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Electrokinetics applied in remediation of subsurface soil contaminated with chlorinated ethenes – A review

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Abstract

Electrokinetics is being applied in combination with common in-situ remediation technologies, e.g. permeable reactive barriers, bioremediation and in-situ chemical oxidation, to overcome experienced limitations in remediation of chlorinated ethenes in low-permeable subsurface soils. The purpose of this review is to evaluate state-of-the-art for identification of major knowledge gaps to obtain robust and successful field-implementations. Some of the major knowledge gaps include the behavior and influence of induced transient changes in soil systems, transport velocities of chlorinated ethenes, and significance of site-specific parameters on transport velocities, e.g. heterogeneous soils and hydrogeochemistry. Furthermore, the various ways of reporting voltage distribution and transport rates complicate the comparison of transport velocities across studies. It was found, that for the combined EK-techniques, it is important to control the pH and redox changes caused by electrolysis

for steady transport, uniform distribution of the electric field etc. Specifically for electrokinetically enhanced bioremediation, delivery of lactate and biodegrading bacteria is of the same order of magnitude. This review shows that enhancement of remediation technologies can be achieved by electrokinetics, but major knowledge gaps must be examined to mature EK as robust methods for successful remediation of chlorinated ethene contaminated sites.

Key words

Electrokinetics, chlorinated ethenes, PCE, TCE, low permeable soil, transport velocities

1. Introduction

Electrokinetic (EK) remediation is a group of remediation techniques utilizing the transport processes obtained when applying an electric DC field to soil. EK has the major advantage of being applicable to fine-grained soils in which other remediation techniques tend to fail. EK enables transport of ions by electromigration (EM), water by electroosmosis (EO) and charged particles by electrophoresis (EP). In recent years, research, development and implementations within EK have combined the unique EK transport processes with already practised remediation techniques to overcome the inefficiency of these latter in fine-grained soils (Lima et al., 2017).

This paper is a focused review on the results obtained with EK (from laboratory scale to full scale) in combination with other techniques for remediation of subsurface soil contaminated by chlorinated ethenes: bioremediation, in situ chemical oxidation (ISCO) and reactive barriers. The objective of the paper is to identify important knowledge and knowledge gaps in order to engineer EK in combination with other in-situ technologies for remediation of heterogeneous subsurface soils contaminated with chlorinated ethenes.

2. Electrode reactions, potential difference and current

When applying an electric DC field to soil, coupled electrode reactions occur; oxidation at the anode and reduction at the cathode. In EK remediation systems, electrolysis of water most often prevails:

Thus, around the cathode, a reducing and alkaline environment develops, whereas the environment around the anode becomes oxidized and acidic. A variety of other electrode processes may occur simultaneously depending on the applied potential, electrode material and solution chemistry. For example, when removed chloride ions reach the anode, there will be oxidization to

or when iron anodes are used the process, the anode corrodes:

In EK remediation, the electric DC field is applied as constant voltage (Bruell et al., 1992), (Chang et al., 2006) or constant current (Chowdhury et al., 2017b). When applying a constant current, the average charge transfer (the current) is the same in every cross section between the electrodes. When the resistivity differs over the cross-section of soil, the current will be highest in the zone with the lowest resistivity. Applying a constant voltage, on the other hand, does not necessarily result in the same potential drops [V cm^{-1}] throughout the soil. Varying resistivities result in different potential differences. Zones with high resistivity will have a high potential drop compared to zones with a low resistivity. In experimental work with EK remediation, a constant voltage is often applied to the electrodes, which is then directly related to an average potential difference in the soil, e.g. 1 V cm^{-1} .

It must be stressed, that there can be huge variations from the average potential gradient in heterogeneous soil systems, not at least because the soil conductivity will change due to geochemical changes caused by the treatment. These changes will not be equally distributed throughout the soil, and the potential differences change accordingly. A primary challenge for engineering field implementation of EK is the development of non-linear geo- and physicochemical conditions between the electrodes (Gabrieli and Alshawabkeh, 2010).

In published research on EK-remediation of chlorinated ethenes, the average potential drop in the soil is calculated directly from the applied voltage. However, a fraction of the potential drop will be at the electrodes, which should be subtracted from the applied voltage before the average voltage gradient in the soil is calculated. As the potential drop at the electrodes is often low compared to the total voltage applied, it is neglected. Ho et al. (1997) studied the relationship between applied voltage and EO in natural clay. The flow rate varied almost linearly with the applied voltage in the range of 0.1-1 V cm⁻¹. Extrapolating the fitted line showed, that at 0.06 V cm⁻¹, the potential gradient would be too low to drive EO. This voltage probably reflects the voltage required to drive the electrode reactions and the over-voltages associated with the particular setup (Ho et al., 1997).

When comparing transport velocities by EM, EO or EP [cm d⁻¹], for different systems or components, it is necessary to relate the velocity to the driving force, i.e. the potential gradient [V cm⁻¹]. The transport velocity per voltage applied thus have the unit [cm² d⁻¹ V⁻¹]. In this review, the potential gradient used in the calculation is the average, calculated based on the applied voltage reported. Hence, the potential differences caused by the electrode reactions are neglected.

3. Electrokinetic transport processes

97

98 EK-transport processes are described in this chapter together with the factors determining their
99 velocities. The basis for EK-transport processes is charge and specifically for EP and EO that particles
100 carry a net surface charge, which is counter-balanced by ions in the liquid phase in the very close
101 vicinity of the particle (the electric double layer). The first layer comprises ions adsorbed onto the
102 positively or negatively charged particle by chemical interactions. The second layer is composed of
103 ions attracted electrostatically. This second layer is diffuse and more loosely associated with the
104 particle. It consists of free ions that constantly move in the thin fluid layer under the influence of
105 electric attraction to the particle and thermal motion. The charge of a particle is often expressed by
106 the zeta potential. However, in principle, the zeta potential is the potential difference between the two
107 layers in the electrical double layer. Hence, the zeta potential is not a characteristic of the actual
108 particle. It is influenced by the chemistry of the soil solution. For example, the zeta potential of
109 bacteria decreases with increasing ionic strength of the solution (Zhang et al., 2015). The sign of the
110 zeta potential can be changed near the electrodes during the EK process due to the electrode reactions
111 and the movement of the acid front near the anode. Hence, the direction of the EO/EP can be reversed
112 if the movement of the acid front is not controlled.

113

114 Table 1 summarizes the major parameters determining the velocity for the different transport
115 processes (based on chapter 3.1-3.3).

116

117 *3.1 Electromigration*

118 While EP and EO are electrokinetic transport processes, EM is the electric current itself. In soil, ions
119 in the soil solution carry the current. Anions move towards the anode and cations towards the cathode.

120 At infinite dilution in water, the ionic mobilities of common ions are in the range of $1 \cdot 10^{-8}$ to $10 \cdot 10^{-8}$

$8 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Mitchell, 1991), which corresponds to $69\text{-}690 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$. The ionic mobility of an ion relates closely to the aqueous diffusion coefficient in non-flowing systems and the dispersion tensor in flowing systems. In soils, however, the velocity is significantly lower as the ions cannot move by EM to the electrodes by the shortest route. Soil particles and air-filled voids block the direct path. The effective ionic mobility of a specific ion is a function of its molecular diffusion coefficient, soil porosity, tortuosity factor, and charge (Reddy and Cameselle, 2009). Also adsorption/desorption and precipitation/dissolution processes influence the amount and type of ions in solution under different conditions, and thereby EM of the specific ions.

The electric current is carried by ions in the electric double layer and by the ions dissolved in the pore water, which have different characteristics (Pengra and Wong, 1996). Charged porous media are filled at least by counter-ions. The dynamics of counter-ions, water molecules and co-ions depend strongly on the water content of the soil matrix. For compact matrices, the water content is low, and EM is slowed down. For less compact matrices, the dynamics of water molecules and counter-ions approach that in the bulk solution (Marry et al., 2003).

3.2 Electrophoresis

Charged particles will move by EP. The applied electric field, which sets the ions in the double layer in motion, acts with an electrostatic force on the particle itself due to the surface charge. The EP will be in the direction of the cathode if the particle has a net positive surface charge, and towards the anode, if the charge is negative. DeFlaun and Condee (1997) found reduced rates of transport for EP of bacteria in soils with silt and clay fractions compared to sand, indicating a major importance from the pore size on the EP mobility. The closer the particle is to a solid surface, the more profound is the boundary retarding effect, which is measured as a reduction in particle EP mobility (Tsai et al., 2011).

Up to a 90% mobility reduction was observed when the thickness of the double layer surrounding the particle was comparable to the particle radius if the particle was sufficiently close to the solid plane. The lower the permeability of the medium, the more profound is this retarding effect (Tsai et al., 2011).

3.3 Electroosmosis

EO is a coupled flow (Heister et al., 2005). When the electric field is applied to soil, ions in the diffuse layer will move. Generally, the diffuse layer in soils mainly consists of cations. They are transported towards the cathode, and push and drag water molecules towards the cathode. This movement of water is EO, and the amount of water moved per ion in solution is large (Ballou, 1955).

EO is only significant in materials with fine pores due to their high relative surface charge. For example, Mikkola et al. (2008) reported insignificant EO in pure sand, whereas EO increased with increasing fraction of silt. Further, EO is most significant when the ion concentration in the pore water outside the electric double layer is low. West et al. (1999) experienced that EO in a clayey soil was significantly lower when the clay was contaminated with Pb above the cation exchange capacity than when below. The pH also influences the surface charge of the particle and hereby EO. At low pH, the flow direction can reverse. For example, Cherepy and Wildenschild (2003) experimentally illustrated the necessity for neutralizing the pH changes at the electrodes to obtain steady EO. They studied a natural clayey soil in which both the EO and hydraulic conductivity decreased over time. When neutralizing the pH changes at the electrodes, steady EO was obtained during 31 days of testing. In this soil, the EO velocity was three orders of magnitude larger than the hydraulic velocity (Cherepy and Wildenschild, 2003). EK-remediation techniques are often targeted towards removal of

contaminants or supply of reagents by EP, EO or EM, thus soil chemistry changes over time, thus continuously influencing EO.

3.4 Influence from non-linear and transient changes on remediation

The soil system changes during EK treatment and strongly influences the transport velocities. This is important to consider when designing full-scale remediation. As Reynolds et al. (2008) states, many complicating phenomena occur due to the application of an electric field, including ion diffusion, ion exchange, development of osmotic and pH gradients, desiccation due to heat generation at the electrodes, mineral decomposition, precipitation of salts or secondary minerals, electrolysis, hydrolysis, oxidation, reduction, physical and chemical adsorption.

Knowledge of the site-specific electrical conductivity distribution and induced changes is important to design the remediation such that the current flow where the contaminants are. The conductivity in homogeneous, inert porous materials depends on the ion concentration, composition and water content. However, soils are heterogeneous, and degradation of contaminants along with the before mentioned changes stated by Reynolds et al. (2008) will influence the electrical conductivity. The overall pattern is highly complex, partly because the changes induced by the applied electric field are transient (time and space dependent). The often non-linear response in remediation time and energy consumption required to degrade a target level of contaminants indicates the need for a site-specific approach and optimization (Wu et al., 2013). In addition, the relatively low permeability of silt and clay soils coupled with the transient and heterogeneous geochemical conditions result in transient fluid flow and development of negative or positive pore pressure (Gabrieli and Alshawabkeh, 2010), which will influence transport patterns. In summary, for the most complicated cases, concentration,

temperature and pressure gradients are in play in addition to the applied potential gradient, i.e. all direct and coupled flows as outlined in Heister et al. (2005) are possible.

Table 2 organizes the outlined phenomena into three categories: (I) effects from applying the DC field to an inert system, (II) changes in the soil in response to the effects in (I), and (III) effects caused by the nonlinear and transient nature of the effects and changes in (I-II).

4. Chlorinated ethene degradation pathways

Chlorinated ethenes are subject to abiotic and biotic degradation (Vogel et al., 1987), following specific degradation pathways depending on the mechanisms involved (Figure 1). Combination of EK with other techniques induce specific degradation pathways.

4.1 Abiotic reduction

The abiotic reduction requires a supply of electron donors, for which zero valent metals can be applied (Roberts et al., 1996). During chemical reduction, chlorinated ethenes can concurrently follow β -elimination with the formation of chlorinated acetylenes (Figure 1, dotted arrows), and hydrogenolysis forming chlorinated intermediates or hydrocarbons (Figure 1, solid arrows) (Arnold and Roberts, 2000). For β -elimination, the formation of toxic chlorinated intermediates is bypassed and the reaction products include chloride ions (Cl^-) and metal ions (Durante et al., 2013), e.g. Fe^{2+} when zero valent iron (ZVI) is used as a reductant. For ZVI it has been shown, that 87% of PCE, 97% of TCE, 94% of cis-DCE, 99% of trans-DCE follows β -elimination (Arnold and Roberts, 2000). Hence, limited formation of vinyl chloride (VC).

EK has been applied to transport chlorinated ethenes towards permeable reactive barriers (PRB) in low permeable soils for abiotic degradation of the contaminants. These PRBs often contain ZVI (details in chapter 6). Hence, in such barriers, the degradation follows these above outlined pathways β -elimination and secondary hydrogenolysis.

4.2 Biotic reduction

Generally, microbial degradation is facilitated only if the reaction can yield energy (Gibbs free-energy below 0), which is true for reduction of chlorinated ethenes and oxidation of the chlorinated intermediates. Microbial reductive dechlorination of chlorinated ethenes follows a sequence with the stepwise formation of the degradation intermediates (Figure 1, solid arrows) (Maymó-Gatell et al., 1997). Specific redox conditions are required for this reductive biodegradation to occur. The *Dehalococcoides* (*Dhc*) group of bacteria enable reductive dechlorination of tetrachloroethylene (PCE) and trichloroethylene (TCE) beyond the dichloroethylene intermediates (cis-DCE, trans-DCE, 1,1-DCE). For complete reductive dechlorination of chlorinated ethenes to the nontoxic end-product ethene, *Dhc* must carry a specific gene for vinyl chloride reductase (*vcrA*) (Lee et al., 2013; van der Zaan et al., 2010). In addition, hydrogen (H_2) must be available as an electron donor for the reduction of chlorinated solvents by *Dhc* (Fennell et al., 1997), possibly supplied by fermentation of a carbon source, e.g. lactate (Scheutz et al., 2008). The *Dhc* are strict anaerobes. Consequently, the surrounding environment must be sulfate reducing and/or methane forming, preferably with an oxidation-reduction potential (ORP) below -100 mV (Kästner, 1991). Furthermore, the activity of *Dhc* is affected by the pH, with pH 6.8-7.8 being optimum (Middeldorp et al., 1999). *Dhc* appear to be inhibited for pH below 5 and above 10, with recovered activity when favorable pH conditions are reestablished (Dennis et al., 2008), however, the duration of low pH exposure affects the ability of *Dhc* to recover activity at circumneutral pH (Yang et al., 2017).

239

240 Application of EK enhanced bioremediation is relying on an active phase with EK applied for delivery
241 of an electron donor and/or bacteria (potentially *Dhc*) into the contaminated soil, followed by a
242 passive phase of biodegradation (details in chapter 7).

243

244 4.3 Abiotic oxidation

245 Abiotic oxidation of chlorinated ethenes requires an external supply of electron acceptors. Common
246 oxidants used include Fenton's reagent, permanganate and persulfate (Siegrist et al., 2014). The
247 chemical oxidation of chlorinated ethenes breaks down the compounds entirely (Figure 1, dashed
248 arrows) and thereby avoids accumulation of the reductive dechlorination intermediates. The end-
249 products of chemical oxidation are hydrogen (H^+), chloride ions (Cl^-), carbon dioxide (CO_2) and the
250 reduced catalytic compound, e.g. $MnO_2(s)$ when permanganate is used as an oxidant (Schroth et al.,
251 2001). Thus, chemical oxidation gradually generates acidic conditions. Successful delivery of the
252 oxidant is crucial for efficient degradation of the chlorinated ethenes.

253

254 The desire of the methods of EK-delivery of chemical oxidants (EK-ISCO) is following this outlined
255 degradation pathway (details in chapter 8).

256

257 5. Electrokinetic remediation of chlorinated ethene contaminated soil – overview

258

259 Table 3 summarizes the different techniques involving EK for remediation of soils contaminated by
260 chlorinated ethenes.

261 Each method is described in the following chapters along with the transport velocities related to the
262 different techniques and a short description of the experimental data leading to the numbers. Results

obtained in experiments using these methods, but targeting other contaminants are included in the discussion to extend the data volume for validation of e.g. EK transport velocities of bacteria. It is important to note that the transport velocities herein reported are calculated from varying fundamentals reported in the literature, since there is no coherency in the way to report experimental data on transport velocities. However, the information is important as it gives the order of magnitude of the transport velocity.

6. EK-reactive barriers. Abiotic reduction

The general PRB concept involves emplacement of a reactive media perpendicular to the flow direction of contaminated groundwater. The contaminant plume passively migrates through the reactive media under the influence of the natural hydraulic gradient. Obiri-Nyarko et al. (2014) reviewed the general PRB technology, while Weng (2009) reviewed the combined EK-PRB technology for contaminated soil in general. When dealing with chlorinated ethenes, the contaminants are mainly transported by electrokinetics to the PRB, and if successful, the contaminants are degraded to nonhazardous compounds by abiotic reduction (Figure 1).

Another possibility for utilizing abiotic reduction in combination with EK is to transport nano-ZVI (nZVI) into the contaminated zone by EP (Pamukcu et al., 2008; Jones et al., 2011; Reddy et al., 2011; Gomes et al., 2012). However, this possibility has not yet been applied for the remediation of soil contaminated by chlorinated ethenes, and thus the transport of these contaminants towards PRBs for abiotic reduction is the principle reviewed here. As early as in the 1990s a technology named LasagnaTM was developed based on this concept (Ho et al., 1997; Ho et al., 1999a,b).

287 *6.1 Transport of chlorinated ethenes by advection in an electroosmotic flow*

288 Bruell and Segall (1992) first reported TCE removal from kaolin columns under the influence of EO.
289 In a laboratory study on EK transport of bacteria in soils, DeFlaun and Condee (1997) observed, that
290 TCE moved in the direction opposite to the bacteria, i.e. towards the cathode. The transport of TCE
291 was suggested to be either due to advection in the EO flow, or that TCE is acting as a polar compound
292 with some positive charge associated with it (DeFlaun and Condee, 1997). Chlorinated solvents can
293 form positively charged ion pairs with protons in the dissolved phase (Chen et al., 2002). Thus,
294 chlorinated solvents can be subject to EM (Chen et al., 2002; Mao et al., 2012). Other researchers
295 explain the transport of TCE towards the cathode solely by advection in the EO flow (Bruell and
296 Segall, 1992; Weng et al., 2003 ; Chang et al., 2006). Yang and Yeh (2011) reported TCE transport
297 in an EO flow within a spiked sandy clay with accumulation in the cathode reservoir without
298 significant TCE degradation. The EO transport rate of TCE was superior to that of PCE in a soil
299 sampled at a contaminated site, explained by the higher water solubility of TCE (Chang et al., 2006).
300 By relating TCE and PCE removal to changes in pore volumes by EO, they found that 85% TCE was
301 removed after three pore volumes and 90% PCE after five pore volumes. This difference was
302 explained by the higher sorption of PCE to the soil.

303
304 The reported velocities to reach a minimum of 70% removal of chlorinated ethenes by advection in
305 an EO flow are:

- 306 • Fine-grained soil: 85% TCE removal from 12 cm spiked fine-grained soil in 5 days under
307 application of 1 V/cm (Weng et al., 2003), corresponding to $2.4 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$
- 308 • Field-sampled clay: Removal of 83-87% TCE throughout 10 cm spiked clay at 2 V cm^{-1} during
309 8.3 days (Chung and Lee, 2007), corresponding to a velocity of $0.6 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$

- Field-sampled clayey/silty soil: At 1.2 V/cm in 7 days, 85% removal was obtained in about 4.5 cm soil for PCE and 6.5 cm for TCE (Chang et al., 2006), corresponding to 0.5 and 0.8 cm² V⁻¹ d⁻¹, respectively.
- Kaolin clay: An initial TCE concentration of 150 mg/kg was reduced with 85% 4 cm into kaolinite from the anode within 5 days at 0.4 V/cm (Bruell and Segall, 1992), corresponding to a velocity of 2 cm² V⁻¹ d⁻¹
- Sandy Clay: 7 days with application of 1 V/cm decreased the TCE concentration in a spiked sandy clay (sampled from farmland) with about 70% in the 5 cm closest to the anode (Yang and Yeh, 2011) This corresponds to a velocity of 0.7 cm² V⁻¹ d⁻¹.

Chang and Cheng (2006) reported an improvement of PRB when combined with EK in sandy soil for degradation of PCE. However, the improvement was obtained during the first 24 hours whereafter the decrease in concentration had a similar slope as standalone EK or PRB. This reveals limited EO towards the PRB in this sandy soil and that EK only increased degradation of PCE initially in the vicinity of the PRB.

6.2 Types and placement of PRB

When combined with EK, different compositions and placements of the PRB have been suggested. Vertical barriers with iron filings in kaolin clay were found effective using the LasagnaTM process (Athmer and Ho, 2009). Chung and Lee (2007) used atomizing slag (PS Ball) and sand as the filter media in the PRB. Chang and Cheng (2006) found that PRB with zero valent Zn (ZVZ) performed better than ZVI for PCE degradation.

PRB is most efficient when placed close to the anode due to the proton production aiding the reduction at the ZVI, and the acidic environment prevented the formation of iron oxides at the ZVI surfaces and thereby passivation (Chang and Cheng, 2006 ; Chen et al., 2010). The advantage of placing an anode near the PRB was also seen in relation to general PRB by Moon et al. (2005), where the contaminated groundwater moves through the PRB in a hydraulic flow; simultaneous application of ZVI and an external DC field enhanced dechlorination of TCE by 1.3-5.8 times compared to ZVI only. However, when utilizing the combined EK-PRB method in fine-grained clayey soils, the contaminants are transported by EM or advection in the EO flow towards the cathode, which suggests placing a cathode downstream the PRB.

6.3 In situ pilot and full scale actions

The LasagnaTM technology has been tested in-situ for treatment of clayey soil contaminated with chlorinated ethenes. The method uses DC current to heat the soil and to mobilize pore water and contaminants into the treatment zones. In the first full-scale field test, horizontal treatment zones were installed (Ho et al., 1999a). However, vertical emplacements were more practical (Athmer and Ho, 2009). With this method, no contamination is brought aboveground, since transport and destruction take place within the soil matrix (Athmer and Ho, 2004; Athmer and Ho, 2009).

Ho et al. (1999b) describe a small field test (4.6 m x 3 m, and 4.6 m deep), which lasted 4 months. The purpose was to prove EO transport of TCE and to collect information for design, installation, and operation. The electrode spacing was 3 m. In between the electrodes, three treatment zones with granular activated carbon were installed to collect and confirm transport of TCE from soil into the treatment zones. A constant current (40 A) was applied. The voltage decreased from 138 V (0.45 V cm⁻¹) to 105 V (0.35 V cm⁻¹), where it stabilized. The decrease was ascribed Joule heating of the soil,

as the temperature increased from 15 to 45 °C. After plant adjustments, the EO flow rate was similar to the level obtained in the lab ($1.04 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$). In total, about three pore volumes were transported with EO. The highest TCE concentration before treatment was 507 mg/kg with a TCE removal of 92–99.8%. About 4% of the removed TCE was volatilized. The remaining fraction of removed TCE was transported to the treatment zones where the concentration at the activated carbon reached 10,000 mg TCE kg^{-1} .

Ho et al. (1999a) describe a larger field scale test (6.2 m x 9.2 m, and 13.7 m deep), which lasted a year. The purpose was to show effective in-situ treatment to a depth of 13.7 m (Athmer, 2004). The electrode spacing was 6.3 m and three treatment zones composed of iron fillings in kaolinite were installed in between. Each electrode comprised of a 3.8 cm thick layer of 50/50 iron fillings and coke to the depth of 13.7 m. The first two months, 150 V was applied (0.23 V cm^{-1}) corresponding to a current of 110 A. Hereafter, the voltage was increased to 200 V (0.31 V cm^{-1}) at 200 A. After about 5 months, the core soil temperature was increased to 80 °C due to Joule heating, and the voltage was reduced to 120 V (0.19 V cm^{-1}). The voltage distribution was reasonably uniform for the first 5 months, where after the anode filling started to dry out. About 2.8 pore volumes were transported by EO. Between the treatment zones, 96–99% TCE was removed. Between cathode and treatment zone the removal was 70% and between the anode and treatment zone, 43% was removed. The removal may be due to both evaporation and EK transport.

Athmer (2014) conducted full-scale remediation at an industrial complex, where two part-areas were remediated. The clayey soil contained aged contamination of TCE with significant levels of cis-DCE and VC. The treatment zone was installed under built infrastructure. The plant depth was 6 m. In part-area-1, two areas were treated (33 m x 21 m and 20 x 15 m). In part-area-2, 15 m x 15 m were treated.

Treatment zones of iron filling mixed in kaolinite slurry were placed vertically at 1.5 m intervals between electrodes. Reductions of TCE in part-area-1 and part-area-2 were estimated to 76% and 83%, respectively.

These in-situ field experiences illustrate the ability of EK to mobilize chlorinated ethenes with EO in fine-grained clayey soils.

7. EK-Bioremediation. Biotic reduction

Bioremediation techniques broadly fall into two categories: biostimulation and bioaugmentation (Lima et al., 2017). Biostimulation is a supply of nutrients, such as electron acceptors or donors, to promote biodegradation of contaminants by indigenous microbes. Bioaugmentation is the supply of microbes possessing specific capabilities to biodegrade the targeted contaminants. The biotic degradation pathways are shown in Figure 1.

Successful bioremediation requires physical interaction between microorganisms, substrates and contaminants (Semple et al., 2004). EK transport processes can overcome the otherwise slow transport of bacteria and/or nutrients in low-permeable soils and thus improve the delivery of e.g. bacteria. Most research on EK-BIO has been on understanding and optimizing the transport processes. A review by Gill et al. (2014) examines the state of knowledge on EK-BIO and conclude that current research needs include analysis of EK-BIO in more representative environmental settings, such as those in physically heterogeneous systems in order to gain a greater understanding of the controlling mechanisms.

Crucial for EK-BIO is that the applied current does not inhibit the microorganisms. When hindering side effects, e.g. pH and redox changes, in developing inside the soil, no significant impact on the microbial activity is seen (Lear et al., 2005 ; Shi et al., 2008a). Jackman et al. (1999) have shown that the application of an electric DC field of 20 mA/cm² stimulates the activity of sulfur-oxidizing bacteria. No research has indicated bacterial growth inhibition by the applied electric field in the range used in EK remediation.

7.1 EK-bioaugmentation

7.1.1 EP transport of bacteria in soil

Bacteria have been transported by EP into sand (DeFlaun and Condee, 1997), Sandy/silty loam (DeFlaun and Condee, 1997) and field sampled clay (Wick et al., 2004; Mao et al., 2012) and bryozoan limestone (Hansen et al., 2015). EP of bacteria depends on the physico-chemical properties of both the porous media (DeFlaun and Condee, 1997) and the surface properties of individual bacteria (Wick et al., 2007 ; Shi et al., 2008b). Most bacterial strains carry a weak negatively charged cell surface at near neutral pH, and thus EP is in the direction towards the anode. EP transport of bacteria in solutions is widely used within the field of micro-electrophoresis for characterization of bacteria (van der Wal et al., 1997). The surface charge of individual bacteria, expressed by the zeta potential, is inconsistent since it is influenced by the surrounding solution. The zeta potential of bacteria decreases with increasing ionic strength of the solution (Zhang et al., 2015). The zeta potential of three microorganisms capable of degrading chlorinated ethenes, *Dhc*, *Geobacter* and *Methanomethylovorans*, at low ionic strength was reported to -25 mV, -40 mV and -51 mV, respectively (Zhang et al., 2015). This reveals different EP transport velocities for those microorganisms since zeta potential and EP mobility are interconnected. Also, the pH of the soil

solution influences the EP of bacteria. DeFlaun and Condee (1997) detected no EP transport at pH 5.5, whereas a high transport rate was seen at pH 8.5.

Soils can restrict EP of bacteria by direct adsorption and by the pore sizes, which need to be larger than the size of the bacteria. Wick et al. (2004) showed that EP transport of weakly negatively charged and moderately adhesive cells was faster than of strongly charged and highly adhesive cells. DeFlaun and Conde (1997) reported that the presence of silt and clay minerals retarded the EP transport of bacteria. Zhang et al. (2015) reported on the microbial cell diameters: *Dhc* 0.62 μm , *Geobacter* 0.70 μm and *Methanomethylovorans* 1-1.5 μm . The pore sizes vary largely in soils, but some examples give indications of the order of magnitudes: For a Brazilian soil, classified as sandy loam, 51.1% of the total porosity was in the 100–500 μm size and a third of total porosity had pores >500 μm (Pieres et al., 2013). In clay, Ninjarav et al. (2007) reported pore sizes of 0.5–1 μm , and in kaolinite, the pore size was less <0.4 μm (Gingine and Cardoso, 2017). Thus, in clayey soils, the diameter of bacteria and pore sizes are in the same order, suggesting a limited possibility for EP transport unless the microbial structure is flexible. Blocking of the fine pores can be a result. Without applied current, high cell concentrations affect the overall retention of cells either positively by providing more surfaces for adhesion or negatively by leaving less favorable surfaces causing blocking (Camesano and Logan, 1998). These effects might also be important when combining with EK.

EP improved the transport of a TCE degrading, adhesion-deficient variant of *Burkholderiucepacia G4 (ICB)* in coarse-grained sand and sandy loam (DeFlaun and Condee, 1997). EP transport velocities of 7.2 – 14.4 $\text{cm}^2 \text{V}^{-1} \text{d}^{-1}$ in sand and 2.4-3.6 $\text{cm}^2 \text{V}^{-1} \text{d}^{-1}$ in sandy/silty loam were observed, while the bacteria did not move without applied current. Similarly, Wick et al. (2004) found no transport of the bacteria *Sphingomonas sp L138* without applied current but reached EP transport

452 velocities of $5.8 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$ in clayey soil. However, they found no EP transport of the bacteria *M.*
453 *frederiksbergense LB501TG*. The two strains have approximately the same size, but the latter is
454 strongly adhesive, which is likely the reason for the different mobilities by EP (Wick et al., 2004).
455 Thus, the characteristics of the bacteria strain are of major importance to the transport by EP.

457 7.1.2 Transport of bacteria by advection in an electroosmotic flow

458 Bacteria can be transported by advection in the EO flow i.e. towards the cathode (Mao et al., 2012 ;
459 Lee and Lee, 2001). Thus, transport of bacteria by EO is influenced by the same factors as EO (Table
460 1). In addition, Wick et al. (2004) reported EO transport of bacteria in soil to depend on bacteria
461 retention by the solid phase. The transport by advection in the EO flow for *Sphingomonas sp L138*
462 and *M. frederiksbergense LB501TG* reached velocities of $0\text{-}3.8 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$ and $3.4\text{-}6.7 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$ in
463 field-sampled clayey soil, respectively (Wick et al., 2004). In another field sampled clayey soil, the
464 *vcrA* copies encoded for VC reductase) moved at least 16 cm into the soil in the direction of the
465 cathode during 56 days of applied current at the average potential gradient of 0.8 V cm^{-1} (Mao et al.,
466 2012). Thus, the transport rate of *Dhc* was 16 cm in 47 days, corresponding to $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$.

468 7.1.3 Electrophoresis vs electroosmosis

469 The transport of bacteria in soil by EP and EO are of opposite directions. The dominating mechanism
470 depends on the bacteria, soil characteristics and soil solution chemistry. *Sphingomonas sp L138* was
471 transported in 80-90% by EO (identified by transport towards the cathode) and 10-20% by EP
472 (transported towards the anode) (Wick et al., 2004). Mao et al. (2012) supported EO to be the major
473 transport mechanism. In contrast, Da Rocha et al. (2009) experimentally showed that EP was the main
474 phenomenon responsible for the transport of bacteria in clayey soil. In summary, the specific soil
475 system and bacteria culture determine the governing EK transport mechanism.

7.2 EK-biostimulation

Hydrogen can serve as an electron donor for biodegradation of chlorinated ethenes, and lactate is considered one of the best hydrogen donors (Wu et al., 2007). Lactate is tested in the literature on EK-biostimulation (alone or in combination with EK-bioaugmentation) for remediation of soil contaminated with chlorinated ethenes, and lactate is negatively charged and transported by EM towards the anode (Wu et al., 2007; Mao et al., 2012; Hansen et al., 2015). Wu et al. (2007) experienced significant EO flow in clay samples, but the opposite directed EM was still the governing transport mechanism for lactate. The EK transport of such organic additives is limited by adsorption, the natural oxygen demand and biological transformation (Wu et al., 2007). Only when the rate of injection is compatible with the rate of consumption, a homogeneous injection is possible throughout the soil (Rabbi et al., 2000). To evaluate the potential enhancement of bioremediation by injection of lactate, it is necessary to assess its reactive transport rates under the DC field (Wu et al., 2007):

- Natural clay: $4 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$ calculated from the reported 3.2 cm d^{-1} and an average potential gradient of 0.8 V (Mao et al., 2012)
- Silty clay: $3.2 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$ (Wu et al. 2012b)
- Clay: Lactate was detected 24 cm into clay towards the anode after 188 hours at 0.8 V cm^{-1} , corresponding to $3.8 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$ (Wu et al., 2007)
- Sand: Lactate was detected 24 cm into the sand towards the anode after 129 hours at 0.5 V cm^{-1} (Wu et al., 2007), corresponding to $8.9 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$.

Efficient supply of lactate by EM into a 40 cm long silty clay spiked with PCE and anaerobic degrading bacteria (culture KB1[®]) showed full degradation to ethene whereas a reference experiment

without application of current resulted in limited degradation (Wu et al., 2012b). Hence, if a bacteria culture capable of degrading the contaminants is present, lactate can be supplied sufficiently by EM in fine grained soils.

7.3 Pilot scale action

Cox et al. (2018) conducted a pilot scale action with the overall goal to demonstrate and validate EK-enhanced amendment delivery for in-situ EK-BIO via enhanced reductive dechlorination of a PCE source area in clay. The EK plant consisted of 9 electrode wells and 8 supply wells located within an area of approximately 12 x 12 m. The depth interval targeted by the treatment was 5-7 m. The remediation amendments distributed by EK included lactate, pH control reagents (potassium carbonate), and a dechlorinating microbial consortium (KB-1®) containing *Dhc*. The action included 2 separate stages, 5-month each, of active operation with a 6-month incubation period between the two active stages. A >60% reduction in average PCE concentrations was achieved in soil and groundwater within the treated area. While groundwater data also showed coupled and comparable increases of dechlorination daughter (including VC) and end products, no such apparent increases of degradation products were observed in soil samples. Ethene was detected at 100% of groundwater monitoring wells and >10x increases of Dhc from baseline was observed at >60% of soil and groundwater samples collected from within the treated area.

8. EK-ISCO. Abiotic oxidation

In-situ chemical oxidation (ISCO) is a remediation technique where chemical oxidants are injected or mixed into the soil for rapid and complete contaminant mineralization. Most of the prevalent organic contaminants can be destroyed using catalyzed hydrogen peroxide (H₂O₂), potassium

permanganate (KMnO_4), activated sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), ozone (O_3) or combinations of oxidants (Siegrist et al., 2014). ISCO is a promising technology, but successful delivery into low permeability zones or uniformly throughout heterogeneous zones is an unresolved challenge (Reynolds et al., 2008). To overcome this, EK-ISCO has been investigated for an optimized supply of permanganate and persulfate.

8.1 EK-ISCO Permanganate

Use of KMnO_4 for ISCO is of significant interest due to its high oxidation-reduction potential, stability in aqueous solution, reactivity over a wide range of pH (3.5-12), ability to work without an activator, and production of non-toxic by-products after reaction with the chlorinated solvents (Chowdhury et al., 2017b). KMnO_4 can dechlorinate chlorinated ethenes completely (Huang et al., 2001).

EK permanganate transport into homogeneous, artificial, non-contaminated soil has been investigated (Roach and Reddy, 2006; Reynolds et al., 2008; Hodges et al., 2013). In experiments without pH neutralization at the electrodes, Roach and Reddy (2006) found that EM of permanganate (MnO_4^-) in kaolinite was limited to the proximity of the cathode due to a low pH in the remaining of the kaolinite. At low pH (< 3.5), MnO_4^- is reduced to Mn^{2+} , i.e. a cation, which EM towards the cathode (Roach and Reddy, 2006). In addition, the oxidation potential of MnO_4^- is lost at acidic pH. Reynolds et al. (2008) obtained EM of MnO_4^- from the cathode reservoir into the anode reservoir through 7 cm mixed glass beads and kaolinite. In experiments with glass beads, the concentration in the anolyte relative to the catholyte was 10% with 10V applied, while 15% with 20V applied after 150 hours. This exceeded the 5% obtained by diffusion but lacked full break-through. In experiments with kaolinite, the concentration of MnO_4^- in the anolyte increased with 13-15% when applying 10-20V for 150

hours. The results indicated a threshold in EM of permanganate due to competing processes or other phenomena (Reynolds et al., 2008). Hodges et al. (2013) defined those limitations as stalling. Hodges et al. (2011) developed an EK set-up in which pH changes were isolated from the soil. Using this set-up, Hodges et al. (2013) showed EM of MnO_4^- through a 10 cm long kaolinite core at neutral pH. After 5.2 days at 1.1 V cm^{-1} , MnO_4^- was measured in the anolyte, corresponding to a transport velocity of $2.3 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$. The concentration in the kaolinite near the anode of 1 g L^{-1} was the lowest inside the core. Such differences in MnO_4^- distribution in the kaolinite is critical when considering implementation of EK-ISCO at full-scale because it can lead to inefficient contaminant degradation (Hodges et al., 2013). Thus, this needs to be overcome.

Reynolds et al. (2008) conducted experiments with fine-grained lenses of glass beads or kaolinite embedded in a non-contaminated artificial soil of coarser glass beads. The pink color of permanganate was qualitatively used to assess EM into these lenses. As opposed to when not applying an electric field, the electric field intensified the pink appearance of the lenses. Thus, EM transport from a coarse medium into a fine-porous medium was shown. Chowdhury et al. (2017b) conducted experiments in a two-dimensional sandbox packed with layers of silt perpendicular to the electric field. The sand and silt were contaminated with aqueous TCE. EK successfully delivered MnO_4^- throughout the silt, while without EK, the MnO_4^- was delivered to the edges of the silt layer fringes only. TCE mass destruction in the silt could not be directly quantified, but image analysis of the silt showed a 240% increase in MnO_4^- delivery when EK was applied. Furthermore, EK-application significantly reduced the back-diffusion of TCE from the contaminated silt after active treatment for 25 days.

8.2 EK-Persulfate

Persulfate offers some advantages over the other oxidants, such as high aqueous solubility, high stability in subsurfaces, lower affinity for organic matter, reduced cost, and nonhazardous end-products (Matzek and Carter, 2016). Persulfate refers to ions or compounds containing the anions SO_2^{5-} or $\text{S}_2\text{O}_8^{2-}$. Matzek and Carter (2016) reviewed in detail the use of activated persulfate for oxidation of organics. Persulfate oxidation requires activation by either heat, mineral-based activators, UV light or high pH (Matzek and Carter, 2016). Selecting the suitable activator depends on site conditions such as geology, hydrogeology and the application strategy (Yukselen-Aksoy and Reddy, 2012). EK assisted ISCO using persulfate is to transport the persulfate into the soil by EM or EO followed by in-situ activation.

The anionic persulfate is transported by EM towards the anode or by EO towards the cathode. Important findings on persulfate distribution in soil using EK can be extracted from papers on laboratory work with non-contaminated soil (Mikkola et al., 2008), soil contaminated with creosote (Isossari et al., 2007) or PCB (Yukselen-Aksoy and Reddy, 2012; Fan et al., 2014). EM of persulfate in sand was found linearly related to the applied voltage in the range of 1-4 V cm^{-1} with transport rates of $12 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$, (Mikkola et al., 2008). A tendency for higher EM velocities with increasing silt content was observed, reaching $19.8 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$ in pure silt. This was ascribed to the higher electrical conductivity caused by higher water content and thus, higher current densities in the silt. Chowdhury et al. (2017a) successfully delivered persulfate with EM throughout a 36 cm silt sample at voltages of 12-18 V ($0.5 - 0.8 \text{ V cm}^{-1}$) in a system where pH was controlled with phosphate buffers at the electrodes. An average transport rate of $2 \pm 0.7 \text{ cm/day}$ was estimated based on the arrival times of 50% of the maximum persulfate concentration (Chowdhury et al., 2017a), corresponding to $3.1 \pm 1.1 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$ based on an average voltage in the range given. The persulfate concentration in the soil solution reached 11 g L^{-1} near the cathode and 9 g L^{-1} near the anode.

595

596 In an EK system without pH control, EO was the most efficient process for transporting persulfate
597 into a field-sampled soil (Fan et al., 2014). Persulfate was delivered 6 cm into the soil by EO within
598 3-6 days. Break-through of persulfate into the catholyte was not observed. On the contrary, break-
599 through into the anolyte with EM was observed, but here the persulfate concentration in the soil was
600 lower (Fan et al., 2014). Addition of persulfate from both electrodes simultaneously did not deliver
601 persulfate uniformly (Fan et al., 2014). This work underlines the necessity to control pH.

602

603 Injection of persulfate at the anode has shown to increase the EO flow velocity (Yang and Yeh, 2011;
604 Fan et al., 2014). Contrary, persulfate has also shown to reduce the EO flow rate significantly (Isosaari
605 et al., 2007). Fan et al. (2016) showed that transport of persulfate by advection in an EO flow towards
606 the cathode was influenced by the persulfate activation method used: alkaline activation > zero valent
607 iron activation > no activation > citric acid chelated Fe^{2+} activation > peroxide activation > iron
608 electrode activation. Thus, the transport of persulfate by advection in EO flow depends on a variety
609 of factors, which possibly are site-specific and thus calls for further assessment. In addition, the
610 simultaneous addition of a suspended activator and persulfate decreased the persulfate distribution
611 into the soil (Fan et al., 2016). Thus, adequate delivery of persulfate into the soil prior to activation
612 is beneficial.

613

614 Efficient degradation (99% removal) of TCE in a 25 cm long, spiked, field-sampled soil under an
615 applied electric field of 1 V cm^{-1} during 7 days with a high dose of 10 g L^{-1} of Na-persulfate at the
616 anode is observed (Yang and Yeh, 2011), corresponding to $3.6 \text{ cm}^2 \text{ V}^{-1} \text{ d}^{-1}$. This high removal was
617 ascribed EO transport of H_2SO_5 , which was suggested produced in the anolyte due to the strongly
618 acidic environment.

619

620 In a study on PCB removal, Fan et al. (2016) reported the removal efficiency order of the activation
621 methods to be: alkaline > peroxide > citric acid chelated Fe^{2+} > Zero-valent iron > no activation > Fe-
622 electrode activation. The removal efficiencies varied between 41 and 31%. The activation methods
623 tested and reported are: (I) *Electrochemical generation of Fe(II) using an iron anode*. This method
624 was evaluated for the oxidation of phenol in a stirred solution with persulfate and phenol (Park et al.,
625 2016). EK-transport was not included in this study, but it showed, that a continuous supply of Fe(II)
626 from the anode was easier to control than direct addition of iron sulfate to the solution because excess
627 Fe(II) impedes the activation of persulfate. Literature available on EK- persulfate for remediation of
628 soil contaminated with chlorinated ethenes is yet scarce. (II) *Thermally Activated Persulfate*.
629 Temperature is a strong activator of persulfate. EK-TAP is an abbreviation for “Electrokinetic
630 Thermally Activated Persulfate”, i.e. a method in the EK-ISCO family. In brief, the persulfate is
631 delivered into the soil by EK followed by a temperature increase by changing to an AC electric field
632 for electrical resistivity heating (ERH). The application of heat is expected more uniformly distributed
633 than other possible activation methods (Chowdhury et al., 2017a), and they also showed full
634 degradation of PCE in soil solution samples after two periods with persulfate supply by EM and
635 activation by ERH. Increase in sulfate concentration simultaneous to decrease in persulfate
636 concentration during ERH indicated activation and decomposition of persulfate. Activation at 36 °C
637 was more efficient in eliminating PCE than at >41 °C. Yukselen-Aksoy and Reddy (2012) found that
638 increasing the temperature to 45 °C was efficient for PCB degradation after EK persulfate delivery.
639 (III) *Persulfate activation with ZVI and nZVI*. Yang and Yeh (2011) reported that with nano-Fe the
640 TCE concentration was reduced from 132-156 mg kg⁻¹ to <10 mg kg⁻¹ all through the 25 cm long soil
641 column, and without nano-Fe the final concentration was about 25-55 mg kg⁻¹ TCE degradation in a

spiked, field-extracted soil was app. 10-30% more efficient when adding nZVI to the catholyte and persulfate to the anolyte than when adding persulfate alone.

Natural soil constituents influence EK-persulfate. Liang et al. (2003) showed that in aqueous systems, significant TCE degradation was obtained after 6 hours at 40 °C. However, longer treatment times and higher doses of persulfate were needed for effective treatment of soil slurries, because the organic matter competed for sulfate free radicals (Liang et al., 2003). Similar, Yukselen-Aksoy and Reddy (2012) observed enhanced degradation of PCB in kaolinite than in glacial till. The difference was attributed to the high buffering capacity, nonhomogeneous mineral content and high organic content of glacial till. In general, the natural oxidant demand in soil is the reaction of permanganate with immobile, sediment-bound reductants such as organic matter, or reduced minerals such as pyrite (FeS_2) (Mumford et al., 2005). Hence, the natural oxidant demand of soil must be accounted for when dosing persulfate. Important findings on changing conditions in soil during persulfate treatment were reported by Isosaari et al. (2007). They periodically injected persulfate to a field-sampled clay and the DC field was applied from external electrodes. Phosphate buffers were added in order to control pH at the electrodes, but without success, i.e. pH changed in the injection wells throughout 8 weeks. Each injection of persulfate resulted in an increased current that leveled out over time. The authors explained the leveling out to be due to precipitation of sulfates, phosphates and hydroxides, which was verified by elemental analyses showing decreasing concentrations of Al and Ca in the soil near the anode and increasing concentrations near the cathode (Isosaari et al., 2007). P concentrations increased significantly throughout the soil originating from the buffer solutions in the electrolytes. The S concentration increased from 780 mg kg^{-1} to $1040\text{-}2980 \text{ mg kg}^{-1}$, peaking in the soil midway between the electrodes, but whether this increase was due to the transport of persulfate or e.g. SO_4^{2-} was not identified. Similarly, Fan et al. (2014) reported an initial increase in current density followed

by a decrease during the continuous supply of persulfate by EO, also ascribed to precipitation within the soil.

The influence of common anions and cations (CO_3^{2-} , PO_4^{3-} , HCO_3^- , SO_4^{2-} , NO_3^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+}) on the Fe^{2+} activated persulfate process for treatment of aniline contaminated groundwater without EK was examined by Zhao et al. (2016). Under the optimum operating conditions, 86% aniline degradation was observed within 60 min. The effects of the cations on aniline degradation were negligible. Anions, on the other hand, decreased the removal of aniline because of radicals generated in the reaction of sulfate radical or hydroxyl radical with these anions. The order of inhibitory effects was $\text{PO}_4^{3-} > \text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^-$. The influence of anions on EK-ISCO of chlorinated ethenes using persulfate needs investigation in relation to EK. Especially of PO_4^{3-} since the phosphate buffering system is often used to buffer pH at the electrodes.

8.3 Modeling EK-ISCO

Wu et al. (2013) took the challenge to model different electrode configurations in EK-ISCO using permanganate. The focus was to achieve optimal coverage of the oxidant. As a supplement to the previous models focusing on electrode placement during EK-remediation, e.g. Alshawabkeh et al. (1999), this model takes into account the contaminant degradation. Greater contact between the injected permanganate and PCE in the model was achieved with horizontal electrodes (Wu et al., 2013). Furthermore, reduced time for remediation can best be achieved by an increased number of electrodes, adopting bidirectional and radial electrode configurations, incorporating oxidant injection wells and a pulsed injection of oxidant (Wu et al., 2013). This will come at the cost of increased capital expenditure and in some cases, increased oxidant or energy consumption. If low-cost remediation is the objective, the electrodes should be placed further apart or fewer electrodes used,

which results in a longer treatment time. In both cases, periodic reversal of the electric field shortened the remediation time and energy consumption (Wu et al., 2013).

9. DISCUSSION

9.1 Summary of transport velocities reported

The transport velocities calculated based on reported experimental results for chlorinated ethenes, lactate, bacteria, permanganate and persulfate are summarized in Table 4. It must be stressed, that the velocities are not directly comparable as available data differed in origin. The velocities gives the orders of magnitude. In general, reported ranges on transport velocities of chlorinated ethenes in different soil types are limited. For designing and operating in-situ full-scale remediation actions with EK-enhanced technologies, velocities are necessary design parameters, and thus must be addressed in future research.

Transport velocities of TCE and PCE by advection in the EO flow are reported in the range of 0.2-2.4 cm² V⁻¹ d⁻¹ (Table 4). Thus, the velocity cannot be neglected in experimental work with all EK-enhanced methods. The main purpose with EK-BIO is to extend the bioremediation to also work in fine-grained soils, and it has been shown, that bacteria are transported by EP and EO in these. The EP-transport velocities for bacteria are 0-7.2 cm² V⁻¹ d⁻¹, and for advection in EO flow 0-6.7 cm² V⁻¹ d⁻¹. EM transports lactate towards the anode and the transport velocities reported are 2.6-8.9 cm² V⁻¹ d⁻¹. Thus, lactate and bacteria are transported with velocities in the same order of magnitude. The transport velocities reported for persulfate and permanganate in EK-ISCO are 1.7–20 cm² V⁻¹ d⁻¹. It has not been possible to conclude the dependency of transport velocities on soil type. Research is needed such that proper design parameters on transport velocities can be determined.

714

715 *9.2 Importance of side effects and transient changes*

716 The pH at the electrodes must be neutralized in all the EK enhanced techniques for remediation of
717 soil contaminated with chlorinated ethenes, since changes in soil pH inhibit remediation, as
718 experienced in many of the studies reported. In EK-PRB, the changes in pH strongly influence EO
719 and hereby the transport of chlorinated ethenes towards the PRB. In EK-BIO, the changes in pH are
720 negatively affecting the health of the bacterial community. In EK-ISCO, pH influences the
721 reactivity and transport of the oxidants. When pH gradients in the soil are prevented, the changes
722 in soil (Table 2) are less sensitive to mineral decomposition and precipitation, which thereby will
723 contribute to a more uniform distribution of the applied electric field.

724

725 More focus needs to be given to the possible changes in soil redox conditions induced by the electrode
726 reactions since these are important for successful remediation. The O₂ containing anolyte can be
727 transported into the soil by EO and diffusion, thus increasing the redox potential. In EK-BIO of
728 chlorinated ethenes, the bacteria *Dhc* require strict anaerobic conditions (Section 4.2), and thus, the
729 oxidizing conditions from the anode must be managed. For EK-ISCO, the oxidant demand must be
730 expected to increase or the remediation efficiency to decrease if the reducing conditions from the
731 cathode are not controlled.

732

733 Joule heating has been investigated in a few studies only (Lageman and Godschalk, 2007; Ho et al.,
734 1997; Ho et al., 1999a), which underline the importance of coming field-scale tests with EK-BIO and
735 EK-ISCO to include an investigation of the effect from Joule heating to take advantage of the possibly
736 increased solubility, reaction rates and transport velocities in the field compared to lab scale.

Evaporation and unwanted transport into buildings etc. need to be considered as well. Also, the energy consumption required for Joule heating needs to be considered in cost calculations.

9.3 EK in heterogeneous subsurface soils

A general need for an understanding of EK in in-situ settings is stressed in recently published reviews. Research needs to include assessment of EK-technologies in more representative environmental settings, such as heterogeneous geologies, in order to I) understand the controlling mechanisms in natural settings (Gill et al., 2014), and II) be able to optimize the EK-technologies for full-scale implementation (Gomes et al., 2012). The field parameters, which influence the modelling and design of full-scale EK-remediation include heterogeneous soils in which the electrical conductivity differs in the different layers. The present review supports this. In the subsurface, the water content may change significantly, from few percentages to saturated, influencing the resistivity, pressure gradients can distribute electrolyte solutions from electrode wells into coarse, unsaturated layers and groundwater flow may counteract or enhance transport velocities, and introduce e.g. vertical flow gradients. The influence from such factors determined by the site geology has not been assessed. The robustness of the EK-methods depends on knowledge on this for sufficient engineering. Following full-scale tests, it may be necessary to step back to redesigned laboratory tests to assess knowledge gaps identified during field-tests to avoid unforeseen situations in large scale, which increase the costs significantly. Acquisition of data in the field is expensive; it is, therefore, critical to identify which processes and system parameters that ultimately determine the success of a remediation strategy (Wu et al., 2012a). For example, transport mechanisms must be fully understood to ensure unintended spreading of the contaminants is avoided. Currently, however, scarcity of data particularly on the EK-parameters and at field-scale, and the related uncertainties, will affect the robustness of both model-based predictions and designs of EK-implementations (Wu et al., 2012a). A comprehensive study,

which quantifies the effects of a wide range of natural and model-parameters on the efficiency of EK-combined technologies is requested.

10. CONCLUSIONS

The concept of EK-enhancement of PRB, BIO and ISCO has shown encouraging results at lab-scale and for PRB and BIO also at full-scale. A major finding is that the already established methods applied in high-permeability soils can be transferred to low-permeability soils when combined with EK. This is unique and calls for a systematic approach to fill in current knowledge gaps towards safe and successful remediation. This review has identified major knowledge gaps, including transport velocities for chlorinated ethenes, changes in redox conditions in different soils due to electrode reactions, significance of the advantageous Joule heating for reaction rates, transport velocities and bacteria activity, and significance of site-specific parameters on transport velocities, e.g. heterogeneous geology and thereby electrical conductivities, water content, pressure gradients, hydrology, hydrogeochemistry, and oxygen demand and buffering capacity of the soil. In addition, there is a lack of coherence on how to report data on voltage distribution and transport rates, which complicate the comparison of studies.

In this review, it was found, that for the combined EK-techniques, it is necessary to manage the induced changes in pH to obtain steady EO transport of chlorinated ethenes, EP of bacteria, a healthy bacteria community, uniform delivery and reactivity of oxidants, and to control mineral decomposition and precipitation for a uniformly distributed electric field. Calculated transport velocities based on reported data show, that for EK-BIO, EM of lactate and EP of the biodegrading bacteria are in the same order of magnitude. When applying EK-techniques, back-diffusion of

contaminants from low-permeable soils is lowered, and periodic reversal of the electric field appears to shorten the remediation time and energy consumption.

This review underlines the promising use of EK for enhancement of remediation technologies, but it also highlights some major knowledge gaps that must be understood for the EK-techniques to be optimized and become robust enough for successful field-implementation at different sites with heterogeneous subsurface.

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Transport process	Transport of:	Transport velocity depends on:
Electromigration (EM)	Ions	Ionic mobility, adsorption/desorption, precipitation/dissolution, water content, pore volume and geometry
Electrophoresis (EP)	Particles, colloids, bacteria	Soil zeta potential, pore water chemistry and conductivity, pore sizes, water content
Electroosmosis (EO)	Water	Soil zeta potential, pore water chemistry and conductivity

1005

1006 *Table 1: Soil characteristics and reactions in soil systems influencing electromigration, electrophoresis and*
 1007 *electroosmosis in the electric field*

1008

I. Effects from applying DC field to an inert system	II. Changes in soil	III. Transient changes
Transport processes	Mineral decomposition	Non-uniform current and voltage
Electromigration	Precipitation/dissolution of salts	distribution
Electroosmosis	Precipitation/dissolution of secondary	Concentration gradients
Electrophoresis	minerals	Pore pressure (negative or positive)
	Physical and chemical	Temperature gradient
At electrodes	adsorption/desorption	pH and redox gradients
Anode: Oxidation and pH decrease	Ion exchange	
Cathode: Reduction and pH increase	Joule heating	
	pH and redox changes	

1009

1010 *Table 2: Possible effects, changes in soil and transient changes when applying an electric DC field to a natural soil*

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Method	Remediation strategy	Substance transported by EK	Transport process	References
EK-PRB	<i>Transport to treatment zone with abiotic reduction</i>	Chlorinated ethenes	Electroosmosis	Bruell et al. (1992), Ho et al. (1997), Ho et al. (1999b), Ho et al. (1999a), Weng et al. (2003), Athmer (2004), Chang et al. (2006), Athmer & Ho (2009), Athmer (2014)
EK-BIO	<i>In situ biotic reduction</i>	Bacteria	Electrophoresis and/or electroosmosis	DeFlaun & Condee (1997)
		Substrate	Electromigration	Rabbi et al. (2000), Wu et al (2007), Wu et al. (2012b)
		Substrate and bacteria	Electromigration, electrophoresis and/or electroosmosis	Mao et al. (2012), Hansen et al. (2015)
EK-ISCO	<i>In situ abiotic oxidation</i>	Permanganate	Electromigration	Chowdhury et al. (2017b)
		Persulfate	Electromigration	Yang & Yeh (2011), Chowdhury et al. (2017a)

1013

1014 *Table 3: Methods involving EK for remediation of soils contaminated with chlorinated ethenes, including substances*
1015 *transported and transport processes utilized*

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Method	Transported specie	Transport process	Soil	Voltage applied [V cm ⁻¹]	Transport rate [cm d ⁻¹]	Velocity [cm ² V ⁻¹ d ⁻¹]	References
EK-PRB	TCE	EO/EM	Field-sampled clay (d ₅₀ = 28 µm, OM 1.8%), spiked	1.0	2.4	2.4	Weng et al. (2003)
	TCE	EO/EM	Field-sampled clay (Particles < 75 µm 90%, OM 6.7%), spiked	2.0	1.2	0.6	Chung & Lee (2007)
	PCE	EO/EM	Field-sampled (48% clay, OM 1.7%/), spiked	2.7	0.6	0.2	Chang et al. (2006)
	TCE	EO/EM	Field-sampled (48% clay, OM 1.7%/), spiked	1.8	0.9	0.5	Chang et al. (2006)
	TCE	EO/EM	Kaolinite, spiked	0.4	0.8	2	Bruell & Segall (1992)
EK-BIO	Lactate	EM	Field-sampled low- plasticity silty clay, non-contaminated	0.8	3.1	3.8	Wu et al. (2007)
	Lactate	EM	Fine grained sand, non-contaminated	0.5	4.5	8.9	Wu et al. (2007)
	Lactate	EM	Field-sampled clay (<10% sand), aged contamination	0.8	3.2	2.6	Mao et al. (2012)

<i>Burkholderiu cepacia G4 (ICB)</i>	EP	Coarse-grained sand, (~750µm), non- contaminated	10	72	7.2	DeFlaun & Condee (1997)
<i>Burkholderiu cepacia G4 (ICB)</i>	EP	Fine-grained sand, (70-350 µm), non- contaminated	10	72	14.4	DeFlaun & Condee (1997)
<i>Burkholderiu cepacia G4 (ICB)</i>	EP	Sandy loam (14% clay, 1.4% OM), non- contaminated	10	36	3.6	DeFlaun & Condee (1997)
<i>Burkholderiu cepacia G4 (ICB)</i>	EP	Silt loam (20% clay, 3.9% OM, non- contaminated	10	24	2.4	DeFlaun & Condee (1997)
<i>Sphingomonas sp L138</i>	EP	Field-sampled clay (59% clay), non- contaminated	2	11.5	5.8	Wick et al. (2004)
<i>M. frederiksbergens e LB50ITG</i>	EP	Field-sampled clay (59% clay), non- contaminated	2	0	0	Wick et al. (2004)
<i>Sphingomonas sp L138</i>	EO	Field-sampled clay (59% clay), non- contaminated	2	0-7.7	0-3.8	Wick et al. 2004
<i>M. frederiksbergens e LB50ITG</i>	EO	Field-sampled clay (59% clay), non- contaminated	2	6.7-13.4	3.4-6.7	Wick et al. (2004)
<i>Dhc</i>	EO	Field-sampled clay, aged contamination	0.8	0.3	0.4	Mao et al. (2012)

EK-ISCO	Permanganate	EM	Kaolinitic pottery clay (28% clay), non- contaminated	1.1	1.9	1.7	Hodges et al. (2013)
	Persulfate	EM	Sand (100% sand) non-contaminated	4.0	48	12	Mikkola et al. (2008)
	Persulfate	EM	Silt (100% silt), non- contaminated	4.0	79	20	Mikkola et al. (2008)
	Persulfate	EM	Fine silt ($d_{50} = 45\mu\text{m}$), Spiked with TCE	0.3-0.5	2	4-6	Chowdhury et al. (2017a)

Table 4: Summary of transport velocities for chlorinated ethenes (>85% removal), lactate, bacteria, permanganate and persulfate in different soils calculated from literature. The velocities are not directly comparable since data available varies between references. The velocities are rather orders of magnitude than exact velocities. (OM = organic matter)

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1027 *Figure 1. Degradation pathways for the chlorinated ethenes tetrachloroethylene (PCE), trichloroethylene (TCE),*
 1028 *dichloroethylenes (DCEs) and vinyl chloride (VC) subject to biotic reduction (solid arrows), abiotic reduction (dotted*
 1029 *arrows) or abiotic oxidation (dashed arrows)*

1030