Bench- and Pilot-Scale Studies: Worthwhile Tools in Optimizing Thermal Remediation Approaches

A. Fortune, G. Heron, S. Nielsen, D. Phelan (TerraTherm/Cascade Thermal)

R. Wenzel, R. Stuetzle (The Dow Chemical Company)

J. Bunton (Parsons Infrastructure)

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Overview of Presentation

- Site History, Site Contaminants, Remedial Objectives
- Treatability Study
  - Thermal Conductive Heating (TCH)
  - Steam Enhanced Extraction (SEE)
  - Hot Water Flushing (HWF)
  - Static Chamber Testing
- Pilot Study
  - Steam Injection and Fluid Extraction Design
  - Corrosion Study
- Summary/Conclusions

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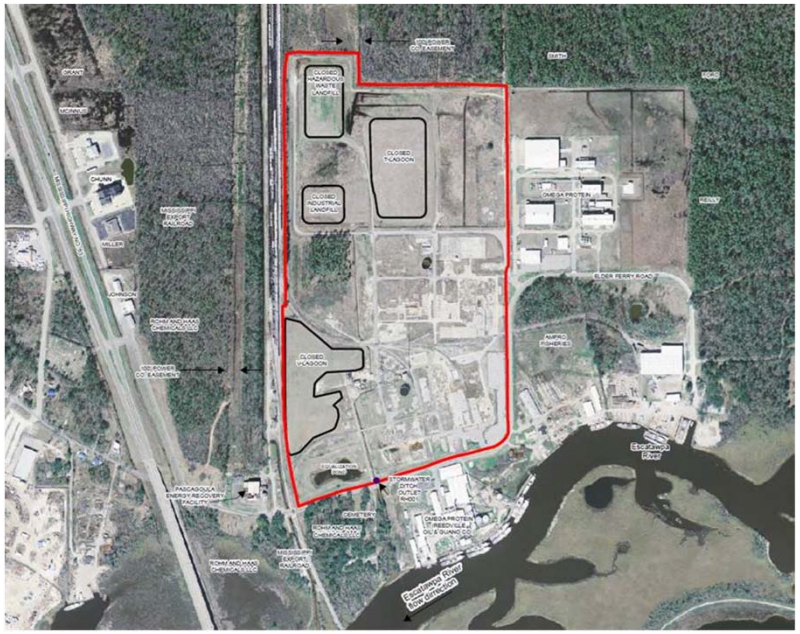
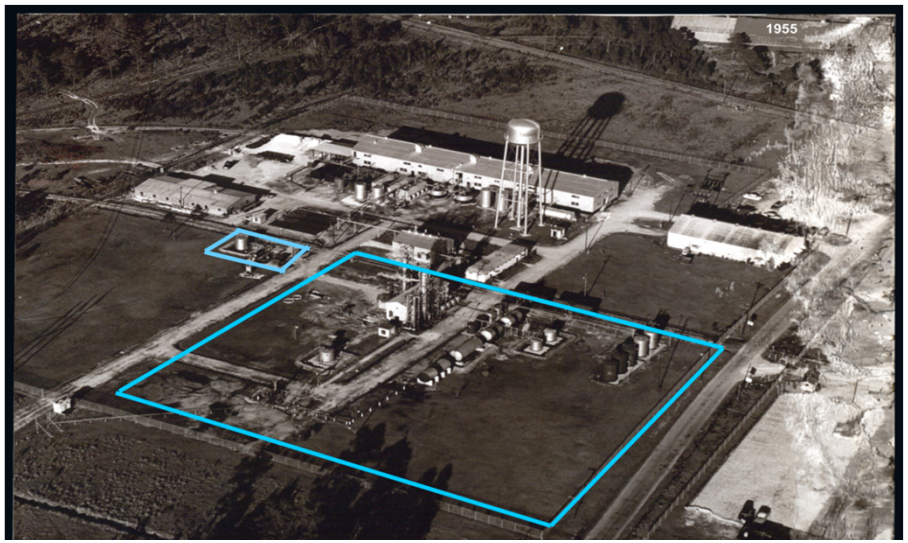
Site History: Former Chemical Plant (Moss Point, MS)

100 Acre Specialty Chemical Plant (Closed 2001, Interim GW recovery)



1955 Photo: Formal Production Area (bis(2-chloroethoxy)methane)



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Site Contaminants (Historical BCEM Production)

Step 1 - 2–Chloroethanol synthesis

$CH_2\text{-}O\text{-}CH_2 + HCl \rightarrow Cl\text{-}CH_2\text{-}CH_2\text{-}OH$

Ethylene Oxide — 2-Chloroethanol

Step 2 – "Formal" – *Bis* 2-Chloroethoxy Methane (BCEM)

Reactive distillation under acidic conditions using 1,2-DCA as entrainer for reaction water. Acid neutralized with NH3 to prevent hydrolysis.

$Cl\text{-}CH_2\text{-}CH_2\text{-}OH + CH_2O \rightarrow Cl\text{-}(CH_2)_2O\text{-}CH_2\text{-}O(CH_2)_2\text{-}Cl$

2-Chloroethanol — Formaldehyde — BCEM

By products: Bis 2-Chloroethyl Ether (BCEE) and 1,4-Dioxane.

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Site Contaminants

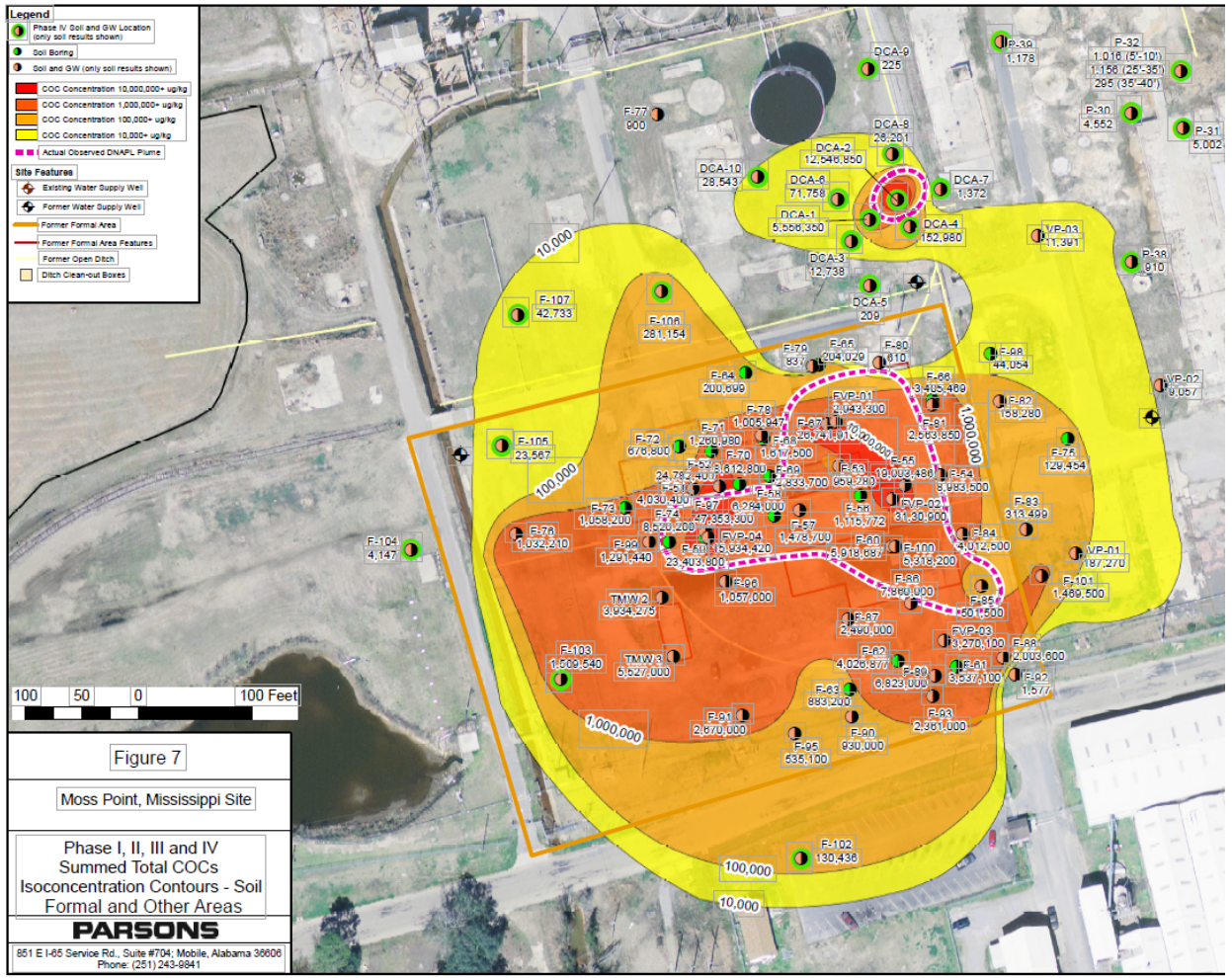
- Bis(2-chloroethoxy) methane (BCEM)
- 2-chloroethanol
- 1,2-Dichloroethane
- Bis(2-chloroethyl) ether (BCEE)
- 1,4-Dioxane
- 1,2,3-Trichloropropane

Soil concentrations 10-10,000 mg/kg

DNAPL present

Approximately 200,000 lbs removed with groundwater pumping

Estimate 650,000 lbs mass remaining



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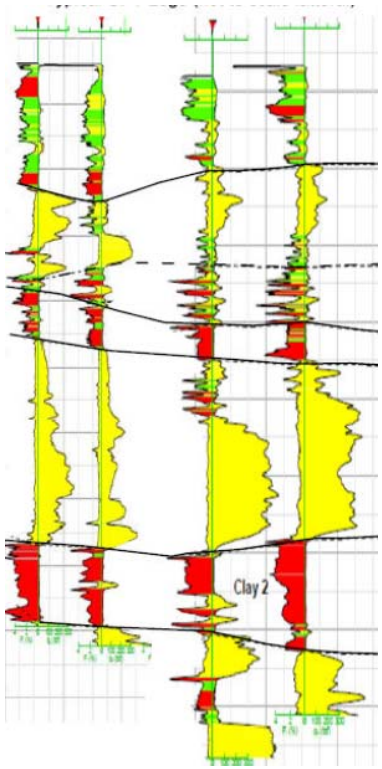
Site History: Cross Section



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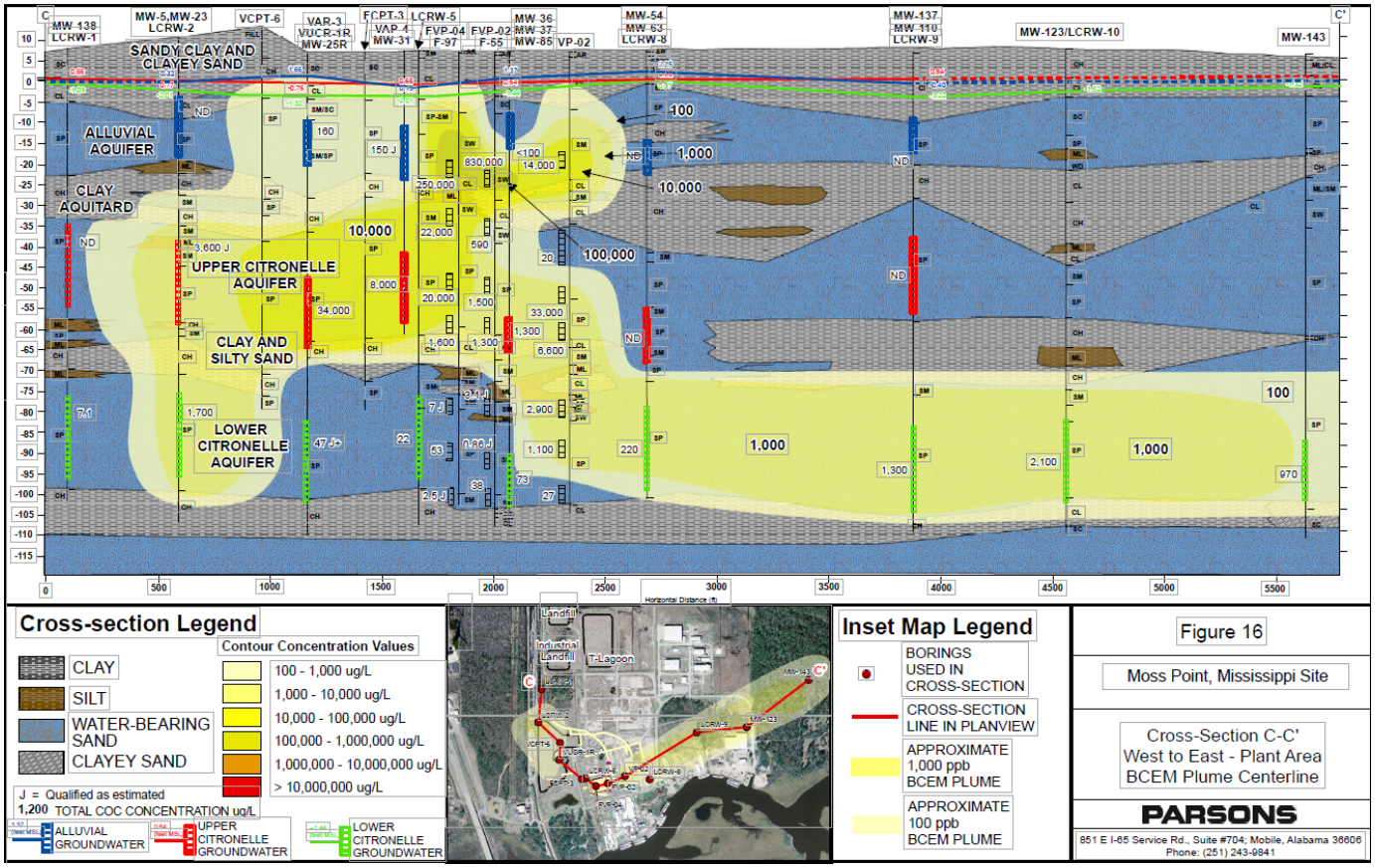

Site History: Remedial Objectives

- Protective of Human Health
- Eliminate DNAPL mass or mobilization
  - Prevent migration of source plume off-site (Short term & Long term)
  - Short term and long term risk reduction
- Achieve lowest COC concentration in soil and groundwater practicable in the treatment zone
  - DNAPL mass reduction
  - Monitor remedy implementation/cost effectiveness

Next Step: Evaluate thermal treatment of site materials via bench scale study

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Treatability Study

Testing performed by KEMRON Environmental Services in Atlanta, GA

Compare performance of 3 thermal treatment technologies

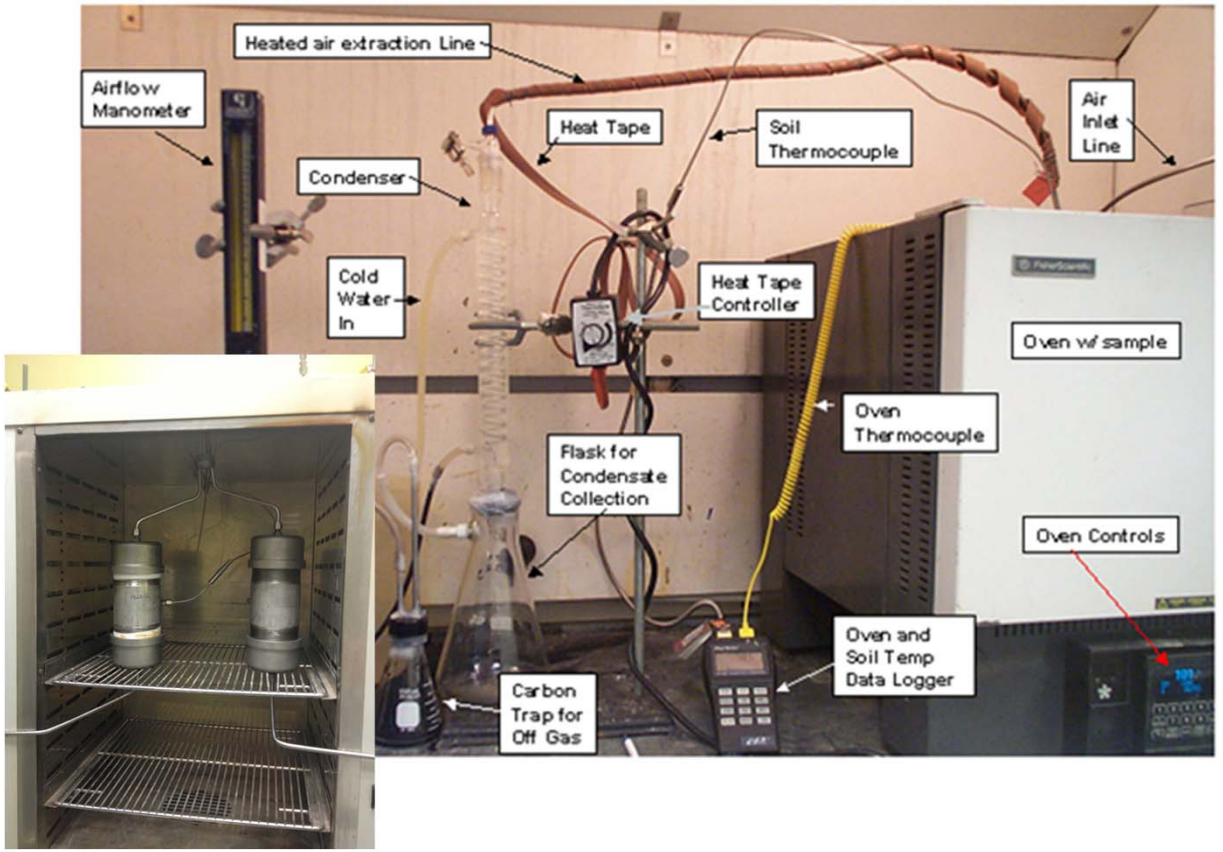
Thermal Conductive Heating (100˚C, 50% PV removal)

Hot Water Flushing: 50˚C (30 PV flush)

Hot Water Flushing: 75˚C (30 PV flush)

Steam Enhanced Extraction (4 PV flush)

Compounds of interest spiked into soils at 500-15,000 mg/kg to simulate worse case DNAPL zones



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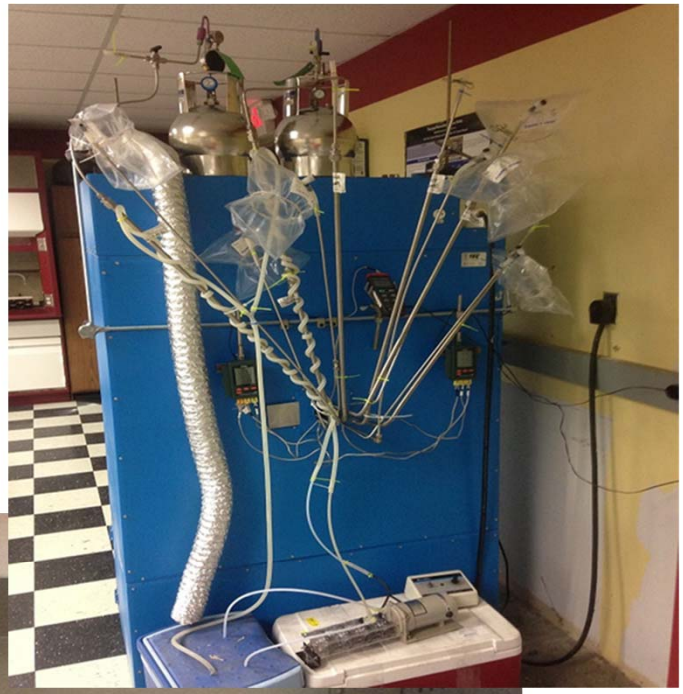
Static Chamber Testing

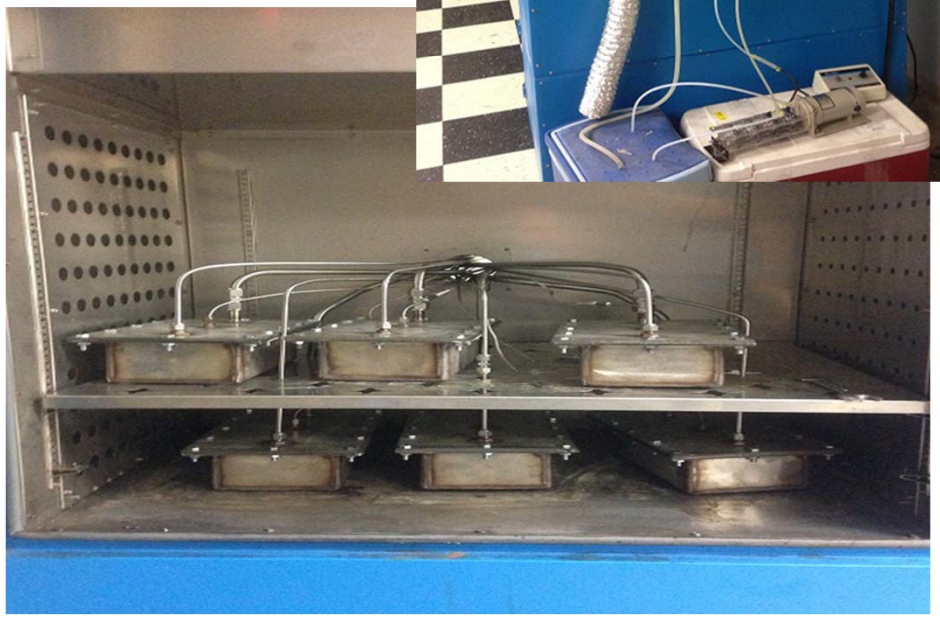
Closed system with site soil (spiked) and groundwater. Outlet connected to vapor collection (Summa canisters) for analysis of vapor.

Slowly ramp temperature in chambers from 60-100˚C.

Chambers for 3 day, 6 day and 10 day analysis

Understand hydrolysis of site contaminants & formation of breakdown products with no flushing





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Treatability Study- Observations

- Breakdown products observed
  - Formaldehyde
  - Chloracetaldehyde
  - Acetaldehyde

  Nearly all seen in condensate
  - Ethylene glycol—known breakdown product
  - Low pH (1-3) & high chloride (2,000-12,000 mg/L) from HCl generated—high potential for corrosion in full scale

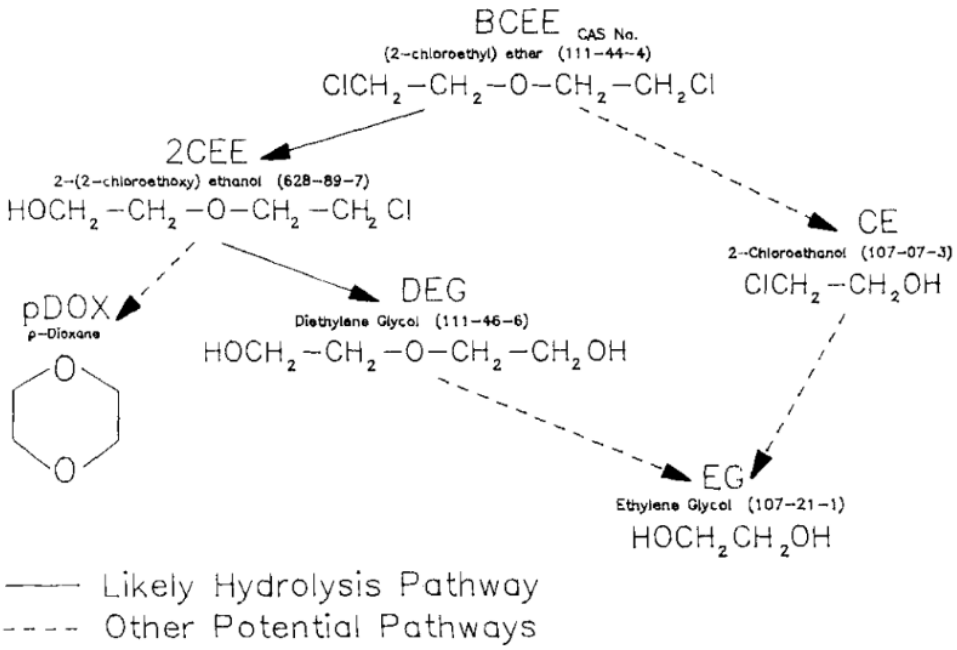

Figure 1

Potential hydrolysis pathways for bis(2-chloroethyl) ether.

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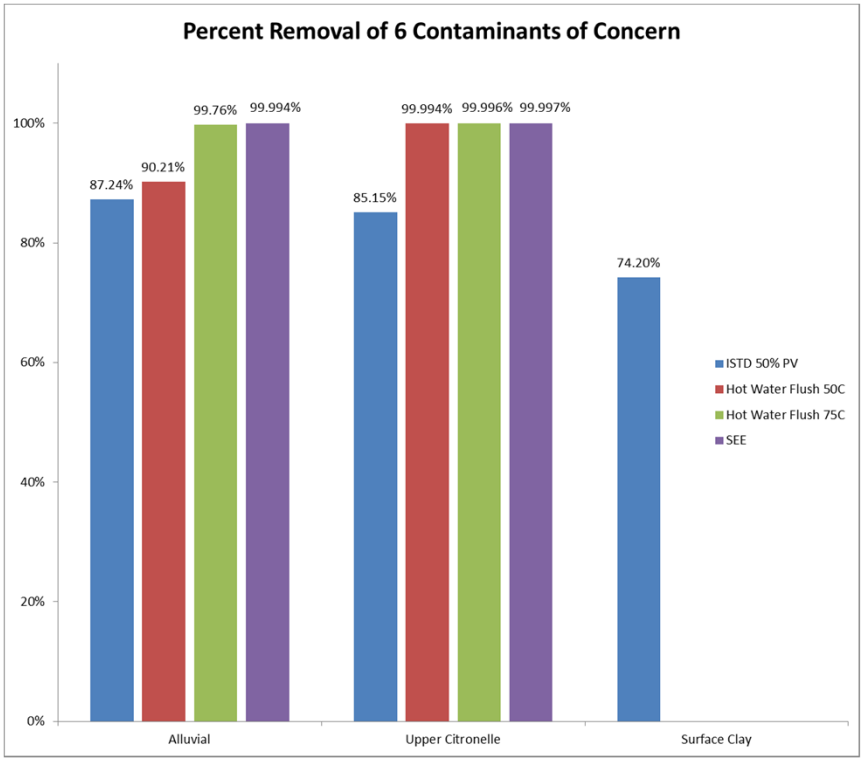
Payne, W. and Collette, T. Identification of Bis(2-chloroethyl) Ether Hydrolysis Products by Direct Aqueous Injection GC/FT-IR. Journal of High Resolution Chromatography, Volume 12 October 1989, 693-696.

Treatability Study- Results



- Steam Enhanced Extraction most effective in Alluvial and Upper Citronelle aquifers
- TCH/ISTD less effective, but still obtained 74% removal in clay
- SEE chosen for pilot testing technology

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Steam Enhanced Extraction Pilot Test

- Near center of proposed full-scale treatment zone
- Most challenging area due to DNAPL (BCEM), presence of thicker Alluvial/Upper Citronelle clay layer, and alternating silt/clays in Alluvial
  - Clay layers may be heated via conduction from steam treated layers above/below
- Target treatment depth: 10-70 ft bgs (approx. 775 cubic yards)
- Two different aquifer zones, 3 steam injection intervals:
  - Shallow = Alluvial
  - Intermediate = Upper Citronelle (Intermediate)
  - Deep = Upper Citronelle (Lower)
- SIW spacing approximately 28’
  distance to extraction was 15’

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SEE Pilot Test (26 days)

- Confirm steam injection well designs, depth & screen locations
- Confirm achievable steam injection rates & pressures
- Collect data to support well spacing & screen location
- Test liquid extraction well design/pump function
- Perform corrosion test to evaluate materials for wells, piping, etc.
- Collect heated subsurface fluids for wastewater treatment system design (Parsons)

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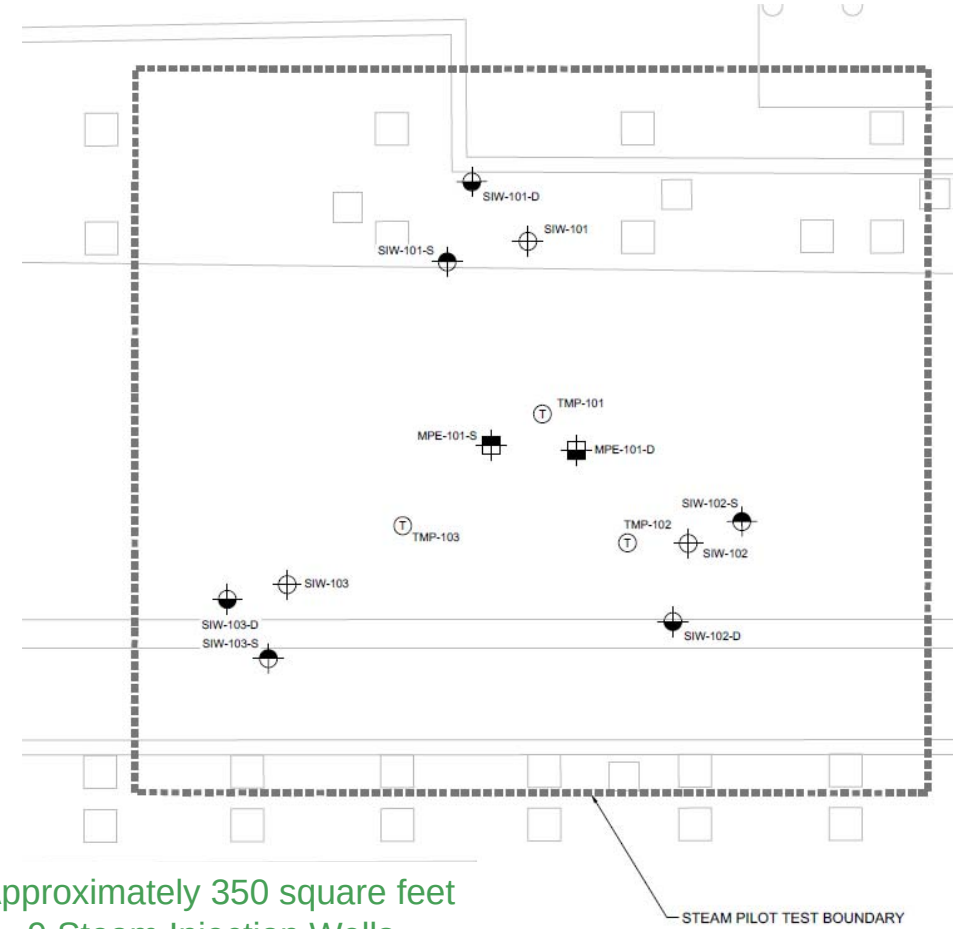
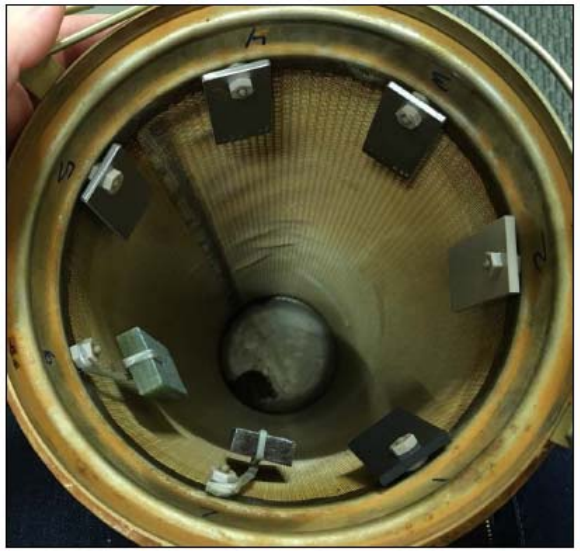


Approximately 350 square feet

- 9 Steam Injection Wells
  - Deep & Shallow
- 2 Multi-phase Extraction Wells
- 3 Temperature Monitoring Points
  - Vertical Arrays

Corrosion Study

316 SS steel and PEEK performed well



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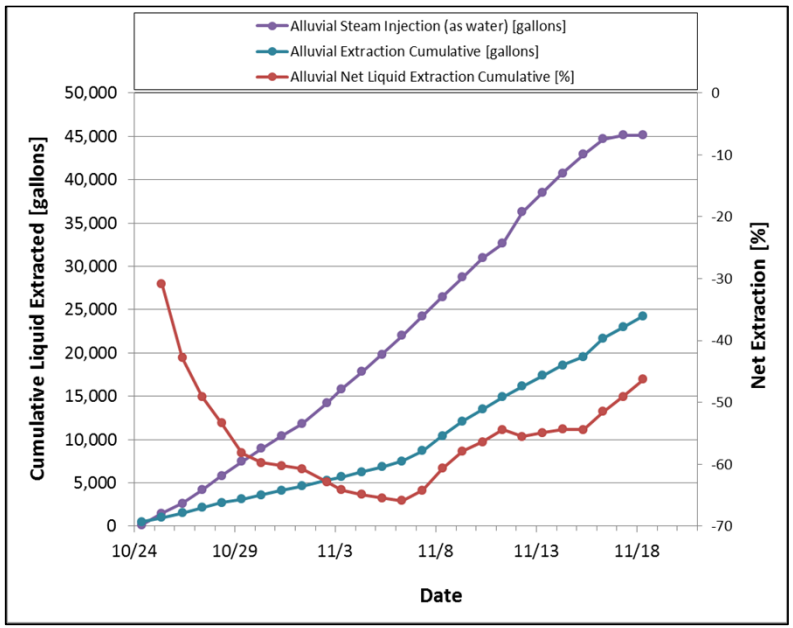
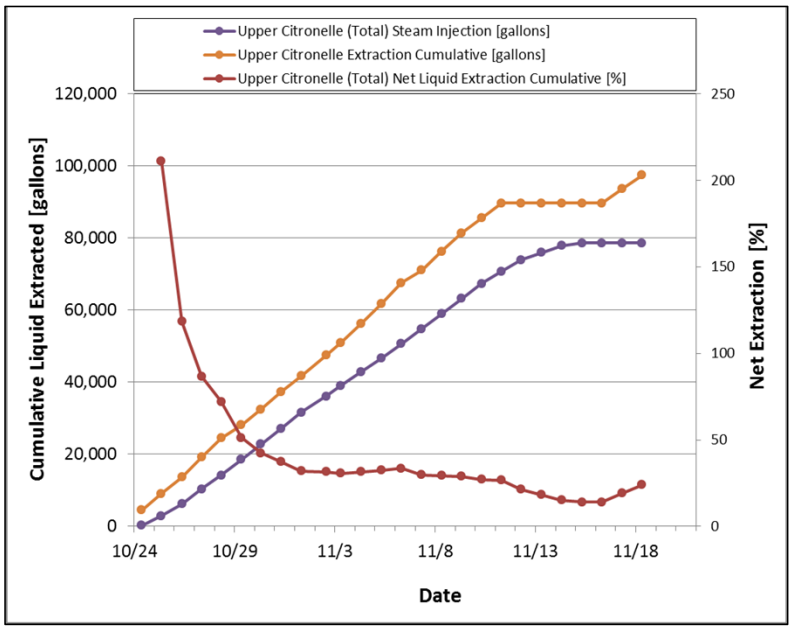
Pilot Test: Results (Water Balance)

Lower than expected permeability observed in Alluvial aquifer, resulting in lower steam injection rate and a negative net extraction



Upper Citronelle aquifer behaved as expected with steam injection rates as modeled and 24% net extraction



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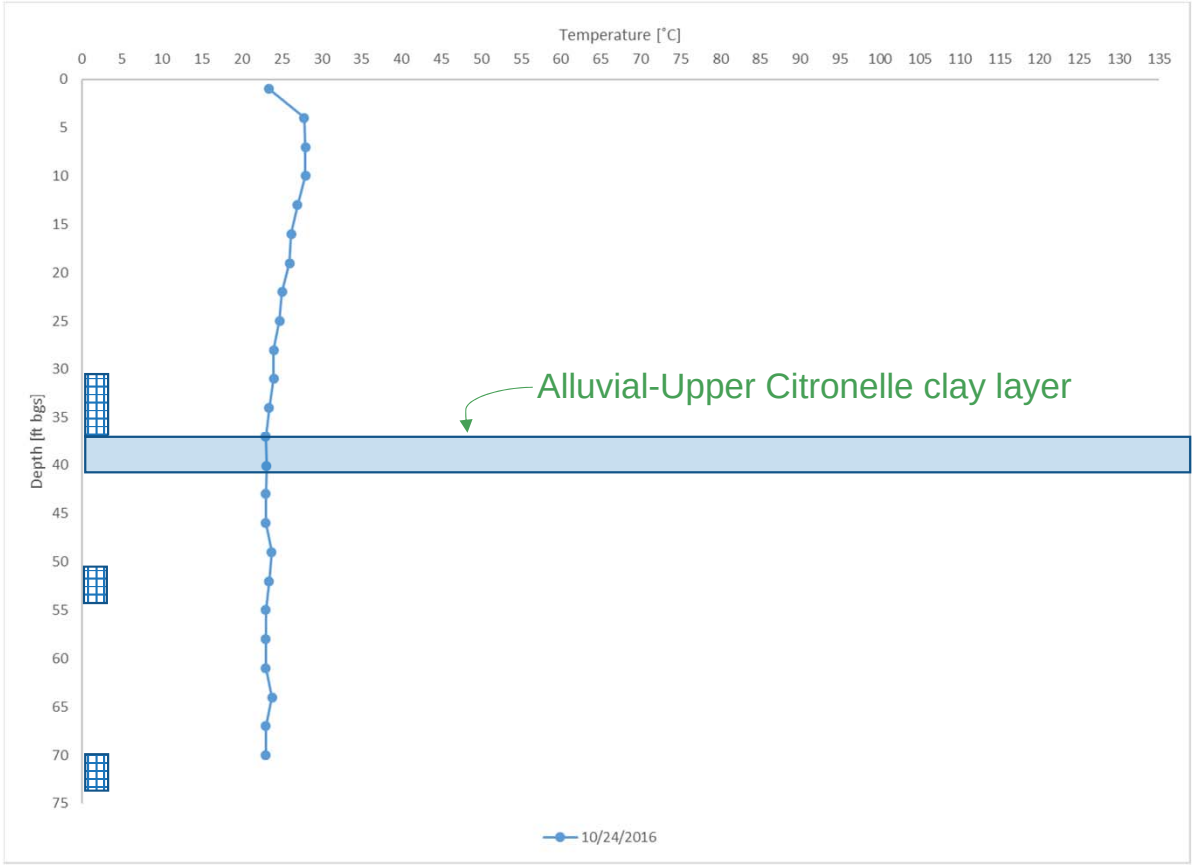
Pilot Test: Results (Temperatures)

Conductive heating in the clay layer in between two steam injection zones was able to close the temperature gap.



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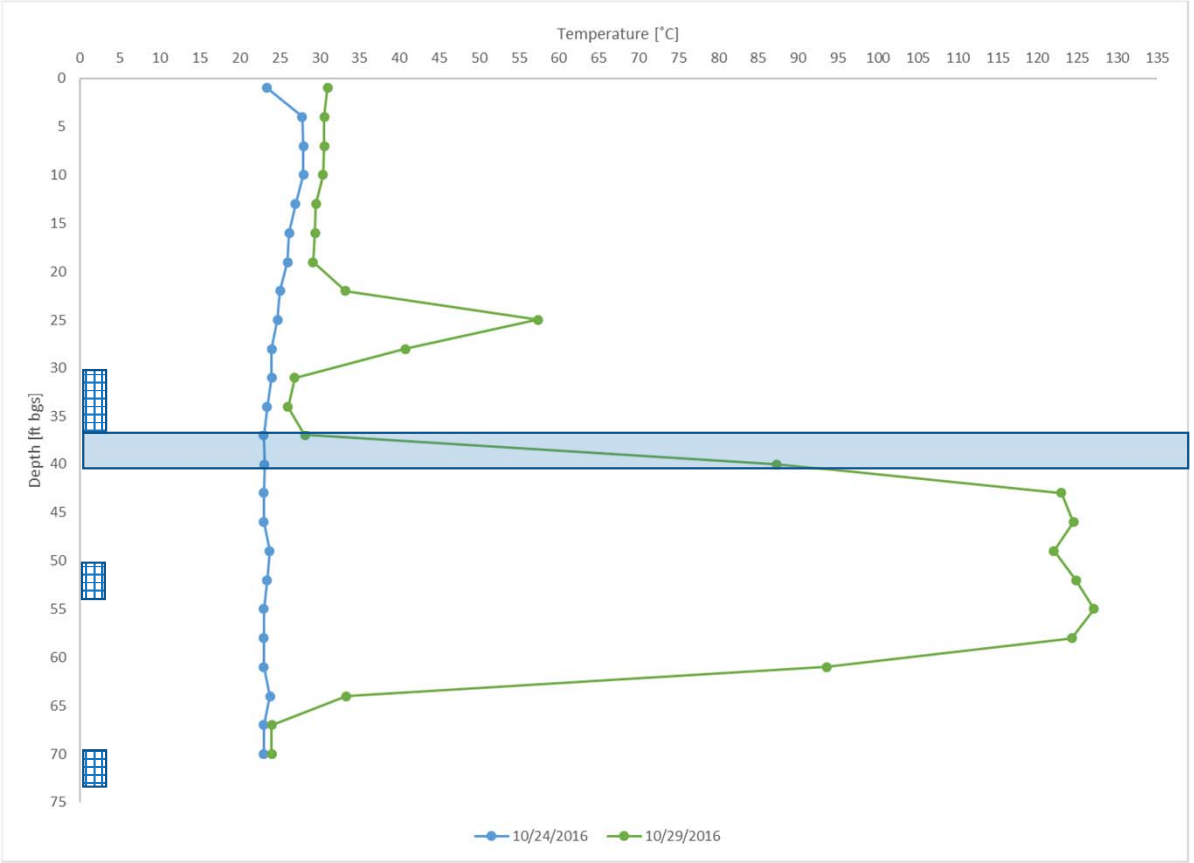

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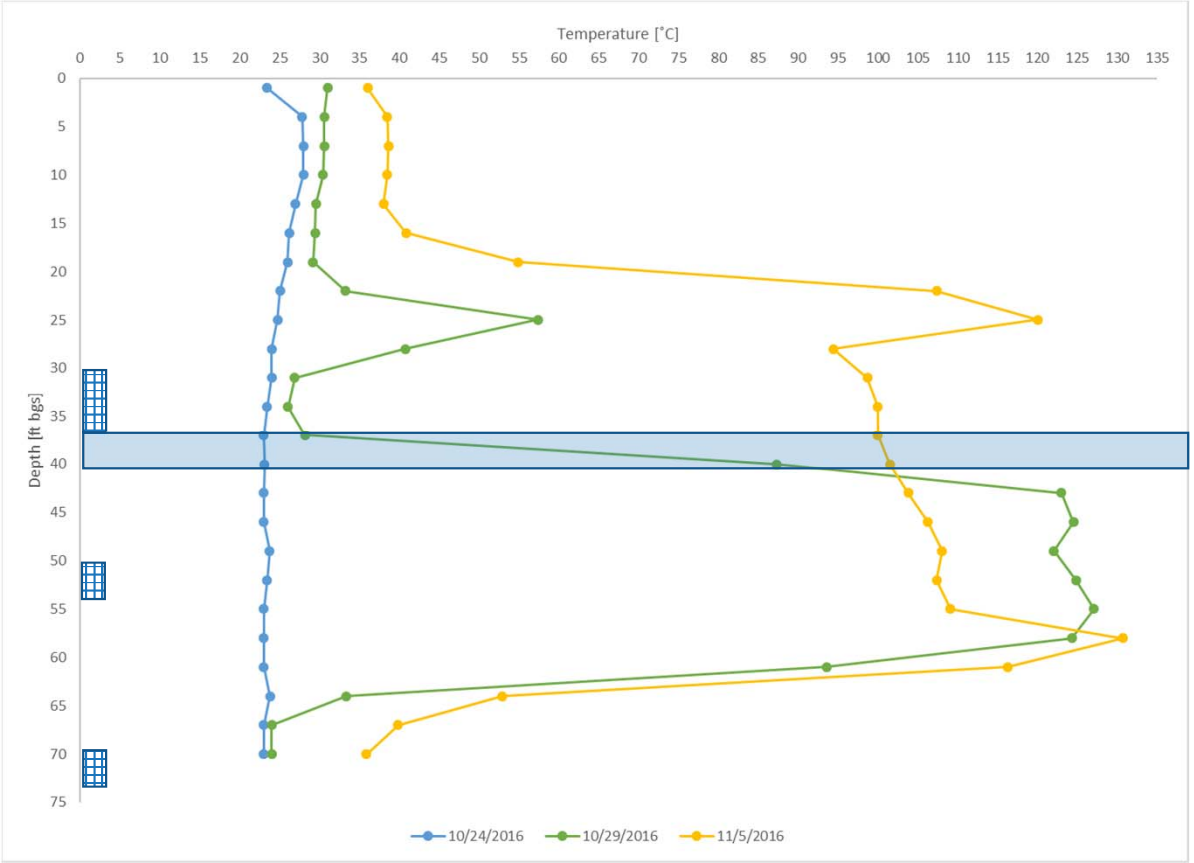

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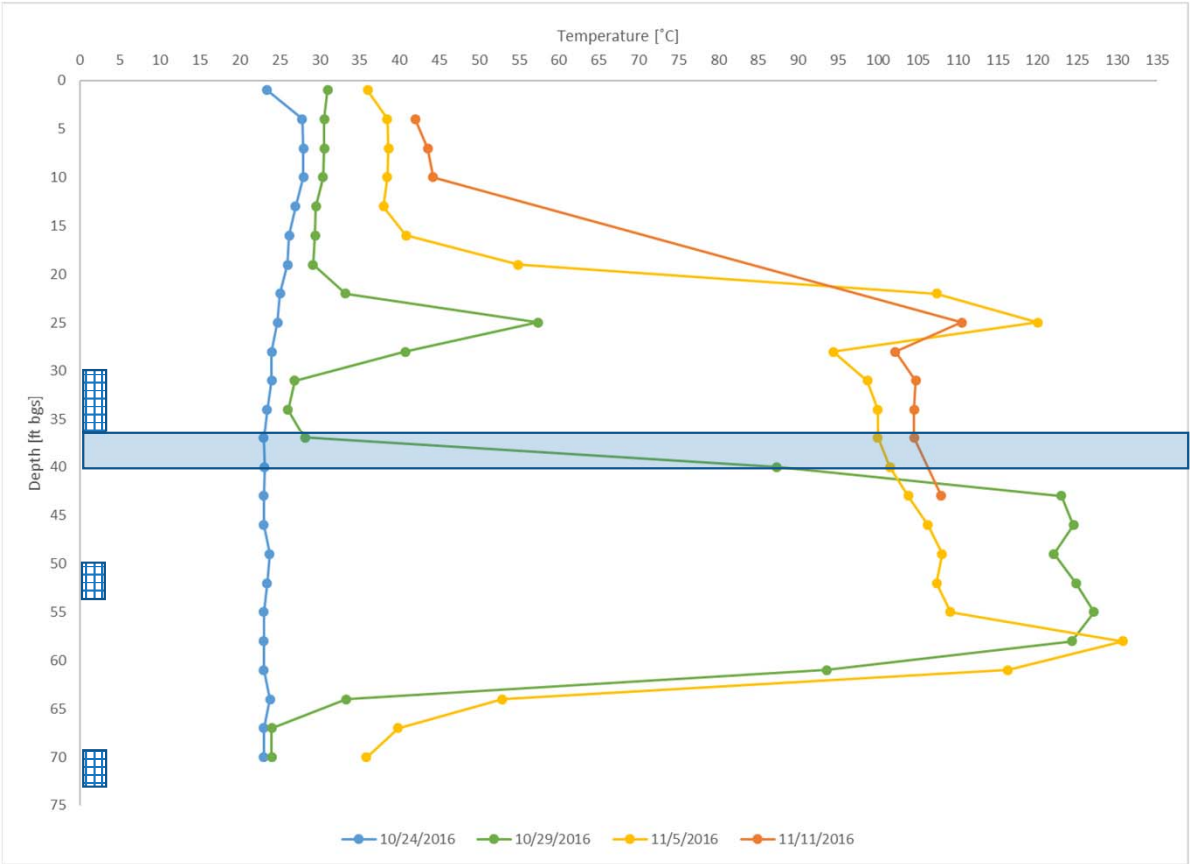

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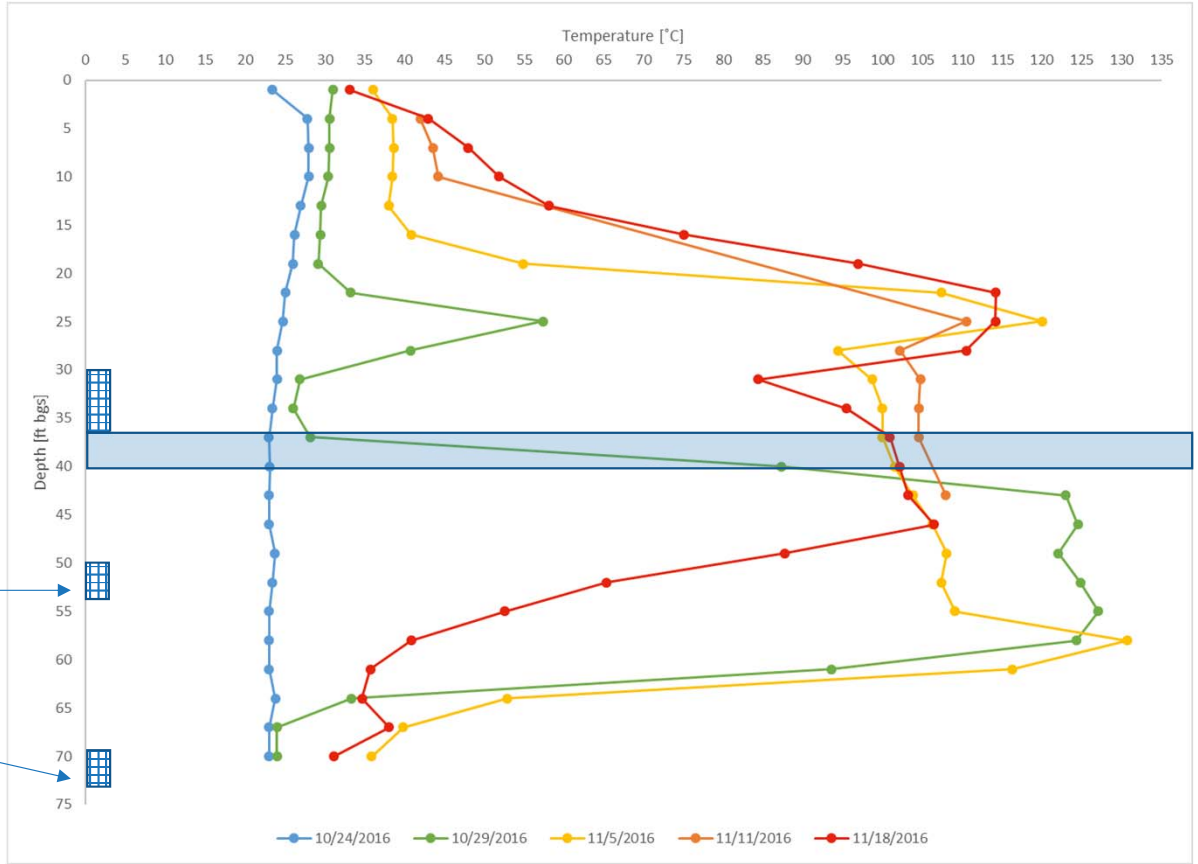
Pilot Test: Results (Temperatures)

Conductive heating in the clay layer in between two steam injection zones was able to close the temperature gap.

Steam injection at intermediate interval stopped on 11/16/2016

Steam injection at deep interval stopped on 11/12/2016



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Conclusions

- Treatability study suggested SEE would be most effective for site overall
  - Physical flushing of soil pores at 100˚C temperature allows for physical displacement of NAPL, heat enhanced hydrolysis in situ and vaporization of contaminants
- Pilot test confirmed the treatment approach
  - Steam and MPE well spacing and design
    - Lower permeability areas than expected– allowed for adjustment of well spacing in full scale design
    - Steam tests documented heterogeneity in subsurface and provided important data for model

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Conclusions, continued

- Corrosion testing showed 316 SS and PEEK would be recommended for any parts coming into contact with process water that are not easily replaced during operations.
  - Other more readily replaceable parts may use standard carbon steel
- Many lessons learned in groundwater treatment (Parsons)
  - Breakdown products formed contributed to high liquid phase granular activated carbon (GAC) consumption; bio treatment coupled with GAC and UV treatment proved most cost-effective.
- We are ready to move forward with full scale thermal design

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978-730-1200
afortune@cascade-env.com

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