

Aided Transport of Nano-Iron in Clay Soils Using Direct Electric Field

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ABSTRACT

The influence of direct current electric fields on the possible electrokinetic delivery of nano-iron slurry in clay for the purpose of fast and effective remediation of soil contaminants has been tested. Nano-iron can be introduced to soil hydraulically in slurry form, but in tight clay soil, delivery of a uniform distribution of the slurry may be difficult to achieve for effective remediation. Additionally, the limited life of the nano-iron particles, previously shown in field studies of being on the order of 4-8 weeks, further emphasizes the need for the nano-iron particles to reach the contaminated site efficiently before the particles oxidize and become ineffective. This study demonstrates that by integrating electrokinetics with nanotechnology, the transport of nano-particles can be electrokinetically enhanced for subsurface remediation of tight clay soils where transport time and process efficiency may be an issue.

Keywords: electrokinetic remediation, nano-iron, redox, electro-osmosis, electro-migration

1 INTRODUCTION

In most field situations, the contaminants are found adsorbed onto soil surfaces, iron-oxide coatings, soil colloids and natural organic matter. Most contaminants are retained in clay interstices as hydroxycarbonate complexes, or present in the form of immobile precipitates and products in soil pore throats and pore pockets that “lace” the vadose zone. This exacerbates the situation as the available technologies, such as in-situ bioremediation, chemical treatment or the traditional pump-and-treat method may not be able to treat the entire site effectively in low permeability soils.

Electrokinetics is the sustainable process of applying a low current electrical field across a porous medium, such as soil, to induce ionic migration and pore fluid movement. The process is a proven, sustainable technology that can transport liquids and slurries in clay soil at a significantly higher rate than hydraulic methods [1, 2].

In previous investigations [3], the application of direct electric current in soils was observed to contribute to the success of the desired transformation reactions by not only providing the “driving force” necessary for the delivery of

active reagents, but also by lowering the energy for the redox reactions to occur. This increase was attributed to the possible over-potential created by double-layer polarization of the clay surfaces leading to spontaneous Faradaic processes under the applied field.

2 BACKGROUND

2.1 Recent Research on Electrokinetics for Soil Decontamination

Remediation of heavy metal contaminants from cohesive, fine-grained soils has presented numerous challenges to geoenvironmental engineers. First, the inherent low permeability of the medium makes traditional pump and treat methods of contaminant removal infeasible. The hydraulic head required to force the flow of water through the soil voids at a predetermined flow rate, would be impractical beyond small-scale laboratory tests. Second, in-situ treatment methods such as bioremediation are generally costly and ineffective in the removal of metallic wastes [1]. Third, heavy metal contaminants have a tendency to sorb onto clay soil particle surfaces, thereby reducing ionic mobility and making conventional treatment methods even more difficult to apply successfully [2].

Recent work on reducing subsurface contamination has been conducted on the effects of changing the oxidation state of heavy metal precontaminated kaolinite clay. It has been shown that ferrous iron Fe (II) can be transported electrokinetically through a Cr (VI) pre-contaminated kaolinite soil bed and result in significantly more Cr (III) present at low to slightly acidic pH regions in the saturated clay [3].

2.2 Nanotechnology in Soil Decontamination

Previous studies have demonstrated that nano scale particles can be used effectively to transform or remove chlorinated hydrocarbons (CHCs) and heavy metals to less toxic or non-toxic hydrocarbons or oxidation states [3,4,5,6,7].

Laboratory tests have proven successful, with greater than 99% removal of TCE using nanoscale iron particles. Pilot field tests of the effectiveness of nano-iron as an environmental catalyst conducted at an industrial research facility waste disposal area showed that nano-iron particles

can remain reactive for 4 to 8 weeks. These tests also determined that nanoparticles had the greatest influence approximately 6 to 10 m around the injection well and could flow with groundwater for over a distance of 20 m. The injection of nano-iron particles in both the field and lab tests showed a drop in the redox potential [7].

2.3 Integration of Electrokinetics and Nanotechnology

Nano-iron can be introduced to soil hydraulically in slurry form and delivered via gravitational flow to the contaminated site. This method has proven successful in remediating a site contaminated by chlorinated solvents [7]. However, in tight clay soil, delivery of a uniform distribution of the slurry may be difficult to achieve for effective remediation due to the limited life of the nano-iron particles before deterioration. Electrokinetics (EK) is a proven, sustainable technology that can transport liquids and slurries in clay soil at a significantly higher rate than hydraulic methods [1,2,3]. The combination of these two technologies has not been studied before and may complement each other in the geoenvironmental field.

3 EXPERIMENTAL PROGRAM

3.1 Nano-iron

Polymer coated dispersed nano-iron, developed at Lehigh University, was used as the iron input into the system. Due to the polymer coating (polyvinyl alcohol-co-vinyl acetate-co-itaconic acid) the iron particles tend to repel each other, and as a result, remain suspended in solution rather than settling over time as occurs with bare nano-iron. The nano-iron particles are zero-valent (Fe^0) and have a diameter less than 100 nm for 80% of slurry batch sample. Zero-valent iron is an effective electron donor regardless of its particle size [7,8].

3.2 Electrokinetic Equipment

A modified electrophoretic (EP) cell (Econo-Submarine Gel Unit, model SGE-020) was used for the experiment and is composed of a rectangular, acrylic, translucent box with a rectangular (20 cm x 18.5 cm) sample tray placed inside it, as shown in Figure 1. To each side of the tray are two liquid chambers, which were used to hold electrolyte salt solution during the experiments.

The tray was modified by the installation of seven platinum wires of 0.25 mm diameter stretched across the tray transversely. The wires were glued to the acrylic tray in three locations using electrically conductive cement adhesive. The wires were labeled E1 to E7 from the anode side, as shown in Figure 1.

The voltage was supplied using an HP E3620A Dual Output DC Power Supply. The reference electrode used to take redox potential readings was an Accumet glass body

Calomel Reference Electrode 13-620-51 (Fisher Chemicals SP 138-500). For pH and temperature readings, the Extech Instruments ExStik II Refillable pH meter PH110, was chosen due to its ability to read the pH of both liquids and wet solids. Finally, the Perkin Elmer AAnalyst 200 Atomic Absorption Spectrometer was used to measure the iron concentration of liquid and soil samples.

3.3 Procedure

Saturated Georgia kaolinite clay and 2.0M NaCl solution was used to make a soil paste with 60% water content. A 2 mm thick uniform layer of the paste was spread onto the EP cell tray over the platinum wires.

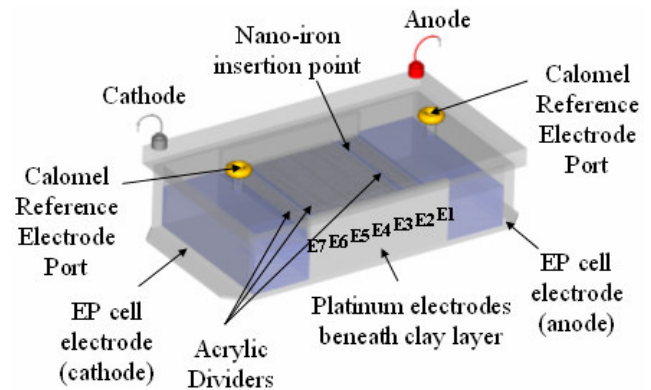


Figure 1: Modified Electrophoretic Cell Schematic

The anode and cathode chambers were filled with 675 mL each of the 2.0 M NaCl solution. The water level was 1.0 mm above the soil bed to ensure saturation throughout the experiment, but to not overtop the acrylic dividers, to ensure that all nano-iron transport in the system occurs through the soil layer. The nano-iron was inserted in the anode side groove, as shown in Figure 1. A constant potential of 5.0 V was applied across the electrodes to remain in the linear range of the power supply and to prevent excessive gas generation caused by electrochemical reactions at the electrodes [3].

Measurements were taken over 46 hours, with more frequent readings earlier on. The redox potentials were measured at each auxiliary electrode (E1-E7) with reference to the Calomel electrode. At the end of 46 hours, three soil samples were extracted above each auxiliary electrode for a total of 21 samples. The samples were diluted and analyzed using U.S. EPA method 7000A for atomic absorption spectrometry [9].

4 RESULTS

4.1 Redox Potential

It was determined that the redox potential reduced across the soil bed from anode to cathode, indicative of

nano-iron transport from anode to cathode, as shown in Figure 2. The presence of nano-iron pushed the redox potential to higher positive values at low pH (anode side), while lowering it to higher negative values at high pH (cathode side) than the electrokinetic effects alone. The diffusion of nano-iron without the electrical field showed no activation of the iron, as indicated by little or no change in the redox potential for the diffusion sample in Figure 2. These results showed that nano-iron was both transported and activated by the applied electrical field.

There were marked spatial and temporal oscillations of redox potential in the electrokinetic tests with nano-iron, as shown in Figure 3. These were more pronounced than those in the control or diffusion control tests, indicating enhanced nano-iron movement in the system. Redox potential fluctuated in time early on and then settled to a constant profile after about 17.5 hrs.

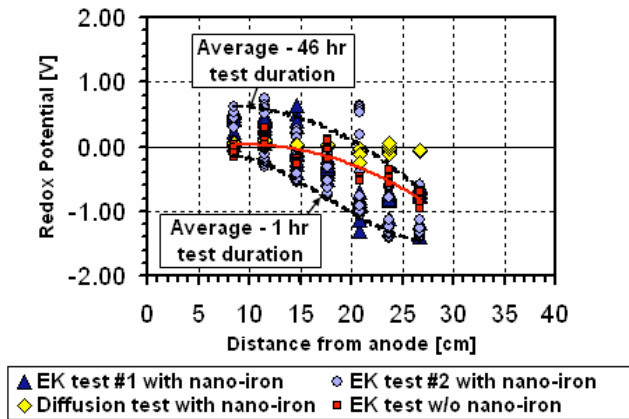


Figure 2: Redox Potential vs. Distance - Test Comparison

The post-test stoichiometric analysis of the measured quantity of Fe^{+2} at the sampling locations versus the corresponding redox potentials was compared to the Nernst equation predictions for half reaction. The data agreed well with the Nernst prediction at higher pH regions and displayed positive shift from the Nernst relation at low pH regions, possibly due to clay surface polarization. A comparison of the nano-iron movement between the electrokinetically enhanced movement and the diffusion test in Figure 4 shows the effect of 5.0 V potential applied to the system at 46.0 hrs. As observed, the electrokinetically enhanced transport activated the nano-iron corrosion at the cathode side, while the diffusive system did not show any sign of corrosion.

4.2 pH

The iso-electric point (IEP) of the nano-iron, which is the critical value at which the net surface charge is zero, occurs at a pH of 8.3 and was found to be independent of iron concentration [8]. The iron nanoparticles will be positively charged when the pH is less than 8.3 and

negatively charged for pH values greater than 8.3. The zeta potential of kaolinite is also a strong function of the pH of the system. Typically, the zeta potential will vary from -50 mV in alkaline conditions to 0 at approximately a pH of 2.0. Therefore, for pH values between 2.0 and 8.3, the nanoparticles will be attracted to the negatively charged clay surfaces and will stay on the surface, contributing to surface reactions. However, for pH values less than 2.0 or greater than 8.3, the iron will be released into the pore fluid and transported through the porous media.

Comparing the pH distributions shown in Figure 5, pH greater than 8.3 typically occurs at electrodes E6 and E7. pH of less than 2.0 was not experienced in the system. Therefore, it is expected that increased nano-iron transport will occur around E6 and E7, which may explain the increased negative redox potentials of E6 and E7 in Figures 2 and 3.

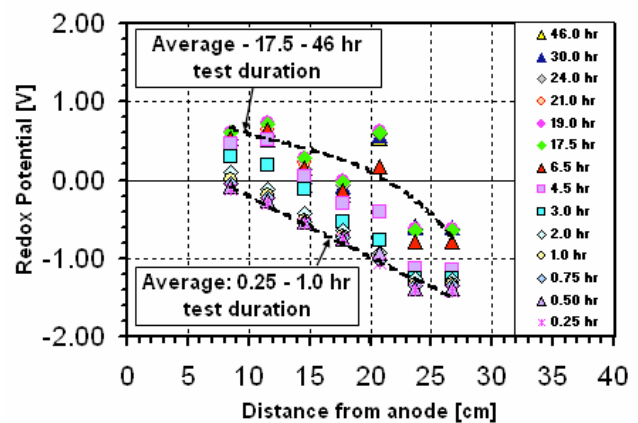


Figure 3: Redox Potential vs. Distance - Time Effects

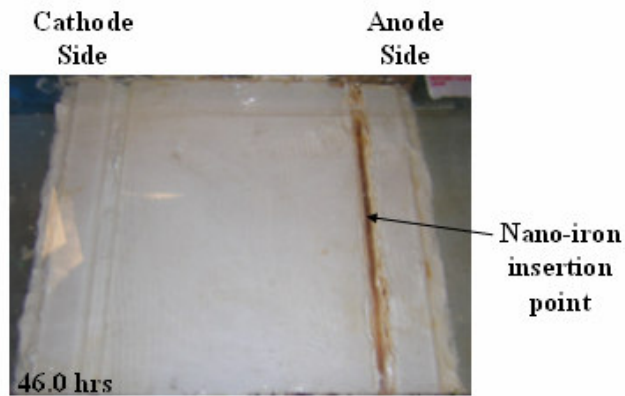
The electrokinetically enhanced transport and activation of nano-iron were evidenced by the higher negative potentials achieved in nano-iron specimens on the cathode side, at the same pH for the same test durations of the control specimens. Figure 6 shows the variation of redox potential (E_h) versus pH. The variation of E_h vs. pH in the electrokinetics only specimen follows closely the lower bound for electrolysis of water, while when nano-iron is transported using electrokinetics the system displays higher oxidation potential for iron.

5 CONCLUSIONS

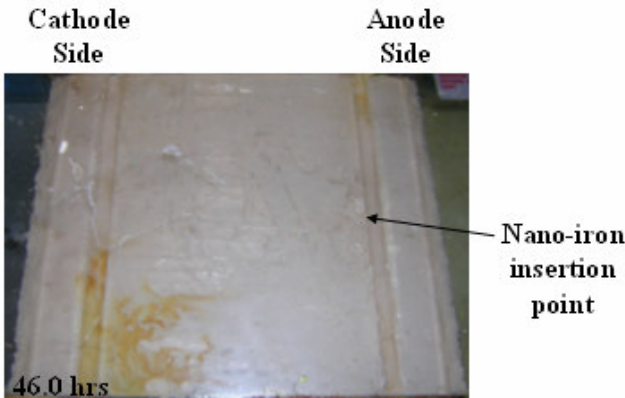
Analyte, containing polymer coated nano-iron particles, was electrokinetically injected into the soil to demonstrate the enhanced transport of nano-iron in clay soils using an applied electric field.

The significance of the results obtained in this study is two fold: 1) electrokinetically enhanced transport of highly reactive nano-particles designed for subsurface remediation is possible in tight clay soils where transport time and process efficiency are critical; 2) direct redox

measurements of the host medium in an integrated application of two technologies as described above can provide adequate evidence of their performance in the field.



(a)



(b)

Figure 4: Soil Bed at 46.0 hrs
(a) Diffusion Only (b) Electrokinetically Enhanced

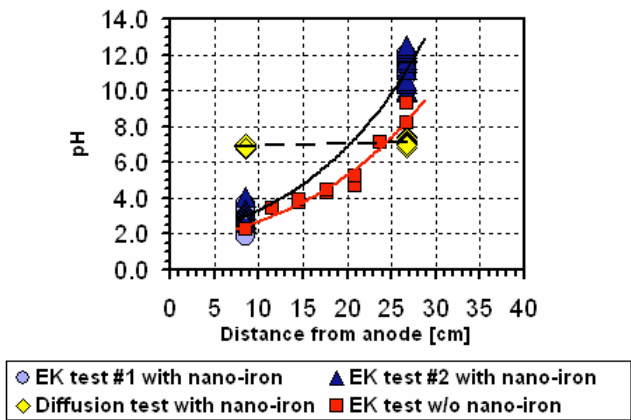


Figure 5: Spatial pH Distribution – Test Comparison

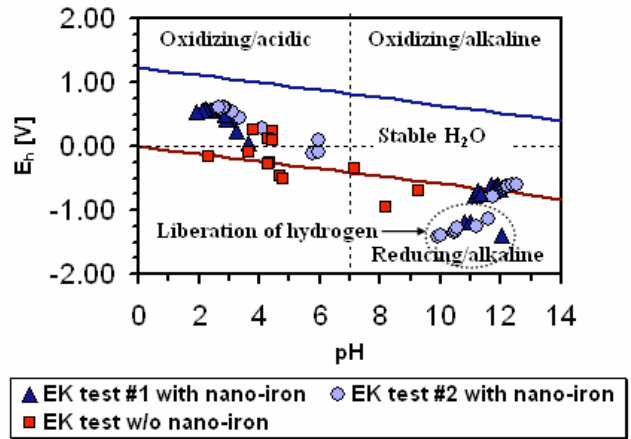


Figure 6: Redox Potential vs. pH – Test Comparison

REFERENCES

- [1] Reddy, Krishna R. and Parupudi, Usha S. (1997). "Removal of Chromium, Nickel, and Cadmium from Clays by In-Situ Electrokinetic Remediation." *J. Soil Contamination*, 6(4):391-407.
- [2] Yeung, Albert T. and Datla, Subbaraju. (1995). "Fundamental Formulation of Electrokinetic Extraction of Contaminants from Soil." *Can. Geotech. J.*, 32:569-583.
- [3] Pamukcu, Sibel, Weeks, Antoinette, and Wittle, Kenneth J. (2004). "Enhanced Reduction of Cr (VI) by Direct Electric Field in a Contaminated Clay." *Environ. Sci. Technol.*, 38, 1236-1241.
- [4] Elliott, D.W. and Zhang, W. (2001). "Field assessment of nanoscale bimetallic particles for groundwater treatment." *Environ. Sci. Technol.*, 35, 4922-4926.
- [5] Engelmann, M.D., Doyle, C.J., and Cheng, I.F. (2001). "The complete dechlorination of DDT by magnesium/palladium bimetallic particles." *Chemosphere*, 43, 195-198.
- [6] Li, F. and Vipulanandan, C. (2003). "Microemulsion Approach to Nanoiron Production and Degradation of Trichloroethylene." *Proceedings of CIGMAT-2003 Conference*, Houston, TX, II-1-3.
- [7] Zhang, Wei-xian. (2003). "Nanoscale Iron Particles for Environmental Remediation: An Overview." *J. Nanoparticle Research*, 5:323-332.
- [8] Sun, Y.P., Li, X.Q., Cao, J., Zhang, W.X., and Wang, H.P. (2006). "Characterization of Zero-valent Iron Nanoparticles." *Advances in Colloid and Interface Science*, 120:47-56.
- [9] U.S. Environmental Protection Agency. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," 3.3, 2004.