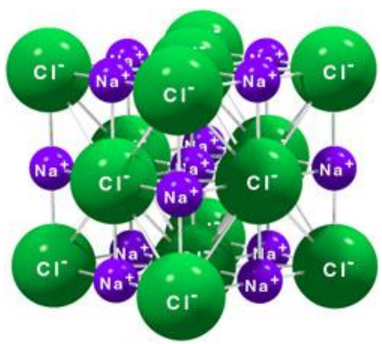
A Method for Remediating Brine Impacted Soil Using Electrokinetics



$$[Na]^+ \; [:\ddot{\underset{..}{Cl}}:]^-$$

Presented by: Dustin Anderson

NDSU Geochemistry

GEOL 628 2020

Project Contributors:

Amy Groseclose with Oasis Petroleum

Christopher Athmer, PE with Terran Corporation

Cody Anderson and Chris Knox with Onecor Environmental

Tetra Tech

American Engineering and Testing

Introduction

- Key terms and takeaways
- How brine influences soil and water infiltration
- Site characterization
- Passive vs Active remediation
- Introduction of Electrokinetic remediation
- Case Study - Schmitz brine remediation, McKenzie County, North Dakota
- Understanding pH and Alkaline fronts with PHREEQC modeling
- Future work

"A nation that destroys its soils, destroys itself" – Franklin D. Roosevelt

Key Terms and Takeaways

Terms

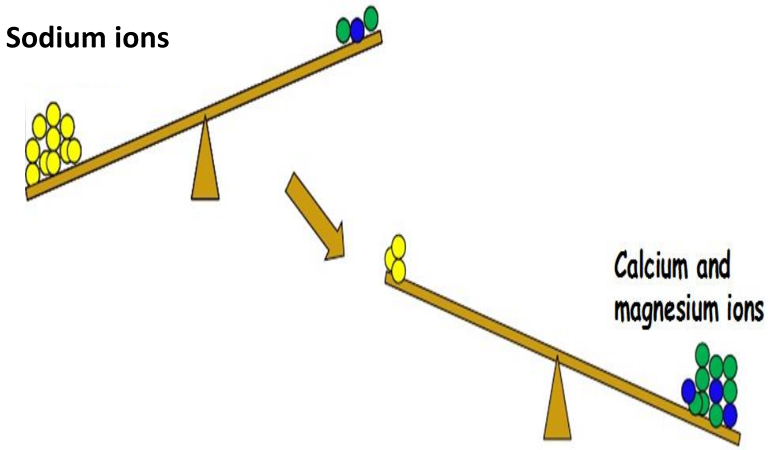
- **Remediation vs Reclamation** – remediation is moving something from a state of non function towards original function. Reclamation is to restore to pre-disturbed function
- **Passive vs Active remediation** – active remediation is short termed high input while passive is long term limited inputs
- **Electrokinetic** – use of direct current to mobilize and recover contaminants of concern

Key Takeaways

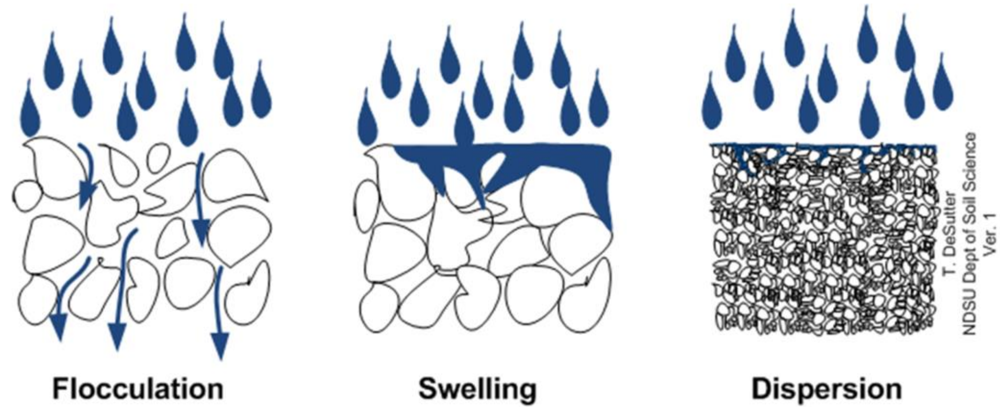
- Research has proven PHREEQC a powerful modeling tool for understanding geochemical processes in electrokinetic (EK) treatment
- Understanding pH fronts are key to EK treatment success
- Geology, hydrology, and chemistry are first order processes
- Chloride removal at the anode is a challenge – 50% to 60% removal
- This application of EK technology is not well understood. Field testing has shown it is effective at mobilizing ions in brine impacted soil

"We know more about the movement of celestial bodies than about the soil underfoot" – Leonardo Da Vinci

How Brine NaCl Impacts Soil

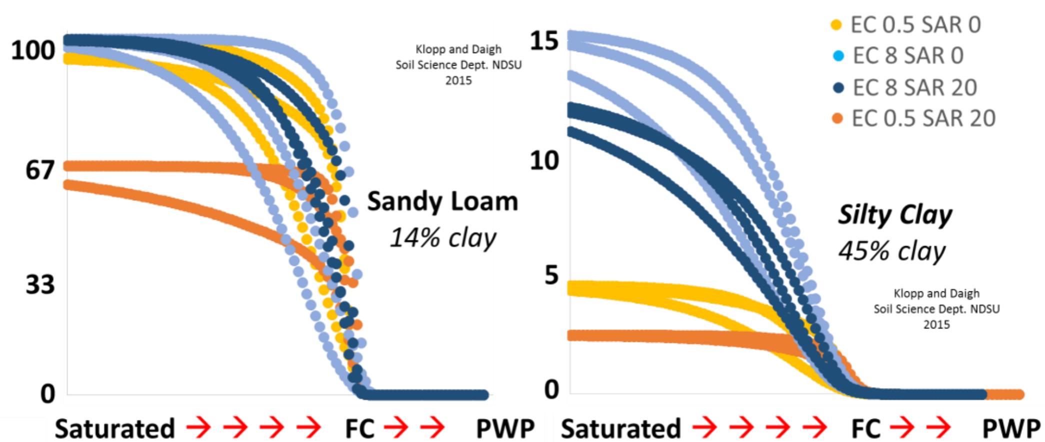


Dr. Kerry Sublette University of Tulsa



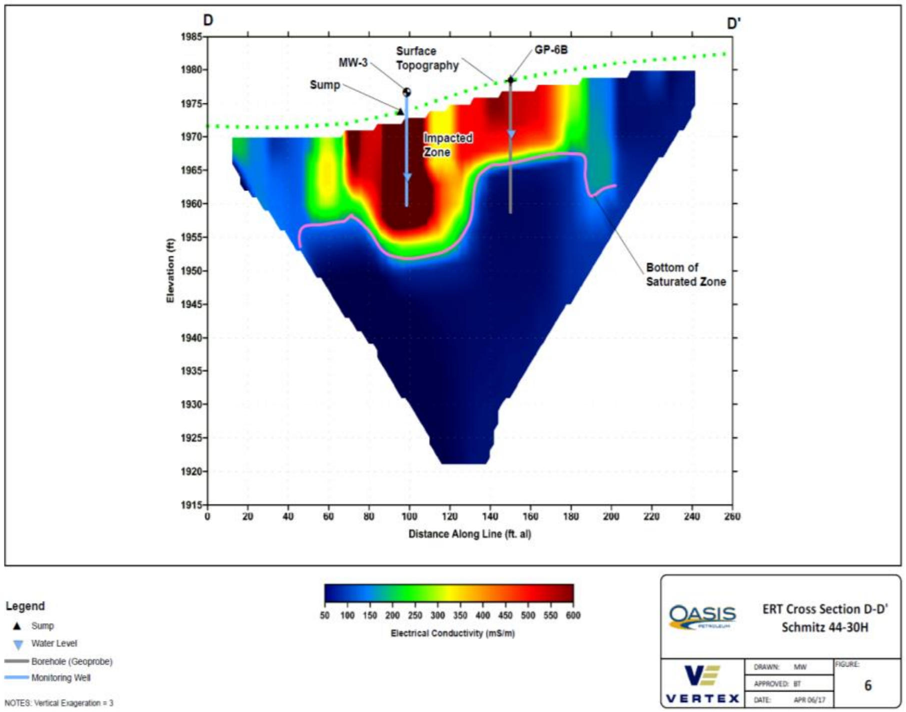
- Flood a natural system with NaCl
- Na^+ impacts soil function by breaking down soil structure which limits water movement in the soil
- Cl^- – has state and federal Risk Bases Screening Levels and is toxic to crops and grasses
- Na^+ binds to clays
- Cl^- is highly mobile
- How to remove these ions?

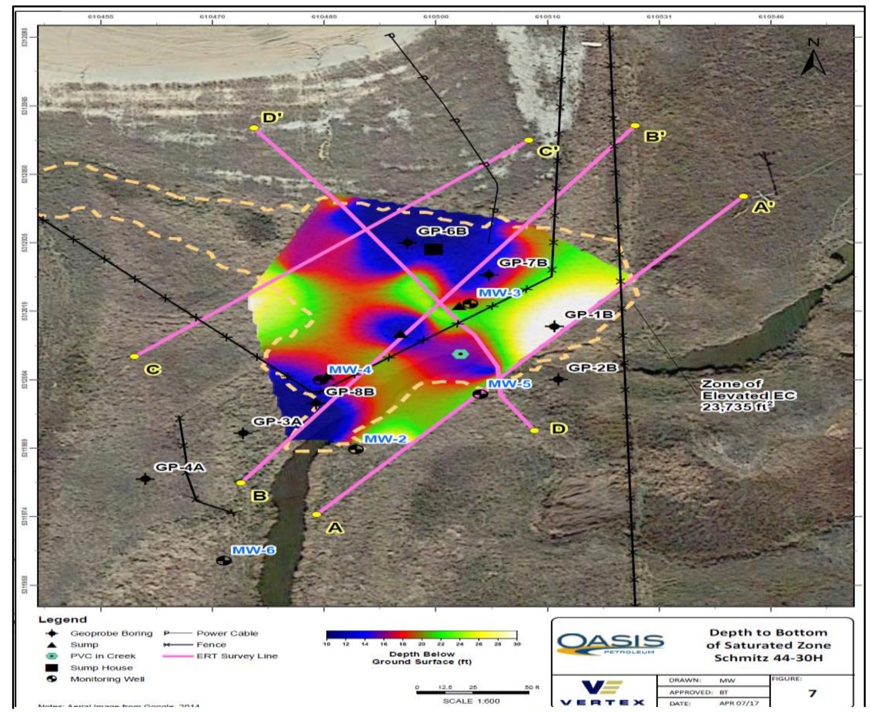
Water Movement in Soil (inches per day)

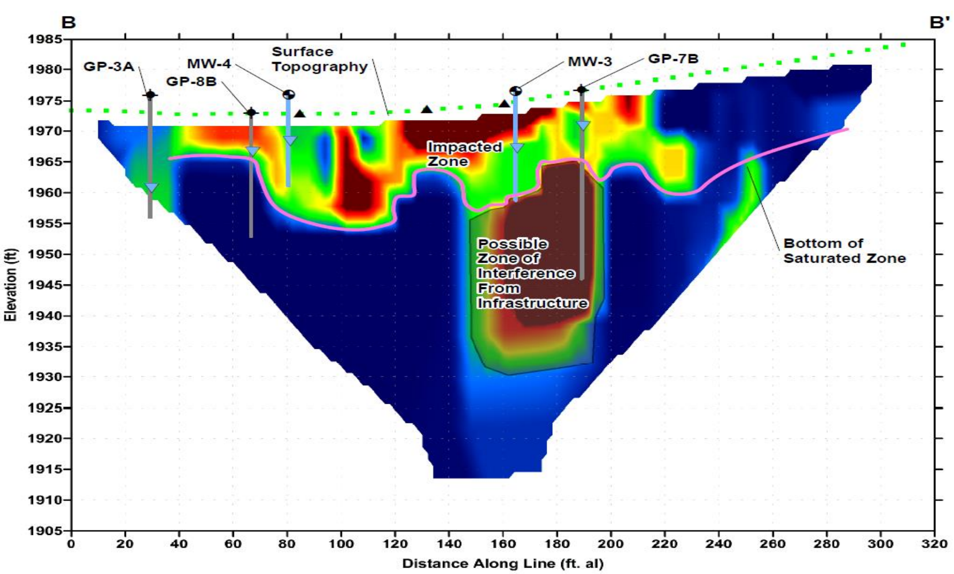


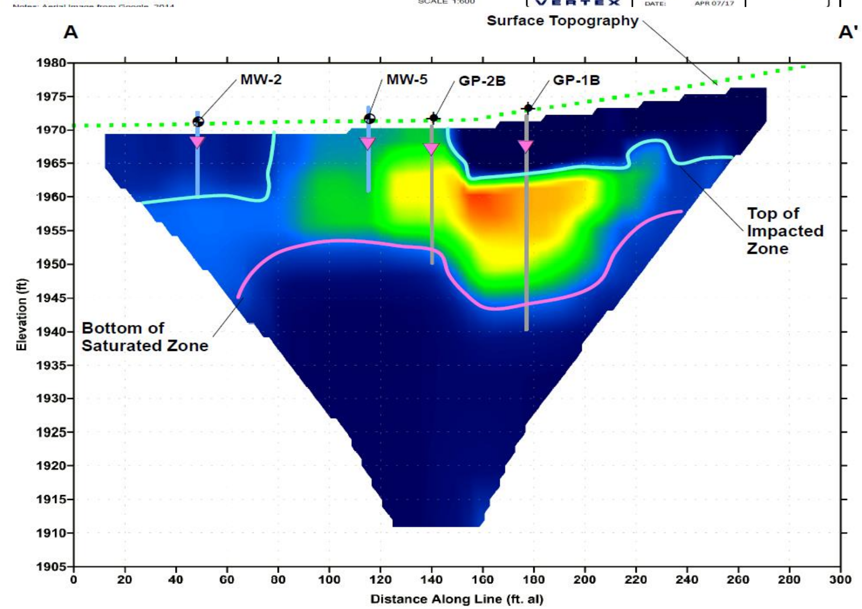
Case Study - Schmitz Remediation McKenzie, ND

Site Characterization

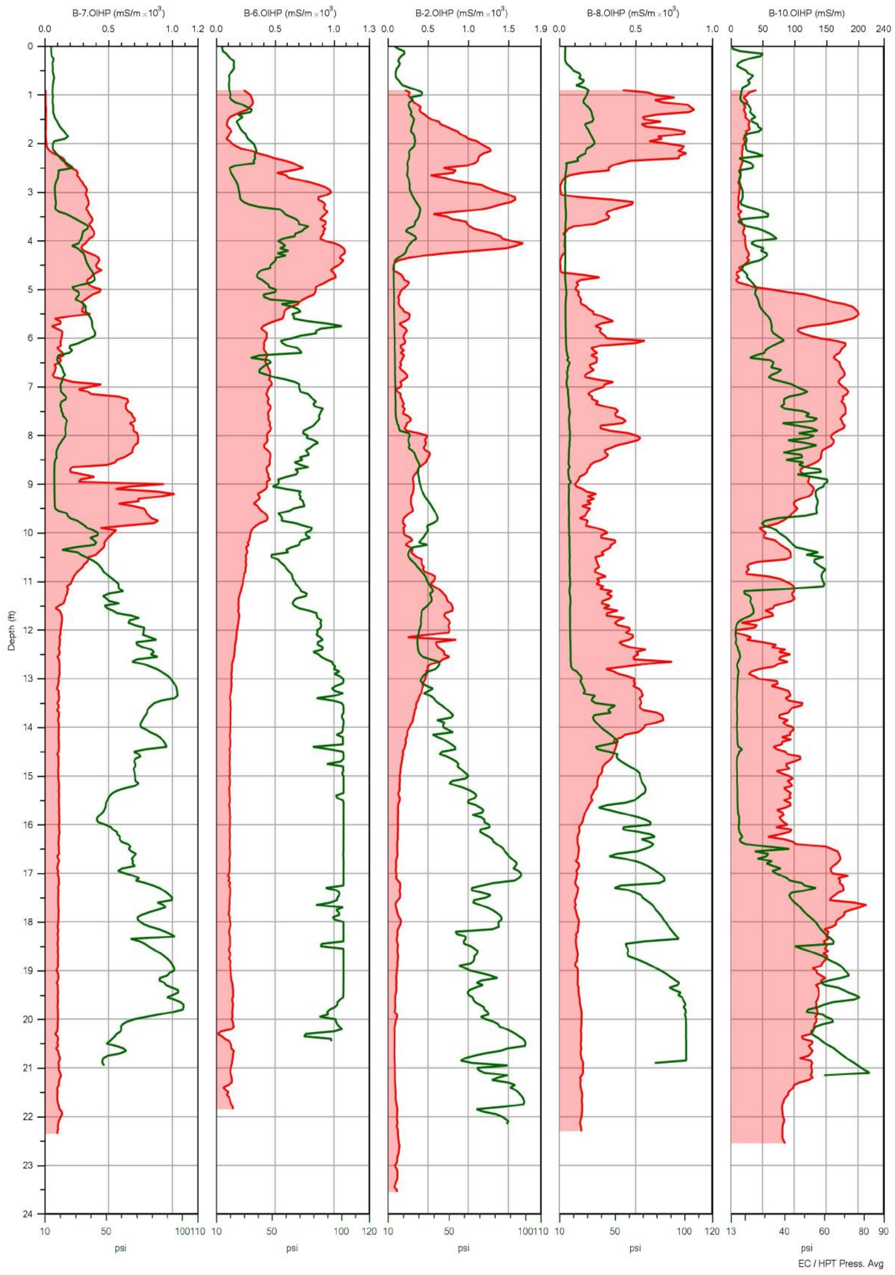


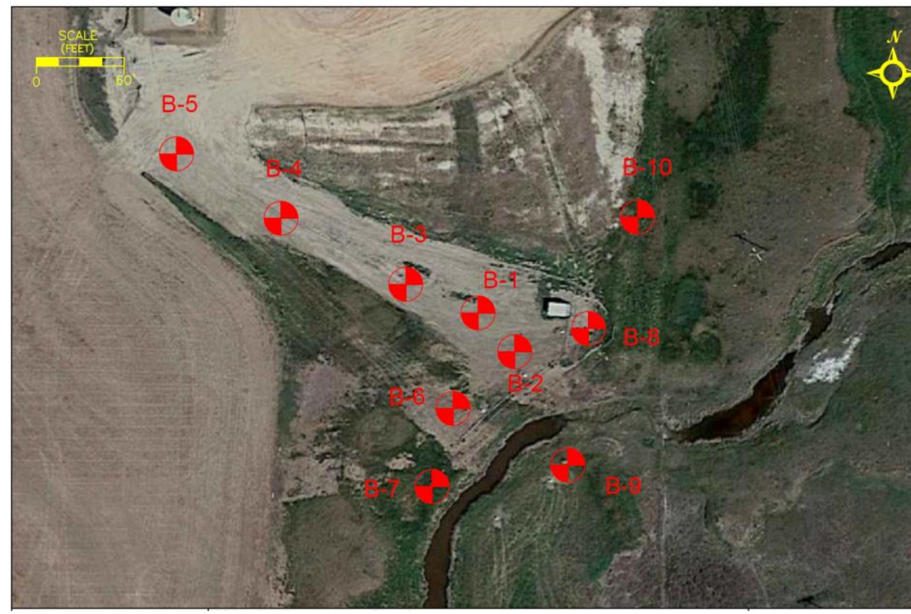




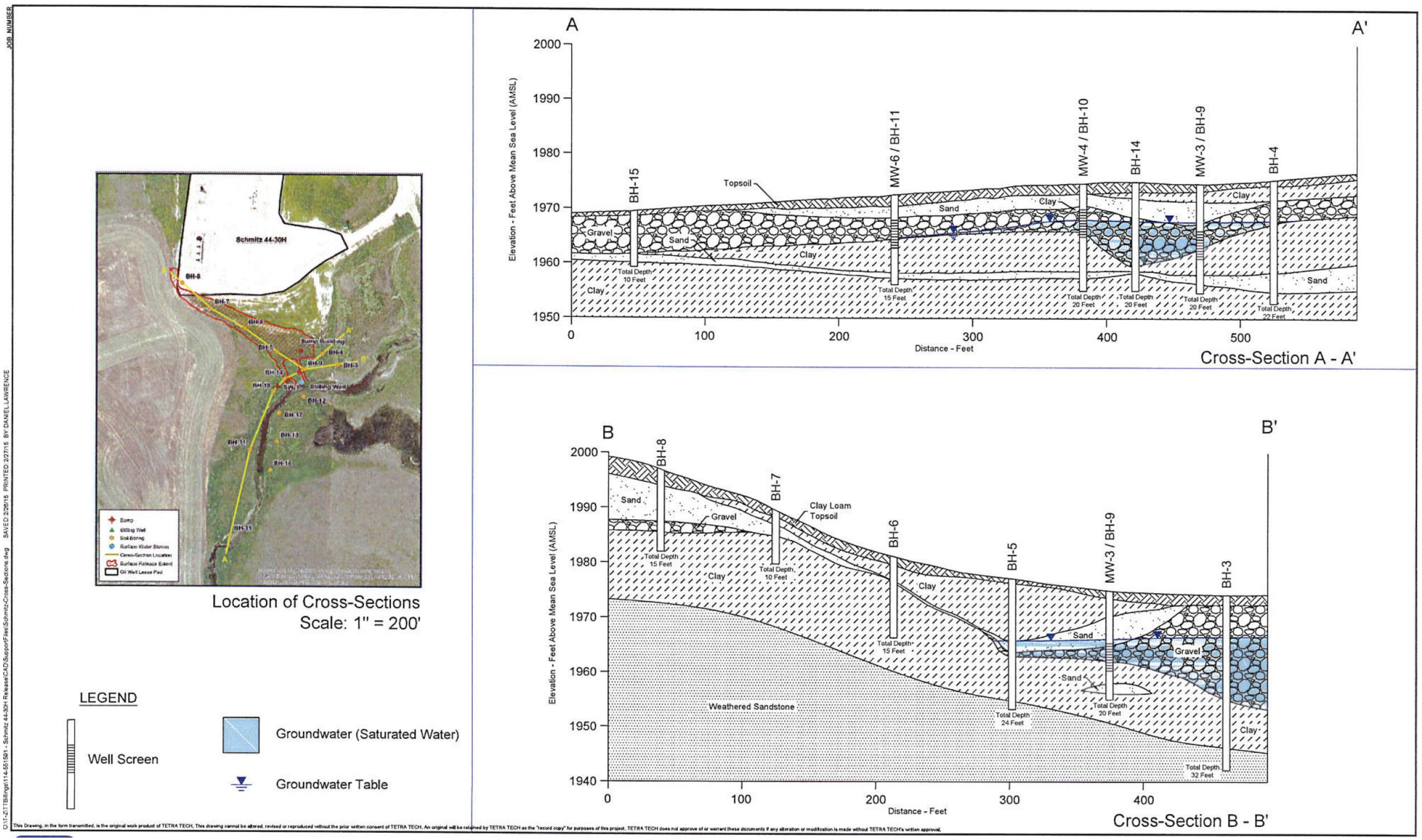


Site Characterization





Site Characterization

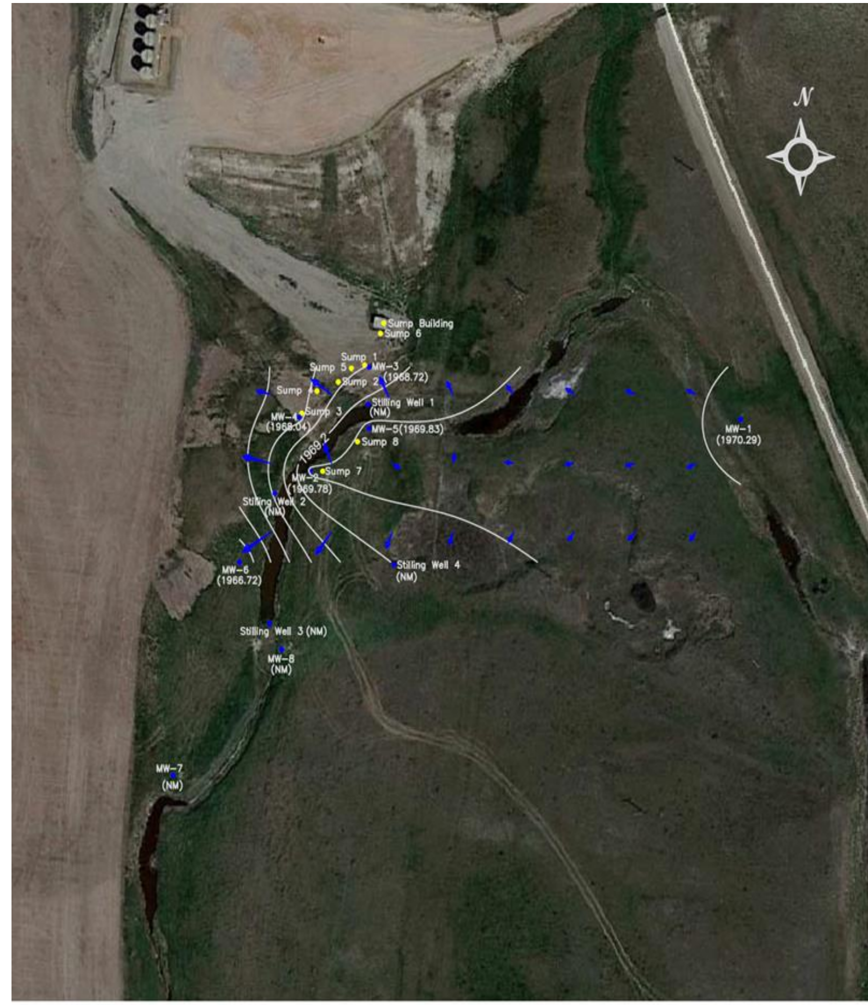


Site Characterization

Contour Intervals = 0.5 foot

SCALE
(FEET)
0 110

Groundwater Contour – August 2017



Contour Intervals = 0.2 foot

SCALE
(FEET)
0 110

Groundwater Contour – March 2017

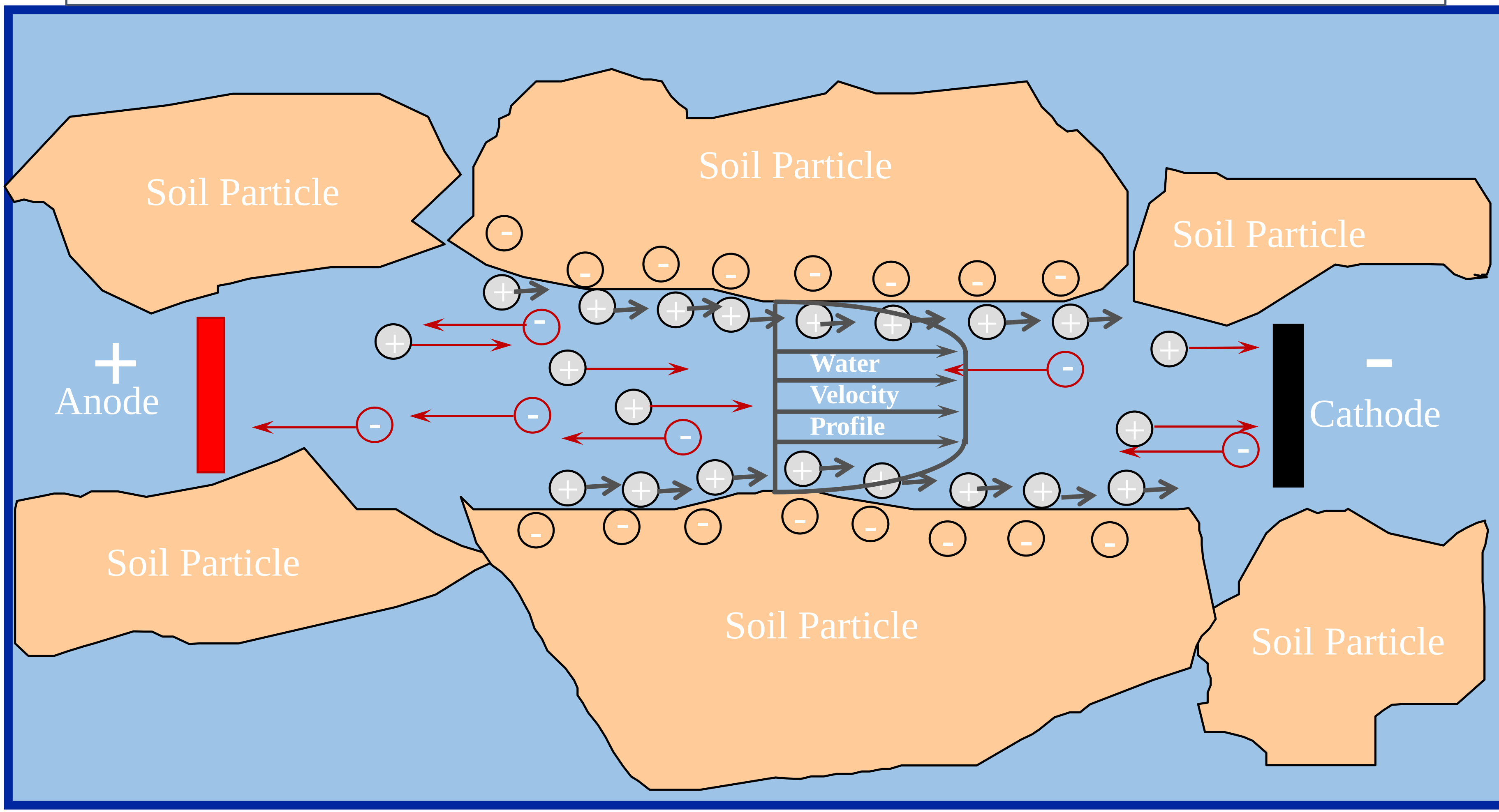
Electrokinetic Remediation

- Application of direct current (DC) electricity to the soil
- Polarized electrodes invoke movement of pore water and ions contained in the pore water, even in low permeability soils
- Electroosmosis – Movement of pore water and contaminants toward the cathode – Na^{+}, Ca^{2+} , Mg^{2+} and other positive charged ions
- Electromigration – Migration of ionic species toward respective electrodes (anions toward anode, cations toward cathode) by electrical attraction – all ions

Principles of Electrokinetics

Electroosmosis = Water Transport from anode to cathode

Electromigration = Ion Transport to the opposite electrode



Electrokinetic Remediation - How EK Desalinization Works

- **Sodium ions** migrate toward the **cathode** by electromigration and electroosmosis where they are removed

- **Chloride** ions migrate toward the **anode** by electromigration, where they are removed or oxidized to chlorine

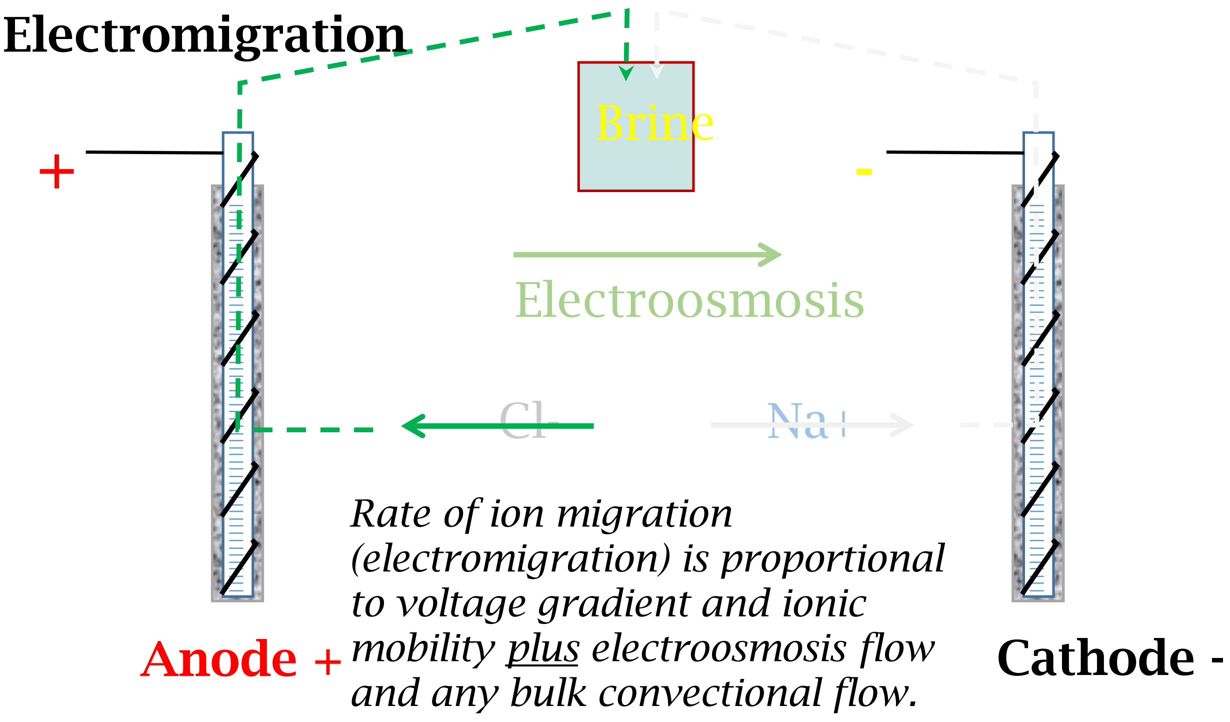
- The removed cathode and anode streams are combined as brine and disposed/injected or beneficially reused

Case Study - Schmitz Remediation McKenzie County, ND

Case Study - Schmitz Remediation McKenzie County, ND

Case Study - Schmitz Remediation McKenzie, ND

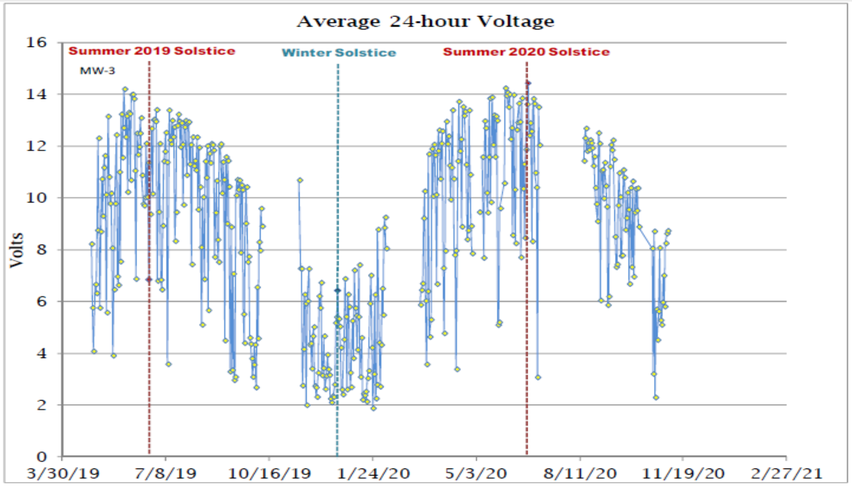
Zoomed in on treatment cell #3



Model Development and Operation

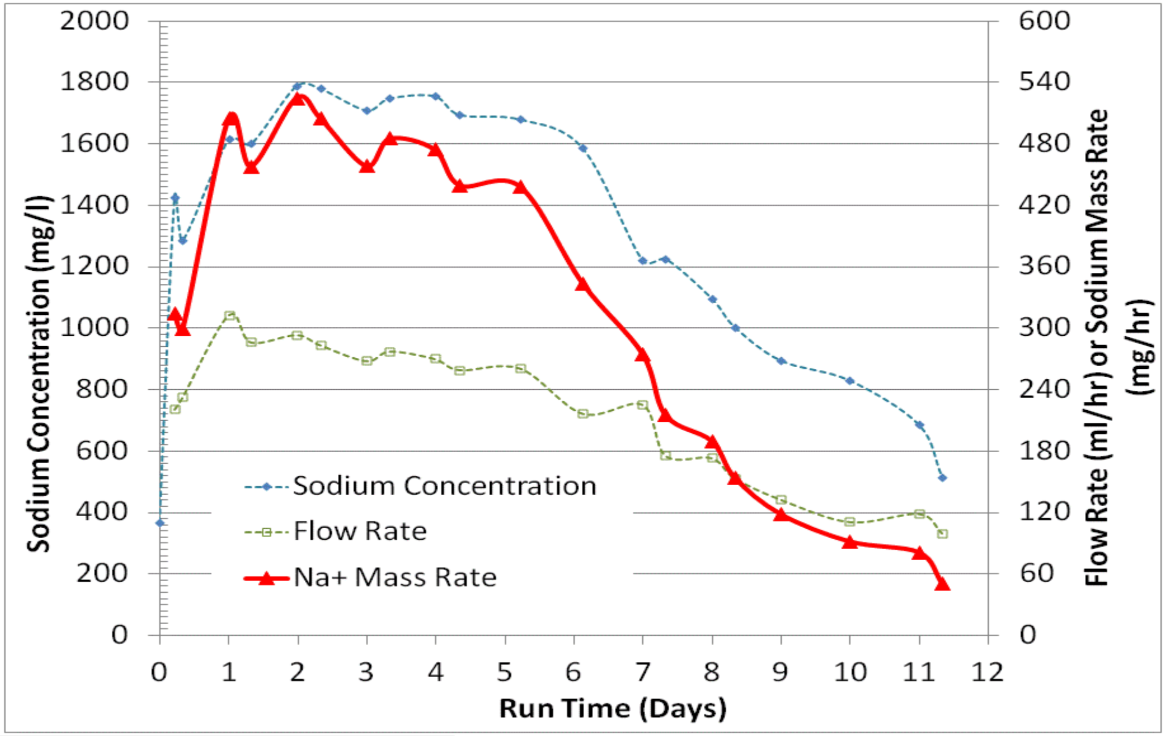
- Model developed to determine appropriate installation and operation
  - 2-Dimensional
  - Cylindrical coordinates (cathode at center)
  - Zero flux boundary at anodes, C = 0 at cathodes
  - Estimates removal times based on electromigration + electroosmosis

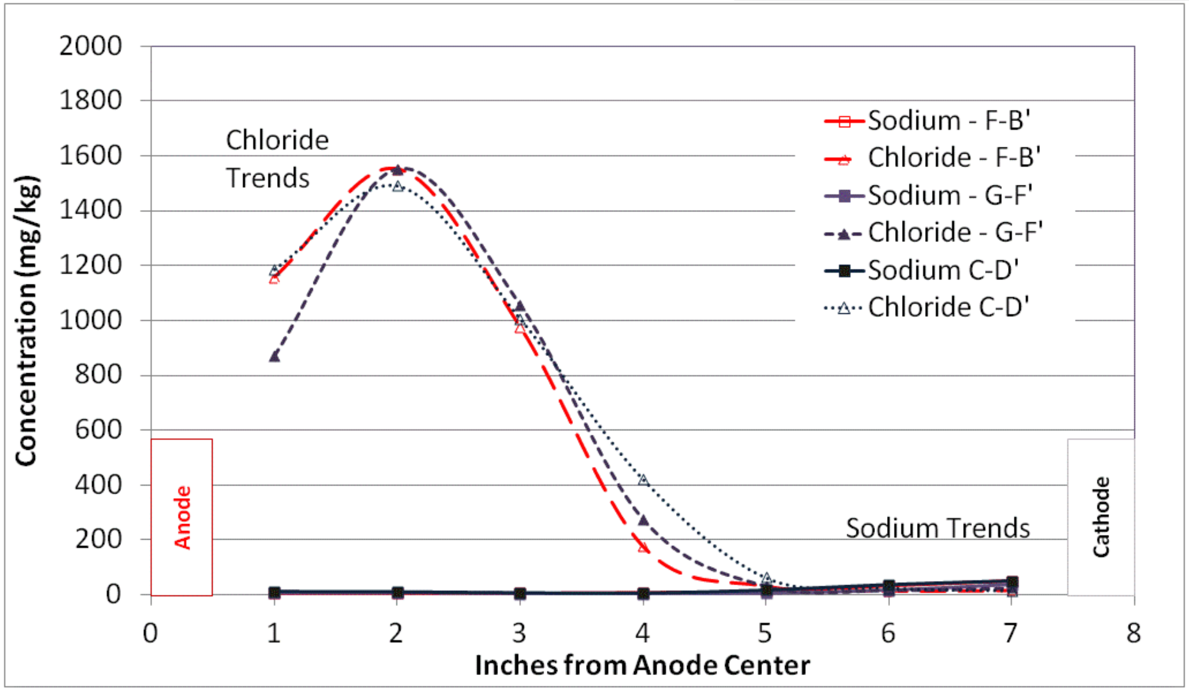
  Excel based model developed by Terran & Dr. Robert Wilkens at University of Dayton



- Operation
  - DC power supply @ 6 - 14 volts
  - Anode – cathode spacing of 5’ to 6’
  - Chloride accumulates and oxidizes to chlorine at anode
  - Sodium accumulates and is recovered at the cathode
  - **Model predicted 4^{+} days to travel 8”**

- Sodium is removed efficiently from the cathode
- Nine days to remediate





- Chloride mounds near the anode

Groundwater Analytical Data from Project Area

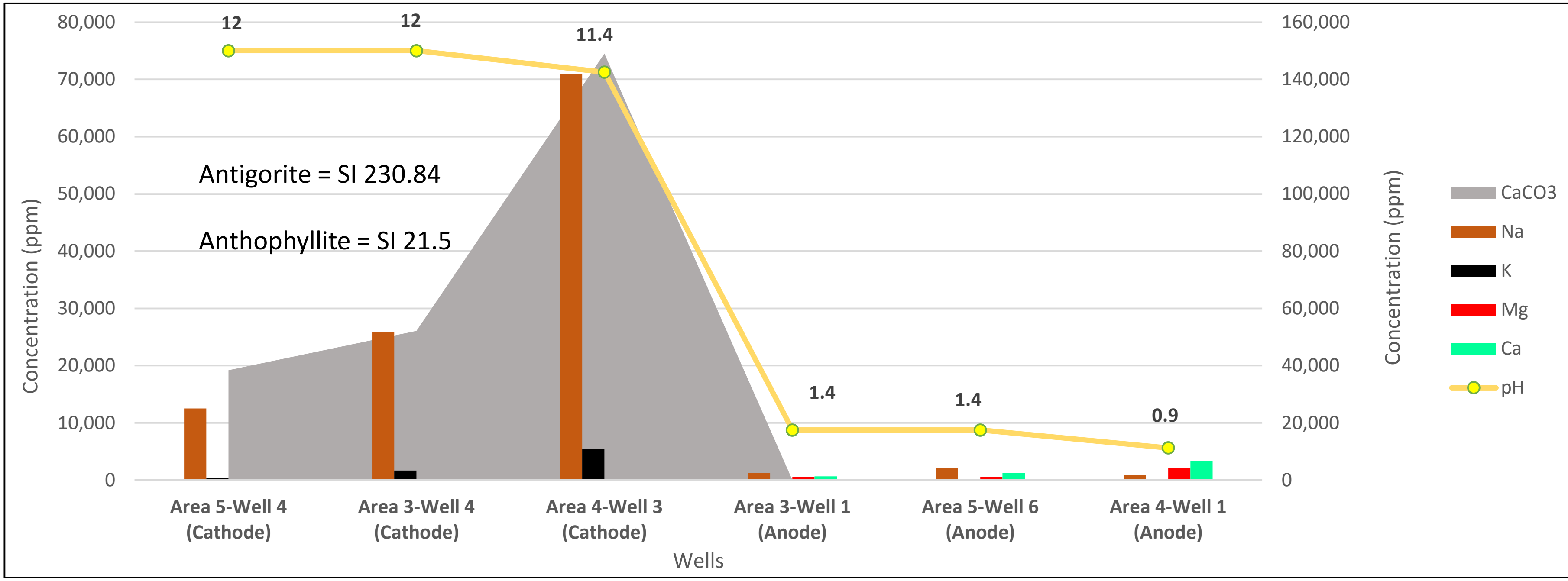
Where is Al?

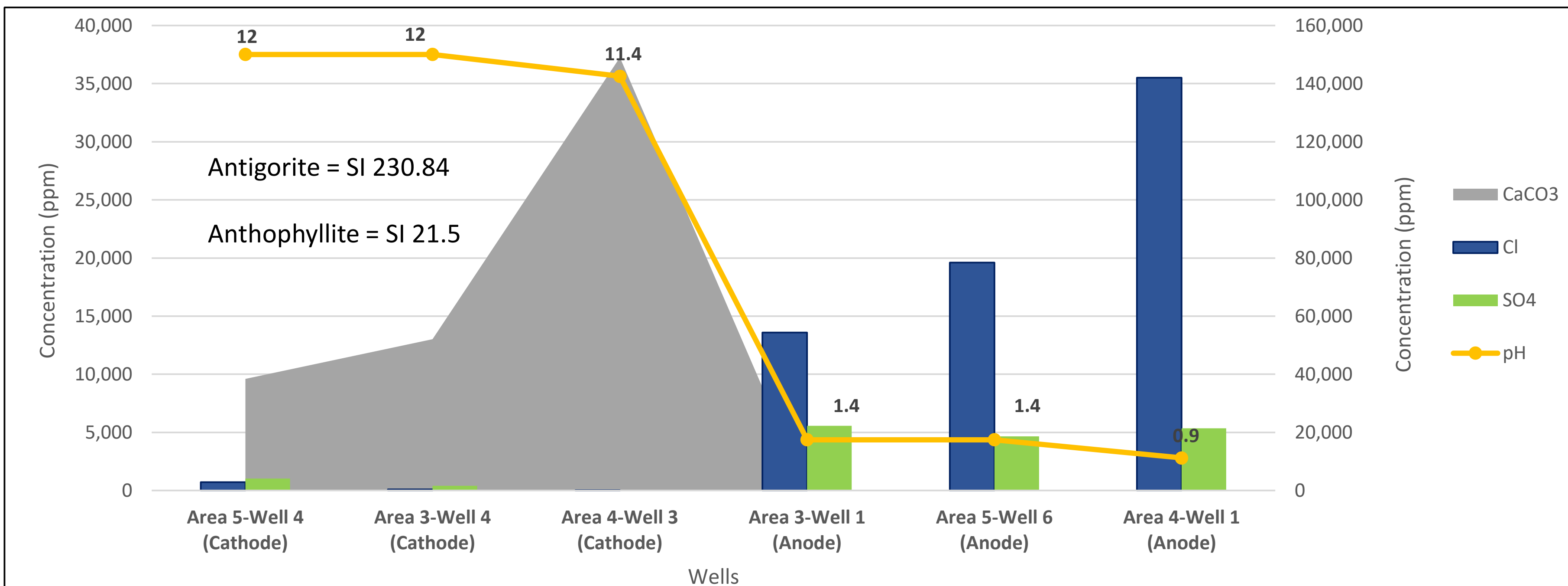
Table 1																	
SampleID	Sampled	pH	Total Alkalinity (as CaCO3)	Silica as SiO2	Bicarbonate as HCO3	Carbonate as CO3	Chloride	Nitrate-Nitrite Nitrogen (as N)	Sulfate	Calcium	Magnesium	Potassium	Sodium	Cation Sum	Anion Sum	Cation-Anion Balance	Dissolved Phosphorus
		s.u.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	meq/L	meq/L	%	mg/L
Background B 6"-4.2'	11/20/20	8.1	151	14.9	182	<5	3	1.3	67	28	11	11	72	5.75	4.81	8.86	0.2
Background B 4.2'-9.3'	11/20/20	8	81	7.1	99	<5	4	0.8	101	16	9	11	73	4.97	3.99	10.94	0.1
Background B 9.3'-15'	11/20/20	8.2	77	4.2	94	<5	14	0.2	27	9	5	4	45	2.87	2.56	5.70	0.4
Background GW	11/16/20	8.6	792.0	21.5	870.0	47.0	9.0	<0.1	1,270.0	87.0	55.0	7.0	769.0	42.43	42.86	0.5	0.8
Area 5-Well 4 (Cathode)	11/16/20	12	**38,400.0**	289.0	<5	**1,160.0**	720.0	2.0	**1,030.0**	42.0	3.0	364.0	**12,500.0**	555.90	814.63	18.9	3.5
Area 3-Well 4 (Cathode)	11/16/20	12	**52,100.0**	91.5	<5	700.0	111.0	<0.1	404.0	20.0	2.0	**1,670.0**	**25,900.0**	1,170.29	1,054.83	5.2	1.3
Area 4-Well 3 (Cathode)	11/16/20	11.4	**149,000.0**	401.0	<5	4,660.0	2.0	<0.1	39.0	80.0	13.0	**5,490.0**	**70,900.0**	**3,229.43**	**2,987.56**	3.9	5.6
Area 3-Well 1 (Anode)	11/16/20	1.4	<5	140.0	-	<5	**13,600.0**	29.1	**5,570.0**	643.0	573.0	43.0	**1,220.0**	133.54	502.71	58.0	19.5
Area 5-Well 6 (Anode)	11/16/20	1.4	<5	82.0	-	<5	19,600.0	52.4	4,660.0	1,250.0	572.0	163.0	**2,130.0**	206.35	655.48	52.1	12.9
Area 4-Well 1 (Anode)	11/16/20	0.9	<5	159.0	-	<5	**35,500.0**	**1,060.0**	**5,360.0**	3,350.0	2,060.0	46.0	828.0	373.81	1,192.24	52.3	44.0

Milligrams per liter = mg/L

Milliequivalent per liter = meq/L

All samples are groundwater


80,000
70,000
60,000
50,000
40,000
30,000
20,000
10,000
0
160,000
140,000
120,000
100,000
80,000
60,000
40,000
20,000
0
Concentration (ppm)
Concentration (ppm)
12
12
11.4
1.4
1.4
0.9
Antigorite = SI 230.84
Anthophyllite = SI 21.5
CaCO3
Na
K
Mg
Ca
pH
Area 5-Well 4 (Cathode)
Area 3-Well 4 (Cathode)
Area 4-Well 3 (Cathode)
Area 3-Well 1 (Anode)
Area 5-Well 6 (Anode)
Area 4-Well 1 (Anode)
Wells


40,000
35,000
30,000
25,000
20,000
15,000
10,000
5,000
0
160,000
140,000
120,000
100,000
80,000
60,000
40,000
20,000
0
Concentration (ppm)
Concentration (ppm)
12
12
11.4
1.4
1.4
0.9
Antigorite = SI 230.84
Anthophyllite = SI 21.5
CaCO3
Cl
SO4
pH
Area 5-Well 4 (Cathode)
Area 3-Well 4 (Cathode)
Area 4-Well 3 (Cathode)
Area 3-Well 1 (Anode)
Area 5-Well 6 (Anode)
Area 4-Well 1 (Anode)
Wells

Cathode @pH 11.4

----------------------------Distribution of species----------------------------

Species	Molality	MacInnes Activity	Log Molality	MacInnes Log Activity	MacInnes Log Gamma	mole V cm³/mol
OH-	6.462e-03	4.242e-03	-2.190	-2.372	-0.183	-1.92
H+	5.811e-12	2.355e-12	-11.236	-11.628	-0.392	0.00
H2O	5.551e+01	9.871e-01	1.744	-0.006	0.000	18.07
C(4)	3.940e-01					
CO3-2	3.898e-01	4.437e-02	-0.409	-1.353	-0.944	0.76
HCO3-	4.200e-03	2.282e-03	-2.377	-2.642	-0.265	27.57
MgCO3	2.221e-06	2.221e-06	-5.653	-5.653	0.000	-17.09
CO2	1.081e-08	1.195e-08	-7.966	-7.923	0.043	34.43
Ca	2.213e-06					
Ca+2	2.213e-06	7.104e-08	-5.655	-7.148	-1.494	-16.40
Cl	2.146e-02					
Cl-	2.146e-02	1.283e-02	-1.668	-1.892	-0.223	19.00
K	9.837e-03					
K+	9.837e-03	5.791e-03	-2.007	-2.237	-0.230	9.91
Mg	4.186e-06					
MgCO3	2.221e-06	2.221e-06	-5.653	-5.653	0.000	-17.09
Mg+2	1.867e-06	5.907e-08	-5.729	-7.229	-1.500	-20.10
MgOH+	9.850e-08	3.843e-08	-7.007	-7.415	-0.409	(0)
Na	5.745e-01					
Na+	5.745e-01	3.130e-01	-0.241	-0.504	-0.264	-0.24
S(6)	1.133e-02					
SO4-2	1.133e-02	1.116e-03	-1.946	-2.952	-1.006	19.54
HSO4-	4.123e-13	2.504e-13	-12.385	-12.601	-0.217	41.15
Si	1.537e-02					
H3SiO4-	1.259e-02	6.388e-03	-1.900	-2.195	-0.295	28.94
H2SiO4-2	2.681e-03	1.845e-04	-2.572	-3.734	-1.162	(0)
H4SiO4	9.573e-05	1.020e-04	-4.019	-3.991	0.028	52.08

- Carbon species are dominant
- Sodium is second most dominant
- Antigorite = SI 230.84; **Mg48Si34O85 (OH)62**
- Anthophyllite = SI 21.5; **Mg7Si8O22 (OH)2**

these are not likely the correct mineral

Anode @ pH 1.4

----------------------------Distribution of species----------------------------

Species	Molality	MacInnes Activity	Log Molality	MacInnes Log Activity	MacInnes Log Gamma	mole V cm³/mol
H+	4.952e-02	3.981e-02	-1.305	-1.400	-0.095	0.00
OH-	4.874e-13	2.509e-13	-12.312	-12.601	-0.288	-2.84
H2O	5.551e+01	9.868e-01	1.744	-0.006	0.000	18.07
Ca	3.210e-02					
Ca+2	3.210e-02	9.524e-03	-1.493	-2.021	-0.528	-16.80
Cl	5.691e-01					
Cl-	5.691e-01	3.660e-01	-0.245	-0.436	-0.192	18.72
K	4.291e-03					
K+	4.291e-03	2.837e-03	-2.367	-2.547	-0.180	9.59
Mg	2.422e-02					
Mg+2	2.422e-02	8.264e-03	-1.616	-2.083	-0.467	-20.52
MgOH+	3.026e-13	3.180e-13	-12.519	-12.498	0.022	(0)
Na	9.537e-02					
Na+	9.537e-02	6.855e-02	-1.021	-1.164	-0.143	-0.59
S(6)	4.993e-02					
SO4-2	3.305e-02	2.962e-03	-1.481	-2.528	-1.048	17.96
HSO4-	1.689e-02	1.123e-02	-1.772	-1.949	-0.177	40.90
Si	1.405e-03					
H4SiO4	1.405e-03	1.451e-03	-2.852	-2.838	0.014	52.08
H3SiO4-	9.960e-12	5.373e-12	-11.002	-11.270	-0.268	28.64
H2SiO4-2	1.242e-22	9.181e-24	-21.906	-23.037	-1.131	(0)

- Chloride is dominant species
- Calcium and magnesium and sulfate are second most dominant

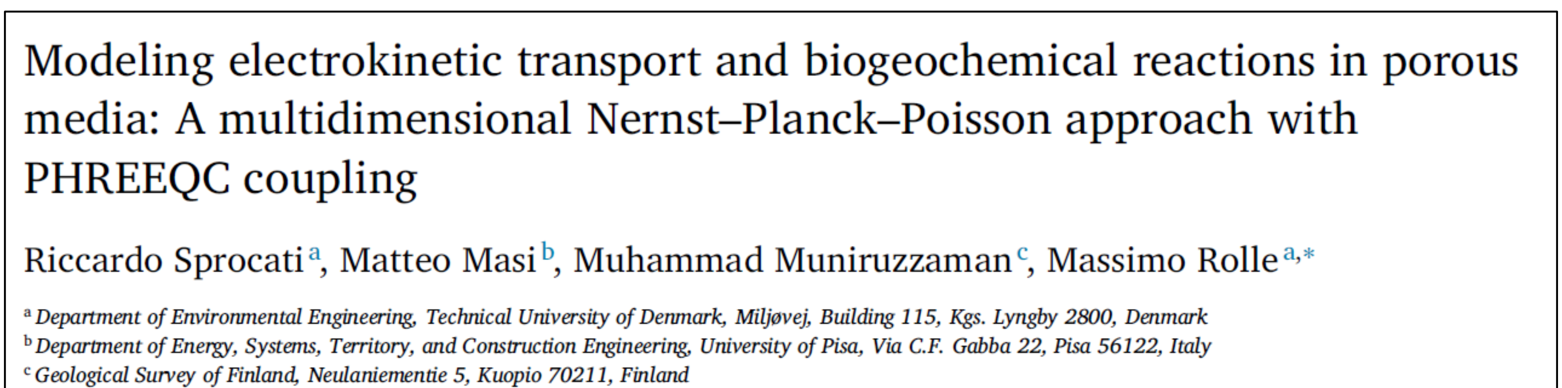
Conclusion and Future Work

Current Conclusion

- Strong alkaline front at the cathode = pH 11.5 – 12
- Strong acid front at the anode = pH 0.9 – 1.4
- PHREEQC shows under saturated conditions, with limited speciation at the anode
- Antigorite = SI 230.84 and Anthophyllite = SI 21.5 are supersaturated at the cathode
- Limited speciation at the anode with chloride being dominant = 5.6×10^{-1} Molality
- Some speciation at the cathode with carbon being dominant = 3.952×10^{-1} Molality

Future work

- Why does chloride mound next to the anode?
- Will reversing the polarity enhance chloride recovery?
- How far from the cathode does the alkaline front extend?
- How far does the pH front extend from the anode? Note other treatments showed slight alkaline conditions at pH 8.8.
- Analyze for Al on future groundwater analysis
- NDSU analyze mineralogy of sediments



Modeling electrokinetic transport and biogeochemical reactions in porous media: A multidimensional Nernst–Planck–Poisson approach with PHREEQC coupling

Riccardo Sprocati[a], Matteo Masi[b], Muhammad Muniruzzaman[c], Massimo Rolle[a,*]

[a] Department of Environmental Engineering, Technical University of Denmark, Miljøvej, Building 115, Kgs. Lyngby 2800, Denmark
[b] Department of Energy, Systems, Territory, and Construction Engineering, University of Pisa, Via C.F. Gabba 22, Pisa 56122, Italy
[c] Geological Survey of Finland, Neulaniementie 5, Kuopio 70211, Finland

Reference Cited

Cameselle, C., and Reddy, K.R., 2012, Development and enhancement of electro-osmotic flow for the removal of contaminants from soil: Electrochimica Acta, v. 86, p. 10-22

Hassan, I., Mohamedelhassan, E., and Yanful, E., 2015, Solar powered electrokinetic remediation of Cu polluted soil using a novel anode configuration, Electrochimica Acta, v. 181, p. 58-67

Sprocati, R., Masi, M., Muniruzzaman, M., and Rolle, M., 2019, Modeling electrokinetic transport and biogeochemical reactions in porous media: A multidimensional Nernst-Planck-Poisson approach with PHREEQC coupling: Advances in Water Resources, v. 127 p. 134-147