

Behaviour of Trinitrotoluene in Electrokinetic Soil Processing

M. Raihan Taha, Yalcin B. Acar, Robert J. Gale
& Mark E. Zappi

ABSTRACT

The behaviour and removal of trinitrotoluene (TNT) in contaminated soil under electrokinetic processes was investigated. The soil used in this study was obtained from the Hastings East Industrial Park site in Nebraska, USA. A current density of 123.3 $\mu\text{A}/\text{cm}^2$ was applied to soil specimens compacted in glass cells. Test with water and a surfactant solution, SDS, as anolytes indicated that TNT concentrations in the soil sample decreased significantly at the sections closest to the cathode. This, however, was not due to removal of TNT away from the cathode. Extensive analysis indicated that the disappearance of TNT was possibly due to the transformation of TNT to TNT anions possibly due to reaction of TNT with base and reductive environment generated during electrolysis. These anions were not detected in initial analysis with high performance liquid chromatography using EPA method. The electrokinetic processes needs further engineering in order to enhance removal of TNT from soils.

ABSTRAK

Kelakuan dan penyingkiran TNT dalam tanah tercemar menggunakan proses elektrokinetik dikaji. Tanah yang diuji datang dari tapak Hastings East Industrial Park di Nebraska, USA. Ketumpatan arus sebanyak 123.3 mA/cm^2 dikenakan ke atas spesimen tanah yang dipadatkan dalam sel gelas. Ujian menggunakan air dan sejenis larutan surfaktan, SDS, sebagai cecair anod menunjukkan kepekatan TNT dalam sampel tanah berkurangan pada bahagian berdekatan dengan katod. Walau bagaimanapun, ini bukanlah sebab penyingkiran TNT daripada bahagian katod. Analisis yang lebih mendalam menunjukkan kehilangan TNT kemungkinan disebabkan oleh transformasi TNT kepada anion TNT akibat tindakbalas TNT dengan bes dan sekitaran penurunan yang wujud semasa elektrolisis. Anion TNT ini tidak dapat dikesan dalam analisis awal menggunakan peralatan kromatografi cecair berprestasi tinggi mengikut kaedah EPA. Proses elektrokinetik ini perlu diperbaiki lagi untuk meningkatkan proses penyingkiran dan pembersihan TNT daripada tanah,

INTRODUCTION

The United States Army has a number of sites contaminated with explosive laden materials such as 2,4,6 - trinitrotoluene (TNT). The contamination is due to release to the environment in the course of production, handling,

loading and packaging of military or civilian devices, and ultimate disposal of explosive residues. TNT is toxic to many organisms and it is a known mutagen (Boopathy et al. 1993). TNT is listed as a priority pollutant by the United States Environmental Protection Agency, USEPA (Keither and Telliard 1979). Therefore, it is important that TNT is removed from the soil to protect against any health hazard.

TNT is the most widely used explosive due to its low melting point, its chemical and thermal stability, low sensitivity to impact, friction, and high temperature, and the availability of safe methods of manufacture. It is also the "standard" explosive material by which the performance of all other explosive compounds are compared. TNT is environmentally stable, yet extremely photo reactive (Zappi et al. 1993). A single TNT manufacturing plant can generate as much as 1.9 million litres of wastewater per day (Yinon 1990). In addition, in shell-loading plants, large volumes of water are used to wash out residual explosives. Wastewaters from the manufacturing of TNT have often been disposed of by discharging into the sea, lakes, unlined lagoons, rivers or streams, landfills and deep ground pumping. A number of techniques have been investigated to decontaminate TNT from the ground. Composting of explosives has proven to be effective and half lives for the breakdown of TNT were found to range between 7 to 22 days (Westonroy 1989). The disadvantage of composting is that it requires large quantities of additives, and only a small amount of the total volume composted is contaminated soil (Boopathy et al. 1994). Incineration has been the only proven technology to cleanup TNT contaminated soil (Lechner et al. 1993). However, the method has high capital cost and low public acceptance. There is a need to find other cost effective solutions to remediate TNT from contaminated sites.

This study attempts to investigate the behaviour of TNT in electrokinetic processes. The main goal is to use electrokinetic process to remediate TNT in contaminated soils. Electrokinetic soil processing is an emerging remediation technology for polluted soil or slurries and the EPA classifies it as a physical remediation treatment for phase separation (EPA 1989). It was hypothesized that this method might provide a cost effective means of removing nonpolar contaminant species such as TNT as well as metal species and water soluble organic contaminants from soils. The method uses low level DC currents (in the order of milliamps per square centimetre), that are applied through electrodes inserted into soil mass to move contaminants across the soil medium. Several reviews, theoretical treatments, laboratory studies and current technology status of this technique may be found elsewhere (e.g. Alshawabkeh and Acar 1992, 1996; Acar et al. 1993a, 1993b; Acar et al. 1994; Ugaz et al. 1994 and Acar et al. 1995).

MATERIALS AND METHODS

SOIL PROPERTIES

The soil used throughout this study was obtained from the Hastings East Industrial Park site in Nebraska, USA. Some basic geotechnical properties of the soil are given in Table 1. More than 85% of the soil particles were

retained on the ASTM No. 200 (74 μm size openings) standard sieve. The soil is classified in the CL or OL region (inorganic clay or organic silts of low plasticity) in the Unified Soil Classification System (USCS) plasticity chart. Soil pH indicated a neutral condition. Brady (1974) reports the range of cation exchange capacity (CEC) to be between 20-26 mmol charge per 100 g of dry soil in neutral conditions. The value of 24.6 obtained in this study fell within the approximate range proposed by Brady (1974). Chemical analysis found that TNT concentrations in the soil sample ranged between 15 000 to 17 000 $\mu\text{g/g}$ of dry soil.

TABLE 1. Basic properties of soil used in experiments

Properties	Values/Observation
Natural water content (%)	16.8
Specific gravity	2.53
Liquid limit (%)	43.9
Plastic limit (%)	21.1
pH	7.2
Cation Exchange Capacity, CEC (mmol charge/100g dry soil)	24.6

EXPERIMENTAL SETUP

The electrokinetic experimental setup is shown in Figure 1. A glass cell which held the compacted specimen and two Teflon end caps was used to minimize possibility of adsorption of TNT or any degradation products onto setup materials. The end caps and the glass cell were connected with threaded rods and tightened with nuts. A horizontal configuration was chosen so that condition of negligible external hydraulic gradient may be set easily between the inflow and outflow. This permits the study of only effects of electrical gradient. Liquid was supplied at the anode through a Teflon tube from a Mariotte bottle. The Mariotte bottle arrangement was used to supply the liquid continuously from a constant elevation. The end caps were furnished with gas vents to allow gases that are produced from electrode reactions to escape. A port with a septum was also provided so that liquids can be sampled by a syringe, and the pH developments at the anode and cathode compartments can then be monitored. The liquid was then injected back into its respective compartment in order to preserve the system. A valve was placed at both the inflow and outflow tubes so that flow into and out of the sample can be stopped during sampling and reinjecting of the liquids. Inert graphite electrodes were chosen to prevent introduction of corrosion products that might cause complicated electrochemistry due to electrode-electrolysis products. The electrodes were 0.31 cm thick and 10 cm in diameter with fifty 0.3 cm diameter holes drilled into them to permit free flow of liquids.

The soil specimens were air dried and compacted in the glass cells having outside diameter of 11.43 cm, inside diameter 10.16 cm and 5.08 cm in height. In this study, compaction characteristics of the soil were not

for the first 24 hours pH were recorded more frequently, i.e., at 0, 1, 4, 10 and 22 hours in order to monitor the pH development more closely. At the end of each test, anode and cathode liquids were collected from the access port. The electrodes and filter papers were taken out and washed with methanol to leach out any adsorbed TNT and the washing liquids were collected. All liquids were then analyzed for TNT concentrations and mass balance purposes. The soil sample was extruded and cut into 5 sections and analysis of TNT concentrations were done after drying. The soil pH before and after tests were also taken.

TNT ANALYSIS

A High Performance Liquid Chromatography (HPLC) instrument was used for the analysis of TNT concentrations. The general procedure follows that of EPA Method 8330 (1990) for analysis of explosives by HPLC. The injection volume for the analysis was set at 25 μ L, the mobile phase being HPLC grade methanol and filtered deaired deionized water (1:1 solution). A flowrate of 1 mL/min was used in the column. These settings were established after long and extensive calibration trials. The UV detection wavelength of TNT is at 254 nm. TNT standards for establishing the calibration curve was purchased from Crescent Chemical Co., New York, USA.

RESULTS AND DISCUSSION

The first test (Cell 1) was conducted with water at both the anode and cathode compartments. This is the control test to which the performance of all other solutions were compared. The second test (Cell 2) was processed with 0.5% sodium dodecyl sulphate (SDS) solution at the anode and water as the catholyte. SDS is a very common surfactant and is known to have an excellent solubilizing strength. It was hypothesised that SDS might be able to desorb TNT from the soil surface and eventually TNT in the aqueous solution would be transported to the cathode by electroosmosis. Batch solubilization of TNT using SDS and other surfactant solutions is described elsewhere (Taha 1996 and Taha et al. 1997). The initial and final specimen properties of Cells 1 and 2 are shown in Table 2. Both samples have almost the same characteristics. A final mass balance of over 80% were achieved in both tests.

ELECTRICAL POTENTIAL

Electrical potential measurements (Figure 2) showed that the reduction of voltage to a constant value (4 to 5 volts) took place within the first 24 hours. In all previous works using a similar setup (Putnam 1988 and Hamed 1990), the voltage profile was the reverse of that observed in this study. The foremost reason is possibly that in those studies the initial soil pH was around 4. The high initial concentration of metallic species such as Pb^{2+} ions in the soil pore fluid renders high ionic strength and therefore high initial electrical conductivity and low voltage. The increase in potential with time (decreasing electrical conductivity and increasing voltage) was related to precipitation of metallic species at their hydroxide solubility limits, or due

to the effect of the high pH environment developed near the cathode (Alshawabkeh 1994). In this study, the initial soil pH was around neutral. The high concentrations of TNT (nonpolar) in the soil and relatively low concentrations of ionic species renders low conductivity and high voltage. The development and movement of acid and base fronts increases conductivity thereby dropping the voltage.

TABLE 2. Specimen properties for Cell and Cell

Property	Cell 1*	Cell 2**
Initial		
Dry density, kN/m^3	12.76	12.44
Moisture content, %	15.77	14.56
Saturation, %	42.22	34.75
Porosity	0.49	0.51
pH	7.15	7.06
Final		
Dry density, kN/m^3	12.40	11.98
Saturation, %	94.37	100
Porosity	0.5	0.52
Applied current density, $\mu\text{A/cm}^2$	123.3	123.3
Test duration, hours	168	168
Total flow, mL [pore volumes]	279 [1.4]	211[1.0]

* Control test - water at anode and cathode compartments.

** SDS (0.5%) solution at the anode and water at cathode compartments.

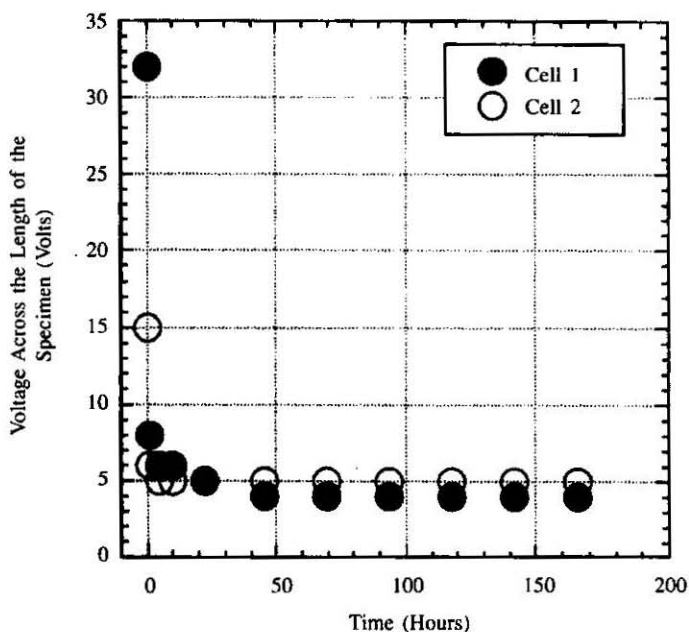


FIGURE 2. Electrical potential across the specimen during electrokinetic test

LIQUIDS PH OF THE ANODE AND CATHODE COMPARTMENTS

The pH developments at the anode and cathode are shown in Figure 3. The theoretical estimation of the pH developments (Taha 1996) are also shown in the figure. The decrease in the pH at the anode and increase at the cathode, as shown in the figure, illustrate that electrolysis reactions were taking place as expected. The pH at the anode was a "reflection" of the pH at the cathode and similarities of both cells displayed repeatability of results. Hamed (1990) estimated that the pH at the anode will drop to a minimum of 2 and cathode will increase to 12. The observations recorded in this study confirms these estimates. The changes in the catholyte and anolyte pH were mostly realized within the first 50 hours of processing. The pH development and its eventual movement across the cell affect zeta potential, fabric and conductivity, which in many ways relate to the flow and movement of contaminants species (Eykholt and Daniel 1994; Acar and Alshawabkeh 1996).

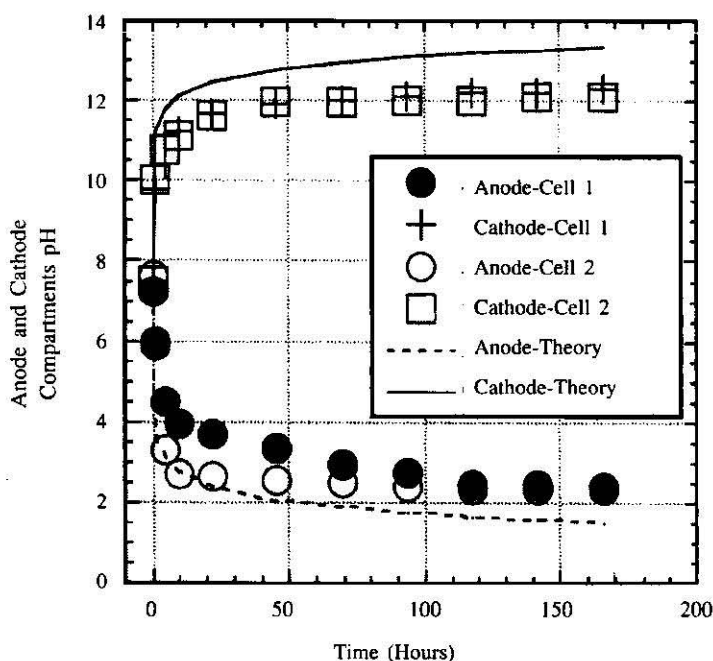


FIGURE 3. The pH developments at the anode and cathode compartments

FLOW

The outflow volume profile (Figure 4) for the testing period shows a continuous but slow flow, especially for the case of surfactant in the anode compartment (Cell 2). The flow totaled about 1.4 and 1.0 pore volumes for Cell 1 and 2, respectively. It is possible that the application of surfactant may have affected flow in the soil system. The evidence for conductivity (hydraulic) loss during soil flushing with surfactants was first reported by Miller et al. (1975). Allred and Brown (1994) measured a maximum hydraulic conductivity decrease of 47% for sandy soil and more than two

orders of magnitude for loam. Surfactant mixtures, soil organic content, added solution electrolytes and pore blockages all affect the degree of hydraulic conductivity losses. In addition, it is probable that addition of a surfactant solution decreased the electrolyte concentration increasing the thickness of diffuse double layer leading to slight fabric changes decreasing the hydraulic conductivity.

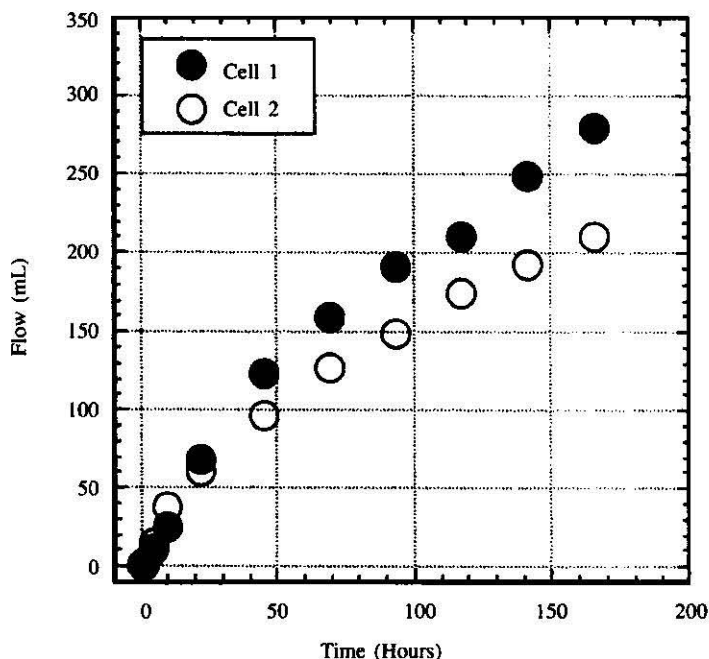


FIGURE 4. The outflow profile during electrokinetic tests

The coefficient of electroosmotic permeability, k_e and the electroosmotic water transport efficiency, k_i can thus be calculated from the flowrate, electrical potential (voltage) gradient, current and cross sectional area of the soil specimen. Fundamentally, k_e is a proportionality constant between hydraulic flow velocity and electrical gradient and k_i is a measure of the efficiency and economics of electroosmotic dewatering. In Figure 5 and 6, it is shown that k_e and k_i first increase and then decrease to a stable value. Similar trends were reported by other workers (Casagrande 1983 and Hamed 1990). The time dependent changes of k_e and k_i demonstrate that significant changes occur in the overall cell resistance and hence the chemistry across the cell during the process. Therefore, k_e and k_i are not constant for a specific soil but they are time dependent variables, presumably controlled by the chemistry generated (Hamed 1990). Modeling the time dependent behavior of k_e represents one of the most difficult tasks in evaluating species transport by electrokinetic processes.

FINAL SOIL PH

The pH profiles in Figure 7 illustrate the advance of the acid front from the anode to the cathode. The drop in k_e is also a consequence of the sweeping

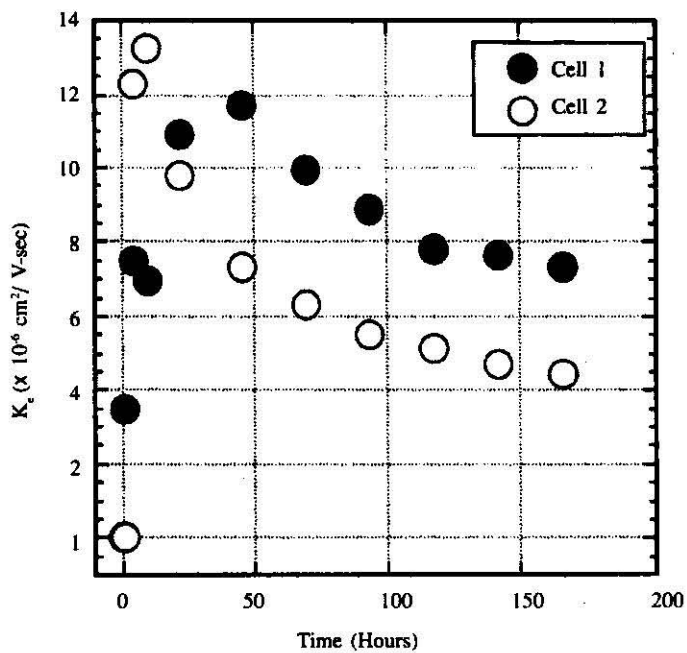


FIGURE 5. The coefficient of electroosmotic permeability, k_e profile in electrokinetic tests

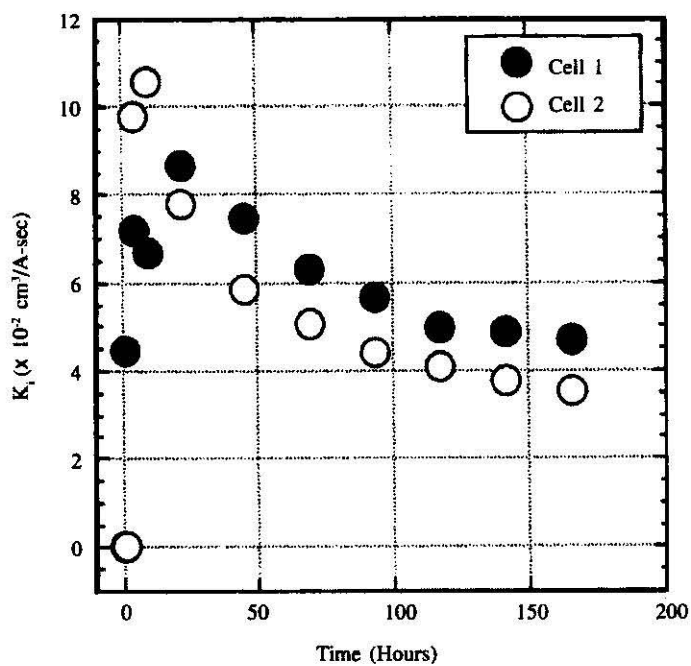


FIGURE 6. The electroosmotic efficiency, k_i profile in electrokinetic tests

acid front which decreases the pH of the system. Decrease in the soil pH and surface charge across the specimen will decrease the zeta potential, ζ , eventually decreasing k_e since ζ and k_e are directly related (Casagrande 1949). Therefore, it is expected that electroosmotic flow will cease at later stages of the process.

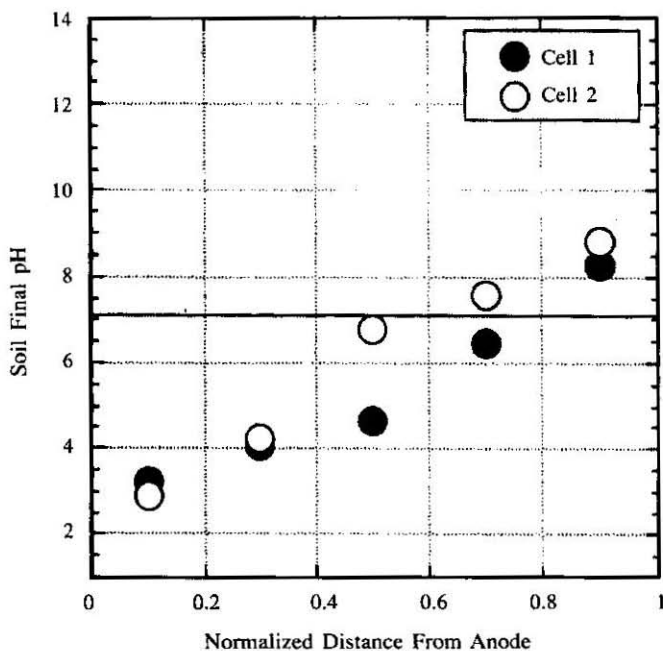


FIGURE 7. The pH of soil across the specimen in electrokinetic test

FINAL TNT CONCENTRATION

TNT concentrations in the soil specimens after 7 days of electrokinetic processing are shown in Figure 8. Soil samples were air dried to eliminate any possibility of TNT losses. Both Cell 1 and 2 showed that at sections closest to the anode there were no significant variations between TNT concentrations before and after electrokinetic processing. This indicated that there was no significant movement or transport of TNT even after treatment with SDS solutions.

At sections closest to the cathode, the test results clearly demonstrated a significant reduction of TNT concentration. Approximately, only one half the initial TNT was detected after a week of electrokinetic processing. Initially it was thought that TNT had been transported to the cathode compartment and was collected in the outflow liquid. However, analyses indicated that no TNT was detected in the catholyte and outflow. TNT concentrations from the wash liquids of the electrode and the filters were very low and quite insignificant in the mass balance calculations. Since TNT is easily biotransformed, it was hypothesized that TNT could have converted into its transformation products such as TNB, 2A-DNT, 4A-DNT, etc. If this was happening, the peaks for these products should have been delineated in

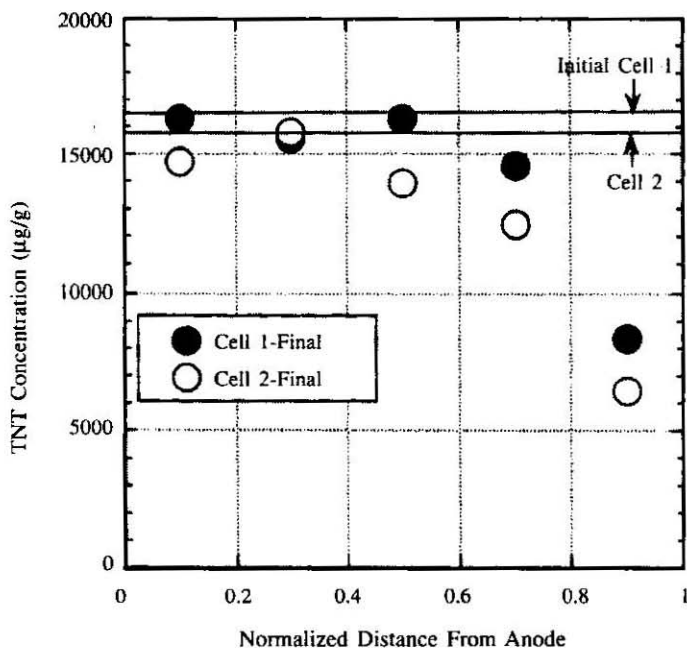


FIGURE 8. Final TNT concentration in the soil specimen after electrokinetic soil processing

the HPLC chromatograms. However, only one peak, i.e. that for TNT, was observed in all analyses. This demonstrates the fact that all other known products were below detection levels, simply did not exist, or an undetectable product was being produced.

Another postulate was possible oxidation of TNT. However, any such oxidation should be less likely to prevail close to the cathode, under strongly reducing conditions. A brief examination of the pH and TNT concentration profiles indicate that the drop in TNT concentrations occur simultaneously when the pH of the soil became greater than seven. This gives an indication that base alone might have reacted with TNT resulting in its disappearance. A simple test was then conducted to investigate if basic conditions could have transformed or degraded TNT. A set triplicate samples of 3 grams of the initially contaminated soil were mixed with 5 mL of 0.01M ammonium hydroxide (NH_4OH) having pH of 10.18. For comparison and discussion purposes, another set of soil samples were mixed with 5 mL of 0.1M HCl (hydrochloric acid) having a pH of 1.16. The soil samples were kept in darkness, then air dried naturally, after which the samples were tested for TNT concentrations. The TNT concentrations for the base and acid reactions were 15 292 µg/g ($\sigma_{n-1}=441$) and 16,245 µg/g ($\sigma_{n-1}=567$), respectively. This result does not indicate significant variation of TNT concentrations upon exposure to base as was initially thought to happen in EK tests at sections close to the cathode. It is possible that the reaction in the soil electrokinetic tests is more complex and may involve other products from the cathode electrolysis.

ANALYSIS OF TNT TRANSFORMATION PRODUCTS

In order to confirm the disappearance of TNT and the possibility of its transformation to other products, the remaining soil samples from electrokinetic tests were sent to the US Army Waterways Experiment Station (WES) Environmental Chemistry Laboratory, Vicksburg, Mississippi, USA for an independent analyses of TNT and all other known transformation products. The TNT concentrations of soil samples after electrokinetic treatment from WES were compared to those obtained by the authors (designated as LSU) in Figures 9 and 10. The results showed higher TNT concentrations in WES analyses at sections close to the anode than those in LSU analyses. However, the discrepancies are not unusual for HPLC analysis of organics by two separate laboratories. They may be attributed to differences in equipment, operator, temperature, test details, etc. Indeed, it is stated that only if calibration standards do not agree within 20%, then the calibration curve needs to be reevaluated (EPA 1990). It may be inferred that the 20% difference is the maximum by which the results can differ. Both WES and LSU analyses conform within 20% of each other. The most interesting fact was the near similarities of TNT concentrations at sections closest to the cathode. This demonstrated that the finding of TNT disappearance close to the cathode was reliable.

The results of analysis for known TNT transformation products are tabulated in Table 3. There was an increase in TNB concentrations at sections closest to the cathode. At the same time, there was a corresponding decrease in the concentrations of other products at these sections. However, the sum of all determined TNT transformation products could not nearly makeup TNT

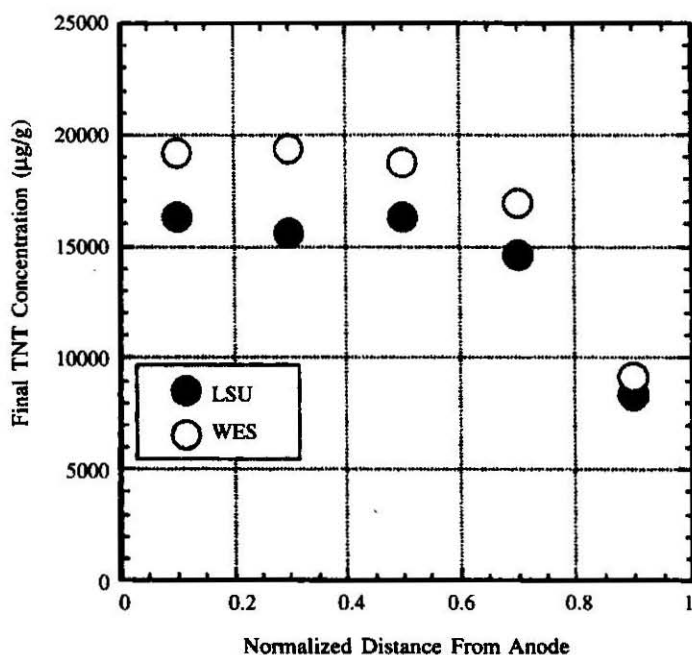


FIGURE 9. Comparison of WES and LSU analysis of TNT for Cell 1

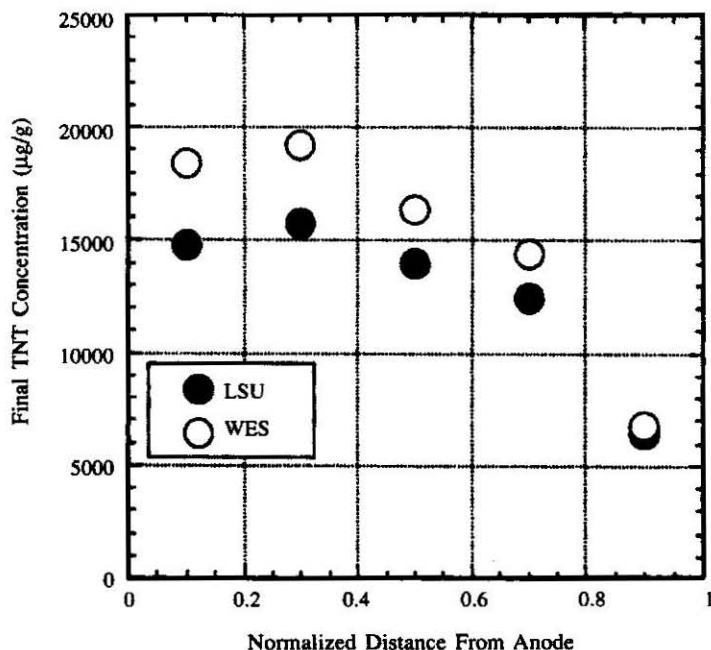
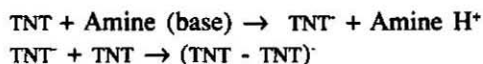


FIGURE 10. Comparison of WES and LSU analysis of TNT for Cell 2

losses from mass balance calculations. In fact the results showed that the concentrations of all the conventionally known compounds were negligible compared to the initial TNT concentrations. It can be hypothesized that TNT could have reacted to form a product(s) that is not detected at 254 nm, the wavelength used for analysis of the TNT and its metabolites.

A possible explanation for the TNT disappearance can be referred to Okamoto et al. (1977) in which they described a colored solution when TNT reacted with strong base. This reaction was first described by Janovsky (1891). The reaction was interpreted as a result of formation of an intermediate, 2,4,6- trinitrobenzyl anion (TNT⁻) which absorbs light in the visible region (500-525 nm). On future reaction, the anions initially produced reacted with unreacted TNT to yield a complex, now known as Janovsky's complex. Thus, according to Okamoto, et al. (1977)



in which (TNT-TNT)⁻ is the Janovsky's complex. Okamoto et al. (1977) cautioned that these hypotheses were suggested with very limited results.

Meisenheimer (1902) and Jackson and Earle (1903) independently arrived at similar structures to explain the phenomenon observed by Janovsky (1891). They proposed a different structure for the highly colored species which are known as Jackson-Meisenheimer (J-M) anions. Jenkins(1990) used the J-M anions to develop a simplified method for in situ detection and determination of TNT concentrations in soils. TNT can be converted into J-M anions by addition of potassium hydroxide (KOH) and sodium sulphite

TABLE 3. Concentration of TNT transformation products in Cell 1 and Cell 2 after electrokinetic soil processing

TNT Transformation products	Cell 1 Concentrations ($\mu\text{g/g}$) Normalized distance from anode					Cell 2 Concentrations ($\mu\text{g/g}$) Normalized distance from anode				
	0.1	0.3	0.5	0.7	0.9	0.1	0.3	0.5	0.7	0.9
TNB	51	77	108	176	229	49.5	94	189	258	260
4A-DNT	44.5	22.5	<25	<25	<25	90	10	<25	<25	<25
2A-DNT	56	20.5	9.5	75	15.5	154	15	10	11.5	14.5
2,6-DNT	<26	<26	<26	<26	<26	<26	<26	<26	<26	<26
2,4-DNT	34	40	37.5	33.5	23.5	22	31.5	31	32.5	19.5
Azoxylol	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
2,6-DANT	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
2,4-DANT	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
DNA	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
TNT ($\times 10^3$)	19.5	19.4	18.7	16.9	9.1	18.4	19.2	16.4	14.4	6.7

TNB = 1,3,5-Trinitrobenzene

2A-DNT = 2-Amino-4, 6-Dinitrotoluene

2,4-DNT = 2,4-Dinitrotoluene

2,4-DANT = 2,4-Diamino-6-Nitrotoluene

4A-DNT = 4-Amino-2,6-Dinitrotoluene

2,6-DNT = 2,6-Dinitrotoluene

DNA = 3,5-Dinitroaniline

2,6-DANT = 2,6-Diamino-4-Nitrotoluene

(Na_2SO_3) within a few minutes. Absorbance is measured at 540 nm using a spectrophotometer. The Jackson-Meisenheimer anions concentration show an excellent correlation to the TNT concentrations. These correlations, however, are derived from tests at low level (<200 ppm) TNT concentrations.

In order to demonstrate the existence of J-M anions in solution, 2.1 mg/L of TNT solution was prepared with 95% acetone and 5% deionized deaired water. A pellet of KOH and 0.2 g Na_2SO_3 were then added to 25 mL of the TNT solution and the solution was shaken for 3 minutes. A dark red solution appeared. Upon addition of sulphuric acid (H_2SO_4) drop by drop, the red colouration diminishes and slowly the solution becomes colorless. The reversibility of the reaction, first by the addition of the base and then the acid, proves the formation of the J-M anions or the Janovsky's complex when bases are added to the TNT solutions.

Two grams of soil from section 5 (closest to the cathode in the region where the reaction is suspected) of Cell 1 and 2 were then shaken for 3 minutes with 10 mL acetone (95%) and water (5%) solution to see if TNT could have transformed into the J-M anions during electrokinetic processing. The extract was then centrifuged for 10 minutes and filtered with 0.5 μm pore size filter. A dark red solution was observed. Sulphuric acid was then added drop by drop to the solution. It was observed that the colour reduced to orange indicating the existence of the J-M anions. It is probable that the J-M anions were formed in the electrokinetic tests although a quantitative assessment needs to be made to assess the extent of this formation.

OBSERVATIONS

Tests results presented showed no removal/migration of TNT in test specimens even with SDS solutions. In batch solubilization tests (Taha et al. 1997), it was shown that removal of TNT into the pore fluid was possible using SDS. Once TNT is solubilized in the pore fluid, theoretically, electroosmotic

process should be able to carry TNT away from the electrodes. The inability of the proses to transport TNT was probably due to inability of the solutions (water and SDS) to solubilize TNT. It must be mentioned that in batch solubilization tests, contaminated soil was shaken rigorously with solutions for 18 hours before TNT was extracted and analyzed. In electrokinetic tests, such dynamic mixing did not occur as the solutions were allowed to pass through the sample under zero hydraulic gradient. The possibility of enhancing removal by improving contact time between solution and contaminated soil, and increasing electroosmotic flow (through neutralization of acid at the anode) also proved to be unsuccessful in improving removal efficiency (Taha 1996). This was probably due to high TNT content in the soil sample (15 000 $\mu\text{g/g}$ - 17 000 $\mu\text{g/g}$) which made small observable loss in TNT concentration (in the range of 200 $\mu\text{g/g}$) insignificant. It may be possible to first flush the TNT with a base, thus converting it into the TNT anions (J-M anions or Janovsky's complex), which are more soluble, then using electroosmotic processes to transport the anions to the anode for removal.

CONCLUSIONS

TNT is toxic to many organisms and is also a known mutagen. Its behavior and removal from soils using electrokinetic processes have been investigated in this study. Electrokinetic soil processing might prove to be a cost effective means for remediation of nonpolar organic contaminants such as TNT. It was found that TNT concentrations were reduced significantly at soil sections close to the cathode after electrokinetic soil processing. This may be due to the transformation of TNT to TNT anions (Jackson-Meisenheimer anions or Janovsky's complex) in the basic, reductive environment. It was observed that significant removal of TNT did not occur even after the supply liquid was changed to SDS solution. It is concluded that there is a need to engineer the process further to enhance the solubility of TNT, or to convert it to a more soluble form, especially when its concentration is high ($\approx 15\,000\text{--}17\,000\ \mu\text{g/g}$).

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support of the US Army Waterways Experiment Station (WES), Vicksburg, Mississippi for this project. Cynthia Teeter of WES Environmental Chemistry Branch performed the analysis of TNT transformation products. Sarah Jones helped the authors in the TNT analysis and other analytical chemistry related matters. Discussions with Dr. Mohamad Qasim of WES and Dr. Thomas Jenkins of US Army Corps of Engineers Cold Regions Research and Engineering Laboratory, Hanover, NH provided helpful insight. Any opinions, findings and conclusions or recommendations expressed in this material are of the authors and do not necessarily reflect the views of the sponsors.

REFERENCES

- Acar, Y.B. & Alshawabkeh, A.N. 1996. Electrokinetic remediation: I. Pilot-scale tests with lead spiked kaolinite. *J. Geotech. Eng.*, ASCE, 122(3): 173-185.
- Acar, Y.B., Alshawabkeh, A.N. & Gale, R.J. 1993a. A review of fundamentals of removing contaminants from soils by electrokinetics. *Environmental*

- Geotechnology. *Proc. Mediterranean Conf. Environmental Geotechnology*, Cesme, Turkey, edited by A.A. Balkema. pp. 321-330.
- Acar, Y.B., Alshawabkeh, A.N. & Gale, R.J. 1993b. Fundamentals of extracting species from soils by electrokinetics, *Waste Management* 13: 141-151.
- Acar, Y.B. Alshawabkeh, A.N. & Gale, R.J. 1994. Removal of cadmium (II) from saturated kaolinite by the application of electric current. *Geotechnique* 44 (2): 239-254.
- Acar, Y.B., Gale, R.J., Alshawabkeh, A.N., Marks, R.E., Puppala, S., Bricka, M. & Parker, R. (1995). Electrokinetic remediation: Basics and technology and status. *J. of Hazardous Materials* 40: 117-137.
- Allred, B. & Brown, G.O. 1994. *Surfactant induced reductions in soil hydraulic conductivity, Ground Water Monitoring and Remediation*, Vol. 14(2): 174-184. Groundwater Pub. Co., Riverside, Dublin OH, Spring.
- Alshawabkeh, A.N. 1994. Theoretical and experimental modeling of multi species transport in soils under electric field. PhD Dissertation, Louisiana State University, Baton Rouge.
- Alshawabkeh, A.N. & Acar, Y.B. 1996. Electrokinetic Remediation: II. Theoretical Model. *J. Geotech. Eng.* 122 (3): 185-196.
- Alshawabkeh, A.N. & Acar, Y.B. 1992. Removal of contaminants from soils by electrokinetic: a theoretical treatise. *J. of Environ. Sci. Health A27(7)*: 1835-1861.
- Boopathy, R., Kulpa, C.F. & Wilson, M. 1993. Metabolism of 2,4,6- Trinitrotoluene (TNT) by desulfobrio sp. (B strain). *Applied Microbiol.* 39: 270-275.
- Boopathy, R., Wilson, M. Montemagno, C.D., Manning, Jr. J.F. & Kulpa, C.F. 1994. Biological transformation of 2,4,6- Trinitrotoluene (TNT) by soil bacteria isolated from TNT - contaminated soil. *Bioresource Technology* 47: 19-24.
- Brady, N.C. 1974. *The Nature and Properties of Soils*, 8th edition. New York: MacMillan Pub. Co., Inc.
- Casagrande, L. 1949. Electroosmosis in soils. *Geotechnique* 1(3): 159-177.
- Casagrande, L. 1983. Stabilization of soils by means of electro-osmosis-State of the art, *J. Boston Society of Civil Engineers* 69(2): 255-302.
- EPA. 1989. *Guide to treatment technologies for hazardous waster at Superfund sites*, EPA/540/2-89/052. Office of Research and Development, Washington, D.C.
- EPA Method 8330. 1990. *Nitroaromatics and nitramines by high performance liquid chromatography (HPLC)*. Office of Solid Waste and emergency Response, Washington, D.C.
- Eykholt, G.R. & Daniel, D.E. 1994. Impact of system chemistry on electroosmosis in contaminated soil. *J. Geotech. Eng.* 120(5): 797-815.
- Hamed, J. 1990. Decontamination of soil using electroosmosis. PhD dissertation, Louisiana State University, Baton Rouge.
- Jackson, C.L. & Earle, R.B. 1903. On certain colored substances derived from nitro compounds. *American Chemical Journal* 29: 89-120.
- Janovsky, J.V. 1891. Uber eine reaction der dinitrokooper. *Berichte* 24: 971-972.
- Jenkins, T.F. 1990. Development of a simplified field method for the determination of TNT in soil. US Army Cold Regions Research and Engineering Laboratory, Special report 90-38, Hanover, Nh.
- Keith, L.H. & Telliard, W.A. 1979. Priority pollutants. I. A perspective view. *Envi. Sci. Tech* 13: 416-423.
- Lechner, C.A. & Feireisel, D.F. 1993. Incineration of soils and sludges contaminated with explosives. Seminar on Technologies for Remediating Sites Contaminated with Explosive and Radioactive Waste, Dallas, USEPA.
- Meisenheimer, J. von. 1902. Uber reactionen aromatischer nitrokooper. *Leibig's Annalen Dr Chemie* 323: 205-246.
- Miller, W.W., Valoras, N. & Letey, J. 1975. Movement of two nonionic surfactants

- in wettable and water repellent soils. *Soil Science Society of America Proceedings* 39: 12-16.
- Okamoto, Y., Chou, E.J. & Wang, J., Roth, M. 1977. The removal of 2,4,6-Trinitrotoluene (TNT) from Aqueous Solution with Surfactants. *Proc. Natl. Conf. Treat. Disposal Ind. Wastewaters Residues*. Inf. Transfer, Inc. Rockville, Md. pp. 249 - 253.
- Putnam, G.A. 1988. Determination of pH gradients in the electrochemical processing of kaolinite. MS Thesis, Louisiana State University, Baton Rouge.
- Rosen, M.J. 1978. *Surfactants and Interfacial Phenomena*. John Wiley & Sons, New York.
- Taha, M.R. 1996. Micellar electrokinetic remediation of TNT from soils. PhD Dissertation, Louisiana State University, Baton Rouge.
- Taha, M.R., Acar, Y.B., Soewarto, I.H., Gale, R.J. & Zappi, M.E. 1997. Surfactant enhanced desorption of TNT from contaminated soil. *Water, Air and Soil* 100: 33-48.
- Ugaz, A., Puppala, S., Gale, R.J. & Acar, Y.B. 1994. Complicating features of electrokinetic remediation of soils and slurries: Saturation effects and the role of cathode electrolysis. *Chem. Eng. Comm.* 129: 183-200.
- Westonroy, Inc. 1979. Composting of Explosive Contaminated Soil Technology. US Army Toxic and Hazardous Materials Agency report No. CCTHA-TC-CR-90027, Aberdeen Proving Ground, MD.
- Yinon, Y. 1990. *Toxicity and Metabolism of Explosives*. Boca Raton Florida: CRC Press Inc.
- Zappi, M.E., Gunnison, D., Pennington, J., Teeter, C., Coyle, C. & Rope, C. 1993. Evaluation of Bioslurry Systems for Treating Explosives Contaminated Soils From the Hastings East Industrial Park. Report submitted to USAE District, Kansas City, Missouri.

M. Raihan Taha
Department of Civil and Structural Engineering
Universiti Kebangsaan Malaysia
43600 UKM Bangi
Selangor D.E, Malaysia

Yalcin B. Acar
Department of Civil & Environmental Engineering
Louisiana State University
Baton Rouge
LA 70803, USA

Rovert J.Gale
Department of Chemistry
Louisiana State University
Baton Rouge
LA 70803, USA

Mark E. Zappi
Department of Chemical Engineering
P.O.Box 9595,
Mississippi State University
MS 39762, USA