REMEDIATION OF SALT IMPACTED GROUNDWATER WITH ELECTROKINETICS.

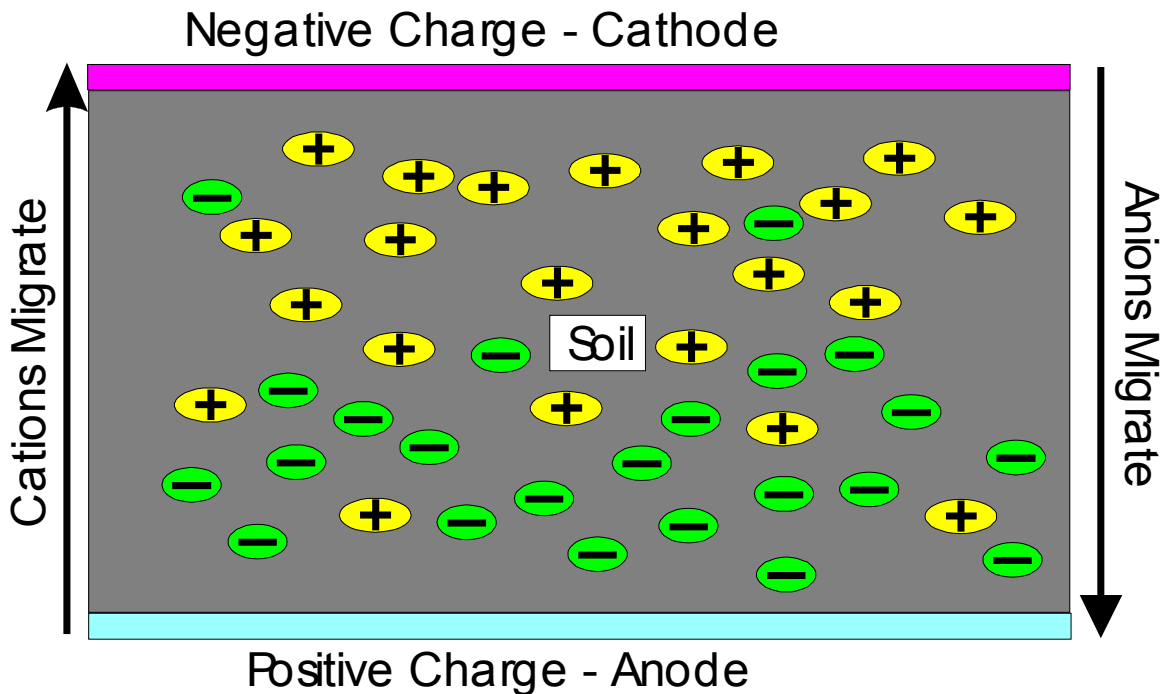*Paper by: Sean Kelly, Rick Churko, Sean Frisky, Anjum Mullick, Stuart Torr.*

Alberta Transportation is supporting leading research in the use of Electrokinetics to enhance the reclamation of salt impacted groundwater. Electrokinetic technology has long been used in applications that require soil dewatering. More recently there has been widespread research and application of this technology to contaminated sites treatment. Electrokinetic remediation is achieved by applying an electric field over the impacted area causing the movement of ions. Pilot studies and research demonstrate that the total voltage will vary from site to site, as it is dependent on the conductivity of the soil and the spacing of the anode and cathode. It is most applicable in low permeability soils, where extraction is difficult, because the soil is typically saturated and is not readily drained. The process has also been used, or is being investigated, for remediation of heavy metals, radionuclides, and organic contaminants. This new innovative research is being conducted at an Alberta Transportation salt storage yard where the impact of salt has caused considerable impact to surrounding vegetation. The pilot study will be in operation for two years to investigate the feasibility of In-situ Electrokinetics combined with vapour extraction and pneumatic fracturing; to enhance the removal of salts from salt impacted soil and groundwater. This paper presents a discussion of the project, including a summary of preliminary results, and economics.

INTRODUCTION

Salt spills in low permeability soils are a challenging remediation problem. High salt concentrations are toxic to vegetation, creating environmental and aesthetic impacts. Groundwater pumping or soil washing are often impractical as the low permeability limits soil/water contact. Electrokinetics is a promising technology, with potential to overcome these difficulties and emerge as a fast and efficient method to treat salt impacted groundwater.

Electrokinetics involves the imposition of an electrical field on a contaminated section of low permeability soil. Charged particles respond to this field by migrating towards the oppositely charged electrode. Once the ions have migrated towards their respective electrodes they can be readily removed by groundwater flushing, extraction, and treatment at the surface. Due to the concentration of the ions at the electrodes, far less water flow is required to remove contamination than would be required without electrokinetics.

Figure 1 – Schematic of electrokinetic principles

This rate of ionic migration can be many times the bulk groundwater flow rate (limited due to complex interactions between water and soil in low permeability soils). Ionic migration facilitates removal of significant proportions of the contamination in very short periods of time, compared to traditional water flushing technologies.

Alberta Transportation is supporting leading research in the use of electrokinetics to enhance the reclamation of salt impacted groundwater. In salt impacted groundwater, high concentrations of sodium ions (Na^+) and chlorine ions (Cl^-) exist in solution. Under the imposed electric field described above, the sodium ions will migrate towards the cathode, while the chlorine ions migrate towards the anode. Removal of these ions over

time through a groundwater pump-and-treat system will reduce the overall salt concentration in the groundwater.

This technology has been tried on a variety of contamination types, such as chlorinated solvents, heavy metals and radionuclides, to a varied degree of success. The US Army has also done a number of studies on chlorinated solvents, zinc, lead and chromium, U.S. DOE, 1995.

A general overview of the use of electrokinetic technologies can be found in Van Cauwenberghe, Liesbet; July 1997 or EPA 1996.

BACKGROUND CHEMISTRY

Predicting the impact of an imposed electric field on a chemical solution requires an understanding of multiple processes, and their interactions. Aqueous chemical equilibrium is largely governed by four parameters:

- Redox Condition - Oxidation-reduction or 'redox reactions' involve a transfer of electrons, and cause changes in the oxidation state of both the reactants and the products. Oxidation is the loss of electrons while reduction is the gain of electrons.
- pH – pH is a measure of the acidity or alkalinity of a solution, increasing with increasing alkalinity and decreasing with increasing acidity.
- Concentration (solubility) – Concentration refers to the amount of solute dissolved in a solution. Solubility is the amount of a substance that can be dissolved in a given amount of solvent under specific conditions.
- Thermodynamics - Thermodynamic conditions impact the equations of state for chemicals in solution. Adding or removing heat in a system creates a dynamic situation until a new equilibrium is reached.

These parameters are interrelated, so a change in one will result in a change in the others. For example, solubility of a chemical may vary at different redox states. Also, solubility often increases with lowering pH.

All of the above parameters will be impacted by electrolysis.

- The addition of a current to the system will result in extreme redox conditions at the anode and cathode.
- Reactions taking place at the electrodes will shift the pH.
- Migration of ions will shift the concentrations of compounds in the groundwater.
- Soil heating will affect the thermodynamics.

Under differing operational conditions, different aspects may be dominant. For example, under high current conditions pH changes may govern the chemical equilibrium, whereas under low current conditions, concentration gradients caused by ionic migrations may dominate.

The following sections describe the chemical reactions resulting from electrokinetic induction of contaminated soil in the pilot study.

ANODE REACTIONS

REDOX REACTIONS

The chlorine donating an electron will result in the formation of a chlorine free radical.

$$Cl^- \Rightarrow Cl^{\cdot} + e^-$$

As chlorine is in high concentrations, the most probable outcome for this free radical is to react with another free radical to form Cl_2 gas.

$Cl^. + Cl^. \Rightarrow Cl_2$

Chlorine free radicals are may react with other reduced compounds before forming Cl_2 gas. However as chlorine is the dominant compound in the pilot solution, the chlorine gas formation reaction should dominate. Some of the chlorine gas will escape and some will dissolve in water to form hypochlorous acid (HOCL bleach) and hydrochloric acid (HCL).

$Cl_2 + H_2O \Rightarrow HOCl$ (pKa = 7.46) + HCl (pKa = negative)
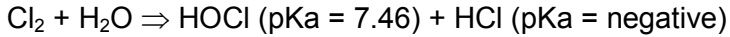
If simple organic acids (formic, acetic acid) are present, chlorinated substances may form through complicated reaction chains, which have significant negative impact on groundwater quality (ie Trichloromethane (chloroform)). Additionally, once the electrical gradient is removed, there will be a charge imbalance that will re-equilibrate. Compounds in the soil matrix may be involved in these reactions (ie iron or carbonate minerals).

An analogous reaction involving the breakdown of water and production of oxygen gas and acid will take place simultaneously, also contributing to a decrease in pH.

$2H_2O \Rightarrow 4H^+ + O_2 + 4e^-$
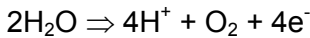
Equations can be found in McQuarrie, Donald A. & Rock, Peter A.

PH REACTIONS

As the chlorine dissolution and water reduction reactions above result in pH drop, various pH sensitive equilibriums will be affected. Lowering pH will increase the solubility of various compounds. Depending on the soil matrix, iron, (bi)carbonate, manganese and other compounds will likely increase in concentration. Initially, the pH increase will be localized to the anode, but the H^+ ions will migrate over time towards the cathode under the influence of the electrical field.

CONCENTRATIONS EFFECTS

Negative ions will migrate to the anode, increasing concentrations. This will result in thermodynamically unstable concentrations of chloride, (bi)carbonate and sulphate in the vicinity of the anode. Concentration gradients will drive solubility reactions, to varying degrees depending on the location between the anode and cathode. The most important of these reactions will likely be the deposition of calcium, sodium and magnesium carbonates. Species that are bound to the soil matrix (i.e. sodium bound to clay particles) may participate in these reactions.

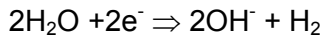## CATHODE REACTIONS

REDOX REACTIONS

Sodium metal, formed through reaction of sodium ions with donated electrons, will react quickly with water to form sodium hydroxide and hydrogen gas.

$Na^+ + e^- \Rightarrow Na$

$Na + H_2O \Rightarrow NaOH$ (pKb = 0.2) + H_2
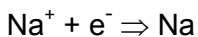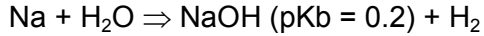
Dissolution of the NaOH will cause an increase in pH, limited by the buffering capacity of the solution. Compounds in the soil matrix may participate in these reactions (i.e. iron minerals).

An analogous reaction involving the breakdown of water and production of hydrogen gas and hydroxide will take place simultaneously, also contributing to an increase in pH.

$2H_2O + 2e^- \Rightarrow 2OH^- + H_2$

PH REACTIONS

The increase in pH will likely be localized to the cathode. An increase precipitation of several compounds will result, dominated by carbonate salts depending on the degree to which carbonate migrates away from the cathode.

CONCENTRATIONS EFFECTS

Positive ions will migrate to the cathode, increasing concentrations. Increased concentrations will affect chemical equilibriums and likely cause precipitation of soluble salts or dissolution of bound species. Additionally, concentrations of NaOH may build up past the saturation point at the cathode itself, leading to precipitation.

PILOT RESULTS

The research program underway is evaluating the applicability of this technology for use on road salt contamination at a road salt storage facility in Alberta. Ground at site consists of a sandy loam with approximately 10% clay content to a depth of greater than 12m. The static water head is at approximately 3 mbgl (meters below ground level).

Several samples of soil from the site have been used in a pilot study to determine the parameters for a planned full-scale field study. Results from this study have been promising.

The pilot study was completed on 0.66 m long columns of undisturbed soil saturated with high concentration saltwater. These samples were taken from two different locations at site (A & B). Soil types analysis results are shown below.

Table 1 – Soil Types

Soil Analysis	Soil Texture	% Sand	% Silt	% Clay
Area A	Sandy Loam	65	27	8
Area B	Sandy Loam	69	19	12

Table 2 – Initial Conditions – Area B

	Well 9 Cathode	Well 9 Middle	Well 9 Anode
Parameter	Concentration	Concentration	Concentration
	mg/L	mg/L	mg/L
Chloride	3340	4340	2890
Sulphate	259	272	193
pH	7.6	7.6	7.6
Calcium	93	220	80
Potassium	70	34	38
Magnesium	28	51	23
Sodium	2310	2430	1800

For chloride concentration this gives an average (mean) of 3520 mg/L and a 95% confidence interval of 2040 to 5000 mg/L. For sodium, the average (mean) is 2180 mg/L and the 95% confidence interval is 1510 to 2850 mg/L. The pH was constant throughout.

A constant voltage power supply was connected across the columns at a range of set-point voltages from 80 to 300 volts. After time intervals of approximately 24, 120 and 240 hrs the columns were disassembled and the soil was sent for saturated paste analysis. Below is a sample of the results.

ANODE RESULTS

After 24 hrs, the results for the soil at the cathode were as follows:

Table 3 – Anode results – 24 hrs

Well	Voltage	Chloride mg/L	Relative to 95 % confidence*	pH mg/L	Relative to 95 % confidence*	Sodium Mg/L	Relative to 95 % confidence*
Area A	80	3500	within	6.4	below	1430	below

Area B	80	4250	within	6.8	below	2090	within
Area A	160	3700	within	6.2	below	113	below
Area B	160	4430	within	5.5	below	1760	within
Area A	300	4670	within	6.0	below	769	below
Area A	300	7460	exceeds	6.4	below	340	below
Area A	300	3400	within	6.4	below	84	below
Area B	300	2390	within	6.2	below	789	below
Area B	300	2210	within	7.1	below	989	below

* = Confidence intervals for the background samples.

The chloride concentrations did not significantly change, regardless of voltage. The pH and the sodium concentrations showed significant changes, more pronounced in the higher voltage samples. Following the 24 hr period, the soil heating in the higher voltage samples became unsustainable, so the 300 volt tests were stopped. After 120 hrs, the results for the 80 and 160 volt samples were as follows.

Table 4 – Anode results – 120 hrs.

Well	Voltage	Chloride mg/L	Relative to 95 % confidence*	pH mg/L	Relative to 95 % confidence*	Sodium mg/L	Relative to 95 % confidence*
Area A	80	5900	exceeds	5.7	below	60	below
Area B	80	5560	exceeds	4.2	below	93	below
Area A	160	7850	exceeds	5.1	below	167	below
Area B	160	3990	within	4.1	below	111	below

*= Confidence intervals for the background samples.

Marked increases in the chloride concentration can be seen at the anode along with significant drops in pH and sodium concentrations. Note that the different voltages seem to have no significant effect.

The results for the 240 hr samples showed more of the same trend, as can be seen below.

Table 5 – Anode results – 240 hrs.

Well	Voltage	Chloride mg/L	Relative to 95 % confidence*	pH mg/L	Relative to 95 % confidence*	Sodium mg/L	Relative to 95 % confidence*
Area A	80	7380	exceeds	5.4	below	54	below
Area B	80	5400	exceeds	5.5	below	150	below
Area A	160	6280	exceeds	5.9	below	129	below
Area B	160	9500	exceeds	3.9	below	150	below

* = Confidence intervals for the background samples.

Chloride concentrations show an approximate doubling from the initial concentrations, while the sodium concentrations drop by more than an order of magnitude. The pH stabilizes and is likely buffered by inorganic salts in the vicinity of the cathode. There is no significant difference between the two voltages.

CATHODE RESULTS

After 24 hrs, the results for the anode soils were as follows:

Table 6 – Cathode Results – 24 hrs.

Well	Voltage	Chloride mg/L	Relative to 95 % confidence*	pH mg/L	Relative to 95 % confidence*	Sodium mg/L	Relative to 95 % confidence*
Area A	80	1080	below	8.7	exceeds	765	below
Area B	80	3020	within	9.7	exceeds	3520	exceeds
Area A	160	524	below	9.9	exceeds	2420	within
Area B	160	2250	below	9.6	exceeds	2640	within
Area A	300	209	below	9.5	exceeds	290	below
Area A	300	493	below	9.9	exceeds	713	below
Area A	300	183	below	10.0	exceeds	459	below
Area B	300	1550	below	9.5	exceeds	1460	below
Area B	300	909	below	9.9	exceeds	2000	within

* = Confidence intervals for the background samples.

Here, the sodium results are somewhat inconsistent. The chloride shows significant decline and the pH shows significant increases. The inconsistent results with the sodium continued in the longer-term samples, as seen below.

Table 7 – Cathode Results – 120 hrs.

Well	Voltage	Chloride mg/L	Relative to 95 % confidence*	pH mg/L	Relative to 95 % confidence*	Sodium mg/L	Relative to 95 % confidence*
Area A	80	229	below	10.1	exceeds	1310	below
Area B	80	2990	within	10.1	exceeds	7920	exceeds
Area A	160	690	below	10.0	exceeds	1290	below
Area B	160	1590	below	10.0	exceeds	3140	exceeds

* = Confidence intervals for the background samples.

The two Area-A sodium samples are showing small but significant decreases in concentration, while the chloride and pH continue to follow their expected trends.

Table 8 – Cathode Results – 240 hrs.

Well	Voltage	Chloride mg/L	Relative to 95 % confidence*	pH mg/L	Relative to 95 % confidence*	Sodium mg/L	Relative to 95 % confidence*
Area A	80	283	below	9.9	exceeds	929	below
Area B	80	208	below	10.1	exceeds	2530	exceeds
Area A	160	781	below	10.1	exceeds	978	below
Area B	160	465	below	10.4	exceeds	8070	exceeds

* = Confidence intervals for the background samples.

The chloride shows a much more significant drop than at 120 hrs and the pH stabilizes, again, likely due to buffering. Even after the full 240 hrs the two Area- A samples continue to show decreases in sodium concentration. This is likely a result of stable

sodium salts forming as a result of the pH increase that are not then detected in the analysis.

It is clear that successful migration is highly dependent on operating conditions. It is unclear at this time how the system will scale and what voltages and currents will be appropriate at full-scale. Further field testing will be taken during the summer to further refine the appropriate operating conditions.

ECONOMICS

To date this technique has only been implemented at pilot scale, so exactly how the installation and operating costs will scale is not known. We can assign an estimated cost of $25 / m^3 on the technique as follows. This cost will be further refined when full-scale trials are complete.

The bulk of the cost associated with the full-scale implementation is expected to be the cost of drilling the wells. The drilling and installation costs for a 2700 m^3 volume is expected to be approximately $60,000 or approximately $25 / m^3.

Full-scale current use is expected to be on the order of 1 amp continuous at approximately 100 Volts. This will lead to a continuous power consumption of about 100 W or 24 kWh over 240 hours of operation to clean up 2700 m^3. Therefore the power costs are negligible.

By comparison, the typical cost associated with excavation and landfill disposal is $80 - $100 / m^3.

CONCLUSIONS

Preliminary studies show significant promise in the use of electrokinetics for salt contaminated soil cleanup in low permeability soils. Although sensitive to operating conditions and soil characteristics it appears that order of magnitude decreases/increases of concentrations are possible.

Field-testing on a large scale will refine estimates of power costs and precise operating conditions, which will be applicable to full-scale operation.

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