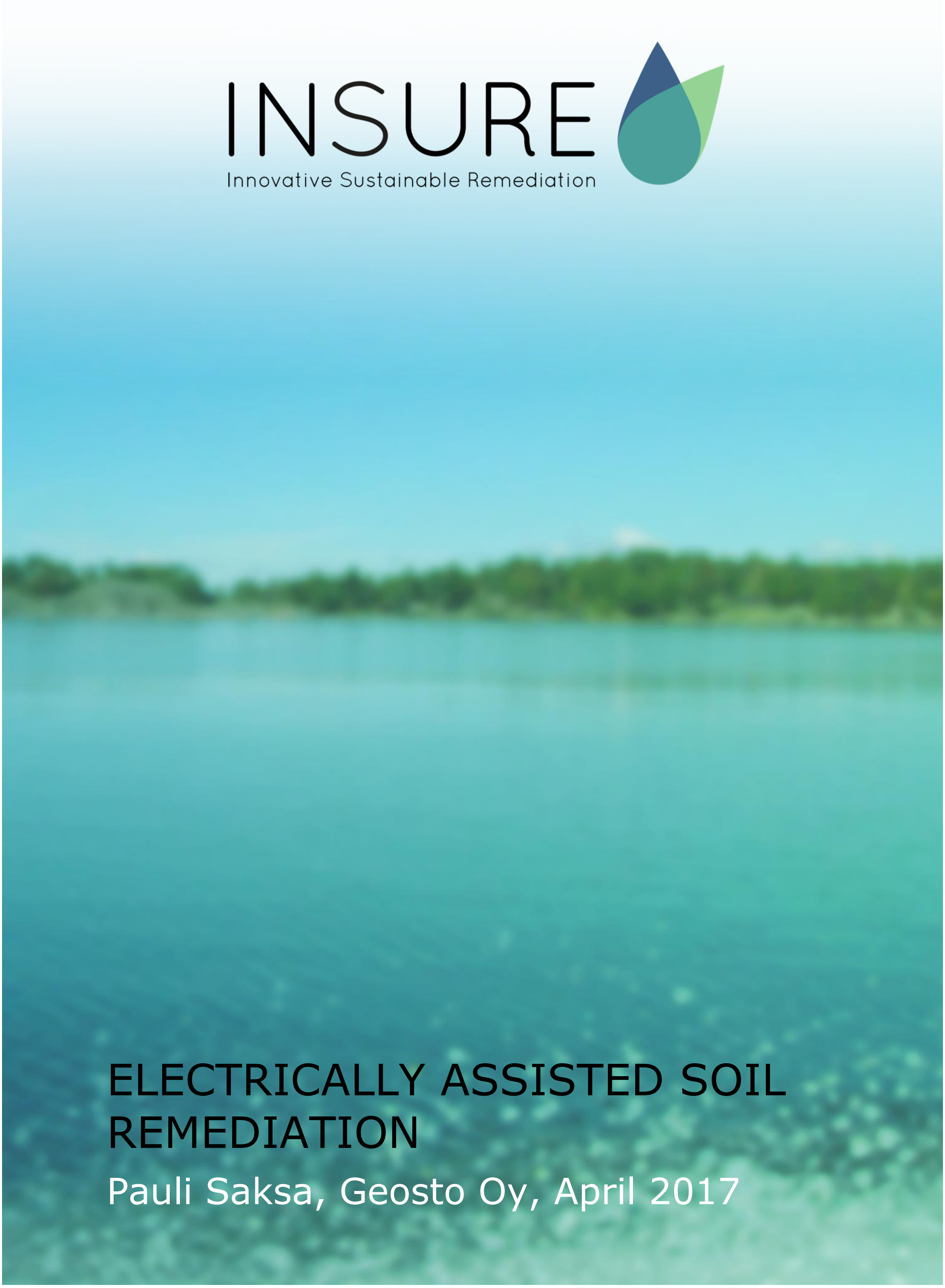

INSURE
Innovative Sustainable Remediation

# ELECTRICALLY ASSISTED SOIL REMEDIATION

Pauli Saksa, Geosto Oy, April 2017

EUROPEAN UNION
European Regional Development Fund

Interreg
Central Baltic

# ELECTRICALLY ASSISTED SOIL REMEDIATION

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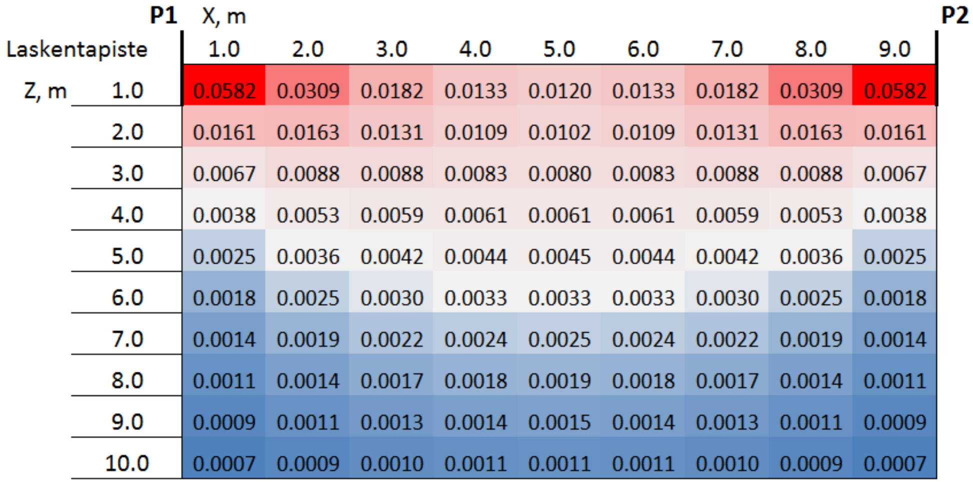
CLIENTS: UHEL, DPT. OF ENVIRONMENTAL SCIENCES, LAHTI, NORDIC ENVICON OY

TRANSLATED BY UHEL, DPT. OF ENVIRONMENTAL SCIENCES, LAHTI



| P1 | X, m | | | | | | | | P2 |
|---|---|---|---|---|---|---|---|---|---|
| Laskentapiste | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 | 7.0 | 8.0 | 9.0 |
| Z, m 1.0 | 0.0582 | 0.0309 | 0.0182 | 0.0133 | 0.0120 | 0.0133 | 0.0182 | 0.0309 | 0.0582 |
| 2.0 | 0.0161 | 0.0163 | 0.0131 | 0.0109 | 0.0102 | 0.0109 | 0.0131 | 0.0163 | 0.0161 |
| 3.0 | 0.0067 | 0.0088 | 0.0088 | 0.0083 | 0.0080 | 0.0083 | 0.0088 | 0.0088 | 0.0067 |
| 4.0 | 0.0038 | 0.0053 | 0.0059 | 0.0061 | 0.0061 | 0.0061 | 0.0059 | 0.0053 | 0.0038 |
| 5.0 | 0.0025 | 0.0036 | 0.0042 | 0.0044 | 0.0045 | 0.0044 | 0.0042 | 0.0036 | 0.0025 |
| 6.0 | 0.0018 | 0.0025 | 0.0030 | 0.0033 | 0.0033 | 0.0033 | 0.0030 | 0.0025 | 0.0018 |
| 7.0 | 0.0014 | 0.0019 | 0.0022 | 0.0024 | 0.0025 | 0.0024 | 0.0022 | 0.0019 | 0.0014 |
| 8.0 | 0.0011 | 0.0014 | 0.0017 | 0.0018 | 0.0019 | 0.0018 | 0.0017 | 0.0014 | 0.0011 |
| 9.0 | 0.0009 | 0.0011 | 0.0013 | 0.0014 | 0.0015 | 0.0014 | 0.0013 | 0.0011 | 0.0009 |
| 10.0 | 0.0007 | 0.0009 | 0.0010 | 0.0011 | 0.0011 | 0.0011 | 0.0010 | 0.0009 | 0.0007 |

Fig: Horizontal current density for pointed electrode

# EXTENDED ABSTRACT

This study concerns the electrically assisted remediation of soil contamination and particularly soil electrical properties, currents and potentials. The original report text is in Finnish and has been translated to English by the University of Helsinki (UHEL). The objective of this report is to investigate the influence of soil electrical structure on remediation and the effectiveness of various electric remediation techniques. This study was commissioned by the UHEL Department of Environmental Sciences and Nordic Envicon Oy to function as background material for the Intereg Central Baltic project INSURE (INnovative SUstainable REmediation).

The electrokinetic method applies direct current (DC) or very slowly alternating current (AC) to move ions, water and colloids to electrodes where collection of transported substances and process adjustments are performed. Electrode system, soil electrical structure, contaminant electrical conductivity and chemical changes (primarily pH) influence how current is distributed within the soil. For a basic homogeneous ground conductivity model electrical field strengths and current densities can be calculated for any electrode configurations.

High levels of DC power shortens the required treatment time and the collected contaminant concentrations are higher, while also generating a beneficial ground heating effect. In addition to Ohmic current conduction there may be weak natural electric fields (self-potential) or current pulse may create chargeability in the form of induced polarisation (IP). The basic electrokinetic method has been applied to remediation of multiple substances.

Alternating current is used in electrical resistive heating where the objective is to achieve evaporation of the contaminants for collection and removal. The inductive effect of alternating current was also studied in the report and found to be marginal and non-influential in the low frequency (< 100 Hz) range.

# 1. INTRODUCTION

Geosto Oy has compiled this report on the topic of soil remediation methods applying electric current and geophysics, as requested by the UHEL Dpt. of Environmental Sciences and Nordic Envicon Oy, in connection with the Interreg Central Baltic funded project INSURE. Client contacts are prof. Martin Romantschuk of UHEL and Hannu Silvennoinen of Nordic Envicon Oy. The first part of this report is based on literature and other collected material regarding electro-kinetics and the functionality of different methods and their variants. The electrical measurement techniques of geophysics and factors affecting conductivity in soil are reviewed, as are the roles of the hydrogeological and geo-chemical circumstances. In the second part, the various electro-assisted and geophysical remediation methods are examined. The goals are to gain information as to whether different electro-assisted methods have potential novel applications in the field of *in situ* remediation, and to review the significance of different parameters and the utilization of geophysical methods. The content of this report has been modified to fit the needs of the customer as requested during a follow up meeting in February 2017.

# 2. FUNDAMENTALS OF ELECTRIC METHODS

## 2.1. THE MAGNITUDE OF THE ELECTRIC FIELD AND CURRENT

The electric field E (V/M) caused by the electro-motoric force (V) forms an electric current (I) in the medium, with the magnitude to surface area as the current density J (A/m^2). The relation between these is conductivity (σ) in Ohm's Law.

$J = \sigma E$ (1)

Electric field and current density are both vector quantities. Conductivity (scalar quantity) S/m indicates the ability of the net electric charge to move in a medium. The unit mS/m is also often used, and electrical resistivity Ωm is its reciprocal. The direction of the electric current is always towards the gradient of the electric field. Electrons or ions function as charge carriers, and are classified as metals, semiconductors, crystalline liquids and electrolytes. In addition to these, the movement of bound charges plays a secondary role: alternating current and/or electrochemical phenomenon cause vibration of the charge carriers and accumulation of charges along conductivity or phase transition boundaries.

In direct current application, direct or low frequency alternating current (<10-100 Hz) is used. In this case, phenomena and parameters can generally be considered as real quantities. Contrary to this, with low frequencies electric polarization also appears. Bound polarized charges also cause an electric field and alter the electrical conductivity values given by Ohm's law. Polarization can be measured as induced polarization (IP), which will be discussed later. IP changes the examination of electric methods in the sense that the total field differs temporally, both in phase and amplitude from the source electric field, and for example conductivity becomes more complex.
Direct current is used in electro-kinetic remediation. In practice the electro-motoric force (power supply) forms a circuit through grounding connections. The direction and magnitude of the resulting field and current are determined by the location and area of the electrodes, groundings and conductivity distribution.

Even with a powerful field, the current density may be low if the soil has low conductivity. From the basis of electro-kinetics the current density should be rather high because the flowing molar concentration is proportional to the current density. When measuring the differences in potential and soil conductivity, low frequency alternating current (~1 Hz) is generally used because of the low expenses (steel electrodes can be used) and direct current theory can still be applied. Artificial or natural direct current field is measured with un-polarizable electrodes (Cu-CuSO4, calomel-KCL and Ag-AgCl). The grounding resistance affects the circuit and the magnitude of the current. This is essential, especially when higher currents are generated into the soil.

In situations with direct current it is easy to calculate the potential from electrodes as well as the current density in the soil for example in the following situations:

-a point-like electrode

-a linear electrode above ground

-vertical linear electrodes below ground

Sufficient geometrics and distances for electrodes and the desired distribution for current densities in different parts and depths of soil, for example near the hot spots of contaminants, can be calculated. The current density is at its highest near electrodes and reduces with increasing distance. For example, current density generated by point electrodes above ground, with distance L, in half depth z (Fig 2.1, Telford *et al*., 1976 ).

Current density also reduces with depth. With an electrode spacing of 10 m, at 5 m depth the current density is approximately 30% of that observed near the soil surface. Likewise only 10 % of the current circulates in depths over 10m .The distribution depends on grounding locations but not on soil conductivity in homogenous soils.

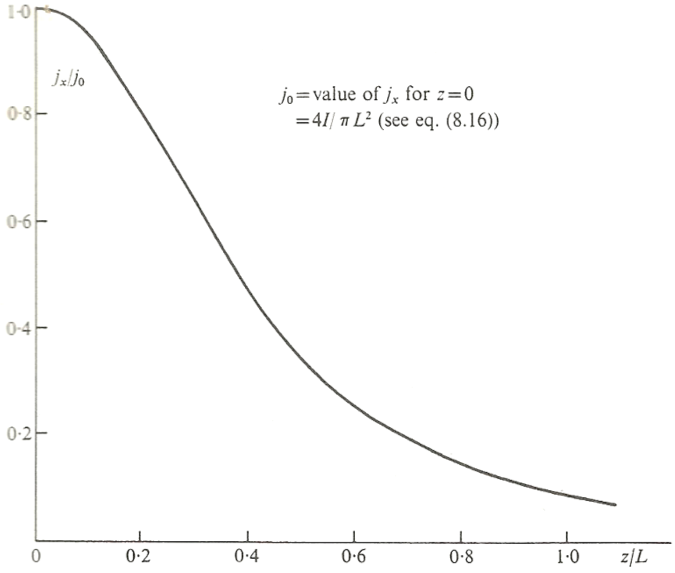


Fig. 8.8 Current density versus depth, fixed electrode spacing.

Figure 2.1.Current density variation along depth in the midpoint between two point electrodes (Telford et al. 1976)

Current density can be set to the desired depth by varying the electrode spacing, and maximum current can be calculated using the formula L = (2z)^0.5. For example if the density is to be maximized at a depth of 3 m in homogenous soil, the distance between the electrodes should be set to 2.45 meters. As an example of variation in current density, there is horizontal variation of the horizontal component ($j_x$) in the vertical plane between the point electrodes P1 and P2 (spacing 10 m) when the current (*I*) has a strength of 1 A. The unit of current density is A/m, which can be divided by ten to convert to mA/cm. As shown in figure 2.2, the density is highest near the electrodes.

| P1 | X, m | | | | | | | | P2 |
|---|---|---|---|---|---|---|---|---|---|
| Laskentapiste | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 | 7.0 | 8.0 | 9.0 |
| Z, m 1.0 | 0.0582 | 0.0309 | 0.0182 | 0.0133 | 0.0120 | 0.0133 | 0.0182 | 0.0309 | 0.0582 |
| 2.0 | 0.0161 | 0.0163 | 0.0131 | 0.0109 | 0.0102 | 0.0109 | 0.0131 | 0.0163 | 0.0161 |
| 3.0 | 0.0067 | 0.0088 | 0.0088 | 0.0083 | 0.0080 | 0.0083 | 0.0088 | 0.0088 | 0.0067 |
| 4.0 | 0.0038 | 0.0053 | 0.0059 | 0.0061 | 0.0061 | 0.0061 | 0.0059 | 0.0053 | 0.0038 |
| 5.0 | 0.0025 | 0.0036 | 0.0042 | 0.0044 | 0.0045 | 0.0044 | 0.0042 | 0.0036 | 0.0025 |
| 6.0 | 0.0018 | 0.0025 | 0.0030 | 0.0033 | 0.0033 | 0.0033 | 0.0030 | 0.0025 | 0.0018 |
| 7.0 | 0.0014 | 0.0019 | 0.0022 | 0.0024 | 0.0025 | 0.0024 | 0.0022 | 0.0019 | 0.0014 |
| 8.0 | 0.0011 | 0.0014 | 0.0017 | 0.0018 | 0.0019 | 0.0018 | 0.0017 | 0.0014 | 0.0011 |
| 9.0 | 0.0009 | 0.0011 | 0.0013 | 0.0014 | 0.0015 | 0.0014 | 0.0013 | 0.0011 | 0.0009 |
| 10.0 | 0.0007 | 0.0009 | 0.0010 | 0.0011 | 0.0011 | 0.0011 | 0.0010 | 0.0009 | 0.0007 |

Figure 2.2. Current density horizontal component between the point electrodes, distance P1-P2 is 10 m.

## 2.2. NATURAL CONDITION ELECTRIC POTENTIALS

The natural conditions and hydrogeological phenomenon in soil can induce electric potential in soil even without an alternative electric input (Parasnis 1986, Reynolds 2011). These are known as streaming potential, zeta potential, diffusion potential, absorption potential and mineral potential. The occurrence of this phenomenon in natural conditions is worth taking into account, especially with low magnitude additional fields and currents. The streaming potential is caused when water is in motion .i.e. hydraulic pressure exists. The magnitude of the electric field formed is given by:

$$E\left(\frac{V}{m}\right) = \left(\frac{\varepsilon\rho\zeta}{4.0\varphi\mu}\right)\Delta(P) \qquad (2)$$

ε= water dielectric permittivity (F/M)

ρ= water resistivity (Ωm)

ζ = zeta/streaming potential (V)

μ = water (electrolyte) dynamic viscosity (Pa s)

Δ(P) = pressure gradient (Pa/m).

The direction of the field formed is the same as that of the flowing water, both of them opposite to the flow of the electrolyte caused by the field. The streaming potential is another phenomenon of significance. The neutrality and the balance between bound and free charges is modified by formation of an electric double layer (Fig. 2.3) (sähköinen maaperän puhdistus ja geofysiikka 1.3.2017, page 6) on the particle water interface. The electric double layer is a very thin layer of opposite charged ions attached to the surface of negatively charged soil particle. The thickness of the layer is usually a couple of nanometers, depending on the ion concentrations. The thickness reduces with growing ion concentrations. Zeta-potential is the potential across the double layer and is usually in the range of 25 – 100 mV and for saturated clays and silts in the range of -10 – -100 mV (Geoengineer.org, 2016) and with major pressure gradient over -2000 mV. According to Gillen (2005), the zeta potential is reduced by the adsorption of hydrogen-ions into soil particles and the addition of electrolyte into the medium. The electric double layer is pictured in figure 2.3.

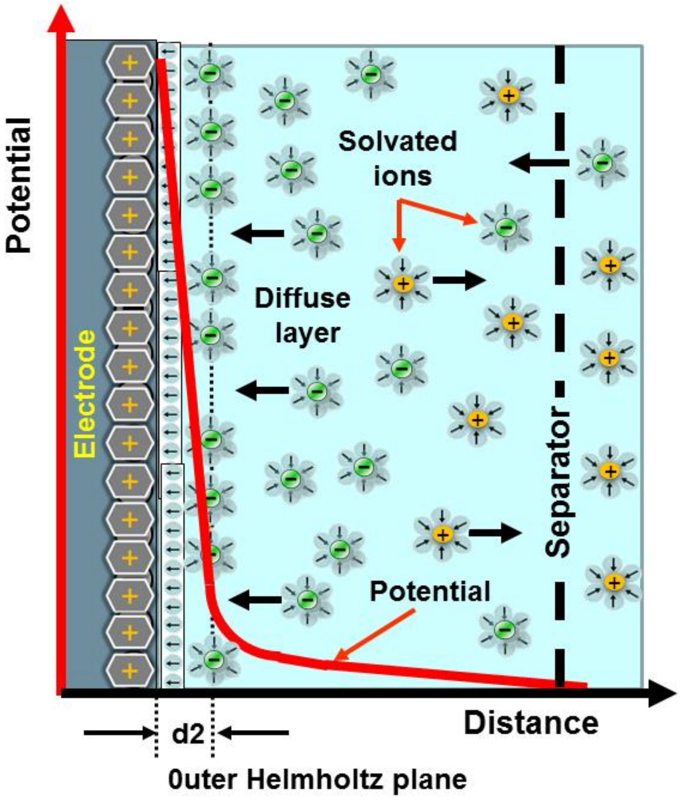


Figure 2.3. Electrical double layer, soil particle boundary on the left, fluid portion in the middle (image source: Wikipedia).

The zeta-potential is significantly pH-dependent, positive in acidic conditions and negative in alkaline conditions. The changes in zeta-potential affect the electro-osmotic movement of ions and water molecules (Buehler *et al*., 1994) The equation of streaming potential shows that one isn't formed without a pressure gradient. Potential is formed to the direction of water escaping the infiltration zone, or in the ground water layer, into the direction of the hydraulic gradient. According to Parasniks (1986) mere pressure difference won't result in a streaming potential, but also soils with zeta-potential need to exist in the streaming direction.

In soil remediation, the field and current created by the power supply needs to release ions and transport water to the desired direction from the influence of the streaming potential (Sähköinen maaperän puhdistus ja geofysiikka 1.3.2017 page 7 (43)). The diffusion potential is formed by concentration differences of the electrolyte in the soil (liquid junction potential). The magnitude is typically from millivolts to several dozen millivolts. The formation of diffusion potential requires that concentration differences exit, which requires a further source for the concentration differences to also remain unlevelled. In pore water concentration differences between fine and coarse soil particles can exist, when the former with higher water detaining capacity also detains more ions. A hydraulic insulator, such as a vertical or horizontal soil layer with low permeability can also uphold concentration differences. One of the most common electrolytes forming these differences in soil is NaCl. Adsorption has been reported to cause electric adsorption potential in pegmatites and quarts in bedrock also below ground. The cause is the adsorption of positive ions into these rock types and the forming of electric current. The mechanism is unclear. The potentials in clays are probably resulting from a similar principle. Positive potential differences caused by adsorption are in the range of couple of dozen mVs from their environment. (Parasnis, 1986).

When minerals with high conductivity are in contact with electrolytes a mineral potential can exist. The phenomenon isn't typical in most soils but can be observed when metals or other solid objects with high conductivity and polarization are present. The resulting differences in potential can be over 1000 mVs but the current densities are suspected low, only 0,01-1,0 µA/m. (Parasnis, 1986). Redox-potential exists over the oxidation-reduction interface. Electric current is generated when one of the electrodes is placed in oxidizing and another in reducing circumstances and the circuit is closed. Bio-electric potentials are generated by vegetation and trees, and they are observed in magnitudes of hundreds of mVs negative difference (Telford *et al*., 1976).

Also telluric streams exist, generated by inter-telluric factors like solar activity that affects earth's magnetic flux and hence the electric currents in the ionosphere. These have a time dimension. Telluric steams in soil are generated from the electromagnetic induction flux and they exists from very low 10^-5 Hz frequencies to audio frequencies 20 kHz. (Telford *et al*., 1976).

Current densities are very low and the electric field with a time dimension is in the magnitude of 10 mV/km (10µV/m). Inducing telluric streams are therefore of very low magnitude compared to the static and hydrogeological and geochemical potentials.

# 2.3. INDUCED POLARISATION

Induced polarization is a phenomenon in which charges aren’t traveling freely in an outer electric field, but a momentarily changing charge still affects the field forming. This is significant because it is connected to the effects of soil structure on electric currents. The two major types of induced polarization are electrode polarization and electrolytic (membrane) polarization.

Electrode polarization is formed when a metal electrode is placed in a fluid with ions. Free electrons aren’t released from the metal to the fluid and no ions from the fluid to the metal. The opposite charges are cumulated into the border zone, and a potential difference is formed. Similarly in soil, metallic particles are polarized in an electric current, thus affecting the field. Polarization can take several seconds in a DC field. Another important mechanism is electrolytic polarization that is formed in run-off channel contractions and on interfaces of clay particles. (Fig 2.5 b and c) In both cases the current is blocked and resulting charge accruals affect the field. Induced polarization can be measured from the soil by feeding transients with opposing polarities in turns and by measuring the discharge in between the transients during the voltage-free period. IP can also be measured with alternating currents with varying frequencies and over a wide frequency spectrum. Typical transient duration is approximately 1s, frequencies 0-10 Hz, and spectrum (0,01Hz-10 kHz) in the IP-method. Induced polarization and the measurements are presented in the figure 2.4 and the charging mechanisms in soil in figure 2.5. The measuring devices use medium or even large power outputs, the current can be over 1 A, voltage over 100 V, and power from 100 Ws up to several kWs when the measuring distances are low (hundreds of meters).

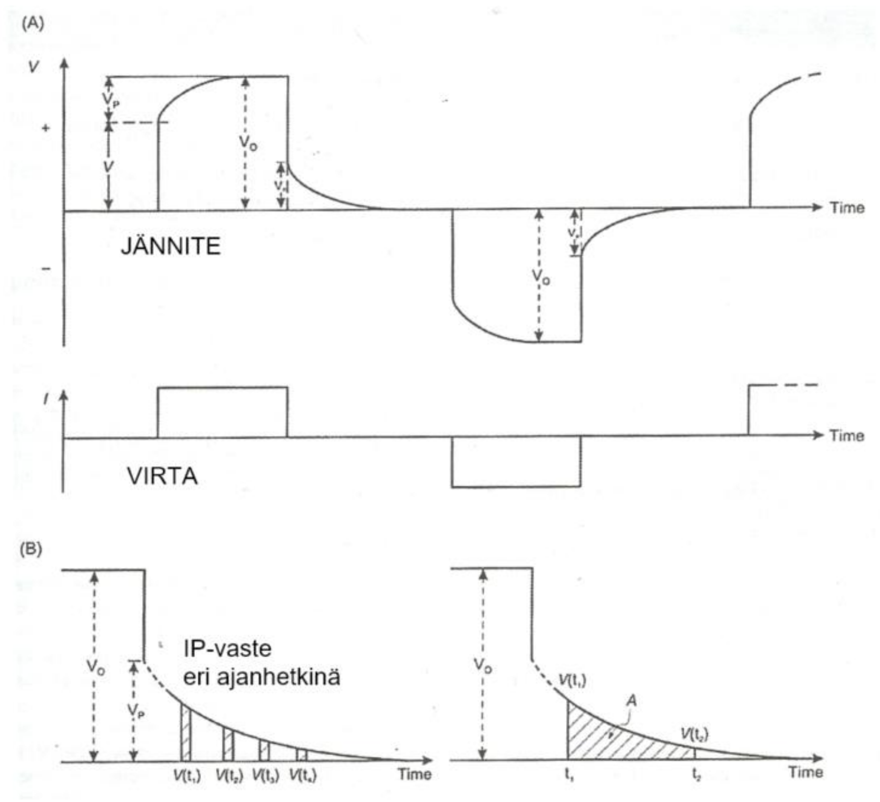
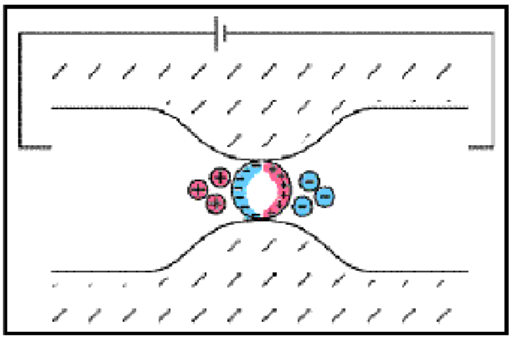


Figure 2.4. Measurement of induced polarisation (edited from Reynolds, 2011). JÄNNITE = charge; VIRTA = current; IP-vaste eri ajanhetkinä = Induced Polarization as a function of time.



a)

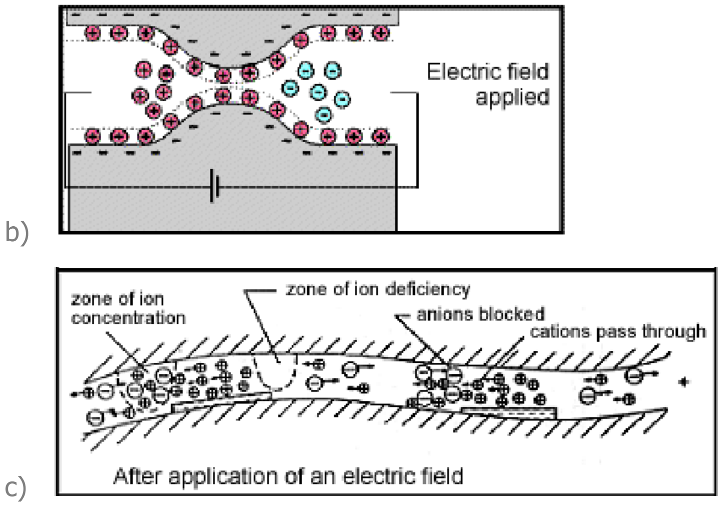


Figure 2.5. Ground mechanisms of induced polarisation, a) metal conductor, b) pore narrows, c) clay mineral.

Induced polarization changes the soil conductivity to a complex physical quantity, where in the end of each pulse, or with low frequencies, a DC conductivity is observed. In the beginning of a pulse, or with high frequencies, the value is higher. The polarizing structure and polarizing degree of the soil are represented as chargeability in the time range and with the cole-cole parameters in the frequency range. Chargeability differs between soil types, minerals and concentrations. Different contaminants change the soil conductivity and soil polarization, which can have some relevance during investigation and contaminant spotting. According to geophysics induced polarization isn't considered as having real significance in soil chemistry. For induced polarization also negative IP responses are known. They can be results of weak electrode contacts (high contact resistance), coupling effects between voltage and current circuit conductors, certain layered polarizing and conductivity structures (for example polarizing top layer and growing conductivity further down or a layer with weak conductivity in between). Negative IP can form also near elongated or three dimensionally polarized objects. Bert (1968) has stated that a negative IP can exist when the electrodes are situated within a polarizable volume. Negative IP has also been observed in soft clays.

## 2.4. ELECTRO-KINETIC METHOD

Traditional electro-kinetic method is based on transporting charged ions or compounds in the soil with an electric current. (mm. Van Cauwenberghe, 1997; Geoengineer.org, 2016; Buehler *et al.,* 1994; Reddy, 2013). In this context we treat only methods based exclusively on electricity, in a section to follow we'll return to methods combined with, for example, chemical techniques. In this method direct current is used. Groundings are done with unpolarizing carbon, graphite or platinum electrodes installed around the zone to be remediated (fig 2.6) (Sähköinen maaperän puhdistus ja geofysiikka 1.3.2017 page 10 (43))

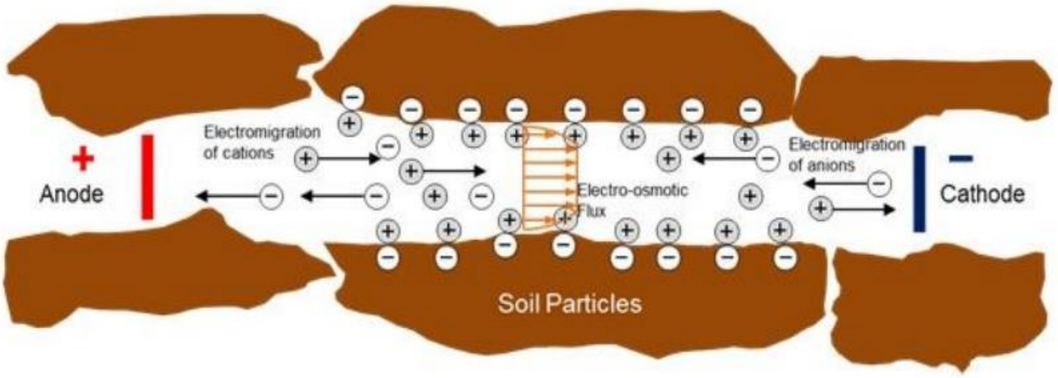


Figure 2: Transportation of ions in the soil (Cameselle et al., 2013)

Figure 2.6. Principle of electrokinetic method, catode and anode situate at the edges of the soil volume treated.

Chemical compounds or ions need to be charged and in a dissolved form or attached to water via adhesion. Pore space and water streams in the soil serve as the transport routes. The method has been used in remediation of soils and soil bound water since the 1990's.

In electro-osmosis soil water or ground water is moved from the anode towards the cathode with the electric current. Osmosis is diffusion from lower concentrations towards higher concentrations. In a liquid media ion groups are organized to form an electric double layer. With an electric field introduced across the stream, an electro-osmotic streaming results. The liquid on the borders of a solid begins to move and creates a stream that is temperature, ion concentration, ion mobility, water viscosity and dielectric permittivity dependent.

Electric double layer plays an important role (additional charges are formed). Solid surfaces gain a surface tension when in contact with the electrolyte. Soil particles are generally negatively charged and in the immediate proximity a layer of positively charged ions is formed. With electric current the electric double layer and its ions are used as the transporters of fluids.

The equation for electro-osmotic velocity vso is (Virkutyte, 2005; Mattson & Lindgren, 1994)

$$vso = \varepsilon * zeta / \mu * Egrad \qquad (3)$$

where $\varepsilon$ =dielectric permissivity of water (C/V*m),

zeta-potential and $\mu$ as in equation (2)

Egrad is the gradient of electic field (V/m). Since $\varepsilon$ and $\mu$ vary very little in water, the electric double layer and the gradient of the field regulate the electro-osmosis to a large extent.

According to Virkutyte (2005, that also refers others like Acar *et al*., (1995)) sand is poorly applicable for electro-kinetics because of the weak double layer (small surface charge density) and the best fit would be either silt, kaolinite, illite or montmorillonite, all with a powerful double layer. The cation exchange capacities are also high so the linkages to soil conductivity model are obvious. CEC is further explored in the context of conductivity models. (Sähköinen maaperän puhdistus ja geofysiikka 1.3.2017 page 11 (43))

Water properties are pivotal in electro-kinetics and water transportation. Even when the water molecule is in a charge balance, it is electrically bipolar because of the orientation of the hydrogen and oxygen atoms. Water molecules have a high cohesion meaning that they attach to each other and form larger structures (fluid, droplet etc.) Water also has high adhesion, meaning high capacity to attach to other charged particles. The movement of water is caused by charged particles, like ions, dragging the water along as they move through the pore space.

Electro-osmosis can be applied in de-watering for soil types of low water conductivity (clay and silt) because the velocity gained with ion-assisted methods is higher than movement gained via hydraulic pumping (Simpanen *et al.,* 2017).

Electro migration (ionic migration) is the movement of ions and ion complexes towards an oppositely charged electrode. The movement is faster than that of water in electro-osmosis. The movement of ions depends on the mobility of ions, valence and concentration of the electrolyte. In electro migration the velocity of ions vsm

vsm= mob * Egrad (4)

where mob is the mobility of ions (m^2/Vs).

The mobility is usually between 4-8 (*10-8) like for $Na^+$ (5.2), $Cl^-$ (7.9), $Ca_2{}^+$ (6.2), and $SO_4{}^{2-}$ (8.4). Mobility of hydrogen $H^+$ (36.2) and hydroxide $OH^-$ (20.6) (*10-8) are somewhat higher.

From equations (3) and (4) the velocity of water and ions can be assessed. The typical values are, for dynamic viscosity $10^{-3}$ Pa*s, permissivity of water $6.93 \cdot 10^{-10}$ C/Vm, zeta 100 mV (= 0.1V) and the result for osmotic velocity vso approximately 7E-08 m/s (~ 0.6 cm/d).

With most ions the migration of ions vsm is similar (6E-08 m/s (~ 0.5 cm/d). In calculations the magnitude of the electric field is 1,0 V/m . If the equations (3) and (4) are wished to represent the actual velocities in pore space, they need to be divided by the square of the route tortuosity (often between 0,1-0,6 depending on the soil type) (Mattson & Lindgren, 1994).

in Geoengineer.org a Paducah-treatment site is mentioned, where a gradient 0.25 V/cm (25 V/m) is used and water velocity 0,43 cm/d achieved. (Buehler et al. (1994)) In this publication the velocity for cromate-ions is 9,6 cm/d with current density 2,26 mA/cm^2). In the different references of Wikipedias “electrokinetic remediation” page alkalis and alkaline metals were found to have moved 50-60 cm/d and heavy metals 10-20 cm/d. With zeta potentials over 100 mV electro-osmotic flow is higher than electro migration which is the case in clays and silts. With coarser soil types with lesser filler concentration, like sand and gravel, the zeta-potential is smaller and the velocity of the ions hence outpaces the osmotic velocity. Likewise the velocities of hydrogen and hydroxide-ions are greater than the osmotic velocity of both water and that of other ions.

At neutral pH the number of hydrogen and hydroxide ions are in balance and in normal near neutral tap water the amount of both ions is very low, $10^{-7}$ M for both (Fig 2.7). In acidic conditions the number of free hydrogen ions exceeds the number of hydroxide ions, in alkaline conditions the other way around. Near anode hydrogen acts as the electron donor oxidizing to H+, leading to acidic conditions, near cathode it is reduced to hydroxide leading to alkaline conditions and hence a pH gradient forming. The changes in acidity are transported in soil faster than either water or ions.

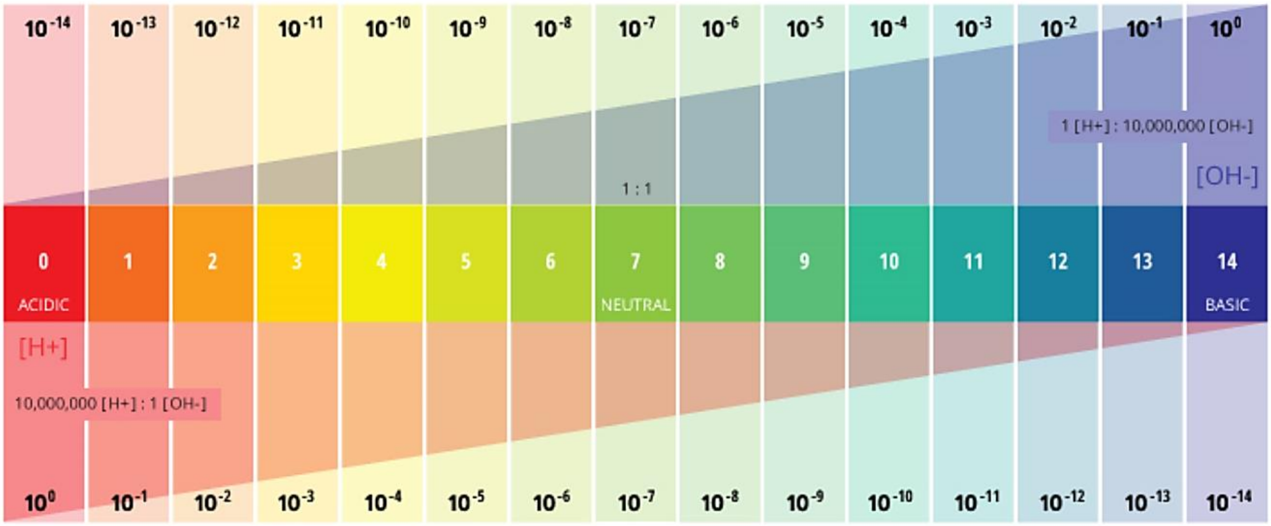


Figure 2.7. Hydrogen and hydroxide ratios at varying pH levels (image: www.fondriest.com/parameters).

The pH value of water is affected by additional chemicals. For example metals dissolve into water to a greater degree in acidic conditions. Electrophoresis is the movement of charged particles or colloids in electric fields in relation to the surrounding liquid medium like water. The movement is negligible in dense soils with low porosity.

The ions or compounds collected at electrodes can be pumped out for further treatment or be treated chemically *in situ*. The electrodes are in principle placed in a bain-marie, for example a drilled hole, to enable both the pumping and grounding of the electrodes. Water can be introduced into the soil to form a sufficient current in the treatable medium. The distance between electrodes in electro-kinetic treatment is several meters. The current density is often in the mA/cm$^2$ range (current 15-50 A) and the magnitude of the field in V/m range (potential difference 100-600 V. Reddy (2013) mentions 1 V/cm to be the optimal value for fields. The method is recommended for *in situ* treatments in soil types with low water conductivity (clay, silt, silt moraine). Electro-kinetic methods can be used as such for collection of contaminants and water, or as electro-assisted alternative methods where electricity is used to transport the contaminant to the desired location (reactive barriers) or to transport reagents (for example nutrients) to hot-spots of contamination. The latter will be discussed in the context of electro-assisted methods.

# 2.4.1. THE RELATED PHYSICAL AND CHEMICAL PHENOMENA

Phenomena related to electro-kinetics are discussed here (Buehler *et al*., 1994). The molar streaming of ions consists of three separate components: movements caused by diffusion, electro-migration and convection. Diffusion depends on diffusion coefficients and differences in the ion concentrations. Convection is the movement of ion concentration carried by water (the flow depends on hydraulic flow (Darcy's flow: hydraulic gradient* hydraulic conductivity) and electro-osmotic component (electro-osmotic permeability*potential difference) (Sähköinen maaperän puhdistus ja geofysiikka 1.3.2017 page 13 (43))

Electro migration is the product of ion valence, faraday constant, ion concentration, effective ion mobility and potential difference, for each ion as an individual ion and as a part of the molar stream.

The electro-osmotic permeability Kc depends on several soil parameters; for that the Helmholtz-Smoluchowski equation is used.

$Kc = \varepsilon * \text{zeta} * \text{porosity} / \mu$ (5)

With low diffusion, the total flow of ions consists of migration caused by potential differences, and the natural movement of the water, with the latter being dependent of the electro-osmotic permeability. Without any flow caused by hydraulic pressure-difference, the convection term is solely dependent on electro-osmotic permeability. Porosity increases electro-osmotic permeability. One benefit of electro-osmosis in comparison to convection is the fact that size of the pores doesn't affect the flow.

Electrical power is the product of voltage and current and electric charge the product of electrical power and duration. Charge is used in chemical reactions on anode and cathode and is transformed to heat through kinetic friction. The charge used in remediation, as found in literature, is 65 – 330 kWh / $m^3$.

The magnitude of current doesn't play a role in electro-kinetics. The movement of ions to electrodes follows Faraday's law

$M = J / (Z * F)$, where

$M$ = molar concentration (mol/cm$^2$*s)

$J$= (A/cm$^2$), $Z$ is ion valence

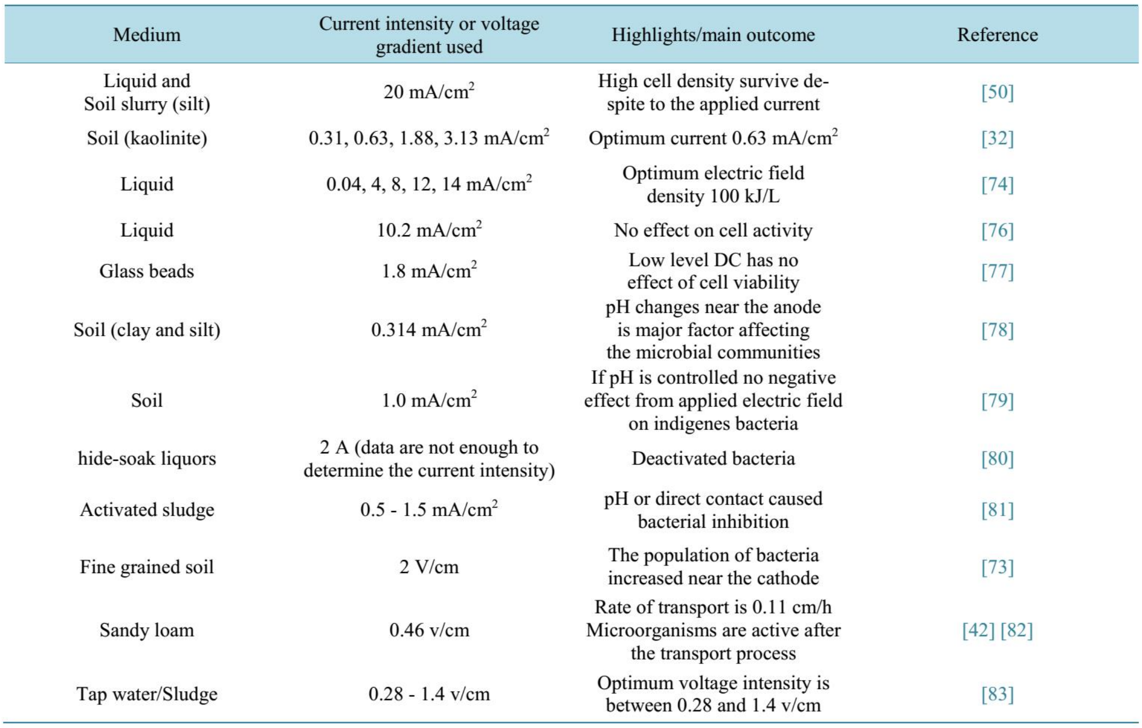
$F$=Faraday's constant (96500 C/mol (=A*s/mol))

The role of current density has been researched by several authors, for example Ottosen *et al*., (2008). According to publication table 1 and figure 1 it appears that, for example, chloride velocity increases with growing current densities. In practice high output voltages and current densities are maintained, because the process accelerates and the concentrations gathered at electrodes and heating effect both increase.

Electric charge in relation to cleansing effect/the amount of transported contaminant is usually rather constant. The current direction can be changed to penetrate the contaminated zone (for example Lasagna method). However, the duration of the electric pulse is long and not of alternating current kind.

The heating effect is mentioned of being of little significance for both osmotic water and ion transportation (Mattson & Lindgren, 1994) . If the direct current is supplied by constant voltage source, one degree rise in temperature can increase the velocity of ions by 3,4 % and the electro-osmotic velocity by 2,1 %. Higher velocity shortens the time required for remediation, but also increases the costs because of the heat excess. Limited heating may be cost-efficient. Current density may affect the micro-organisms. Hassan *et al.,* (2016) has listed effects reported in different sources. The message of the table 2.1 is somewhat vague, and the current densities can't be derived from currents alone (with current density itself being the noteworthy parameter for micro-organisms).

Table 2.1. Effects of current density on micro-organisms (Hassan et al., 2016).



| Medium | Current intensity or voltage gradient used | Highlights/main outcome | Reference |
|---|---|---|---|
| Liquid and Soil slurry (silt) | 20 mA/cm$^2$ | High cell density survive despite to the applied current | [50] |
| Soil (kaolinite) | 0.31, 0.63, 1.88, 3.13 mA/cm$^2$ | Optimum current 0.63 mA/cm$^2$ | [32] |
| Liquid | 0.04, 4, 8, 12, 14 mA/cm$^2$ | Optimum electric field density 100 kJ/L | [74] |
| Liquid | 10.2 mA/cm$^2$ | No effect on cell activity | [76] |
| Glass beads | 1.8 mA/cm$^2$ | Low level DC has no effect of cell viability | [77] |
| Soil (clay and silt) | 0.314 mA/cm$^2$ | pH changes near the anode is major factor affecting the microbial communities | [78] |
| Soil | 1.0 mA/cm$^2$ | If pH is controlled no negative effect from applied electric field on indigenes bacteria | [79] |
| hide-soak liquors | 2 A (data are not enough to determine the current intensity) | Deactivated bacteria | [80] |
| Activated sludge | 0.5 - 1.5 mA/cm$^2$ | pH or direct contact caused bacterial inhibition | [81] |
| Fine grained soil | 2 V/cm | The population of bacteria increased near the cathode | [73] |
| Sandy loam | 0.46 v/cm | Rate of transport is 0.11 cm/h<br>Microorganisms are active after the transport process | [42] [82] |
| Tap water/Sludge | 0.28 - 1.4 v/cm | Optimum voltage intensity is between 0.28 and 1.4 v/cm | [83] |

Significant electrolysis takes place on electrodes. Oxidation on anode produces hydrogen ions $4H^+$ and releases oxygen as gas. Hydroxide ions are produced at cathode and hydrogen gas is released. Gasses form bubbles that serve as obstacles for the electricity. pH affects the outcome and chemical conditions in a significant manner. Alok *et al*., (2013) lists the following phenomena and effects:

-pH affects the following surface properties of the soil particles: cation exchange capacity (CEC), adsorption capacity, magnitude of zeta potential and polarity.

-The occurrence and dilution degree of contaminants may also be pH-dependent.

-geochemical reactions like precipitation and dilution, adsorption, sorption and redox-reactions are pH dependent. The dilution of metals Pb, Ni and Cd near anode, transportation to cathode and precipitation near cathode in high pH is an example of this (Reddy, 2013).

- Through different factors pH also affects the advancing of electric current in soil by altering the conductivity. However, for example in the experiments of Alok *et al.,* (2012) voltages and currents varied independently in different pH values.

The mobility of hydrogen and hydroxide ions is 5-10 time higher than that of other cations and anions. This results in major pH differences in the current itinerary, apparently especially near anode and cathode. The soil pH is observed to have dropped to value 2 near anode and raised to 11-12 near cathode. Acidic conditions may result in mobility of metals. Alok *et al.*, (2012) mentions that metals precipitate near the cathode. Neutral pH point and highest potential gradient are located on the cathode side.

Diffusion is the balancing of concentrations towards the gradient. The significance of the phenomenon is low if the contamination is aged and the concentrations haven't been balanced already (Sähköinen maaperän puhdistus ja geofysiikka 1.3.2017 Sivu 15 (43))

The physical structure of the soil affects the electro-kinetic treatment. Soil physical structure is scrutinized in part 2.5.

For example the saturation degree plays a role. According to EPA, the efficiency of electro-kinetics weakens with saturation degrees under 10 %. The maximum efficiency is achieved with 14-18 % moisture (silts and clays). Moisture level can be way higher, up to 100 % with entirely saturated soil. With saturation degree lower than 10 %, no current is achieved without water additions to secure the minimal threshold for conductivity.

## 2.5. MODELS OF CONDUCTIVITY FOR SOILS

Soil is defined here as a solid or as a medium consisting of a solid phase and the bound water. Soil water content is the mass of the soil bound water in relation to the dried solid material. Soil density can be expressed as the density of the mineral matter (matrix density) or as bulk density. Soil conductivity is described and calculated with different mixture models often including mineral particles, fines (clay) and pore space filled with water, air or some other substance, like oil. If the pore space is filled partially with water and partially with air, the water filled part of the space is called the saturation degree (0-1).

In clays the porosity is high, the size of the pores smaller than in the mineral soil types and the soil particle area is large. The latter is related to the high cation-exchange capacity i.e. the double layer occurrence. Soil types including fine-grained ones also restrain high amount of water in the pore space, meaning that these soil types are rarely dry.

Water conducts electricity more efficiently than mineral particles and air, and in many models conductivity is a function of conductivity of water, porosity and saturation. The structure of the soil, orientation and pore size distribution are taken into account with empirical coefficients. More advanced models also consider fine matter concentrations. Here we talk about Waxman-Smits (Schön, 1996) and Connectivity Equation (CE) (Montaron, 2009) models, both applicable for soils.

Waxman-Smits model consists of two parts: the conductivity of the mineral part is calculated with Archie's Law and the conductance increasing effect of the fine-grained soil is added with an additional term. The variables in the model are water conductivity, porosity, saturation degree, soil density, clay content and cation exchange capacity of the fine soils (CEC), in unit mill equivalent / 100 g rock (meq/ 100g). Cation exchange capacity can be analysed separately for each soil type in a laboratory setting and lots of values are found in literature.

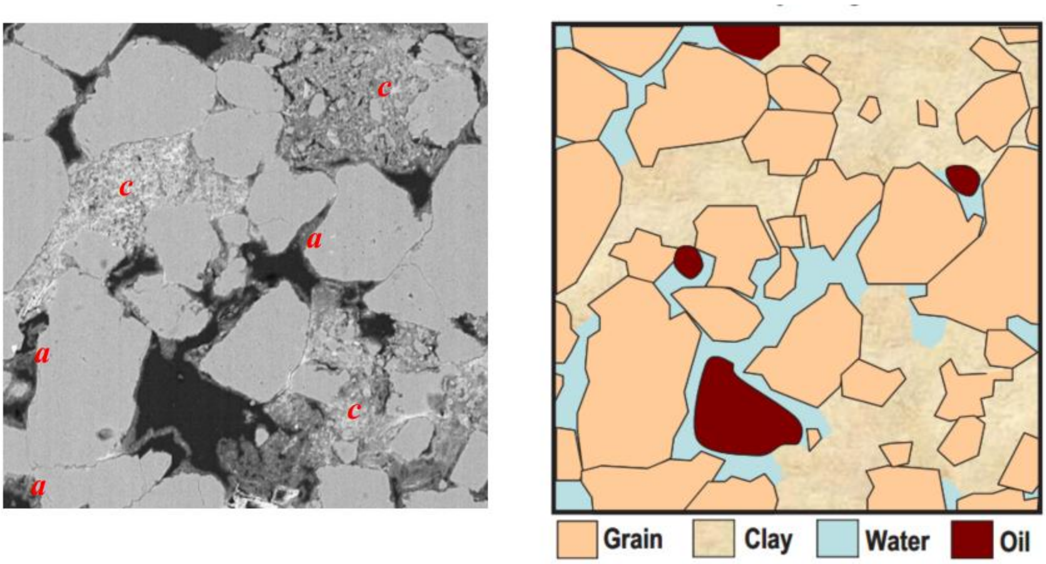


Figure 2.8. Sandstone structure example and its constituents. Oil can be substituted by air, for example (Montaron, 2009).

CE-model is based on mathematical mixture model. The conductivity of water, porosity and saturation for the whole soil mass are used as the calculation parameters. Other components like oil can be added to the mixture (fig 2.8).

The significance of water in different conductivity models is underlined by the fact that the conductivity of the mineral matter is excluded altogether. In principle both soil particles and pore air are insulators. The use of conductivity models leads to following advantages in remediation:

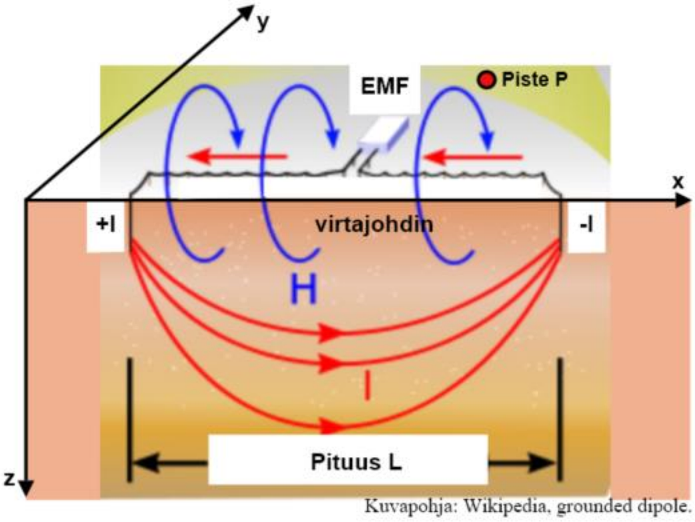
-The total concentrations of ions can be calculated from the conductivity differences in soil

-The effect of chemical additions on soil conductivity can be calculated.

-If the conductivity of water is known, porosity and clay-concentration can be calculated (if certain assumptions can be made)

## 2.6. THE ROLE AND APPLICATIONS OF ALTERNATING CURRENT

Electro-osmosis and the transportation of ions and colloids require static direct current. If alternating current is used instead, the phenomenon changes from electro-statics to electromagnetism. Direct current fed to conductors creates a primal electromagnetic source field and acts as a transmitter. The source field induces secondary magnetic and electric fields into the soil, both of which have a time dimension and amplitudes and phase differences in relation to the source field. The magnitude of the field is affected by the current I, the distance between groundings, distance from the transmitter, the frequency of the alternating current and conductivity of the soil closing the circuit. The field components in soil are affected by the galvanic term and inductively generated term (Nabighian *et al*., 1991; Kaufman *et al*., 2014). The situation is visualized in figure 2.9 where current I is fed into the conductor with the frequency f. The observation point P is also situated aboveground. The red arrows indicate the movement of the electric current and the blue ones the primary magnetic fields generated by the conductor.



Kuvapohja: Wikipedia, grounded dipole.

Figure 2.9. Grounded current wire for study of electromagnetic fields.

Calculation of components of electric and magnetic fields is complex especially if the point P is near the conductors and the distance r from the conductor of the same magnitude as the length of the conductor. The situation is less complex, if for example the component Ex of the electric field is observed far away from the conductor and with low frequencies. The electro-magnetic field is regulated by wavenumber k determined as

$$k = (i^* \boldsymbol{\sigma} * \mu_0 {}^*\Omega)^\wedge(1/2) \qquad (7)$$

where $\sigma$= conductivity, $\mu_0$ = soil magnetic permeability, $\Omega$ = angular frequency $2^*\pi^*f$, f = frequency. i is the complex number (-1)^(1/2).

If the condition $|k^*r| << 1$ is true, calculation of the field components is simple. If the frequency is under 100 Hz the conductivity is 0,01 S/m, the condition is true when the distance to the conductor is less than 50 m. Limitations set on distance and frequency are applicable when using electro-kinetics.

With low frequencies, the field components are reduced to mere direct current element as induction becomes insignificant. In a simple example DC 1 A is fed into the soil, with 10 m distance between grounding points. When observed above ground level from 50 m, with soil conductivity 0,01 S/m, the magnitude of the primary DC electric field Ex to the direction of the conductor is 2,5 mV/m. When the inductive element (frequency 100 Hz) is also taken into account, the magnitude of the field total differs less than 3% from the DC field. With frequencies lower than 100 Hz, the difference is even less. Also, if the field is being measured near the conductors, the inductive element is reduced and hence the DC element will increase and dominate to a larger degree.

When the electromagnetic induction is small, only the DC terms remain. With low (<100 Hz) frequencies alternating current is similar to direct current. In each moment voltage and current level can be handled as static portions than can be summed together for the timely effect. In the conductor also static magnetic field is generated (Fig 2.9, marked H and with blue arrows) that can be calculated using Biot-Savart's Law. The role of the magnetic field hasn't been covered in literature.

Alternating current doesn't have time to transport charges over significant distances before the polarity of the current changes and the direction is inverted. The supplied voltage and current are converted into heat in the circuit (thermal power, W) and integrated over time, to quantity of heat (Wh). Also the inductive element is wasted in soil as Joule heating.

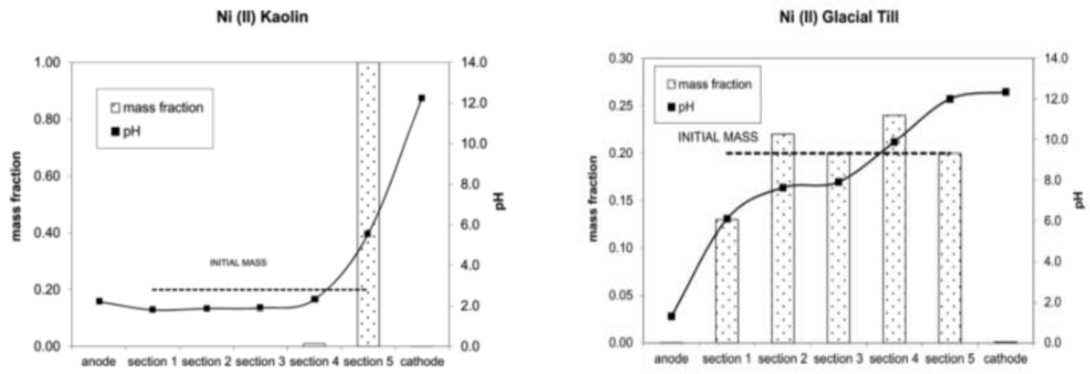
## 2.7. USE IN REMEDIATION, COMMERCIAL APPLICATIONS AND EXAMPLES

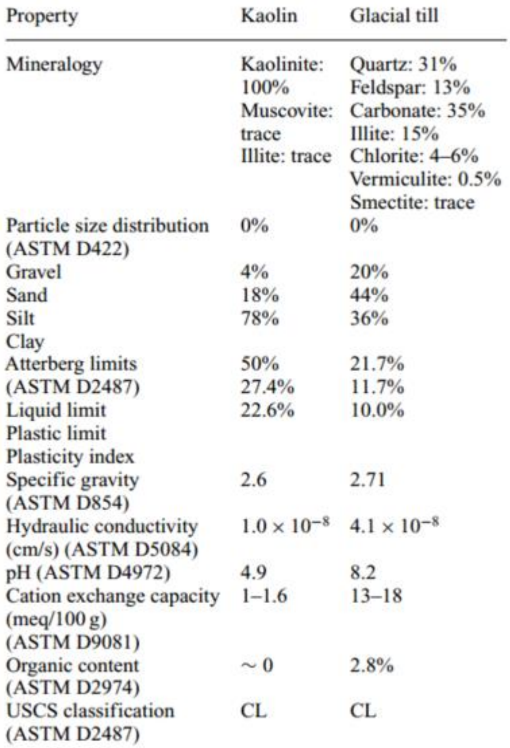
Dewatering with electro-osmosis has been in use from the 1930's onwards and the transportation of soluble compounds with electrodes is the basis of electro-migration.

Electro-kinetic method is mentioned of being applied for heavy metals, radioactive compounds, toxic anions (nitrates, sulphates,) dense DNAPL's, cyanides, oil hydrocarbons (diesel, petroleum, kerosene, lubricating oils), explosives, organic pollutants, halogenated hydrocarbons (TCE), non-halogenated organic pollutants (BTEX) and PAHs (Van Cauwenberghe, 1997). The requirement is that the respective ions, compounds or colloids appear as solutes in water.

Reddy (2013) shows various examples of lab scale remediation pilots for soils contaminated with heavy metals (Cr, Ni, Cd and Hg) both for homogenic clays (kaolin) and un-homogenic moraine. As an example the movement of ion $Ni^{2+}$ is shown in figure 2.10 with the medium characteristics also listed. The example was chosen for the major variation in different soils.

Ni was transported effectively in clay, but with reduced efficiency in moraine, because of the high pH in the latter. In moraine the acidity decreased only near anode, from where the metal was transported to the reductive zone. In clay, pH stayed low apart from the region near the cathode.





| Property | Kaolin | Glacial till |
|---|---|---|
| Mineralogy | Kaolinite: 100%<br>Muscovite: trace<br>Illite: trace | Quartz: 31%<br>Feldspar: 13%<br>Carbonate: 35%<br>Illite: 15%<br>Chlorite: 4–6%<br>Vermiculite: 0.5%<br>Smectite: trace |
| Particle size distribution (ASTM D422) | 0% | 0% |
| Gravel | 4% | 20% |
| Sand | 18% | 44% |
| Silt | 78% | 36% |
| Clay | | |
| Atterberg limits (ASTM D2487) | 50% | 21.7% |
| Liquid limit | 27.4% | 11.7% |
| Plastic limit | 22.6% | 10.0% |
| Plasticity index | | |
| Specific gravity (ASTM D854) | 2.6 | 2.71 |
| Hydraulic conductivity (cm/s) (ASTM D5084) | $1.0 \times 10^{-8}$ | $4.1 \times 10^{-8}$ |
| pH (ASTM D4972) | 4.9 | 8.2 |
| Cation exchange capacity (meq/100 g) (ASTM D9081) | 1–1.6 | 13–18 |
| Organic content (ASTM D2974) | ~ 0 | 2.8% |
| USCS classification (ASTM D2487) | CL | CL |

Figure 2.10. Nickel consentration in kaoline clay and moraine in electrokinetic field and material properties (Reddy, 2013).

The effect of water and heavy metal content has been tested (Reddy, 2013). The increase of the former didn’t affect the mobility of the metals, but increased the magnitude of the electric current and electro-osmotic flow. Higher metal concentrations and synergy effect of different metals weakened the migration. Addition of water doesn’t hence increase the mobility of metals in soil. According to Gillen (2005) increasing moisture decreases the zeta-potential and the reduction of zeta-potential also weakens the electro-osmotic flow as can be seen in equation 3.

Metals occur with different valences and this phenomenon also plays a role. For, for example, chrome the mobility in clay is highest for $Cr^{3+}$ , and in moraine for $Cr^{4+}$, since the latter is able to form a soluble compound with increased migration in reducing conditions. Reddy also sums that reducing or oxidizing compounds (especially sulfites) occurring in natural conditions, that have an effect on redox and pH, should be surveyed when the applicability of the method is being studied.

EPA CLU-IN mentions several limitations:

- LNL has observed that dense non-water soluble DNAPL compounds can clog the system.
  DNAPL (Dense non-aqueous phase liquid) is a general term for non-water soluble compounds heavier than water, like chlorinated solvents, creosote, mercury and heavy oil hydrocarbon fractions.
- in non-saturated conditions addition of water can flush contaminants away from the zone of electro-kinetic influence
- metallic structures in soil hinder the process and greatly affect the distribution of, for example, the electric current distribution
- metallic electrodes dissolve in electrolysis and produce corrosion materials into the soil

The efficiency of electro-kinetic remediation can be enhanced with several direct methods. Electro-assisted methods where additives are injected and transported electro-kinetically are excluded from this list. Methods to increase the efficiency of electro-kinetic methods are:
-Increasing the magnitudes of voltage and electric current.
-the utilization of the electric field with direct current, with long duration on/off pulsing, by increasing the duration.
-the use on cation/anion exchange membranes on electrodes
-circulation of electrolytes
-threating electrodes with, for example, organic acids.

Water and/or heat transportation towards the contaminant and micro-organisms can perhaps also be included in the list.

Lasagna is a patented electro-kinetic remediation method that combines electro-kinetic technique and *in situ* electro-assisted treatment (Fig 2.11). The *in situ* half is comprised of parallel iron fillings suspended in clay slurry, situated between the electrodes. The aim is to transport the contaminant through at least two of the iron fillings. Lasagna has been developed by DuPont, General Electric and Monsanto companies together with US EPAn and US DOEn in 1990s (The first experiment was done in in 1995). Water is moving together with the contaminant from anode to cathode and circulated gravitationally back to the anode. The circulation of water has been found to decrease electrolysis and electrode reactions and buffer pH changes. The distance used is 6-30 m.

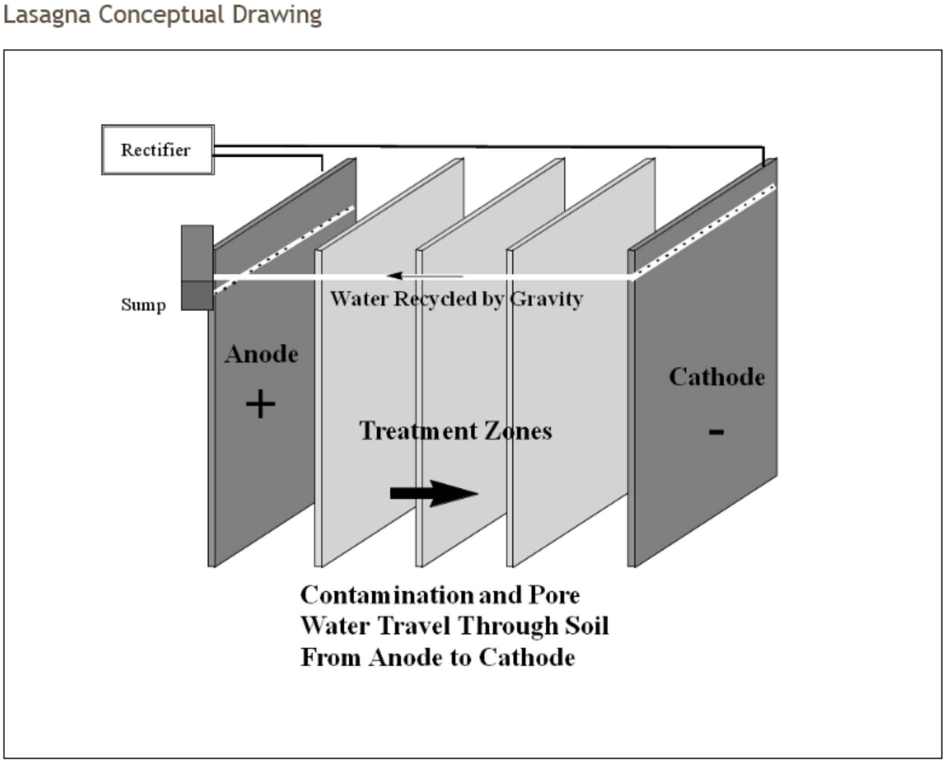


Figure 2.11. Electrokinetic Lasagna-method (Geoengineer.org, 2016).

GEOSTO Oy, 20.4.2017

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