The Use of Electrokinetic Technology to Enhance Chemical and Biological Remediation of Contaminated Sands and Soils

Brian Wartell, PhD, Michel Boufadel, PhD, Lucia Rodriguez-Freire, PhD, Lisa Axe, PhD

With assistance from Stewart H. Abrams, PE, and Ali Ciblak, PhD (Langan Engineering, Lawrenceville, NJ, USA)

Department of Civil and Environmental Engineering,

The New Jersey Institute of Technology, Newark, NJ 07102

Problem Statement
and
Objectives

- *Problem:* Contaminant spills occur regularly in terrestrial environments.
    - Via pipeline and other leaks, manufacturing, transport, natural disasters.
    - Pollutants can include: Crude oil, Industrial dyes, Heavy metals, and various emerging contaminants.
    - Traditional approaches such as dredging, digging, and pump-and-treat, et al. are disruptive and costly.

- *Primary Objective:* To understand the electrokinetic (EK) process and its applicability to enhance pollution cleanup in subsurface media
    - EK is a remediation technology where a DC voltage is applied to porous media to enhance transport of specific compounds of interest.
- *Sub-Objective:* To investigate different rates of EK phenomena, primarily electromigration in sand and in clay.
- *Sub-Objective:* To investigate changes in the pH Gradient of an EK system over time in different media.

Electrokinetics

- *Includes three parts:*
  - **Electromigration** - the movement of charged particles in the form of ions in subsurface media due to the presence of a magnetic field
  - **Electroosmosis** - can be used to migrate fluids (e.g. groundwater) as well as the contaminants
  - **Electrophoresis** - used to transport charged (colloidal) particles, sediment, and bacteria

- Can be used to migrate charged contaminants such as heavy metals (+) or toxic dyes (-,+)
- Can be used as a flushing technique
- Can enhance bioavailability and make electron donors, acceptors, and nutrients more accessible. All of this potentially enhances biodegradation.
- Can combine with surfactants for increased efficiency:
  - Resolves the concern of microbes tending to attach to organic matter and soil/sediment particles

Electrokinetic Setup Example

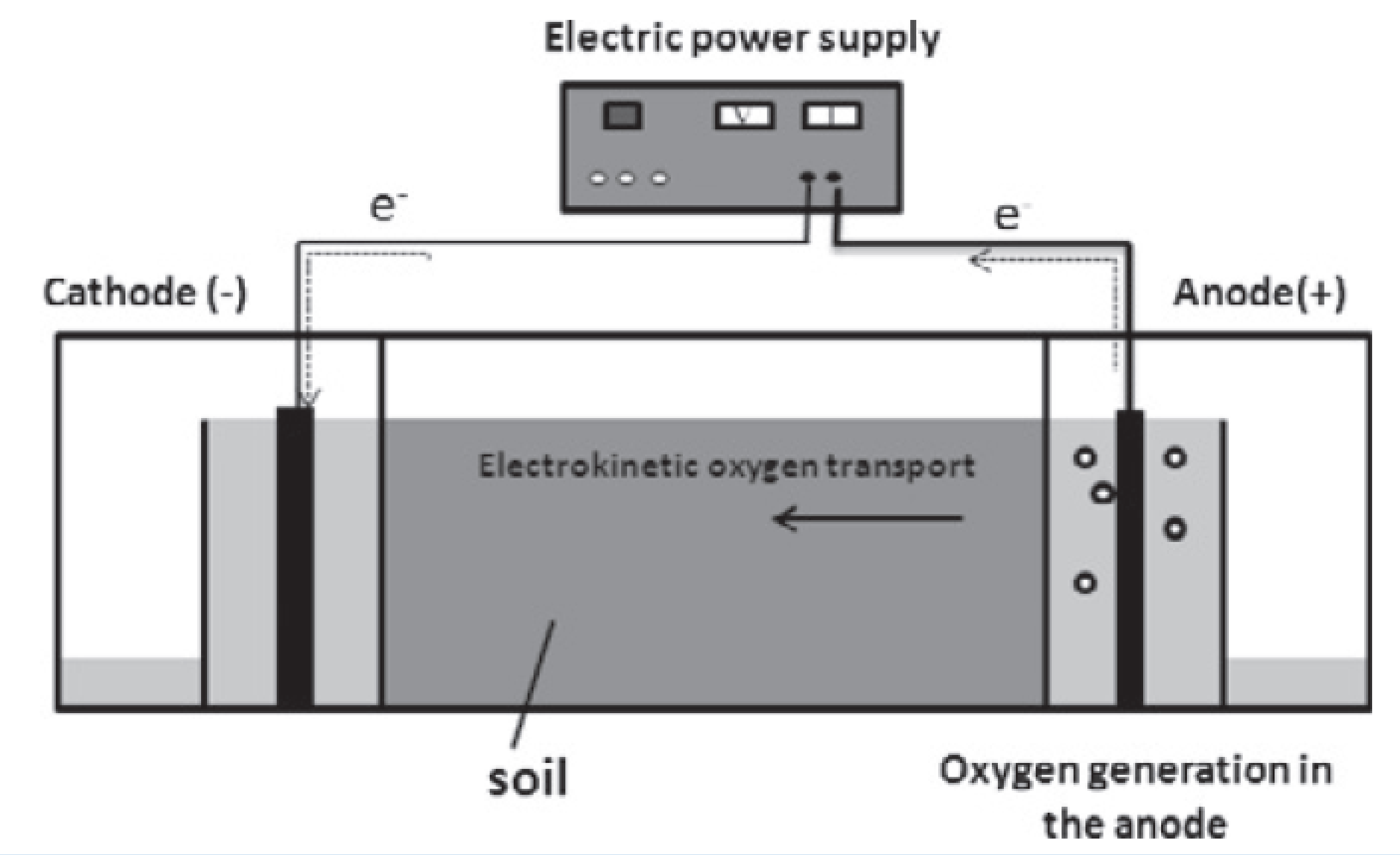
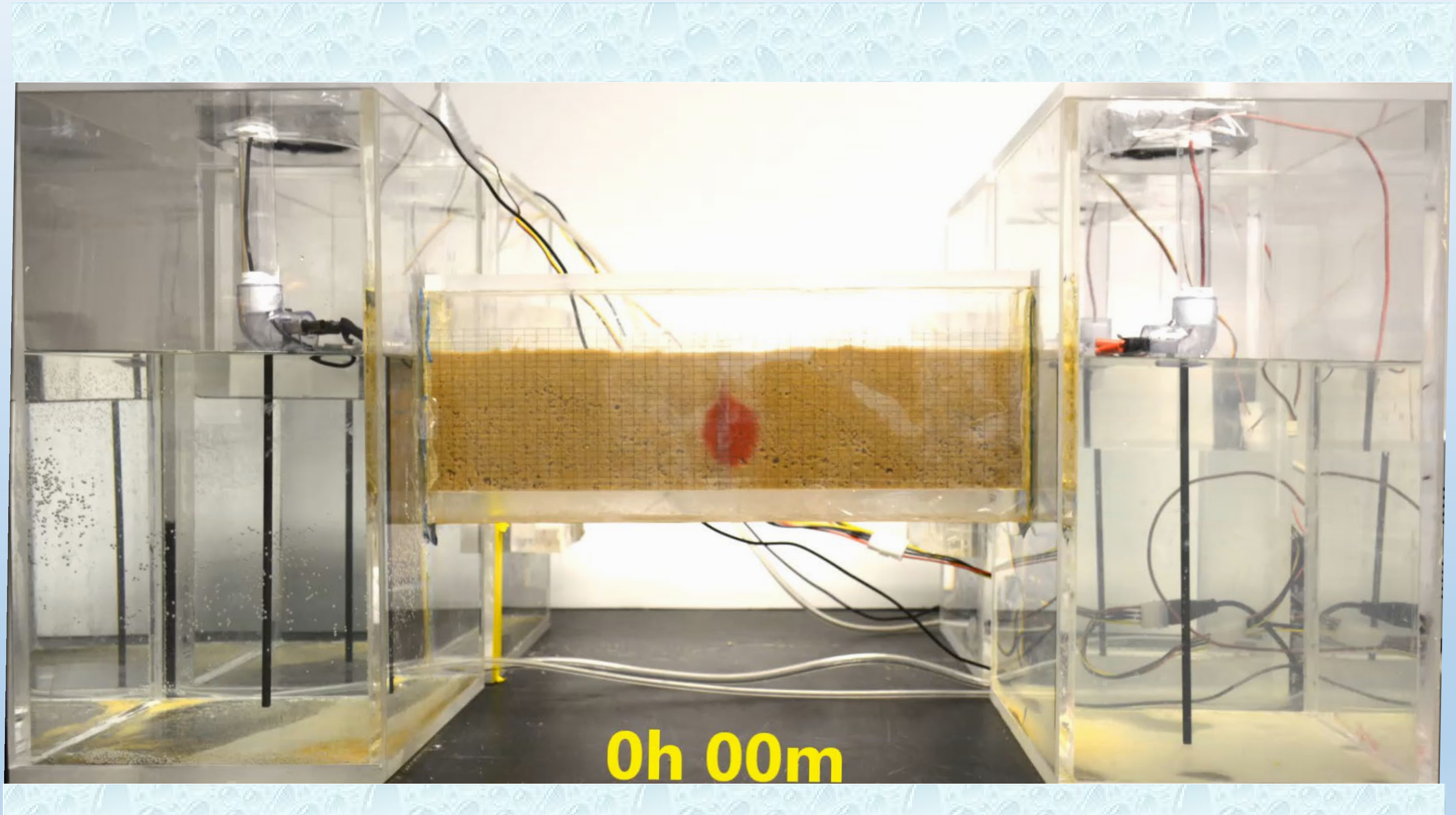


Image source: Ramírez, E. M., J. V. Camacho, M. R. Rodrigo, and P. C. Cañizares (2014), Feasibility of electrokinetic oxygen supply for soil bioremediation purposes, *Chemosphere*, *117*, 382-387.

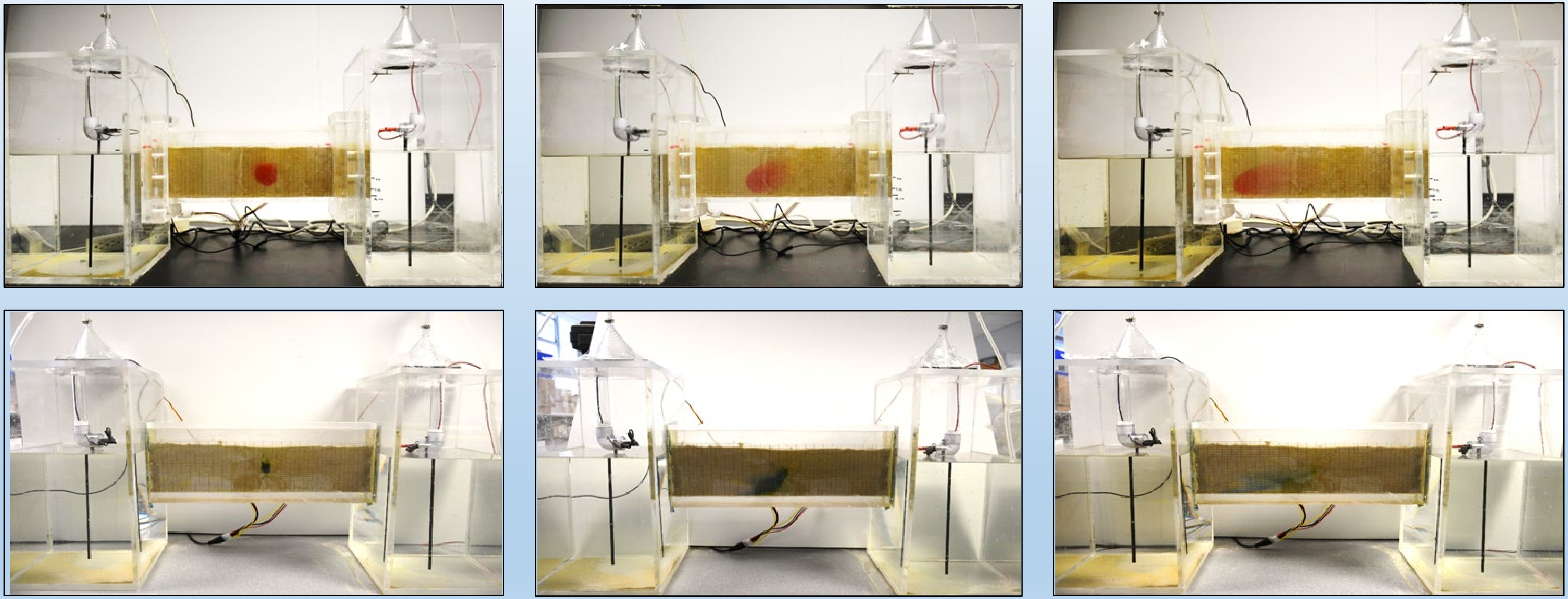
A Study in Electrokinetic Migration Rates in Sand and in Clay

- **Objectives:** To investigate different rates of electrokinetic phenomena, primarily electromigration, in different media (soil, sand) and compare two dyes with different charge properties and how their migration rates change accordingly.
- Red dye: Anionic, Green dye: amphoteric properties, could function as Anionic, Cationic, depending upon pH.
- ***Specific Objectives:***
  - The migration of Anionic vs Amphoteric dye in sand
  - The migration of Anionic vs Amphoteric dye in clay
  - Comparing the migration of the Anionic dye in sand vs clay and fitting to theoretical values
  - Understand the nature of how and why the Amphoteric dye migrates in both media types

Movement of Anionic Dye in Sand

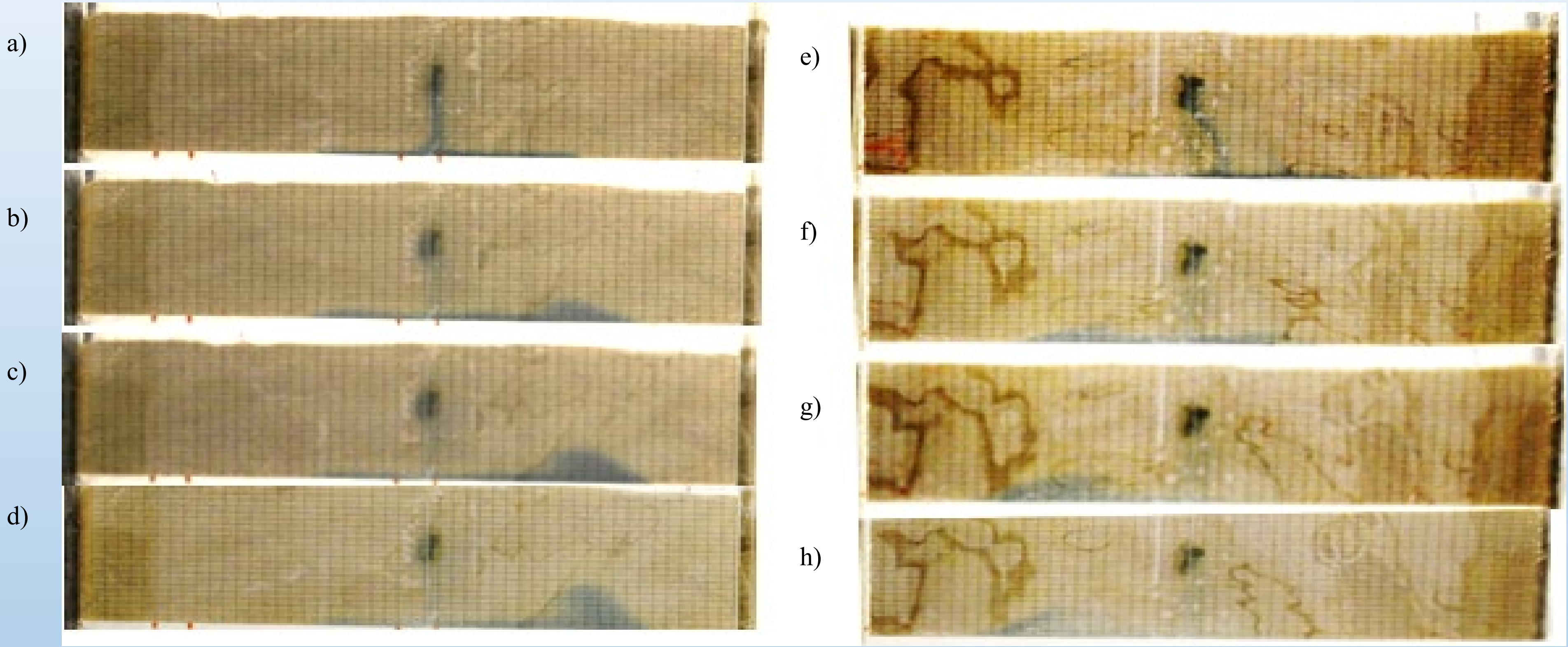


Migration of Anionic (red) and Amphoteric (green) Dye through Sand



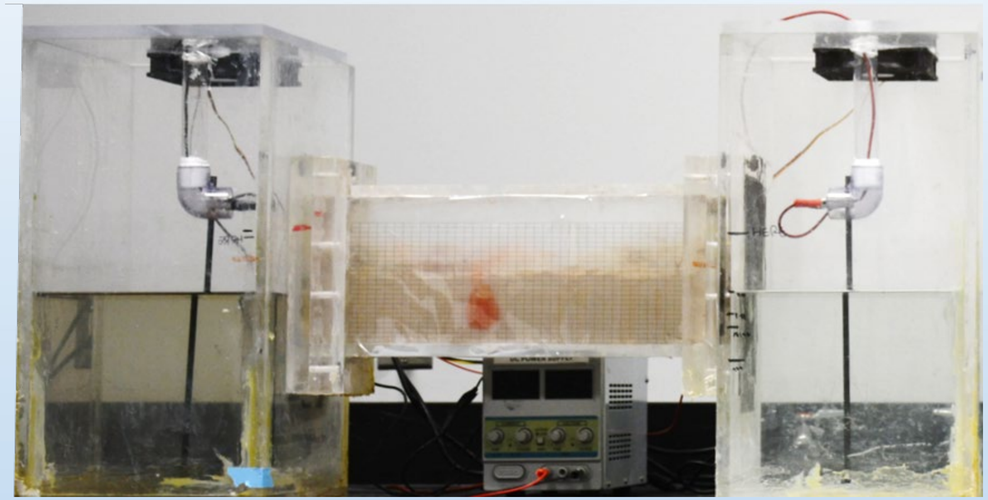
0 h 24h 50h

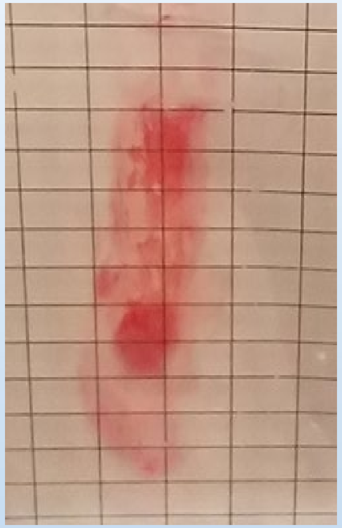
Amphoteric (green) Dye Experiment
[Confirmational]

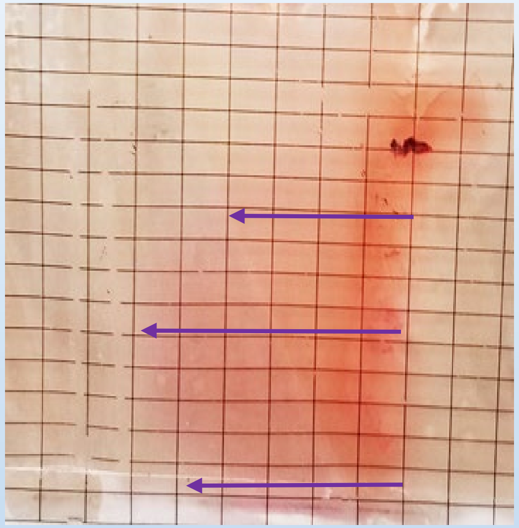


- System 1 at various times (anode on right) - a) 0h ; b) 24h ; c) 48h ; d) 72h.
- System 2 at various times (anode on left) - e) 0h ; f) 24h ; g) 48h ; h) 72h

Migration of Anionic (red) Dye in Clay

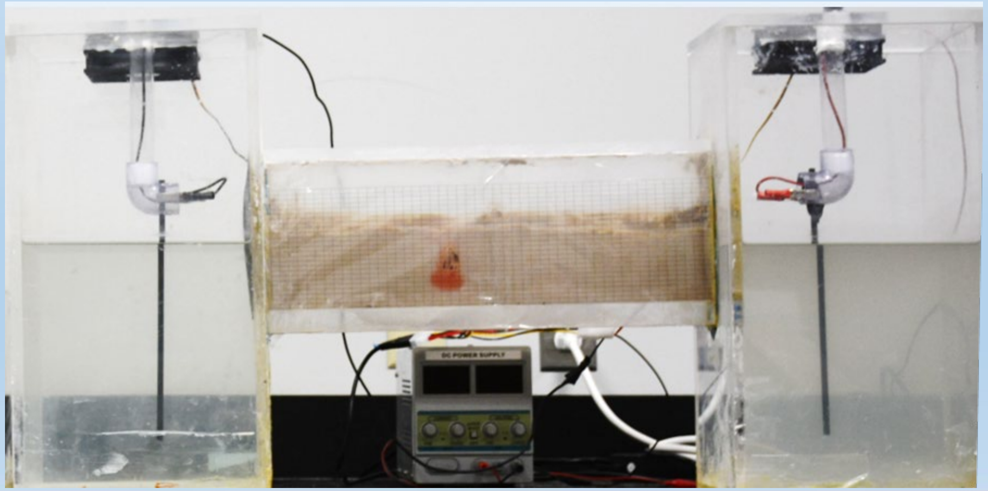


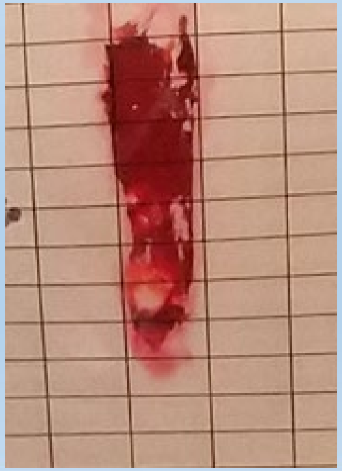


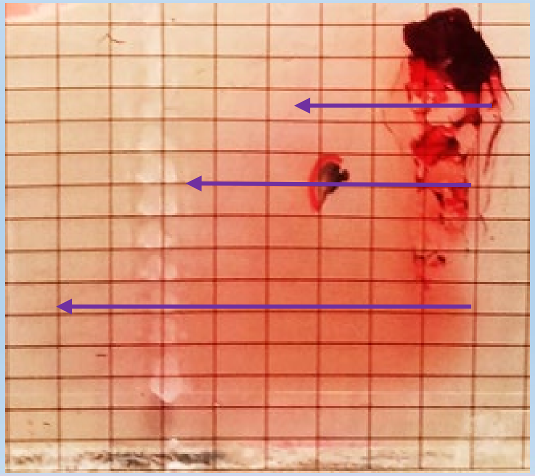


0h

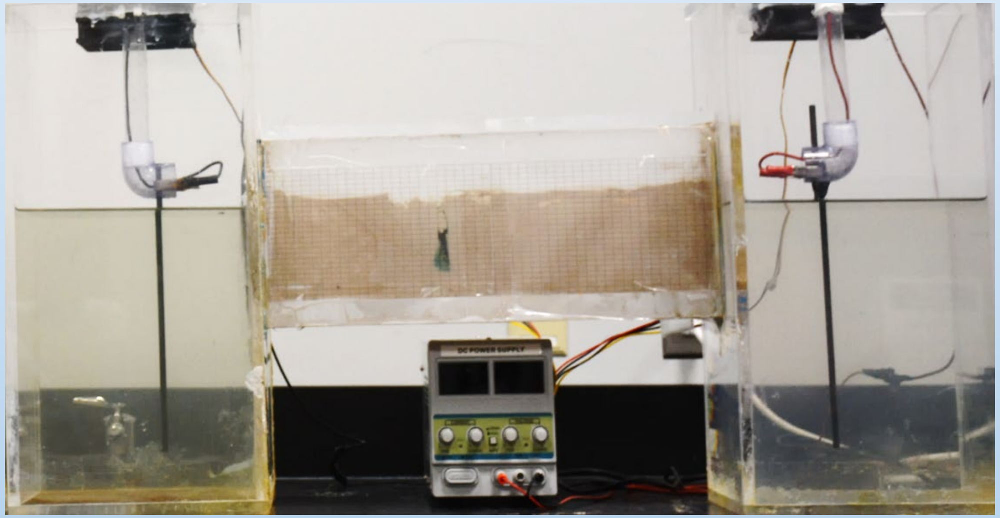
96h 50m



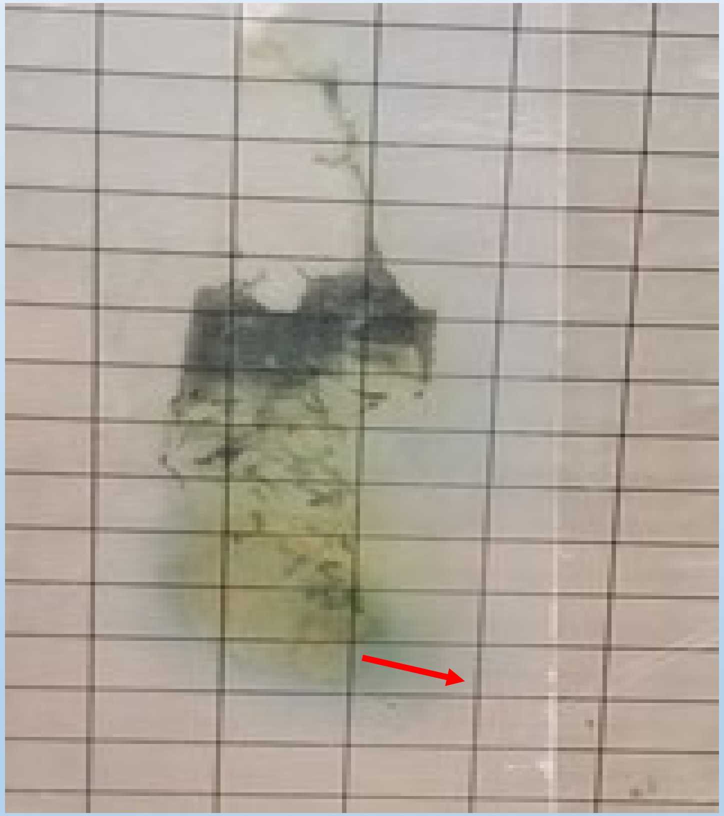




Migration of the Amphoteric (green) Dye in Clay



The green dye is composed of a mixture of turmeric (yellow) and Spirulina Blue – the primary pigment is C-Phycocyanin.

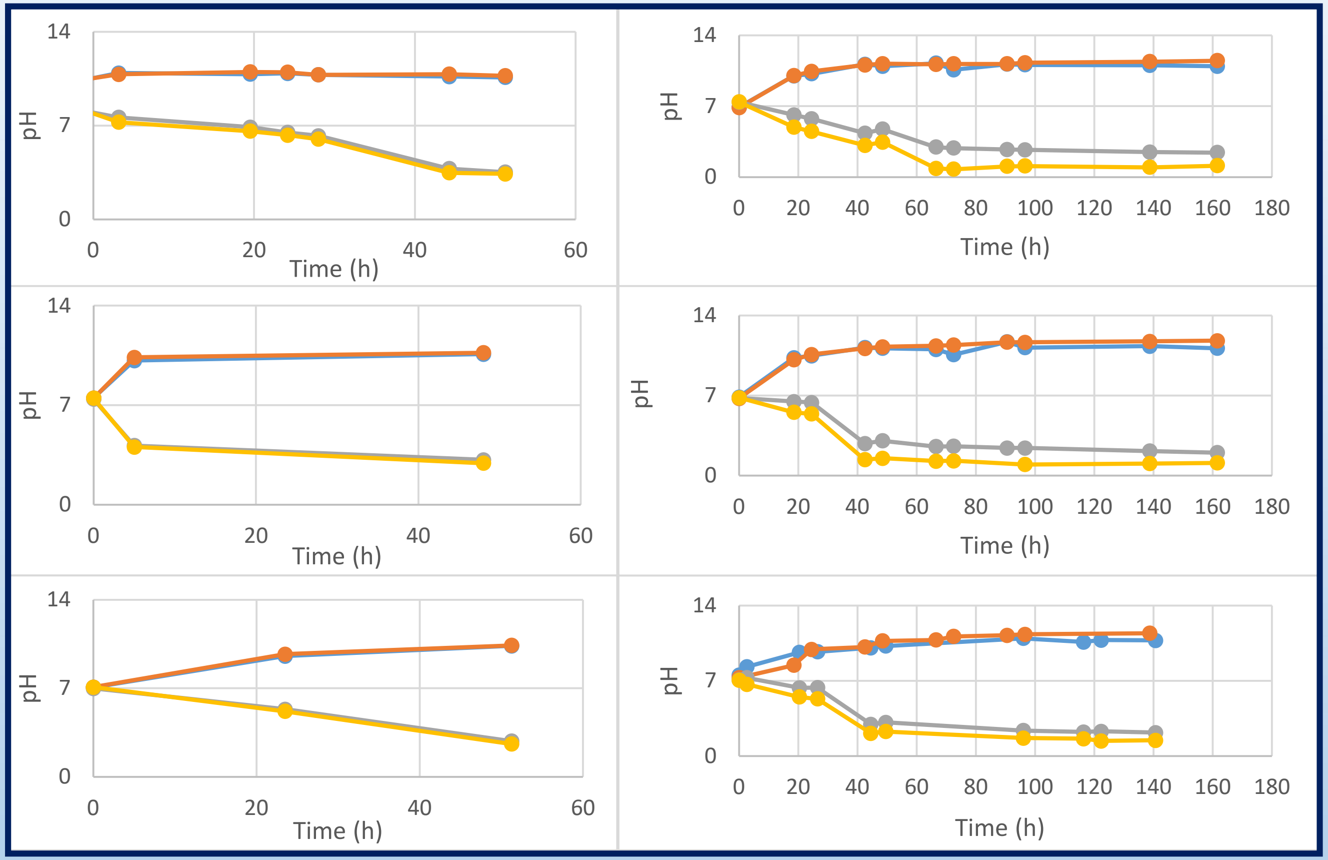


140h 40m

Average Migration Rates

	Sand (red dye)	Sand (green dye)	Clay (red dye)	Clay (green dye)
Migration rate (cm/d)	9.12 ± 1.57	7.28 ± 0.57 / 6.60 ± 0.20	0.93 ± 0.16	0.17
Migration Type	Electromigration	Electromigration*	Electromigration	(likely) Electroosmosis

Extreme pH Values

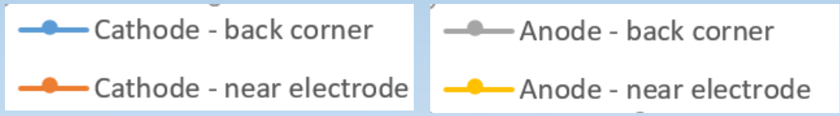


pH changes in reservoirs over time:
Sand experiments (left) ; Clay experiments (right)

At the anode: $2H_2O - 4e^- \rightarrow O_2 + 4H^+$

At the cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

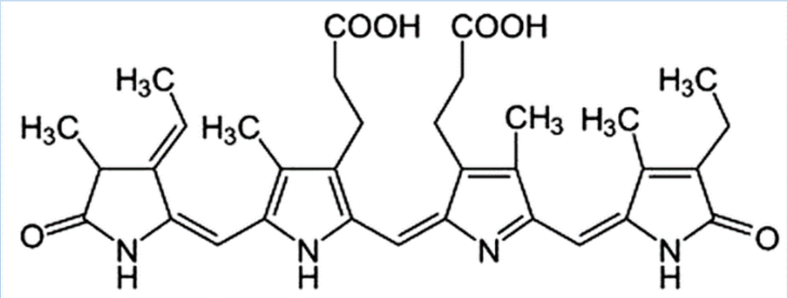
- The pH in each reservoir quickly reached extreme values.
- Anode reservoir reached 1-2, depending upon duration
  - A result of the production of H^+ ions
- Cathode reservoir reached 11-13, depending upon duration
  - A result of the production of OH^- ions
- Extremes reached in ~3 days but did not extend much farther, irrespective of media type.



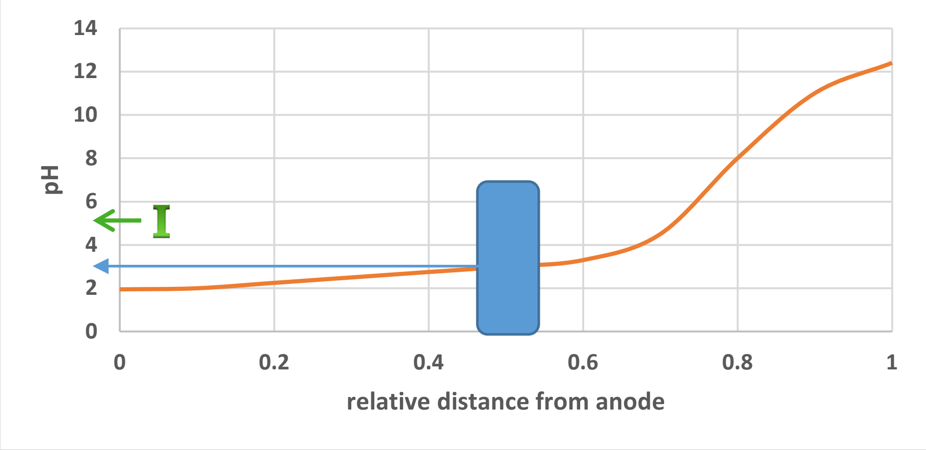
Analyzing the Strange Behavior of the "Amphoteric" Dye

- The use of an amphoteric substance such as *Spirulina* dye highlights an unforeseen obstacle that can take place in electrokinetic systems:

  The alteration of a chemical migrational pattern due to changes in pH values.



Molecular structure of C-Phycocyanin, the primary component of the Spirulina Blue dye



An estimation of a pH profile in an EK system based upon multiple literature reports.

Anionic Migration is Counter-Intuitive

- C-phycocyanin can become heavily positively or negatively charged.
- Based upon assumed pH gradient, where dye was inserted (horizontal center) pH value would be ~3.
  - This is well below the isoelectric point (pI), implying the molecule should become strongly positively charged (cationic).
- <u>**Anionic migration rather than Cationic migration was observed and confirmed.**</u>

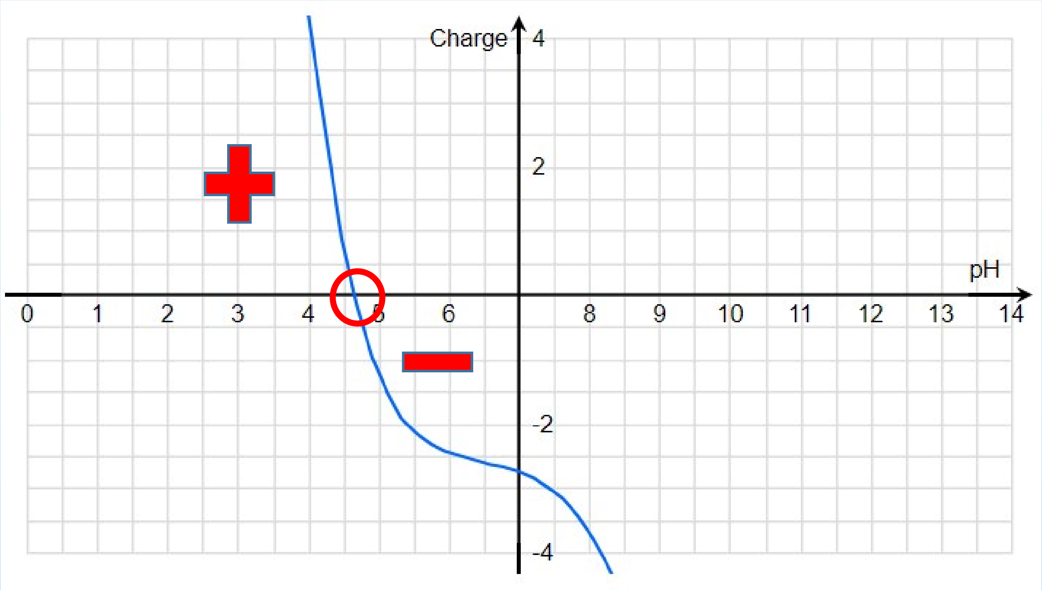


Illustration of an approximate isoelectric curve of C-phycocyanin with respect to pH

(obtained via ThermoFisher Scientific's Peptide Analyzing Tool).

Hypotheses

- Only pH gradients found in the literature were for soil – **is sand different?**

- The steep pH gradient seen in papers was for experiments that took place over several days or longer.

  - The migration of the green (blue) dye in sand experiment occurred in less than 3 days (ceased ~ 65h), with most of the migration in the first 24-36 hours.

COULD TIME BE A FACTOR?

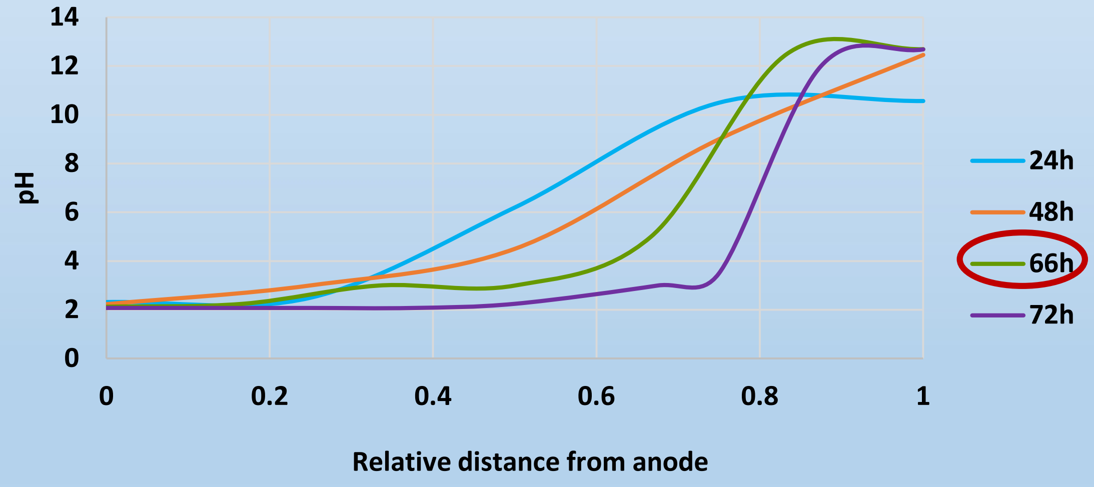
Investigation via Mini-Setups

The reservoir boxes (without lids) measured 9.5 x 9.5 x 12 cm (L x W x H) and the bridge area measured 20 x 3.8 x 6.5 cm.

- Miniature EK setups similar to the larger setups were constructed. Similar voltage gradient and current density. Same electrodes (half the length)
- ***Objective:* To investigate how the pH profile changes over time in sand.**
- Due to size constraints and delicateness of probe, pH indicator strips were used. Values obtained were therefore approximate but provided very clear trends.

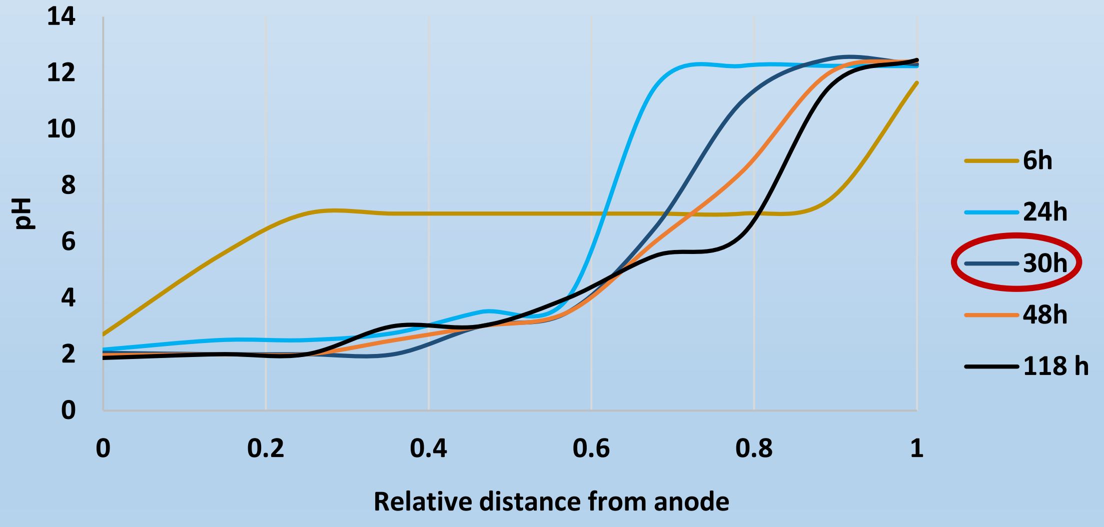
Initial and Confirmational Results

- Voltage gradient: 10 V applied over 20 cm = 0.5 V/cm
- Current density: ~ 2.13 mA over 76 cm^2 = 0.028 mA/cm^2



Example from Initial Experiment

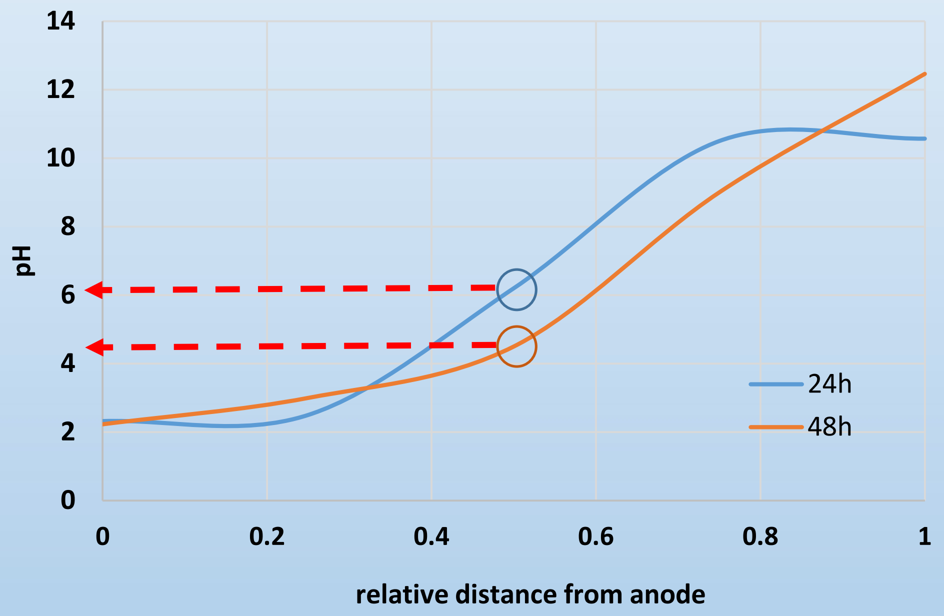
- Voltage gradient: 13.3 V applied over 20 cm = 0.67 V/cm
- Current density: ~ 2.91 mA over 76 cm^2 = 0.038 mA/cm^2



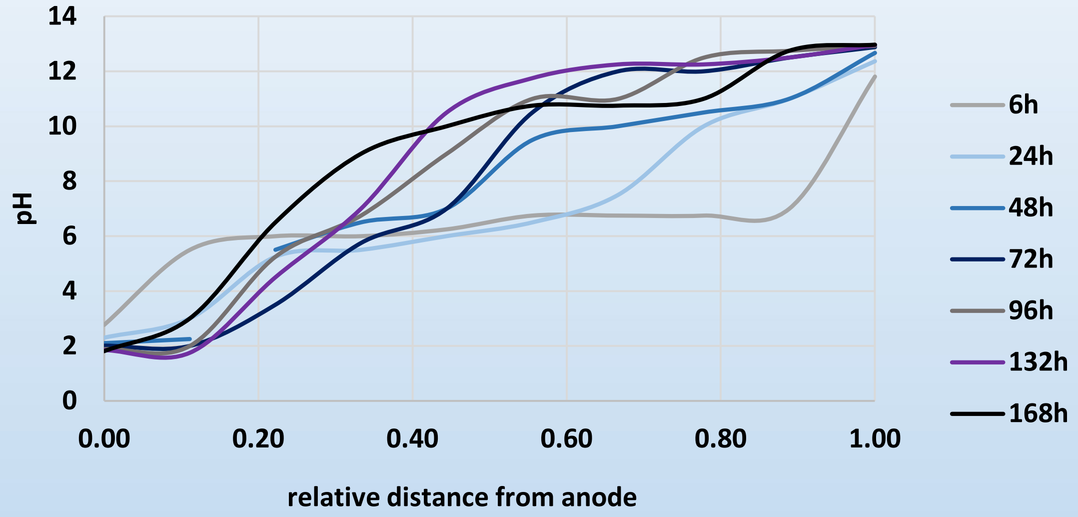
Example from Confirmation Experiment

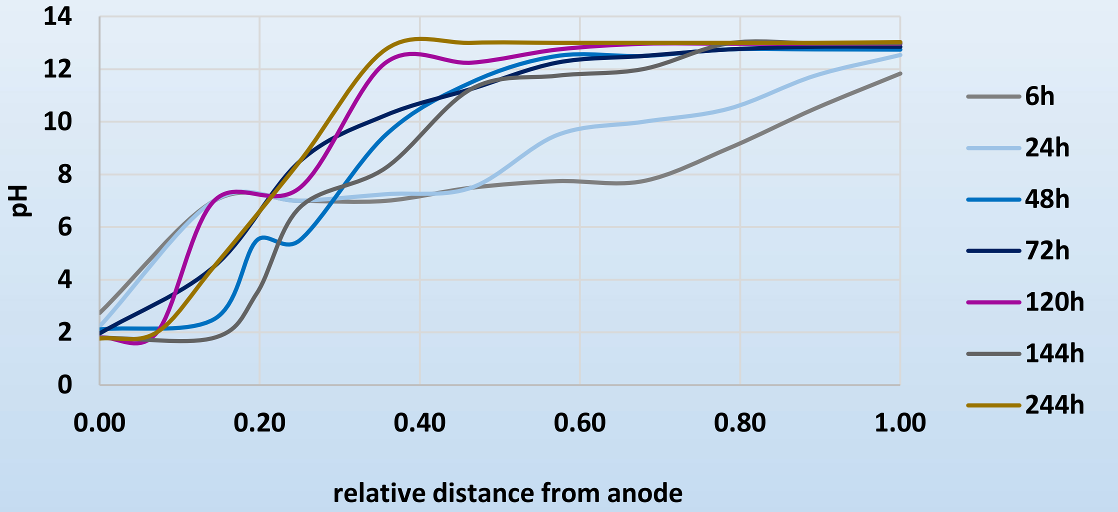
Implications of the Findings

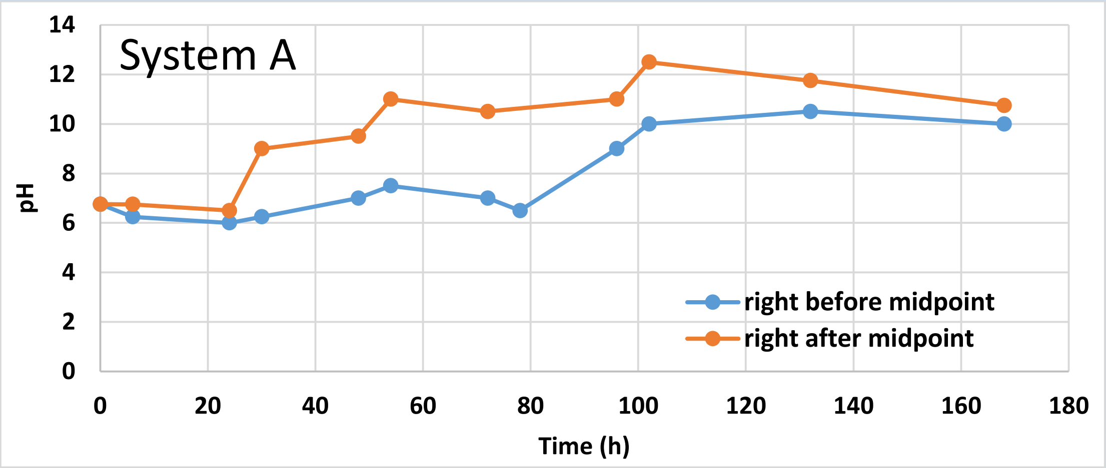
- pH profile initially had a linear trend from anode to cathode – only takes shape similar to pH gradient as seen in literature, after 2-3 days.
- Thus, when dye migrated, mostly before this time, pH would have been near or > pI (~ 4.8).
    - At least for first 24 hours, pH would have been ~6, significantly above the pI.
    - When above the pI, the dye would be anionic, explaining the migration pattern.
    - Should stop migrating after ~ 48 h.



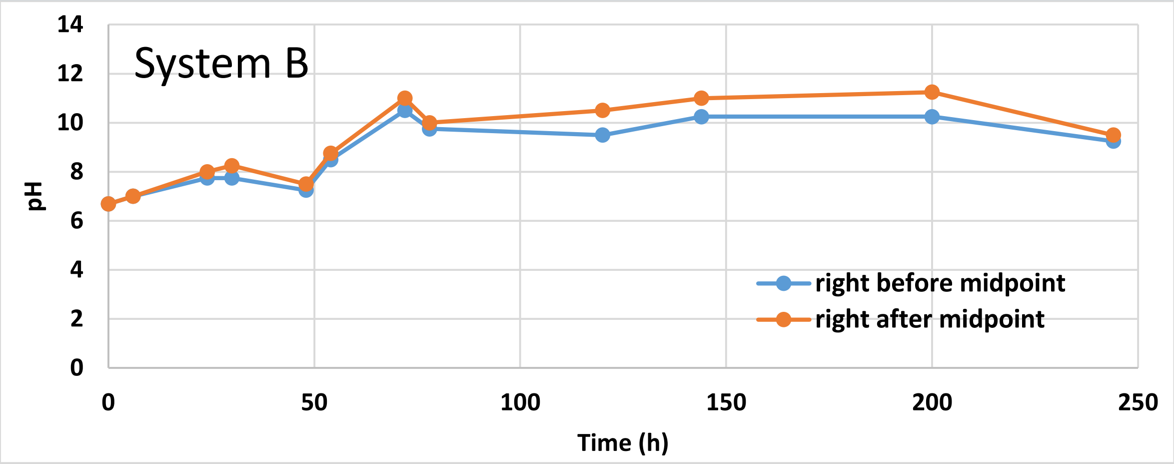
pH Gradients in Soil (by system)





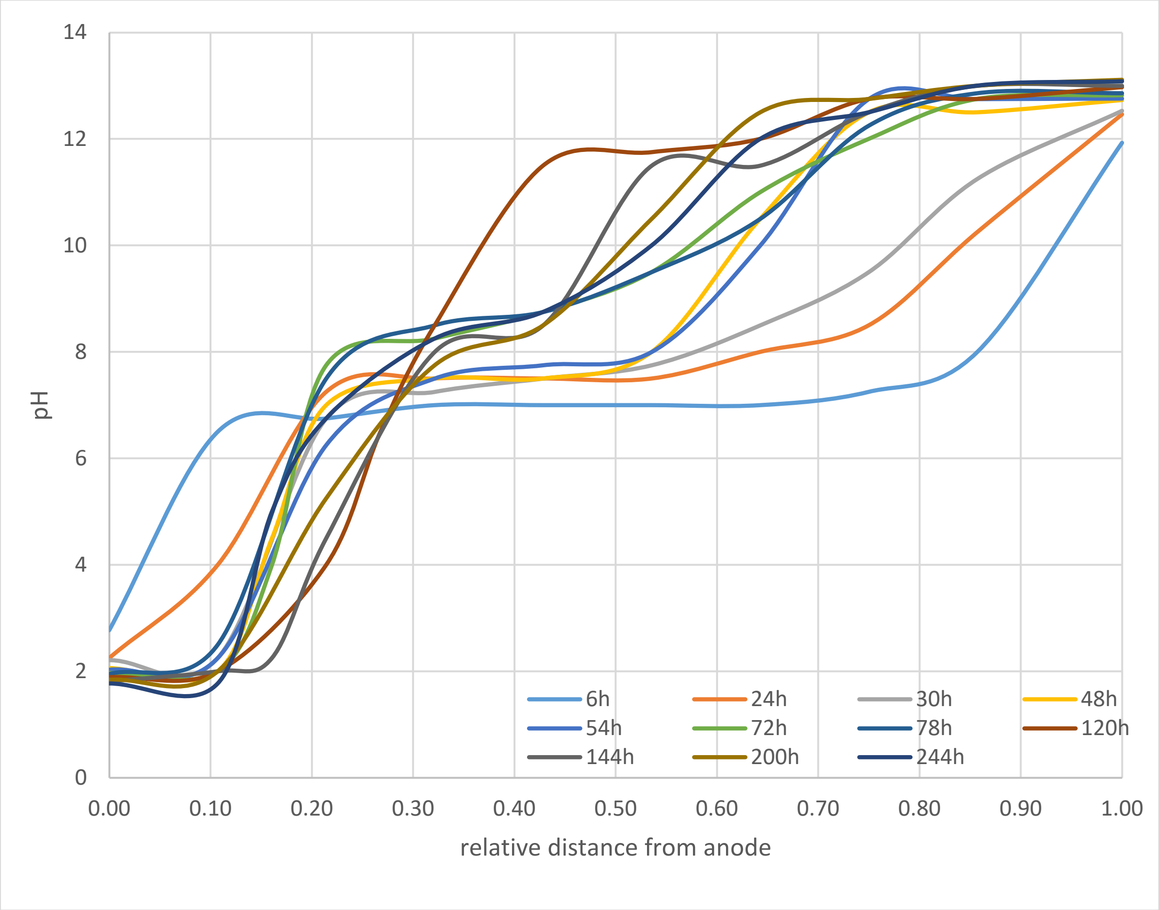


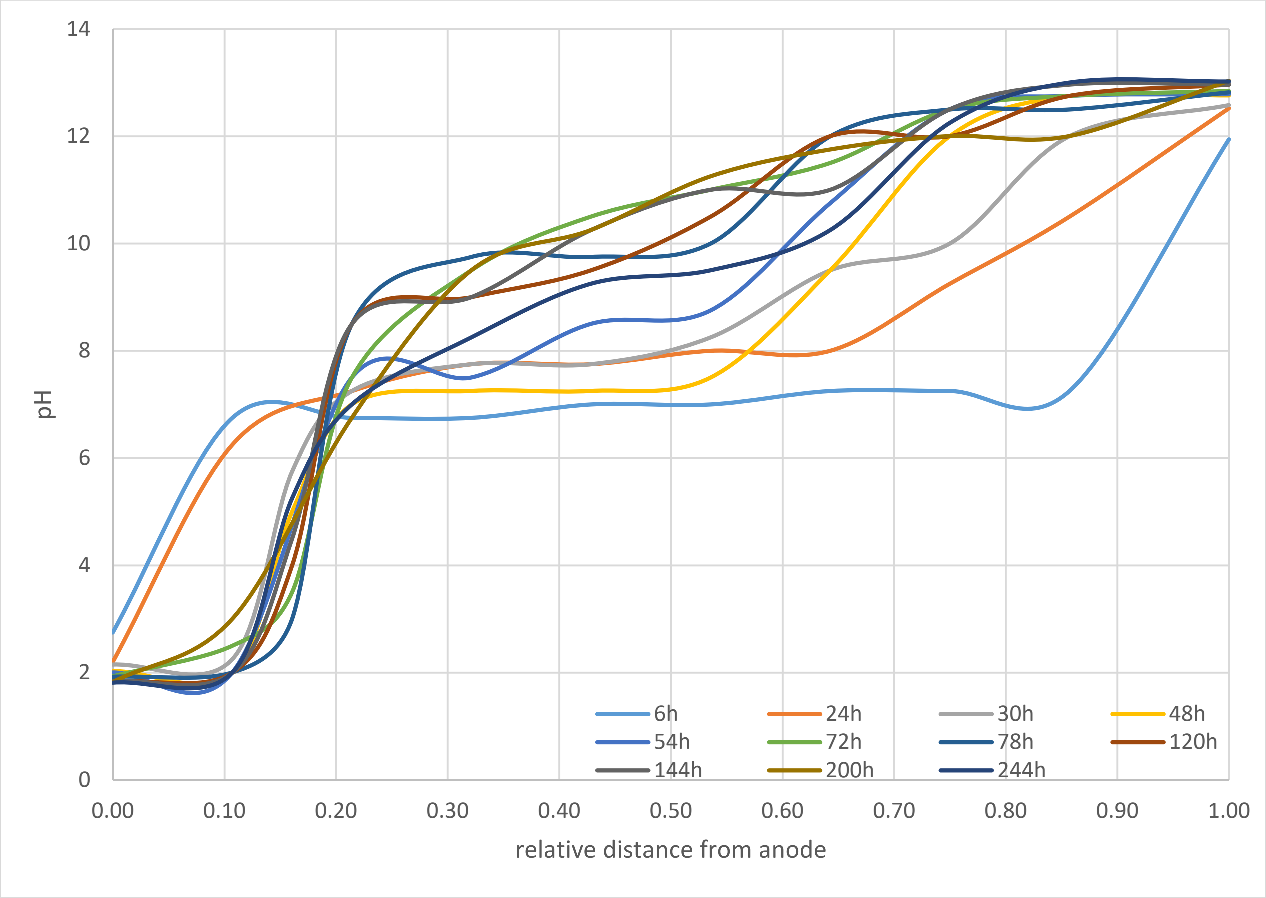
relative distance from anode



relative distance from anode

Gradient Shifts Over Time in Soil (Systems B and D)





Conclusions

- **Key differences in migration rates for different media types (sand, clay)**
  - Most indicative for anionic (red) dye – 10x greater migration in sand, values observed similar to calculated (expected) values and literature values
  - Relevance: How to control the migration of ionic substances
    - Such as certain heavy metals (e.g., chromium), which can be mimicked by this type of anionic dye.

- **Key differences in dye types**
  - Amphoteric (green) dye more complex, difficult to model, pH dependent
  - Discovery of pH gradient

- **Key differences in pH gradients for different media types (sand, soil)**
  - pH in sand reach literature depiction of near-anodic pH level until ~60% distance only after 2-3 days
  - Shift in time – initially more linear
  - pH in soil surprisingly opposite of literature-based trend
  - Also shifts over time, more investigation needed

Thank You!

Questions?

Summary of Migration Rates in Sand

Dye	Migration Distance 1 (cm)	Time 1 (h)	Migration Distance 2 (cm)	Time 2 (h)	Migration Rate 1 (cm/d)	Migration Rate 2 (cm/d)	Avg. Migration Rate (cm/d)	Voltage Gradient (V/cm)	Current Density (mA/cm^2)
Red Dye	13 cm	30.5 h	16.75 cm	50.16 h	10.23	8.01	9.12 ± 1.57	0.667	0.054
Green Dye	13.75 cm	48 h	16 cm	50 h	6.88	7.68	7.28 ± 0.57	0.667	0.054
Green Dye	16 cm	60 h	17 cm	60 h	6.40	6.80	6.60 ± 0.20	0.667	0.040

Flux Calculations

$$N_i = -zu_i F c_i \nabla \phi - D \nabla c_i + c_i v$$

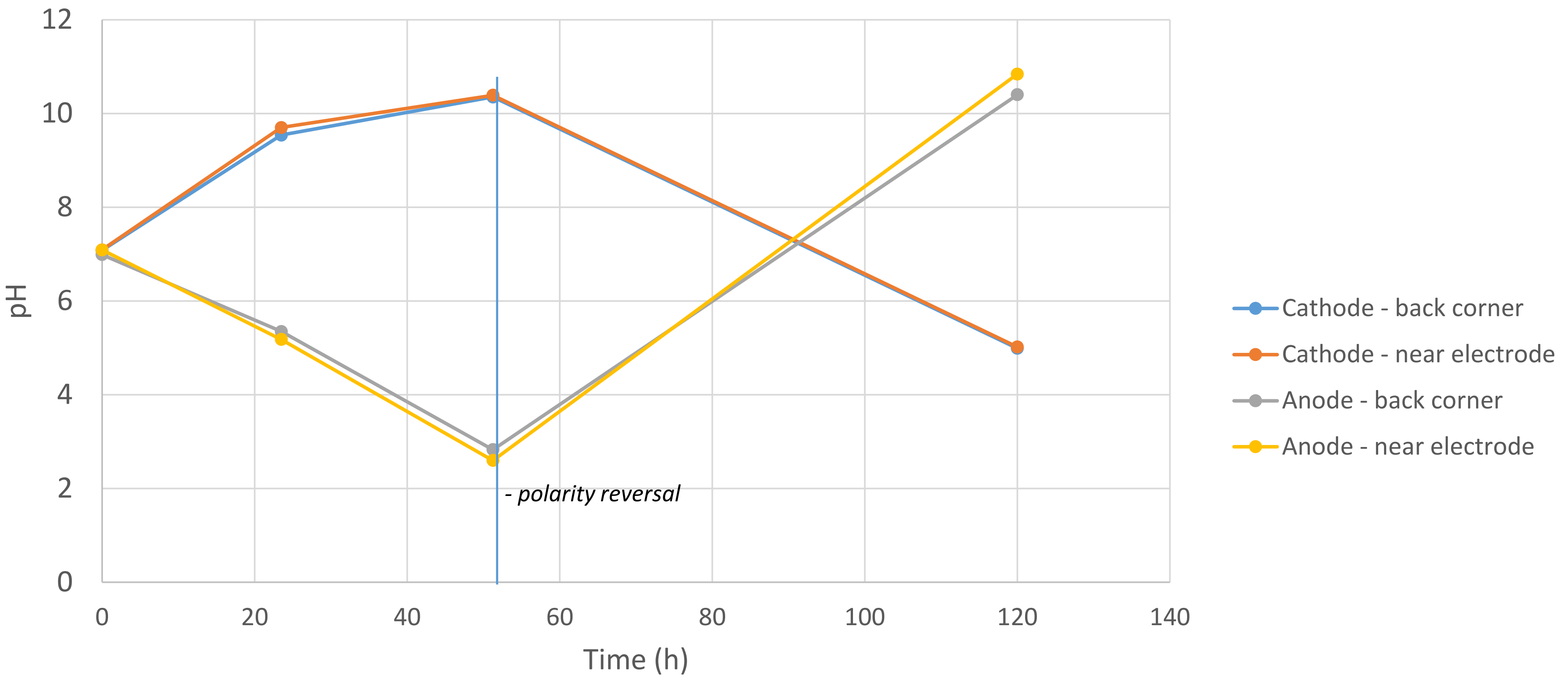
N_i = total flux (mol cm^{-2} d^{-1}), u_i = ionic mobility (cm^2 V^{-1}s^{-1}), z = molecular charge of the migrating species, F is Faraday's constant (C/eq), $\nabla \phi$ = voltage gradient (V/cm), D = effective diffusion coefficient (cm^2/s), ∇c_i = is the change in concentration (mol/L), c_i = overall concentration (mol/L), v = velocity of the fluid flow.

Experiment	Migrational Mass Flux (mol cm^{-2} d^{-1})	Migrational Mass Flux range (mol cm^{-2} d^{-1})	Diffusion Flux (mol cm^{-2} d^{-1})	Electroosmotic Flux** (mol cm^{-2} d^{-1})	Total Flux (mol cm^{-2} d^{-1})
Red Dye - sand	3.242	2.848-3.637	3.04×10^{-6}	N/A	-3.24 ± 0.56
Green Dye (exp1) - sand	0.109	0.103-0.115	1.43×10^{-8}	N/A	-0.11 ± 0.01
Green Dye (exp2) - sand	0.099	0.096-0.102	1.43×10^{-8}	N/A	-0.099 ± 0.004
Red Dye - clay	0.18	0.16-0.20	3.23×10^{-5}	N/A	-0.18 ± 0.02
Green Dye - clay	7.87×10^{-5}*	7.87×10^{-5}	6.22×10^{-7}	~ 10^{-8}	$+7.93 \times 10^{-5}$

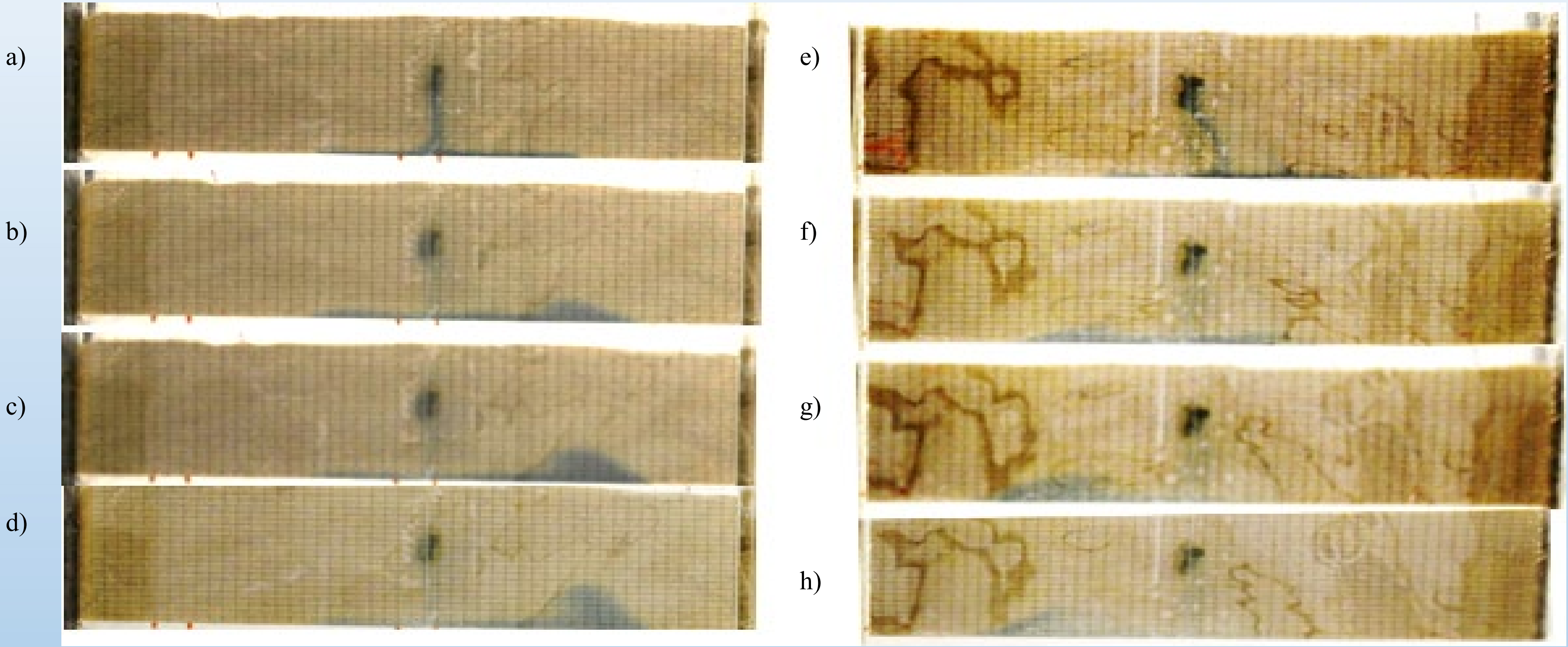
**Value for flux due to electromigration only, **Based upon calculations of system parameters*

During the Electrokinetic process, the electrolysis of water forms hydrogen and oxygen gas at each electrode, respectively.

Polarity Reversal



Looking Again at Migration Times

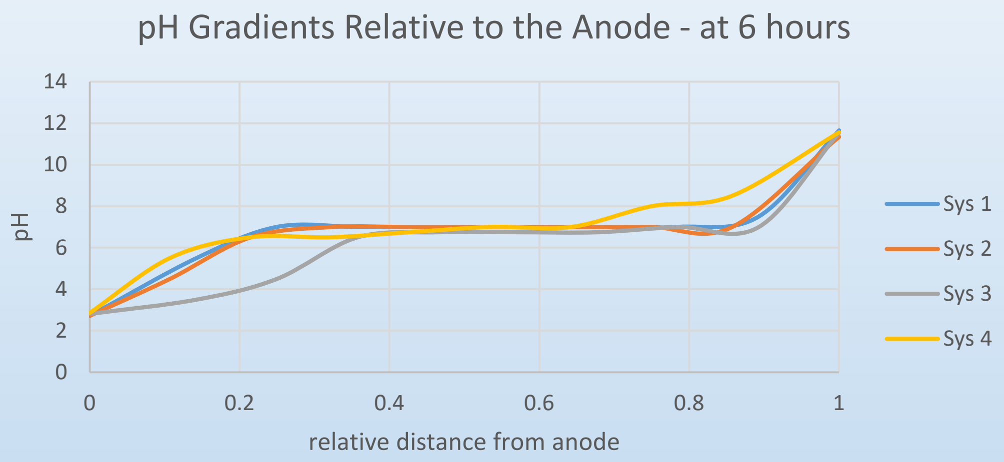


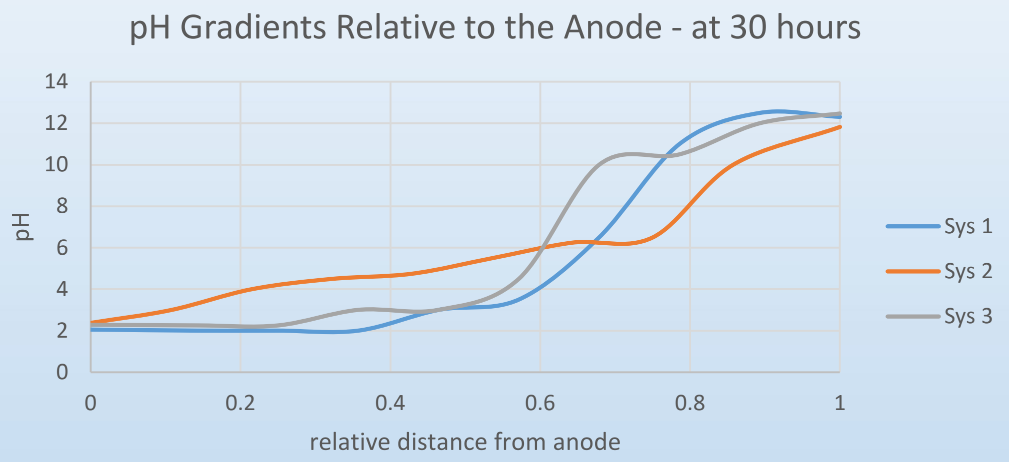
- System 1 at various times (anode on right) - a) 0h ; b) 24h ; c) 48h ; d) 72h.
- System 2 at various times (anode on left) - e) 0h ; f) 24h ; g) 48h ; h) 72h

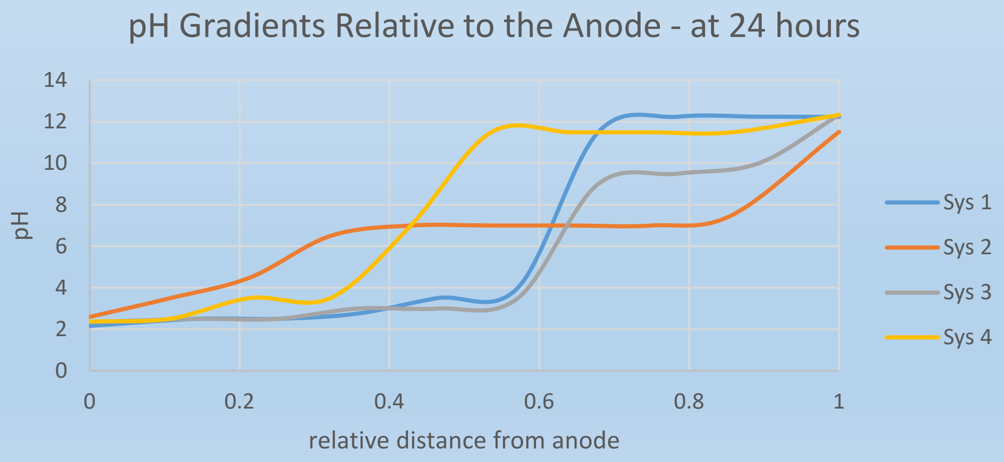
Confirmation of Findings with Increased Voltage Gradient and Current Density

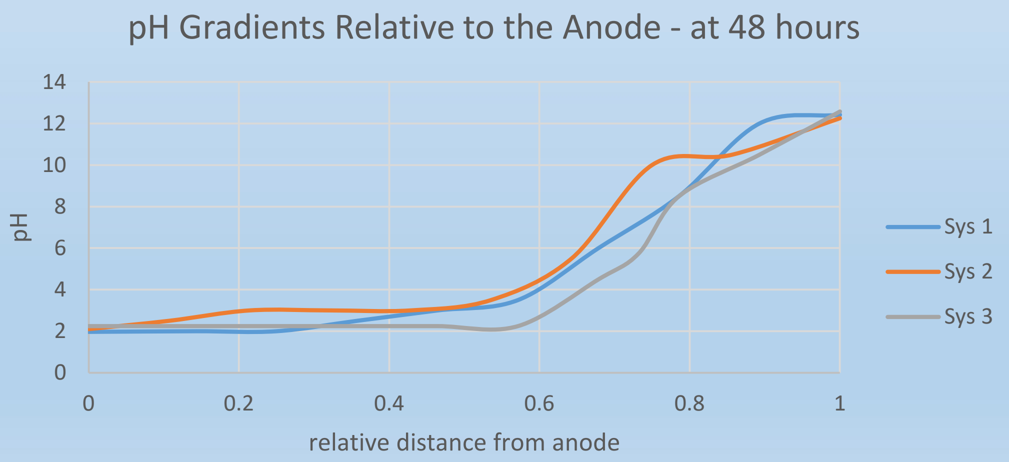
- Mini-setups used again to confirm findings and variation with changes in voltage and current:
  - Larger setups had 0.667 V/cm and 0.040 mA/cm^2
  - New mini-setups had 0.667 V/cm and 0.038 mA/cm^2
- Conducted as 2 sets of duplicates (Systems 1-2, Systems 3-4)
  - Each with one with anode on right, one with anode on left – to eliminate bias

Results (by time)

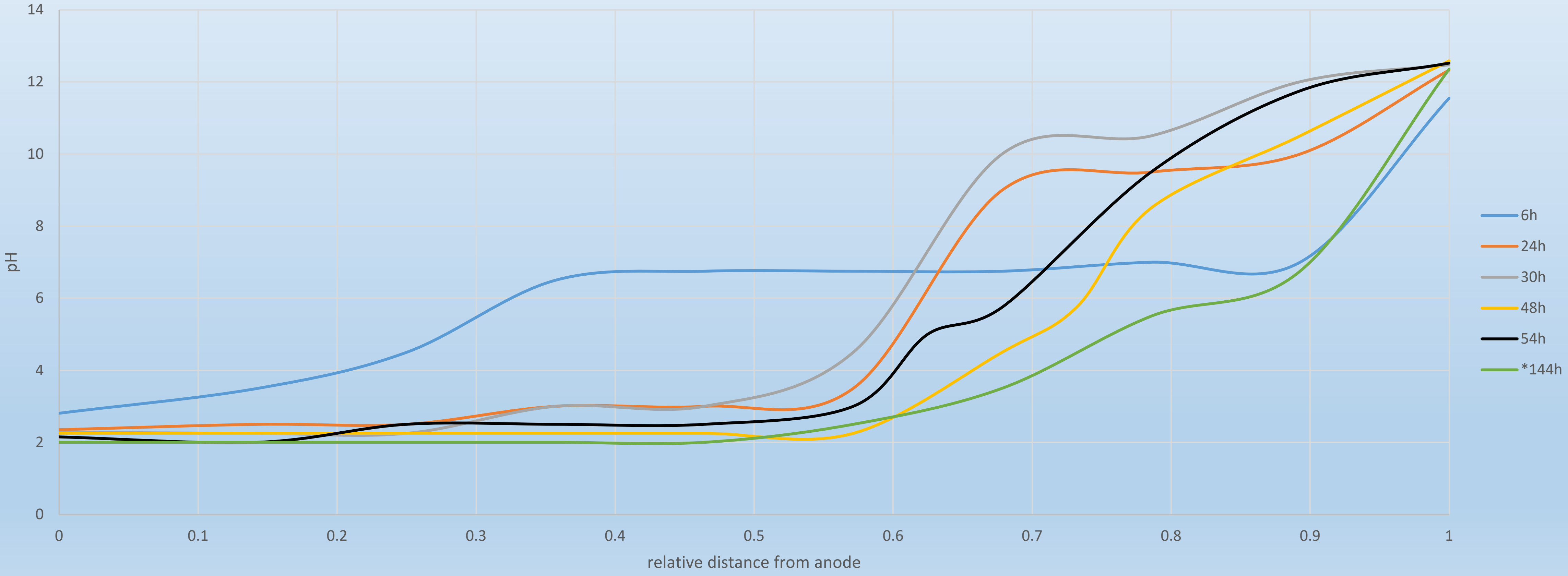




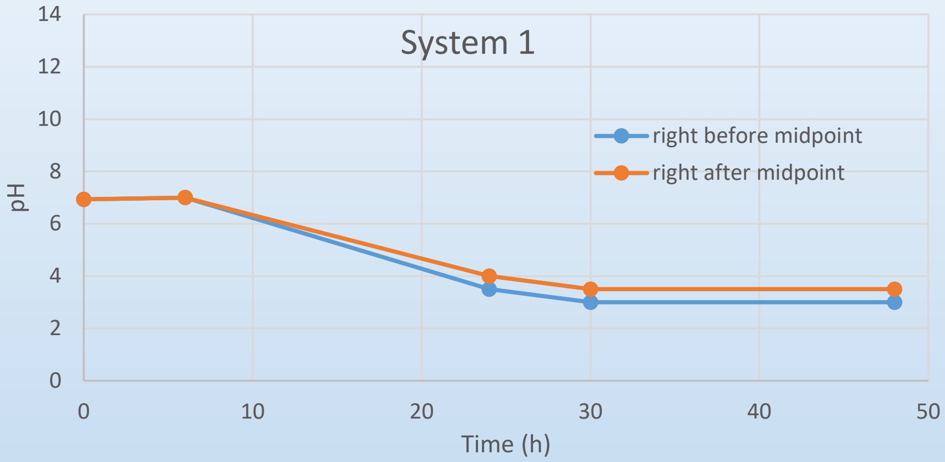


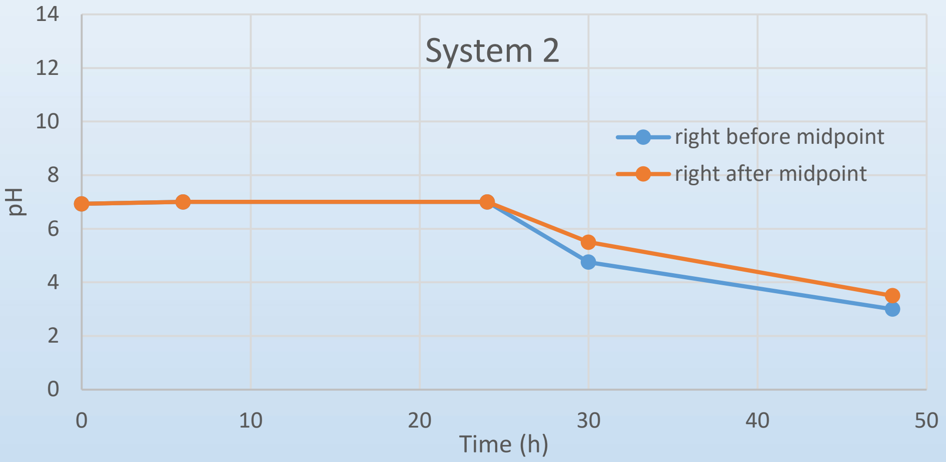


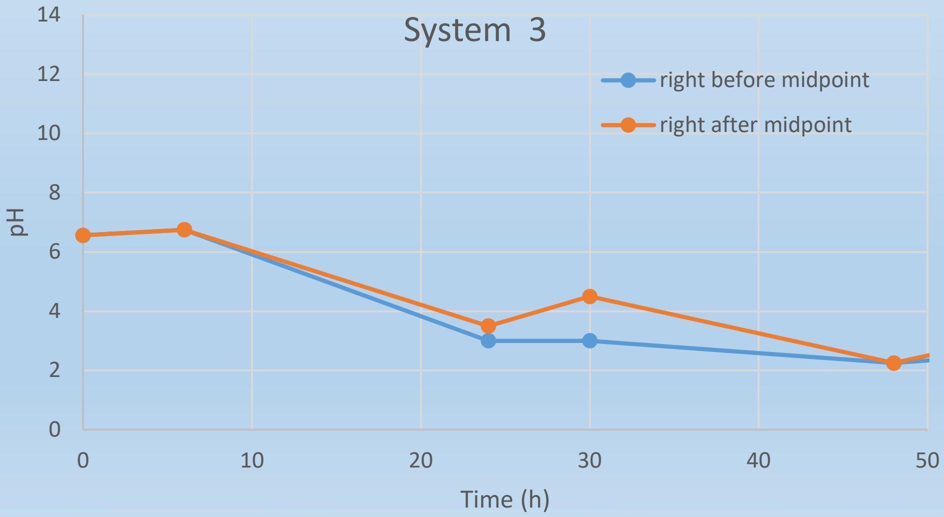
Gradient Shifts Over Time (System 3)



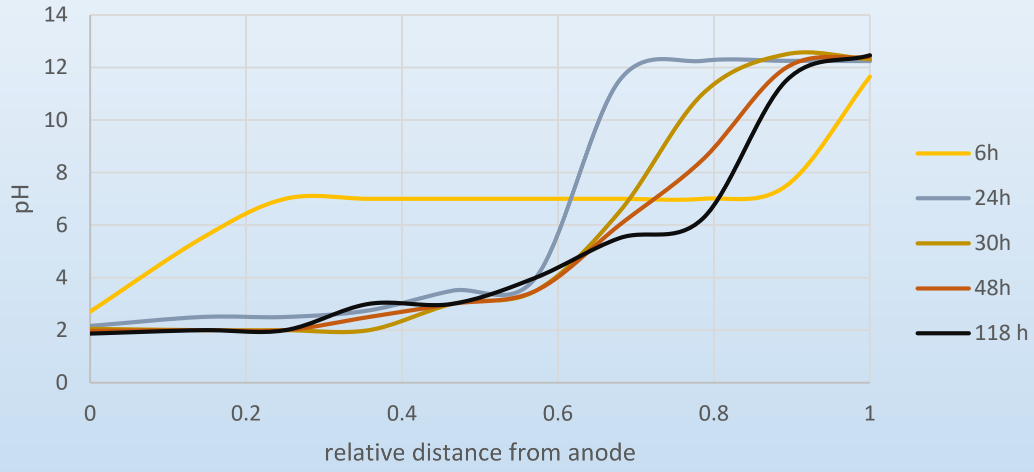
pH Shifts near Sand Center





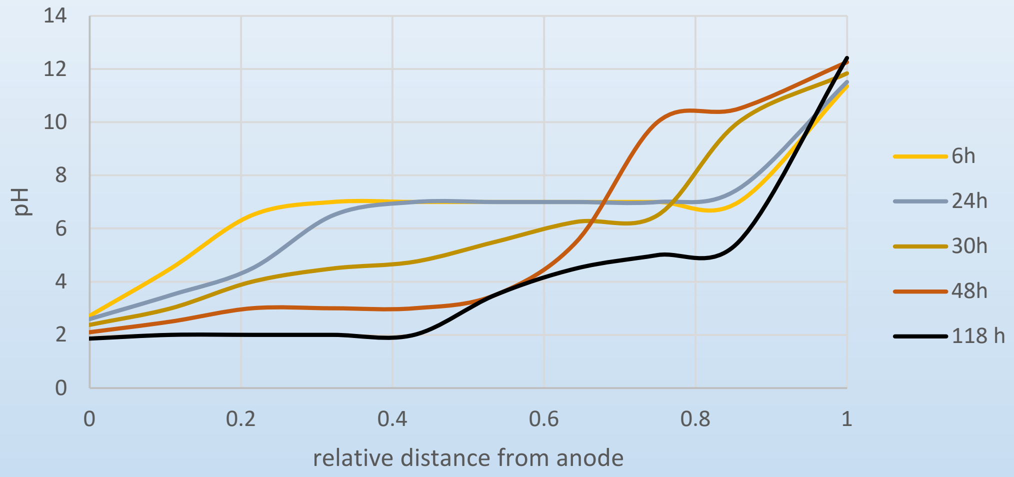


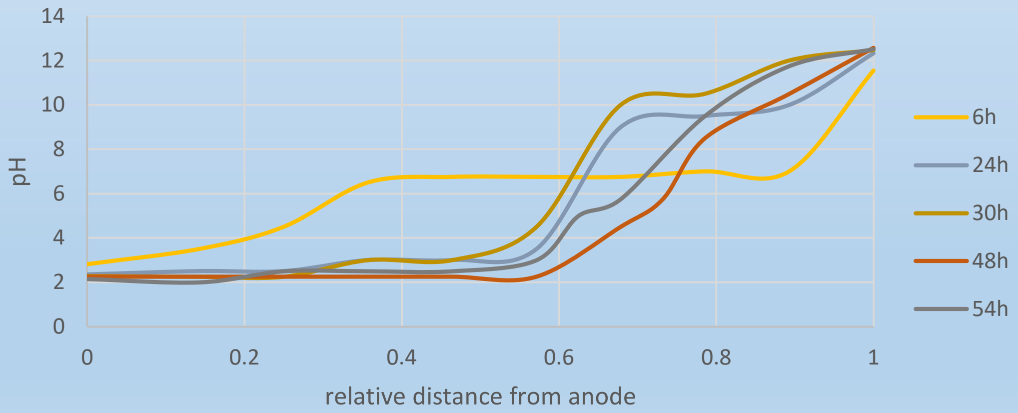
pH Gradients in Sand (by system)



Measured Current in Reservoirs (mA)

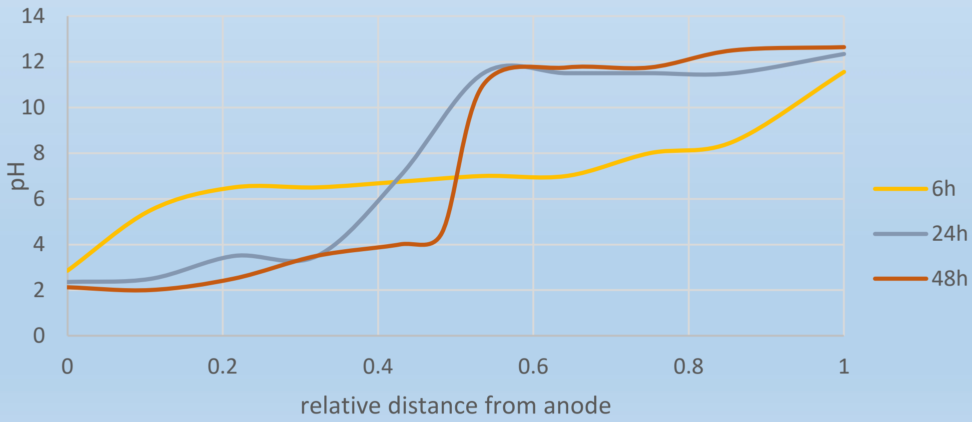
Sys	24h	118h
1	2.29	1.55
2	1.95	1.28



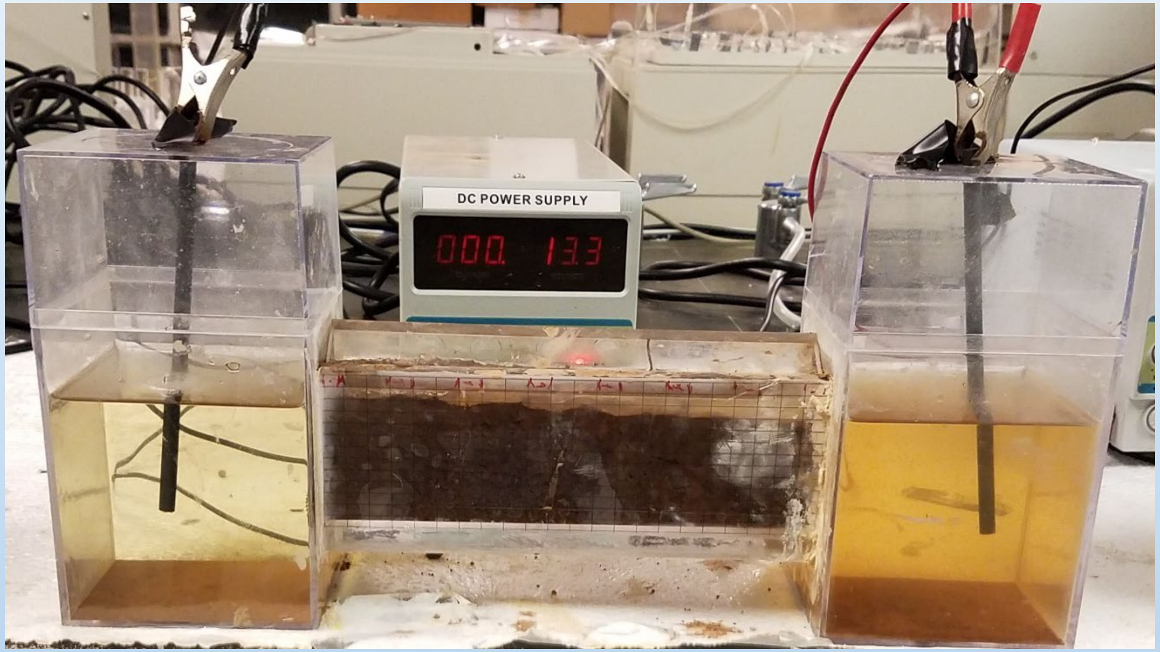


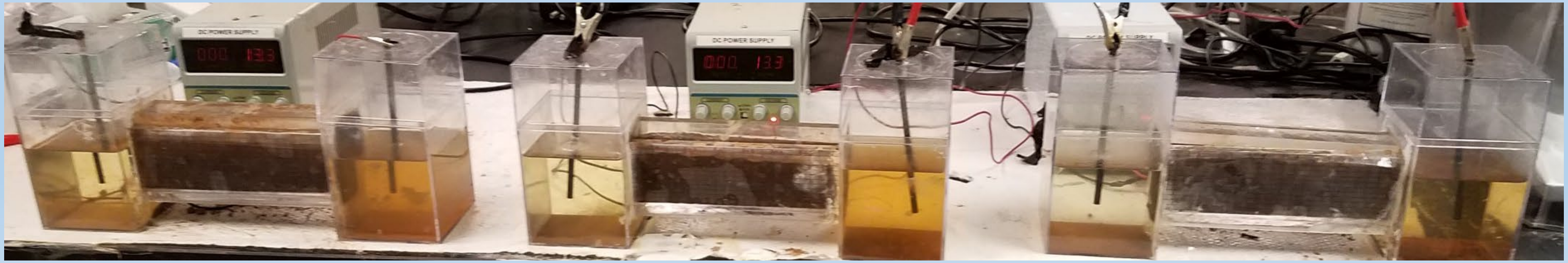
Measured Current in Reservoirs (mA)

Sys	0h	48h
3	2.59	2.41
4	2.39	2.14



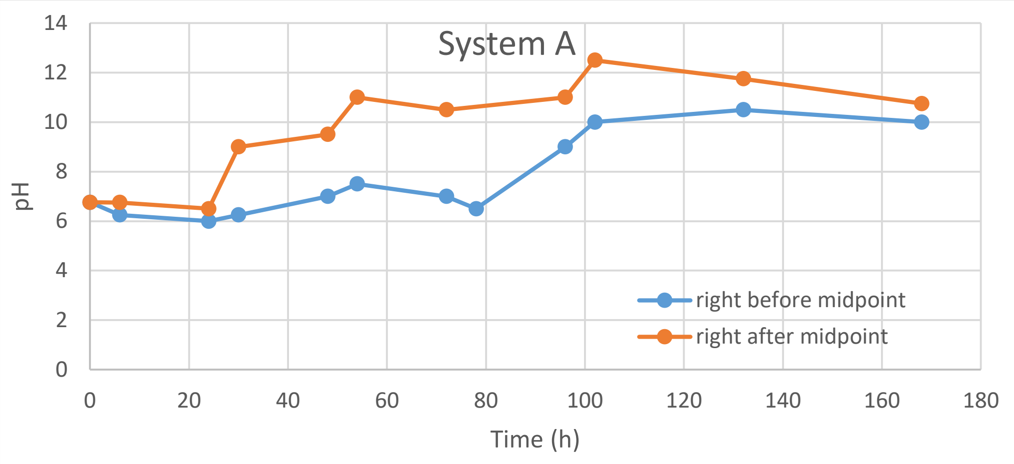
Looking at pH Gradients in Soil

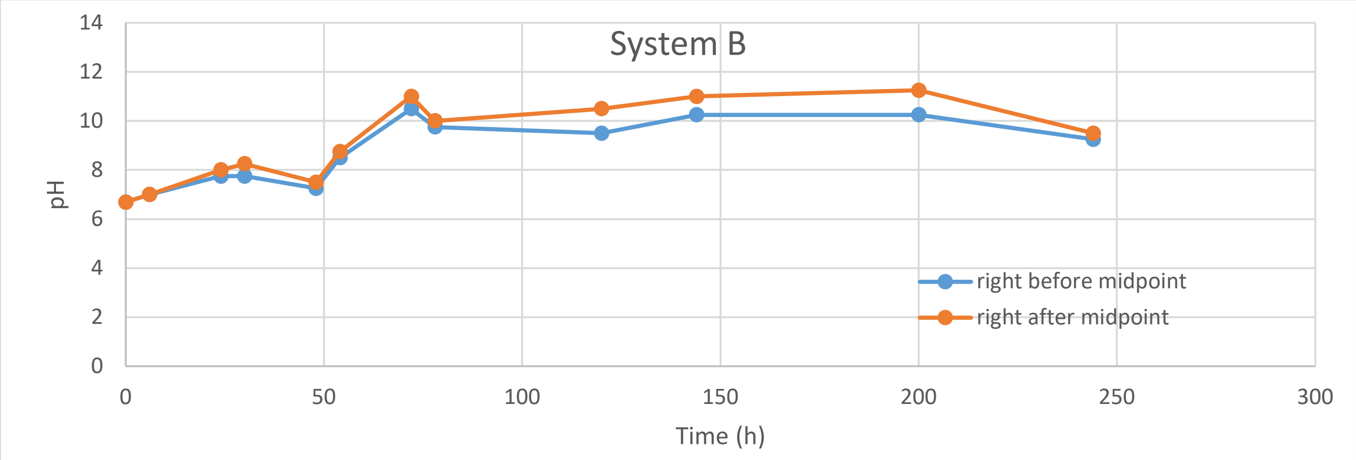


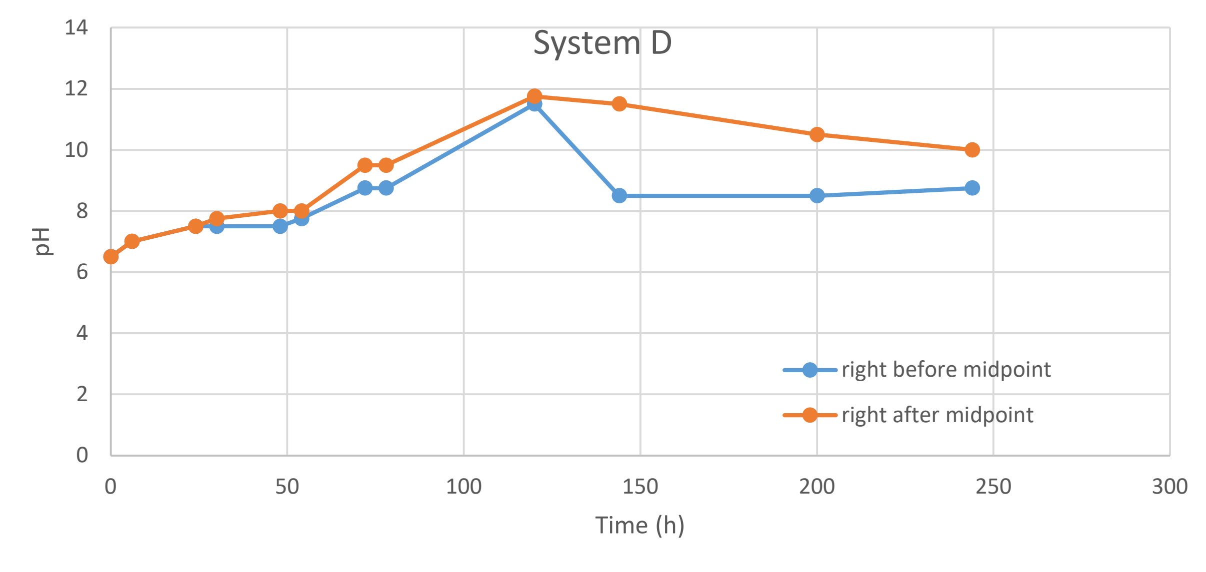


Gradient Shifts Over Time in Soil (System B)

pH Shifts near Soil Center







Explanations and Resolutions

- These mini-setups can explain what occurred in the larger setups
- Central point in the sand where green dye was inserted – initially had pH > pI
- For up to 24 hours, or if taking into the account the preliminary results, up to 48 hours, the green dye would have been anionic and thus been prone to migrate towards the anode.
- Also explains why migration stopped when pH < pI
- However, Results from this experiment with correlating voltage gradient and current density indicate that migration should have stopped or slowed significantly by 24 hours, rather than 48-72 hours.
- Although voltages and current densities were near-identical, proportions of setups were not.
- The overall designs of the two sizes were similar but bridge height relative to the position of the reservoirs was different.
  - Larger setups - bottom of the sand (bridge) @ 39% of the reservoir height, fill height ~64% of the reservoir height.
  - Mini setups - bottom of the sand (bridge) @ 33% of the reservoir height, fill height ~75% of the reservoir height.
    - In mini-setup, a greater portion of reservoir liquid (42% by height) came in contact with the sand bridge in the than in larger setups (25% by height). This may have led to a faster shift in the pH gradient, and therefore for the larger setups, the pH may have only dropped below the isoelectric point after 48-72 hours.