERIMENTAL

Dye in Unsaturated Soil

The experimental setup and procedures used for the unsaturated dye electromigration experiments are described in more detail in a previous paper (2) with a few exceptions. A new plastic test cell was used with internal dimensions of 15.2 cm high, 25.4 cm wide and 1.9 cm thick. The cell was prepared by packing the cell with sand moistened to the desired moisture content. The water used to moisten the oven dried sand was a synthetic groundwater (0.005 M CaSO₄ in distilled water). A 0.6 cm wide spacer along the cell center line produced a void when removed after the cell was packed. This void was packed with contaminated soil. The 0.64 cm diameter graphite electrodes were sharpened and driven to the bottom of the test cell ~21 cm apart. A constant current was applied to the electrodes and photographs were taken of the test cell at timed intervals to record the location of the migrating dye. In all experiments shown, the anode is on the right hand side of the test cell and the cathode is on the left. The advantage of visualization experiments is that the dye location can be monitored *in situ* by photography and no chemical analyses are required.

Pure FD&C Red No. 40 was used in all the dye runs presented in this paper. The dye concentration in all cases was equivalent on a molar basis to 100 ppm_w Cr (dry soil basis). The structures of FD&C Red No. 40 is shown in Fig. 3. The dissociation behavior of this molecule can be estimated by

assuming one of the sulfate groups behaves similarly to naphthalenesulfonic acid with a $pK_1 = 0.57$ and the other sulfate group behaves like benzenesulfonic acid with a $pK_2 = 0.70$.(3) This infers that the dye is completely dissociated even at low pH. Chromic acid has a $pK_1 = 0.74$ and a $pK_2 = 6.49$.(3) Thus, chromate is over 90% completely dissociated at pH over 7.5. At a pH = 6.5 half the ions will be CrO₄⁼ and half will be HCrO₄⁻. In neutral to slightly basic pore water (typical of New Mexico), the dye and chromate should be similarly dissociated. However, it is recognized that chromate electromigration behavior will likely be more effected by pH than will the dye analog.

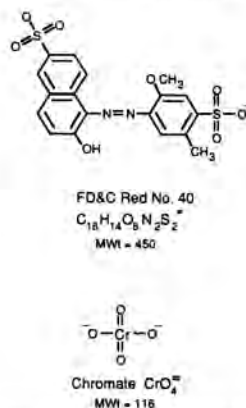


Fig. 3. Chemical structures of FD&C Red Dye No. 40 and chromate ion.

The soil used was obtained near the CWL. The soil was wet sieved into 50 to 100 mesh (medium) and 100 to 200 mesh (fine) fractions. A moisture content of 10 wt% was used with the medium sand and 13.8 wt% was used with the fine sand. one goal of this set of experiments was to conduct electrokinetic experiments in unsaturated layered media. In unsaturated soils, the soil matrix tension and gravity potential are the hydraulic driving forces that determine moisture flow. Therefore, one must match the soil matrix tension in layered unsaturated experiments to establish equilibrium conditions and prevent the redistribution of moisture between the layers.(4) The desired matrix tension was approximately 0.33 bar. This tension corresponds to soil moistures of 10 wt% in the medium sand and 13.8 wt% in the fine sand.

Unsaturated Layered Soil

A layered experiment was setup by packing a 6.2 cm high layer of medium sand with 10 wt% moisture followed by a 4 cm high layer of fine sand with 13.8 wt% moisture and a 5 cm high top layer of medium sand. The dye contaminated soil matched the grain size and moisture content of each layer. The dye concentration was equivalent to 100 ppm_w Cr.

Chromate in Unsaturated Soil

The run using chromate ions as the contaminant was set up and operated exactly like a homogeneous dye run. The run was made with medium sand with 10 wt% water. The center line of sand was contaminated with sodium dichromate to a concentration of 100 ppm_w. The cell was operated at 10.3 mA of current for 22 hours. The cell was then destructively sampled and analyzed for water soluble chromium and moisture content. Deionized water was added to each of the soil samples, stirred, and allowed to settle for one hour. The

supernatant water from each sample was drawn into a syringe and then filtered through a 0.2 μm PTFE syringe filter. The filtered water was then analyzed for chromium with an emission spectrometer. The detection limit for the technique used was approximately 0.05 ppm_w (dry soil).

RESULTS AND DISCUSSION

Chromium and Dye Comparison

Chromate Contaminated Medium Sand

The results of a homogeneous run with chromate contaminated medium sand with 10 wt% moisture are depicted in Fig. 4. This figure illustrates the cell setup, the initial chromate location and the approximate chromate location after 22 hours of 10.3 mA current. The current remained constant at 10.3 mA throughout the entire run. The voltage required rose from 89 volts initially to 150 volts after 22 hours. Figure 4 also shows where each of the samples were taken at the end of the run. Each rectangle depicted represents an area sampled and the number inside each rectangle is the concentration of chromium measured (ppm_w dry sand).

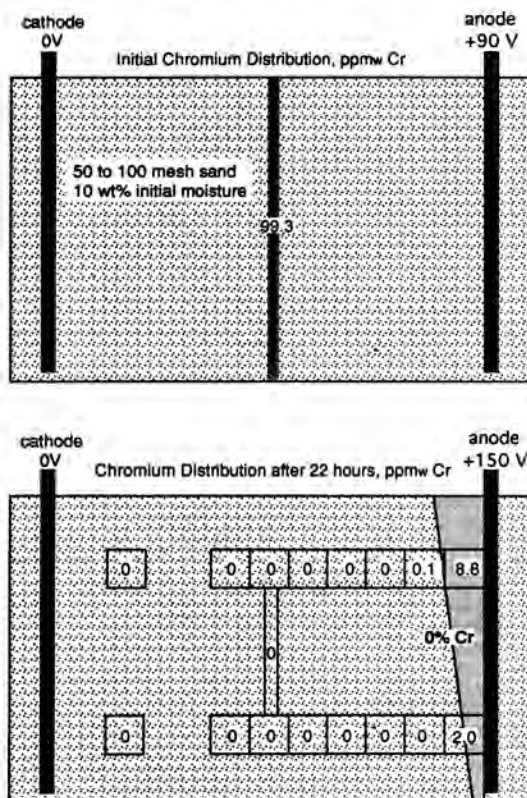


Fig. 4. Experimental setup and chromate position initially and after 22 hours of operation at 10.3 mA

Typically, the current density is determined by dividing the total current by the cross sectional area of the cell. This results in a cell current density of 0.35 mA/cm² for this run. However, it is reasonable to assume all of the current travels through the pore water suggesting a more appropriate way to define current density, especially in unsaturated soils. The pore water current density is simply the cell current density divided by the volumetric water content of the soil, and thus will vary inversely with moisture content. Assuming a typical

bulk density for sand is 1.6 g/cm³, the pore water current density for this run was 2.26 mA/cm².

No chromium was detected except adjacent to the anode and the region of the sand containing all the initial chromium spike was cleansed of the contamination. For this initial chromium run, the estimated final mass of chromium detected was less than the initial amount of chromium used. It is possible that the chromium concentrated on the surface of the electrode (which was not analyzed) or very close to the electrode (which was inadequately sampled). Another explanation is that the chromium changed valence states from Cr⁺⁶ (as in CrO₄⁼) to Cr⁺³. Since Cr⁺³ is cationic in solution, it tends to adsorb strongly to soil and may not have been extracted by the water washing technique used in the chromium analysis. Subsequent runs with chromium will be conducted to investigate these uncertainties.

The apparent migration rate of the trailing edge of the chromium was 0.40 cm/hr along the top samples and 0.45 cm/hr along the bottom samples. When normalized by the pore water current density, these rates are 0.049 and 0.056 cm³/C, respectively (see Table I). This rate can be thought of as the pore volume swept per coulomb of electricity passed through the soil. Such normalization is necessary for comparing runs of different current densities.

As shown in Fig. 5, the analysis of the samples for moisture showed that water moved downward and toward the cathode. The downward movement of water has been determined to be due to both gravity and a small increase in the bulk density of the soil due to packing. The wetter soil near the bottom of the cell probably conducted more current which could explain the faster migration rate at the bottom of the cell.

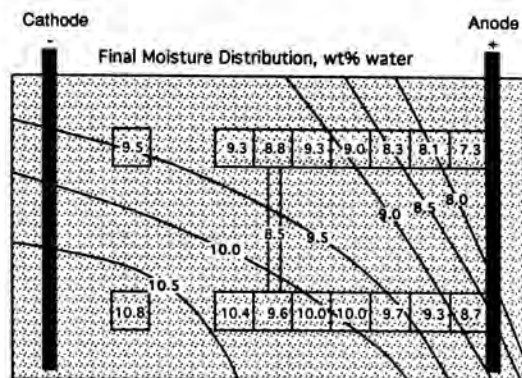


Fig. 5. Moisture distribution of chromium run after 22 hours of operation at 10.3 mA.

Water also migrated toward the cathode by *electroosmosis*. The rate of electroosmosis estimated by mass balance was 0.02 cm/hr. The electroosmosis rate is 20 times slower than the electromigration rate which indicates that for the conditions of this experiment, the rate of electromigration was affected very little by electroosmosis.

Dye Contaminated Medium Sand

A run was made with dye contaminated soil under conditions similar to the chromate run. Figure 6 shows the results of a homogeneous run with the 50-100 mesh sand at 10.3 wt% moisture initially and after 22.2 hours of 8.5 mA average current. Initially, 10.3 mA of current required 81 volts, the current dropped 1 mA over the first 12 hours of the run when the maximum voltage of 110 volts was reached, the current

then dropped more rapidly to 7.2 mA after 22 hours. The average pore water current density dropped from an initial value of 2.14 mA/cm² to 1.51 mA/cm². The average leading edge dye migration rate near the top of the cell dropped from 0.50 cm/hr at 11.7 hours to 0.49 cm/hr at 16.5 hours and finally to 0.44 cm/hr at the end of the experiment. When normalized by the average pore water current density the rates are 0.069 cm³/C, 0.070 cm³/C and 0.069 cm³/C, respectively. Thus, the average normalized rate apparently remained constant with time.

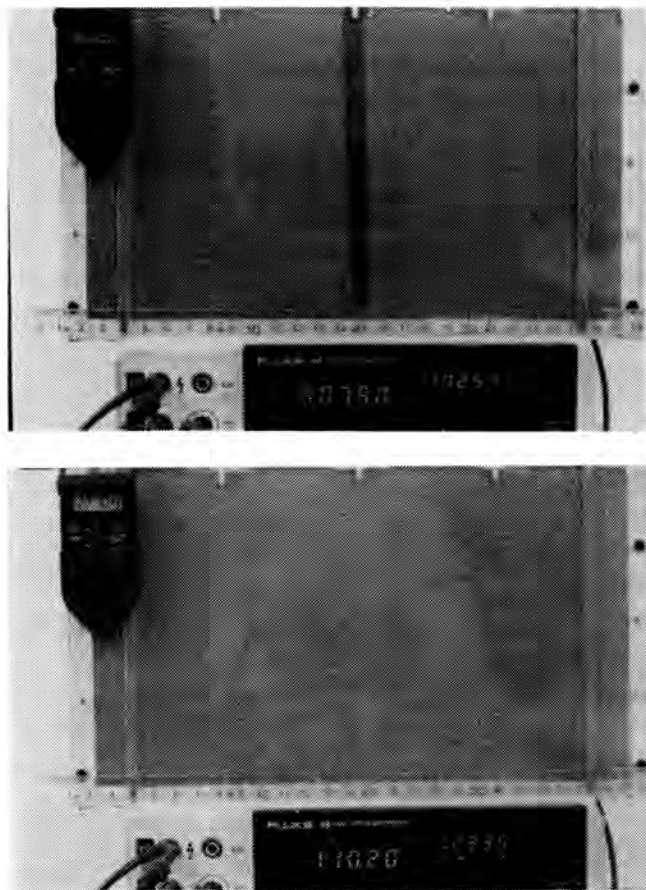


Fig. 6. Unsaturated medium sand with 10.3 wt% water and dye contamination, initially and after 22.2 hours of operation at 8.5 mA.

The same slanted final profile is evident in the experiment with dye as was apparent in the chromate run. After 11.7 hours, the average leading edge migration rate near the bottom of the cell was 0.63 cm/hr or 0.086 cm³/C which is 25% faster than the rate at the top of the cell. Analysis of the moisture distribution after the run again showed that water had moved downward and toward the cathode.

The average leading edge migration rate was on the order of twice as fast as the trailing edge migration rate. At the end of the 22 hour run the average trailing edge migration rate was 0.032 cm³/C near the top of the cell and 0.054 cm³/C near the bottom. The leading edge was 0.069 cm³/C near the top and 0.086 cm³/C near the bottom. This may be due to a concentration effect where the more dilute leading edge migrates faster than the more concentrated trailing edge. This hypothesis will be thoroughly tested in future experiments.

Comparison of the chromate run and the corresponding dye run is made in Table I. The current normalized chromate migration rate of the trailing edge was 50% faster than the dye migration rate along the top portion of the cell. However, the rates were essentially identical along the bottom portion where both the dye and the chromate had reached the electrode. From this single comparison it seems that the dye is a reasonably good analog for chromate ions, however, more experiments are needed before a definitive comparison can be made.

Homogeneous and Layered System Comparison

Dye Contaminated Fine Sand

Figure 7 shows the results of a homogeneous run with fine sand at 13.8 wt% moisture initially and after 22 hours of 10.3 mA average current. Initially, 10.5 mA of current required 25.0 volts. In this run the current dropped to only 10.1 mA after 22 hours of operation and the average pore water current density was 1.58 mA/cm². At the end of the run the average leading edge migration rate was 0.14 cm/hr or 0.024 cm³/C (see Table II). Unlike the medium sand experiment, the migration velocity at the bottom of the cell was only slightly faster than at the top portion of the cell even though water moved downward and toward the cathode as in the other runs.

Dye Contaminated Layered Sand

The results of the unsaturated layered experiment are shown in Fig. 8 initially and after 21 hours of operation at 9.5



Fig. 7. Unsaturated fine sand with 13.8 wt% water and dye contamination, initially and after 22.0 hours of operation at 10.3 mA.

TABLE I

Comparison of Contamination Migration Rates for Chromium and Dye (Trailing Edge)

Run Type	Cr	Dye
Run Time (hr)	22.0	22.2
Sand Type	Medium	Medium
% Moisture (by weight)	9.8	10.3
Average Current (mA)	10.3	8.5
Current Density (mA/cm ²)	0.35	0.29
Pore Water Current Density (mA/cm ²)	2.26	1.78
Average Migration Rate (cm/hr)- Top (cm/hr)	0.40	0.20
- Bottom	0.45	0.35
Normalized Migration Rate (cm ³ /C) - Top	0.049	0.032
- Bottom	0.056	0.054

experiment. After 21 hours, the leading edge migration rate in the top layer was 0.31 cm/hr, in the middle layer was 0.27 cm/hr and in the bottom layer was 0.44 cm/hr (see Table II). Normalization by current density is not possible until the current density in each layer is estimated.

Comparisons of the average leading edge migration rates for the layered run and the two homogeneous runs are made in Table II. The dye in the fine sand is migrating twice as fast in the layered system than in the homogeneous system, conversely, the dye in medium sand is migrating 30 % slower in the layered system. The differences can be explained by considering the current density in each layer of the layered system.

The current density in each layer can be calculated from the resistivity determined in the homogeneous experiments. Soil resistivity is calculated as shown below:

$$\rho = R A \theta / l \quad (\text{Eq. 1})$$

where:

ρ is resistivity [Ωcm]

R is initial resistance from Ohm's Law $R = V/I$ [Ω]

where V is the initial voltage [volts]

I is the initial current [amps]

A is the cell cross sectional area [cm^2]

θ is the volumetric water content [cm^3/cm^3]

l is the length between electrodes [cm]

This definition of resistivity has been modified to account for the cross sectional area available for current flow through the pore water and will compensate for small differences in moisture content.

From the initial resistivity of each of the sand types measured in the homogeneous runs and the geometry of the sand layers in the layered run, the resistance of each layer can be calculated from Eq. 1 (solved for R). Using this method, the effective resistance of 5006 ohms is calculated for the layered system by considering each layer as a parallel resistor. The calculated resistance compares well with the resistance of 5320 ohms measured at the beginning of the layered experiment. Using Ohm's Law and the resistance of each of the layers, the current density in the top, middle and bottom layers is 1.30, 3.18 and 1.30 mA/cm², respectively. Thus the current density normalized migration rates are 0.067, 0.024, and 0.094 cm³/C, respectively. These normalized rates compare well with the rates in the homogeneous runs (see Table II) indicating the difference in migration velocity is mostly explained by current density differences.

CONCLUSIONS

Electromigration of chromate ions has been demonstrated in unsaturated sands. The initial region of sand contaminated with chromate ions was completely cleansed of contamination. Water soluble chromium was only detected near the anode. The chromium migrated at an average velocity of approximately 0.4 cm/hr. The counteracting movement of the pore water by electroosmosis was considerably less (~0.02 cm/hr) than the electromigration rate. This implies that electromigration is the dominate transport mechanism for the unsaturated soils studied.

The migration rate of the chromate ions was faster than FD&C Red Dye No. 40 in a similar experiment, however, the final dye concentration profile was qualitatively similar to the chromate run. The qualitative similarity of behavior in an

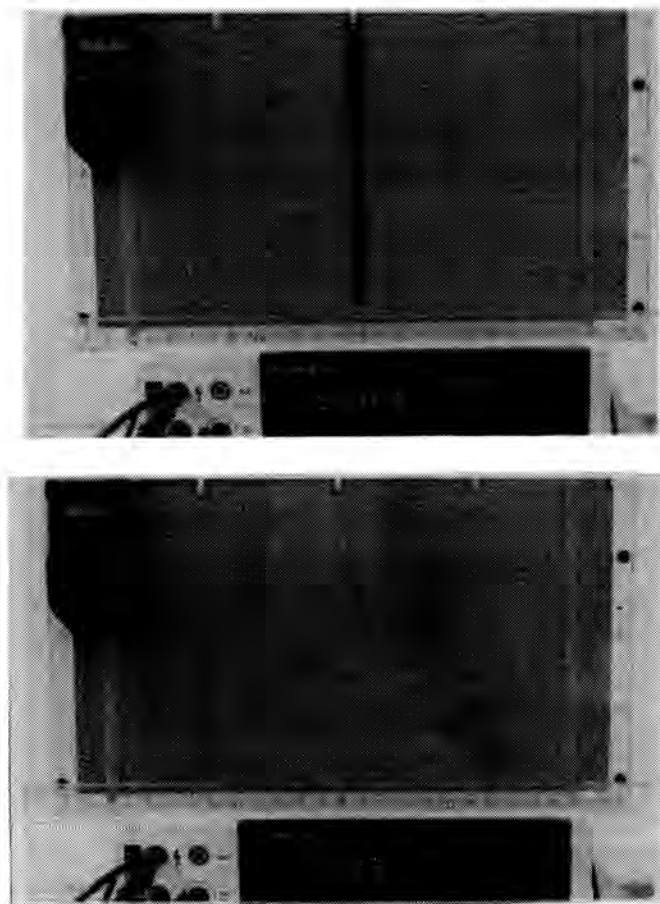


Fig. 8. Unsaturated layered system with dye contamination, initially and after 21.0 hours of operation at 9.5 mA. The top and bottom layers are medium sand with 10 wt% moisture and the middle layer is fine sand with 13.8 wt% moisture.

mA average current. The contact zones are visible between the layers of 50 - 100 mesh sand with 10 wt% moisture on the top and bottom and the 100-200 mesh sand with 13.8 wt% moisture in the middle. Initially, 9.8 mA of current required 52.2 volts and the current dropped to 9.1 mA by the end of the

