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The Performance of Electrochemical Remediation Technologies in Soil Mechanics

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In this paper a review is presented about studies involving the electrochemical remediation technologies in soil mechanics. The previous works include electrochemical technologies based on important approaches for effective and efficient pollution remediation, both on their own and in concert with other remediation techniques. Electrochemical remediation technologies for polluted soils, sediments and groundwater provides a systematic and clear explanation of fundamentals, field applications, as well as opportunities and challenges in developing and implementing electrochemical remediation technologies in geotechnical engineering. Results from these approaches reveal that ionic contaminants are absorbed to sediment particles and are often not available for removal by the simple flushing action of water. The pH shift produced by the electrolysis of the water effectively desorbs contaminating ions. In clayey sediments, hydraulic flow through pores can be extremely limited. Electrokinetic remediation is an effective method of inducing movement of water, ions, and colloids through fine-grained sediment. The aim of this paper is to provide an updated summary of the works in this field and the works have been done summarized together with the outcome of electrochemical science in soil mechanics.

Keywords: Electrochemical Remediation, Soils, Electrokinetic remediation, ECRT, In-Situ, Ex-Situ

1. INTRODUCTION

Electrochemistry is a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte), and which involve electron transfer between the electrode and the electrolyte or species in solution. If a chemical reaction is driven by an external applied voltage, as in electrolysis, or if a voltage is created by a chemical reaction as in a battery, it is an electrochemical reaction. In contrast, chemical reactions where electrons are transferred between molecules are called oxidation/reduction (redox) reactions. In general, electrochemistry deals with situations where oxidation and reduction reactions are separated in space or time, connected by an external electric circuit.

2. ELECTROCHEMICAL REMEDIATION TECHNOLOGY (ECRT)

Electrochemical Remediation Technology (ECRT) uses a proprietary AC/DC electrical signal to mineralize organic compounds, and to mobilize and remove metal contaminants. Electrochemical remediation technologies (ECRTs) are part of a broader class of technologies known as direct current technologies (DCTs). These technologies use an electric current in the treatment process to either mobilize or break down contaminants in soils or sediments. The technologies can be applied to both organic and inorganic contaminants. Proprietary AC/DC converters produce a low-voltage, low-amperage electrical field that polarizes the soil or sediment, causing soil particles to charge and discharge electricity. This causes redox reactions that occur at all interfaces within the soil, groundwater, and contaminant and electrode system, mineralizing organics and increasing the mobilization of metals. Metals migrate to the electrodes where they are deposited and removed with the electrodes. There are several distinctions between ECRTs and traditional electrokinetics. First, relatively low energy input is required to perform remediation. Second, ECRTs generally are effective within months, instead of years, and they can be performed in-situ or ex-situ. Third, metals generally migrate to and deposit at both electrodes, unlike classical electrokinetic techniques, in which metals migrate in the direction of only one electrode.

2.1. Electrochemical Remediation Theory

Electrochemical remediation involves the application of a low density direct current to a pair of positive (anode) and negative (cathode) electrodes placed in the soil to mobilize contaminants in the form of charged species. The contaminants within the electric field are transported to the anode or to the cathode where they are removed by one of the following methods: electrodialysis into electrolyte solutions, adsorption onto the electrode, precipitation or co-precipitation at the electrode, pumping next to the electrode, completing with ion exchange resins, or capturing in permeable reactive barriers. In the United States and Europe, there is a patent for Electrochemical Remediation Technologies (ECRTs), which consist of two types. Electrochemical GeoOxidation (ECGO) uses a low voltage, low amperage DC/AC current to induce a polarization field within the sediment. The sediment acts as a capacitor, discharging and charging electricity resulting in redox reactions, which cause desorption of the contaminants from the sediments and mineralization of the organics to their inorganic constituents (e.g., carbon dioxide and water). Empirical evidence indicates that reaction rates are inversely proportional to grain size, such that ECRTs remediate faster in finer-grained material typically found at sediment sites. The second method of removal, Induced Complexation (IC), significantly enhances the mobilization of metals and radio nuclides in a sediment matrix through redox reactions that desorb the contaminants from the sediment and create ionic metal complexes. [5]. Electrochemical remediation was originally developed for remediation of heavy metal polluted soil. [22]. the electrokinetic phenomena in porous media are based on the relative motion between a charged surface and the bulk solution at its interface. The formation of an electric double layer at the charged surface of clay particles explains the processes mobilizing the charged particles via three phenomena: electromigration, electroosmosis, and electrophoresis. These processes force the aqueous phase and ions to desorb from the sediment surface and migrate through the electric field either towards the anode or the cathodes, depending on the speciation.

Electromigration is the movement of ions and ionic complexes in a soil solution due to an applied electric field. The ions move towards the electrode of opposite charge: anions towards the anode and actions towards the cathode. Electromigration is the most important transport mechanism aiding electrochemical remediation [17] and is dependent on tortuosity, porosity, and the charge of the ion. [1]. Electroosmosis is the movement of water in a porous media in an applied electric field. Soil particles are negatively charged, which creates a diffuse double layer of water and dissolved captions around the soil particles. When an electric field is applied, the captions will migrate in the direction of the cathode along with the water molecules. Whereas values of hydraulic conductivity can vary many orders of magnitude for different soil types, the electroosmotic conductivity lie in a narrow range of 1x10-9 to 1x10-8. Thus, an electric field is a much more effective force driving the fluid through fine grained soils of low hydraulic conductivity than a hydraulic gradient. [3]. Furthermore, electroosmosis is independent of the pore size distribution or the presence of macro8 pores. The effect of the electroosmosis process to the total mass transport varies according to soil type, water content, types of ion species, and pore fluid concentration of ions. [2]. the final phenomenon affecting electrochemical remediation is electrophoresis. Electrophoresis is the transport of particles in an applied electric field and includes all charged particles (e.g. colloids, clay particles, organic particles). [1]. Since only released ions in the pore water are transported in the electric field during electrochemical remediation, the precipitated and adsorbed metals in the sediment must be converted to mobile ionic forms before they can be removed. Mobilization is enhanced in an electrochemical reactor by pH changes in the sediment during the treatment. Water splitting at the anode occurs via the following reactions (Equations 1 and 2) and results in an acidic front that moves from the anode to the cathode. [12].

$$\text{(1) Cathode: } 4\,H_2O + 4\,e^- \rightarrow 2\,H_2(g) + 4\,OH^-$$

$$\text{(2) Anode: } 2\,H_2O \rightarrow O_2(g) + 4\,H^+ + 4\,e^9$$

Theoretically, in an electrochemical reactor, equal amounts of current are carried by anions and cations in solution. Closer to the electrodes, the concentration of anions and cations decreases compared to the bulk concentration. When the concentration reaches zero, the limiting current density has been reached. Operation at current densities higher than the limiting current results in the water splitting phenomenon (formation of H^+ and OH^-). The limiting current is lower at the anode than at the cathode, thus an acidic front is formed desorbing metals and transporting them with water and soil particles towards the cathode. For metals of concern that are not mobile at low pH (e.g. As or Cr (VI)), surfactants and complex agents have been used to assist in the migration. [24] Surfactants have also been used to assist transport of organic contaminants in electrochemical remediation. [6].

2.2. Limitations and Concerns in ECRT

ECRTs reaction rates are inversely proportional to grain size, so ECRTs remediate faster in clays and silts than in sands and gravels. The working depth of the technology is limited by the availability of drilling technology to install the electrodes.

2.3. Applicability

Electrochemical remediation technologies (ECRTs) are part of a broader class of technologies known as direct current technologies (DCTs). These technologies use an electric current in the treatment process to either mobilize or break down contaminants in soils or sediments. The technologies can be applied to both organic and inorganic contaminants. ECRTs are patented in the United States and Europe and include the Electro Chemical GeoOxidation (ECGO) process to destroy organics in soil, and the Induced Complexation (IC) process to mobilize and remove metals in soil and ground water. ECRTs have been successfully applied to soil, sediment and ground water both *in-situ* and *ex-situ.* Among the contaminants remediated to below regulatory standards are VOCs, CVOCs, SVOCs, PAHs, PCBs, phenols, fuels, hydrocarbons, explosives, mercury, cadmium and lead. In many of the more than 50 successful projects, multiple contaminants have been removed with a single system, including combinations metals and organics. ECRTs remediate metals, radionuclides, and organic compounds in soil and groundwater. Metals remediated include mercury, arsenic, lead, cadmium, chrome, copper, nickel, and zinc. Organic compounds remediated include semi-volatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs); volatile organic compounds (VOCs), and total petroleum hydrocarbons. Substances composed primarily of carbon and hydrogen atoms that have boiling points greater than 200° C. Common SVOCs include PCBs and PAHs. A chemical compound that contains more than one benzene ring. They are commonly found in petroleum fuels, coal products, and tar. One of a group of carbon-containing compounds that evaporate readily at room temperature. Examples of VOCs include trichloroethane, trichloroethylene, benzene, toluene, ethyl benzene, and xylene (BTEX). Typically, ECRTs are implemented in-situ. In some applications they have been used ex-situ. [27].

2.4. Developments in Electrochemical Remediation

The first electrochemical remediation experiments were performed in soil at the Technical University of Denmark. In their PhD theses, Ottosen et al. [24] described the development of the experimental cell and first electrodialytic remediation experiments and Hansen et al. [11] tested the suitability and advantages of different ion exchange membranes for use in the electrodialytic cell (Note that the difference between electro kinetic and electrodialytic experiments are that the former applies current directly to the soil with electrodes in the soil and the latter uses an ion exchange membrane and separate electrolyte solution compartments). From 1995 to 2000, three more PhD studies were completed on electrodialytic soil remediation: Jespersen [28] built the first pilot and full scale plants and Ribeiro [29] and Kliem [30] studied the changes in soil characteristics by different analytical methods during and after electrodialytic remediation. Together with developing the soil remediation technique, the electrodialytic remediation process was also used to remediate other porous materials, such as fly ash (Pedersen [31]), impregnated wood waste (Ribeiro [29]) and waste water sludge (Jakobsen et al. [12]). Pedersen introduced the stirred electrodialytic treatment cell in her PhD thesis to combat problems of high electrical resistance and hardening of the material. Christensen [32] used oxalic and phosphoric acid as a desorbing agent to remove Cu, Cr, and as from impregnated wood waste, in the laboratory, bench, and pilot scale. This was the first time large scale experiments were made for other materials other than soil. There is definite potential for remediating harbor sediments as well by the electrodialytic method (Nyostrom [33]). Dredged sediment is often too contaminated to be dumped at sea. Sediment consists of many similar components as soil: clay, silt, organic matter, oxides, and carbonates. Therefore, the expectations for the remediation of sediment were based on the past experiences from the electrodialytic remediation of soil. The greatest difference is in the effect of salinity on remediation success, because heavy metals can form uncharged complexes with chloride, thus not being mobile in an electric field. Grande and Gent [9] conducted an electro kinetic field scale in-situ experiment in a 2000 m^2 waste lagoon located in a tidal marsh in the United States. The saline sediment was remediated for both heavy metals and chlorinated solvents (PCEs). The field experiment lasted 96 weeks and showed that the heavy metals moved towards the cathode. In 77.5% of the area the chromium level was reduced to under background level (<109 mg/kg) and in 78.8% of the area the cadmium level was reduced to under background level (<3.1 mg/kg). Degradation of up to 99.0% of PCEs was also experienced. The current density had to be lowered during the remediation because of formation of Cl_2 (g) at the anodes. The chloride gas reacted with dissolved organic carbon in the system and formed trihalomethanes, especially chloroform. Air sparing at the anodes and replacement of the electrolytes were used to reduce the production of chloride gas.

Roulier et al. [34] studied the feasibility of electro kinetic soil remediation in horizontal Lasagna TM cells and described some problems related to the installation and operation of horizontal electrodes. A hydraulic fracturing process (adapted from oil field practice), where a horizontal layer of porous electrode material (e.g. graphite) can be installed, was suggested as a suitable installation method. No major problems were anticipated installing electrodes this way, but in an initial assessment some problems maintaining flow of liquids and electrical current in the electrode layers seemed to occur. Good hydraulic as well as electrical conductivity in the electrode material are critical to the success of the electrochemical process. Evolved gases at the electrodes must be removed continuously to maintain satisfactory electrical conductivity. In a vertical electrode design, the gases can bubble out and do not cause problems, but in horizontal electrodes the gases do not vent readily but may displace water, thereby reducing the contact between the electrodes, leading to decreased electrical conductivity. It was claimed that the use of horizontal Lasagna cells only beneath the water table would reduce the problems with water flow in electrode fractions that exhibit reduced transmissibility due to evolution of H_2 and O_2 from electrolysis of water.

3. CONCLUSION

Electro kinetics may be an appropriate remediation technique in sediment remediation based on advantages and disadvantages of electrochemical remediation because:

- There are currently no other viable in-situ methods for treating inorganic and organic compounds in porous media simultaneously.
- Ionic contaminants are absorbed to sediment particles and are often not available for removal by the simple flushing action of water. The pH shift produced by the electrolysis of the water effectively desorbs contaminating ions.
- In clayey sediments, hydraulic flow through pores can be extremely limited. Electro kinetic remediation is an effective method of inducing movement of water, ions, and colloids through fine-grained sediment.
- The process is competitive in cost and remediation effectiveness to other methods currently in use.

However, electrochemical remediation does have associated limitations, such as:

- The electro kinetic process is limited by the solubility of the contaminant and the desorption of contaminants from the soil matrix. Heavy metals in metallic states are difficult to dissolve and separate from soil samples. Organic compounds may be tightly bound to natural organic matter. The process is also not efficient when the target ion concentration is low and non-target ion concentration is high.
- Acidic conditions and corrosion of the anode may create difficulties in in-situ efforts.
- Precipitation of species close to the electrode is an impediment to the process. Heavy metals can prematurely precipitate close to the cathode at their hydroxide solubility value.

References

1. Y.B. Acar, *Civil Engineering*, 62(1992) 58-60
2. Y.B. Acar, and A.N. Alshawabkeh, *Environmental Science and Technology*. 27(1993) 2638-47.
3. N. Akram, N. Alshawabkeh, A. T. Yeung, M.R. Bricka, *Journal of Environmental Engineering*, (1999) 27-35
4. T.D. Bucheli, and O. Gustafsson, *Chemosphere*, 53(2003) 515-22
5. F. Doering, N. Doering, J.L. Iovenitti, D. G. Hill, and W. A. McIlvride, Electrochemical Remediation Technologies for Soil, Sediment and Ground Water. *The Annual International Conference on Soils, Sediment, and Water*. (2000)

6. M. Elektorowicz, and J. Lin, Removal of PAH using Electrokinetic Transport of Biosurfactants in Clayey Soil, *3rd Symposium on Electrokinetic Remediation*. (2001)
7. N.R. Francingues, and D.W. Thompson., Innovative dredged sediment decontamination and treatment technologies, DOER Technical Notes Collection (ERDC TN-DOER-T2), U.S. Army Engineer Research and Development Center, Vicksburg, MS (2000)
8. A. Giannis, E. Gidarakos. *J. Hazard. Mater.*, B123 (2005)165-175
9. S. Grande and D. Gent, Electrokinetic remediation of contaminated sediments. In: Remediation and Beneficial Reuse of Contaminated Sediments. *Conference Proceedings. Edited by Hinchee, R.E., A. Porta, and M. Pellei. Battelle Press, Columbia Richland*. (2002) 205-212
10. G. Orjan, F. Haghseta, C. Chan, J. Macfarlane, and P.M. Gschwend. *Environmental Science and Technology*, 31(1997) 203-9
11. H.K. Hansen, *J. Chem. Technol. Biotechnol.*. 70(1997) 67-73
12. M.R. Jakobsen, J. Fritt-Rasmussen, S. Nielsen, L.M. Ottosen. *J. Hazard. Mater.*106B (2004)127-132
13. K. Abidin, Y. Yukselen, *J. Hazard. Mater.*, B120 (2005)119-26.
14. R. Lageman, W. Pool, G. Seffinga, *Chemistry and Industry*, 18(1989) 585-590.
15. R. Lohmann, J.K. Macfarlane, and P.M. Gschwend, *Environ. Sci. Technol.*, 39(2005) 141-48.
16. G. M. Nystrom, Electrodialytic removal of heavy metals from contaminated harbour sediments. Department of Civil Engineering, Technical University of Denmark, PhD thesis, (2004)
17. H. Niroumand, K.A. Kassim, *Int. J. Phys. Sci.*, 6 (2011) 3938-3942
18. H. Niroumand, K.A. Kassim, *Int. J. Phys. Sci.*, 6(2011)1583-1590
19. H. Niroumand, K.A. Kassim, *Electronic Journal of Geotechnical Engineering*, 15L(2010) 1151-1158
20. H. Niroumand, K.A. Kassim, *Journal of applied science*, 28 (2011) 2012-2016
21. H. Niroumand, K.A. Kassim, R. Nazir, *American journal of applied science*, 7(2010)1396-1399
22. L.M. Ottonsen, H.K. Hansen, S. Laursen, A. Villumsen, *Environmental Science and Technology*. 31(1997) 1711-15
23. L.M. Ottensen, H.K. Hansen, L. Hansen, B.K. Kliem, G. Bech-Nielsen, B. Pettersen, A. Villumsen, *Contaminated Soil*, (1998) 471-8
24. L.M. Ottosen, H.K. Hansen, C. Hansen, *J. Appl. Electrochem.*, 30(2000)1199-1207
25. A.J. Pedersen, L.M. Ottosen, A. Villumsen, *J. Hazard. Mater.*, B122(2005)103-9
26. M. Roulier, M. Kemper, S. Al-Abed, L. Murdoch, P. Cluxton, J. Chen, W. Davis Hoover, *J. Hazard. Mater*, B77(2000)161 – 176
27. F. Doering, N. Doering, J. L. Lovenitti, D. G. Hill. *Symposia Papers Presented before the Division of Environmental Chemsitry American Chemical Society, Sandiego, CA*, 41:1(2001) 1075-1079
28. R.D. Jespersen. Elektrokinetisk jordrensning. Department of Geology and Geotechnical Engineering and Department of Chemistry, Technical University of Denmark and A/S Bioteknisk Jordrens. PhD thesis (1996)
29. A.B. Ribeiro. Use of electrodialytic remediation technique for removal of selected heavy metals and metalloids from soils. Department of Geology and Geotechnical Engineering and Department of Physical Chemistry. Technical University of Denmark. PhD Thesis (1998)
30. B.K. Kliem. Bonding of heavy metals in soil. Department of Geology and Geotechnical Engineering and Department of Chemistry, Technical University of Denmark. PhD Thesis (2000)
31. A. J. Pedersen. Electrodialytic Removal of Heavy Metals from Fly Ashes. Department of Civil Engineering, Technical University of Denmark. PhD Thesis (2002)
32. I.V. Christensen. Electrodialytic Remediation of CCA-Treated Waste Wood. Department of Civil Engineering, Technical University of Denmark. PhD Thesis (2004)
33. G.M. Nystrom. Electrodialytic removal of heavy metals from contaminated harbour sediments. Department of Civil Engineering, Technical University of Denmark, PhD thesis (2004)

34. M. Roulier, M. Kemper, S. Al-Abed, L. Murdoch, P. Cluxton, J. Chen, W. Davis - Hoover.. *J. Hazard. Mater*. B77(2000) 161 – 176.