# Complex Sites and Recalcitrant Compounds:

***Combining thermal technologies for more efficient remediation efforts***

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# Foreword

In situ Thermal Remediation (ISTR) - Thermal can treat almost all organic contaminants in almost any Site condition. But not always economical.

In Situ Chemical Oxidation (ISCO) – Can be economical and effective when the reagent is delivered well, and only a few injection events are necessary. Low K zones and high mass areas can be an issue.

In Situ Bioremediation (ISB) – Effective in large, diffuse, dissolved phase plumes, but less so where there is NAPL, high contaminant mass, unfavorable geochemistry, and in Vadose zone.

Often, the best solution for a site is to COMBINE TECHNOLOGIES spatially and(or) temporally. Picking the best suited technology for each zone and at varying stages in the project when it is more cost-efficient than using one technology past its sweet-spot.

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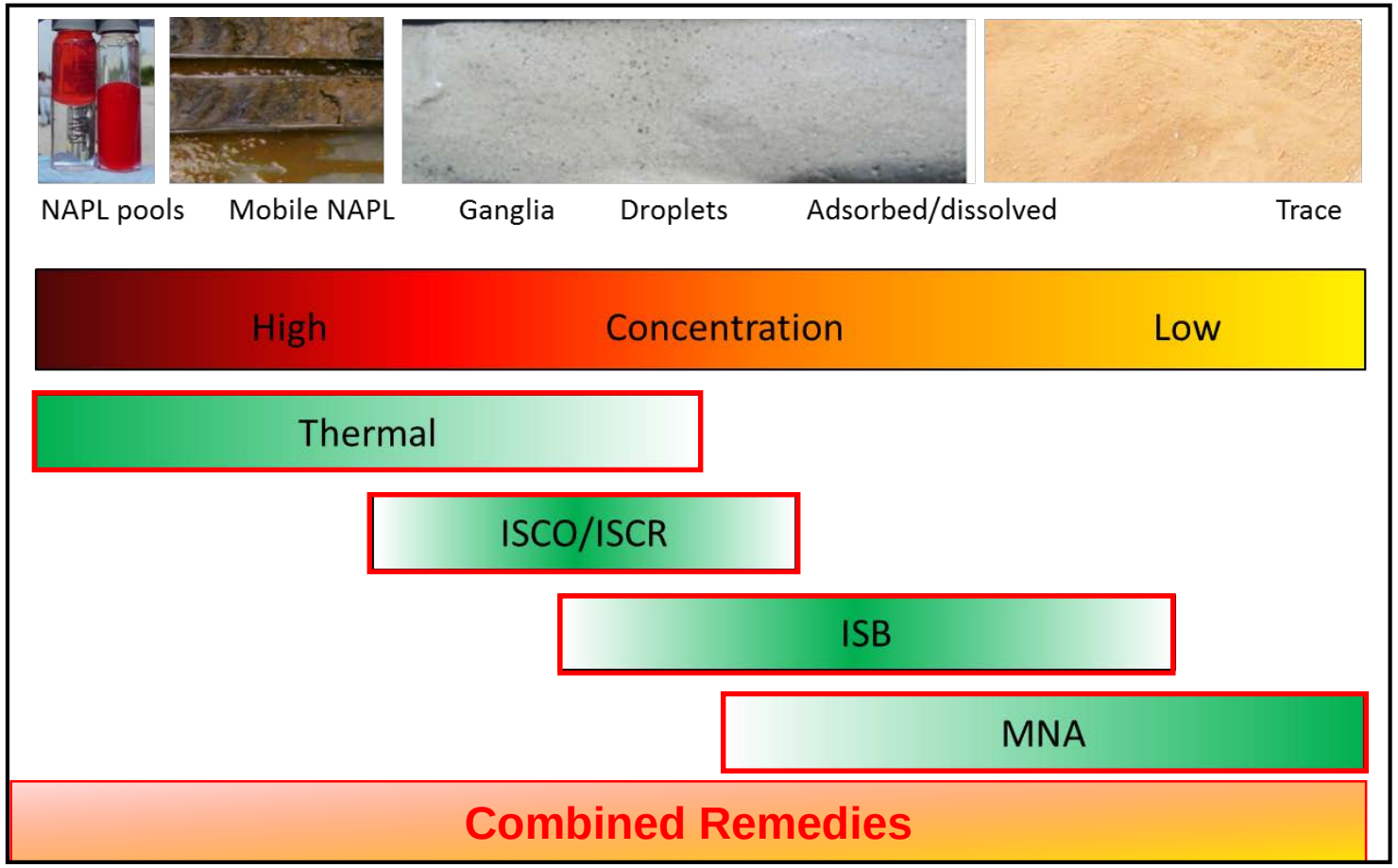
# Exploiting Technical Advantages – Optimizing Approach

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# Presentation Overview

- **ISTR Technologies**
  - Overview of Different ISTR Technologies Available
  - Comparison of ISTR Technologies
- **Combining ISTR Technologies**
  - TCH-SEE
  - ERH-SEE
  - ERH-TCH
  - ERH-TCH-SEE
- **Combined Remediation Approaches**
  - ISTR-Bio
  - ISTR-ISCO
- **Designing Smarter ISTR Systems**

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# Dominant Heating Technologies

| Thermal Conduction Heating (TCH / ISTD) | Steam Enhanced Extraction (SEE) | Electrical Resistance Heating (ERH) |
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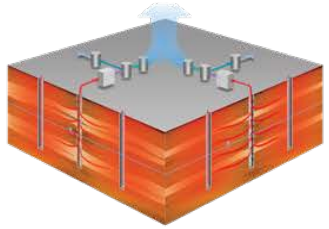
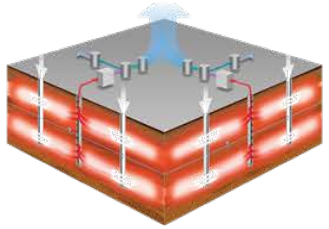
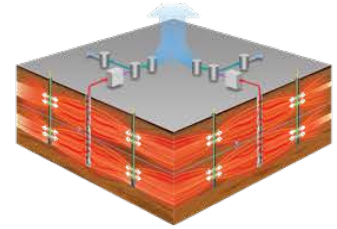
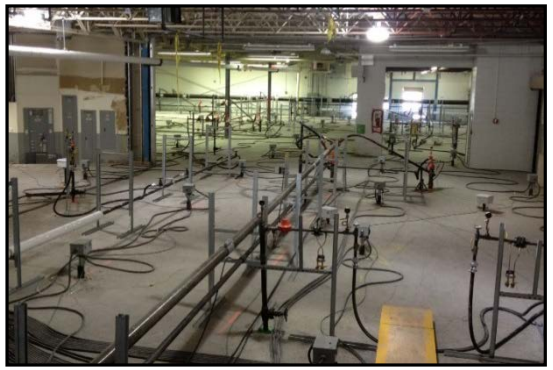
|  |  |  |
|  |  |  |

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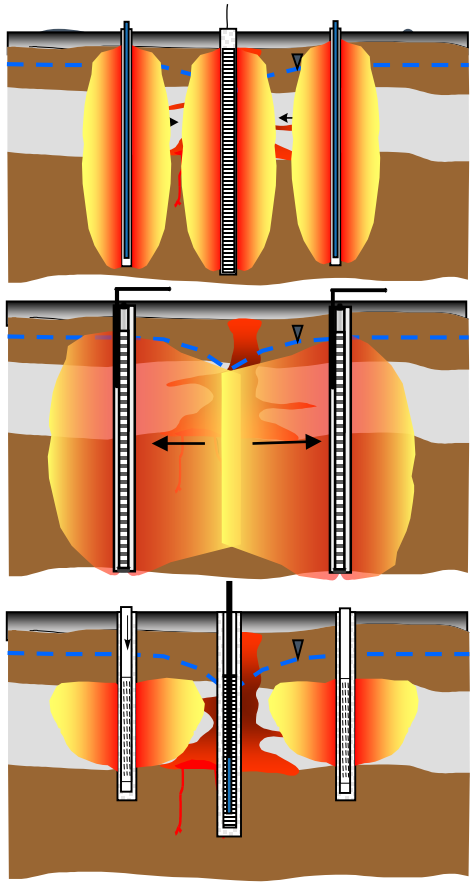
# Dominant Heating Technologies



## THERMAL CONDUCTION HEATING (TCH)

Utilizes circuits of electrically powered heaters which generate heat from the heater location and propogate heat through thermal conduction as heat energy is transferred from the heaters to the subsurface.

**20°C to 400°C**

## ELECTRICAL RESISTANCE HEATING (ERH)

Electrodes are installed in the subsurface such that current passes from one electrode to another. The soils resistance to that current flow generates heat within the subsurface.

**20°C to 100°C**

## STEAM ENHANCED EXTRACTION (SEE)

Ideal for free product and VOCs at sites with greater soil permeability and groundwater flow. Steam is injected through screened wells at designated depths and locations.  SEE is commonly used in combination with ERH and TCH, and is particularly effective for LNAPL sites with mobile product.

**100°C**

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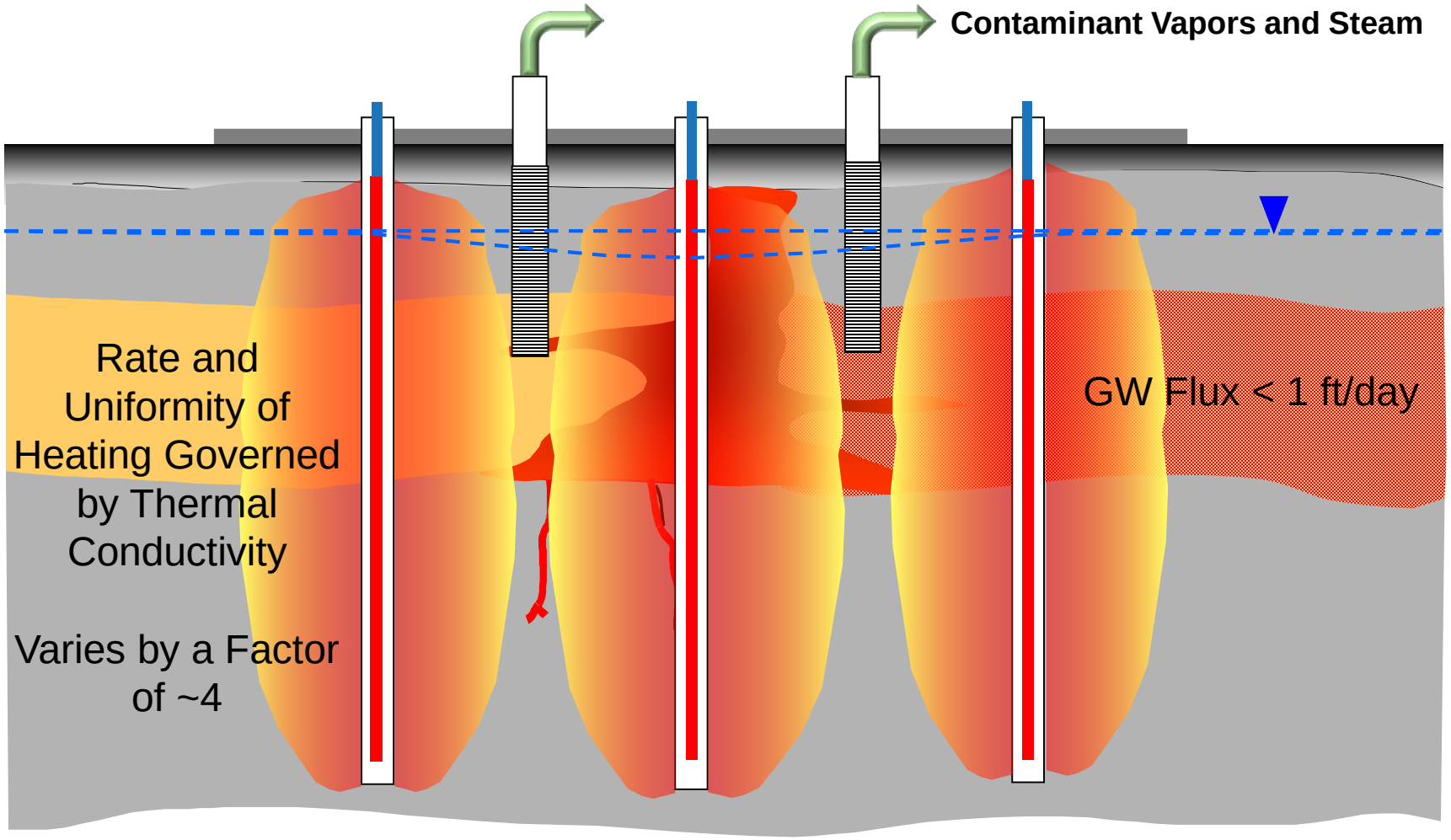
# Thermal Conduction Heating (TCH) – Electric Heaters




TCH + vacuum extraction = In Situ Thermal Desorption (ISTD)

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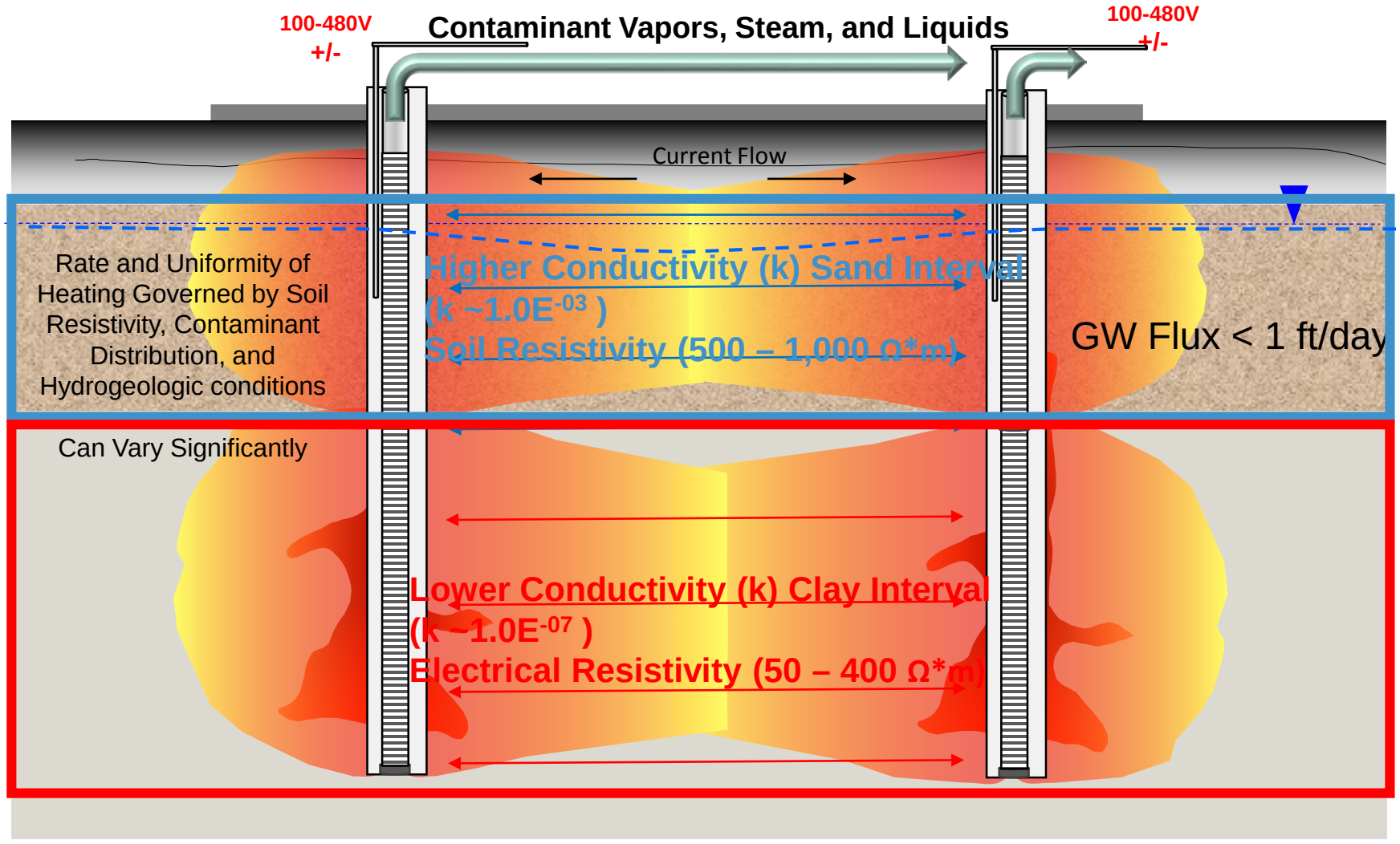
# Electrical Resistance Heating (ERH)

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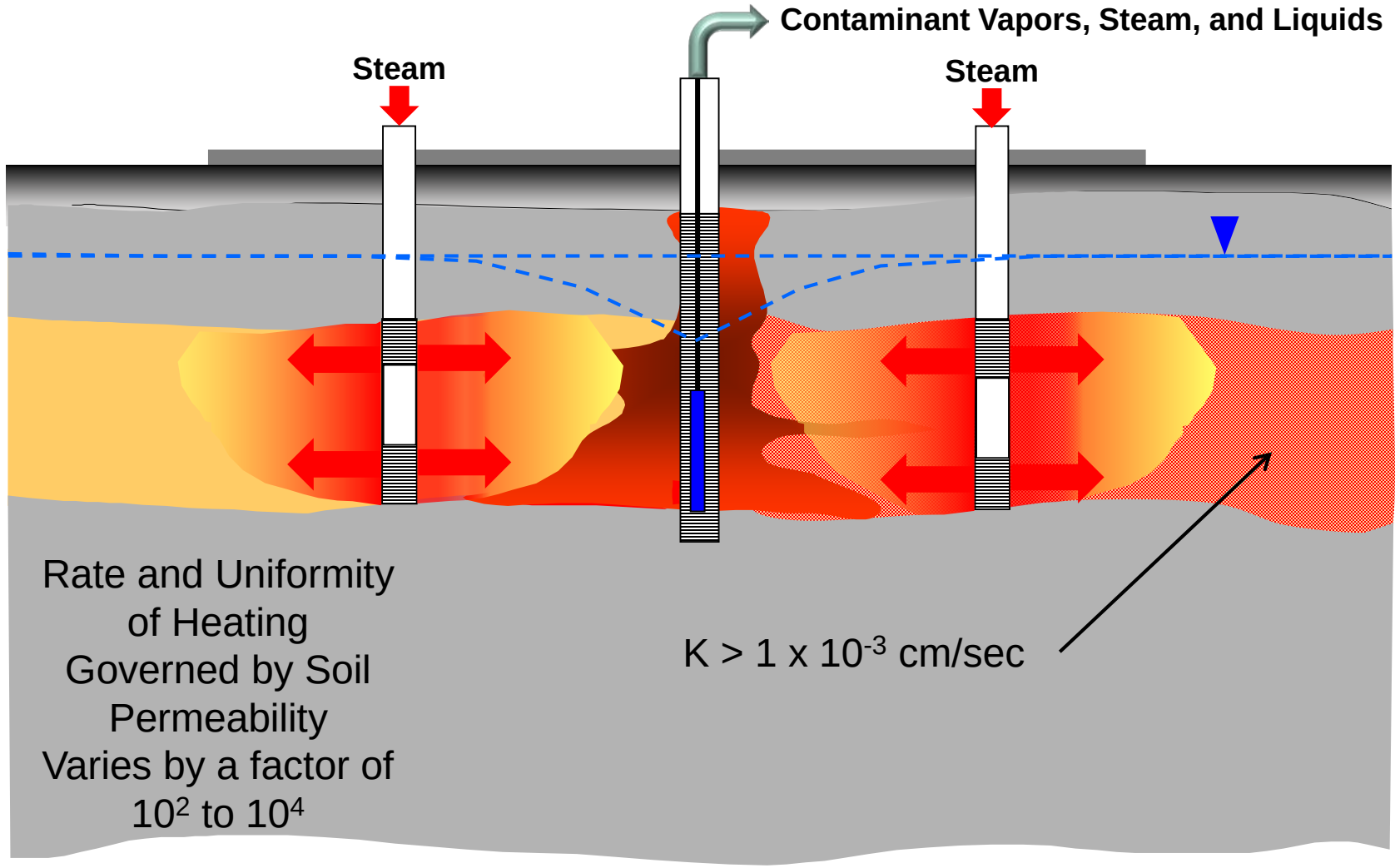
# Steam Enhanced Extraction (SEE)




K = Hydraulic conductivity

# Combined Approaches

- **Combined ISTR Technologies**
  - TCH-SEE
  - ERH-SEE
  - ERH-TCH
  - ERH-TCH-SEE
- **ISTR – Enhanced Bio & Enhanced Injection**
  - Post ISTR Bio-polishing
  - Low Temp ISTR – Heat Enhanced Bio
  - ISTR Source –Enhanced Bio Downgradient Plume
  - ISTR Source – Thermally Catalyzed Injection (Red/Ox)

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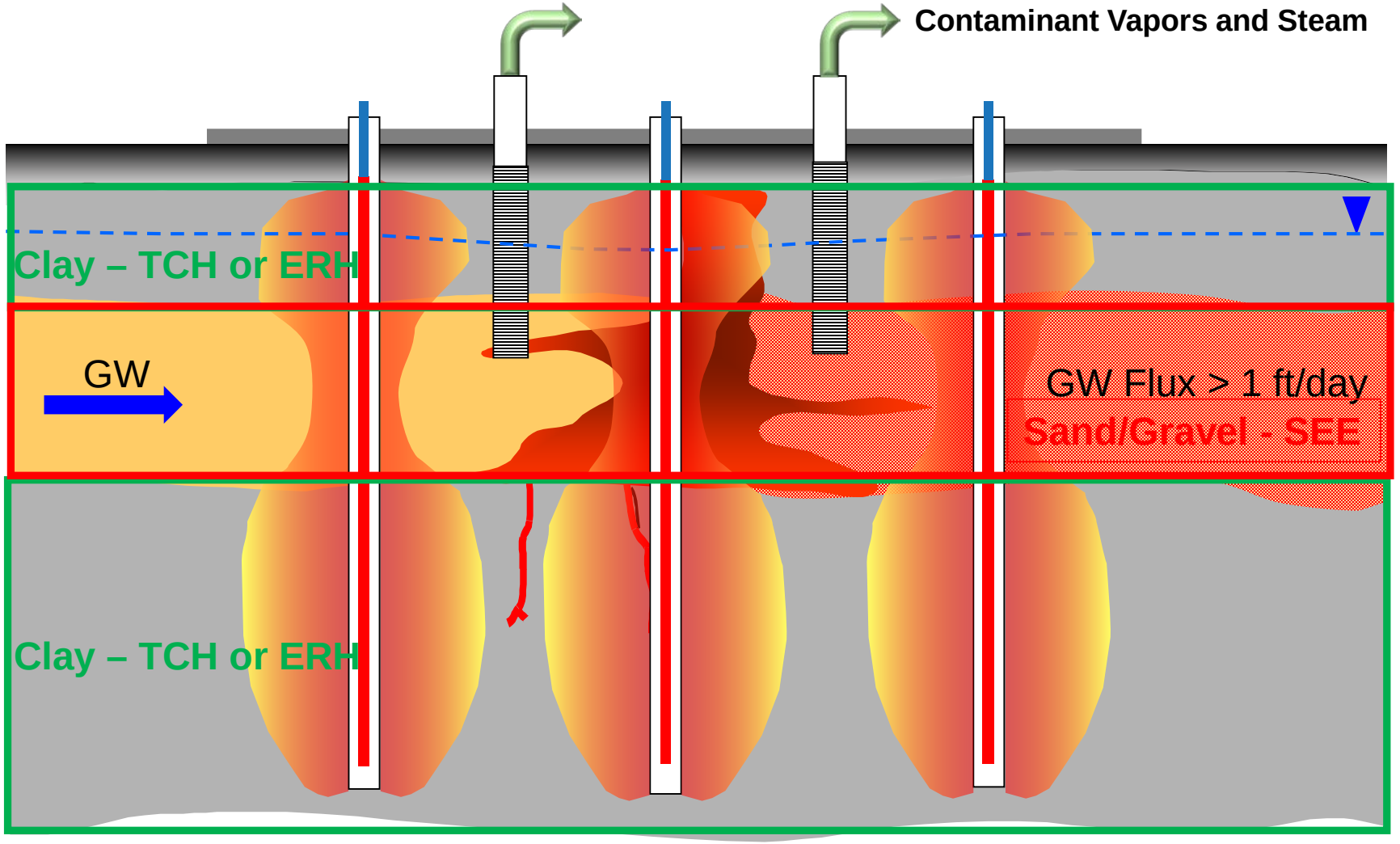
# Sometimes One Technology Alone Won't Get the Job Done

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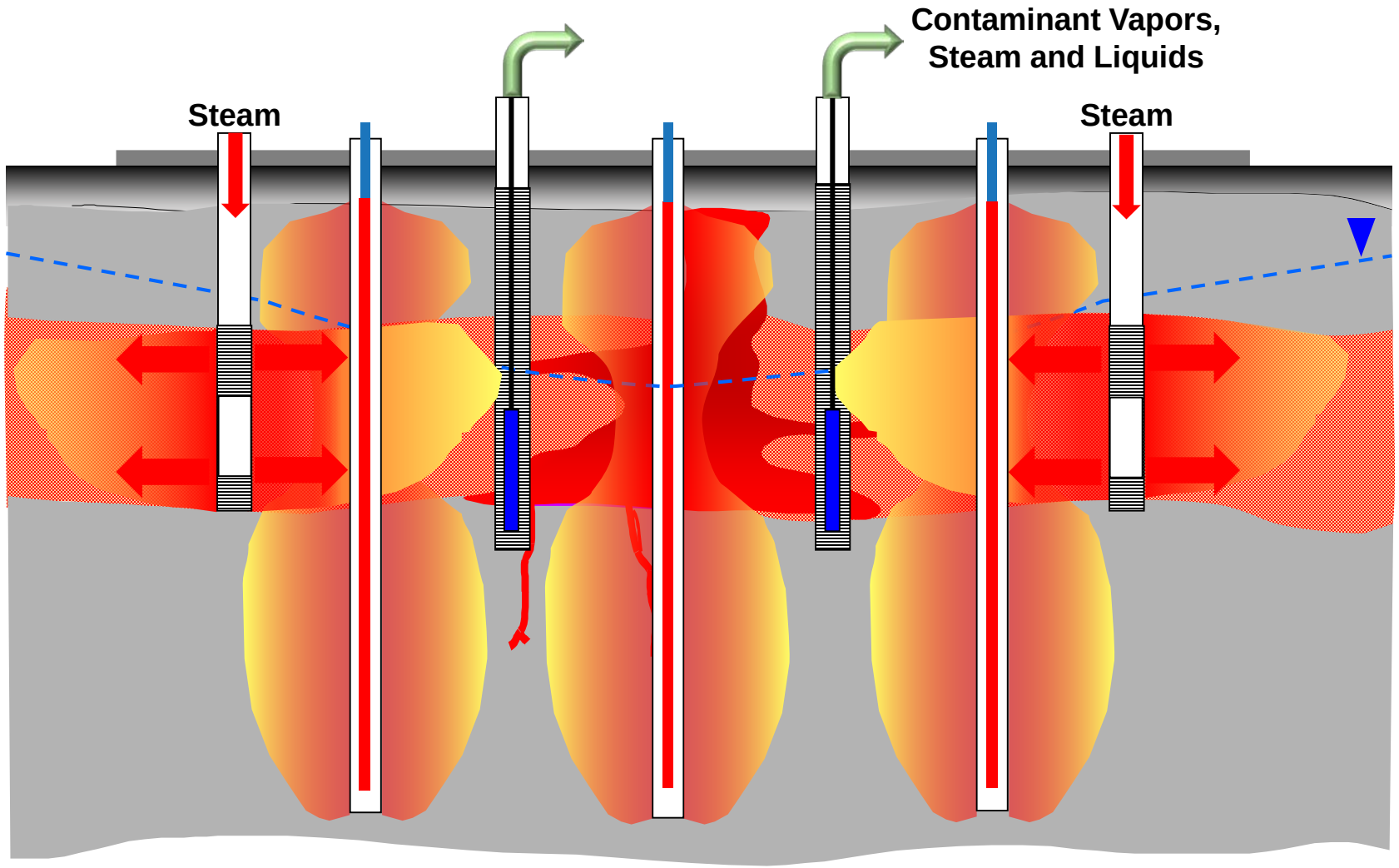
# TCH-SEE or ERH-SEE

Combine ISTR Technologies to Match Site Conditions

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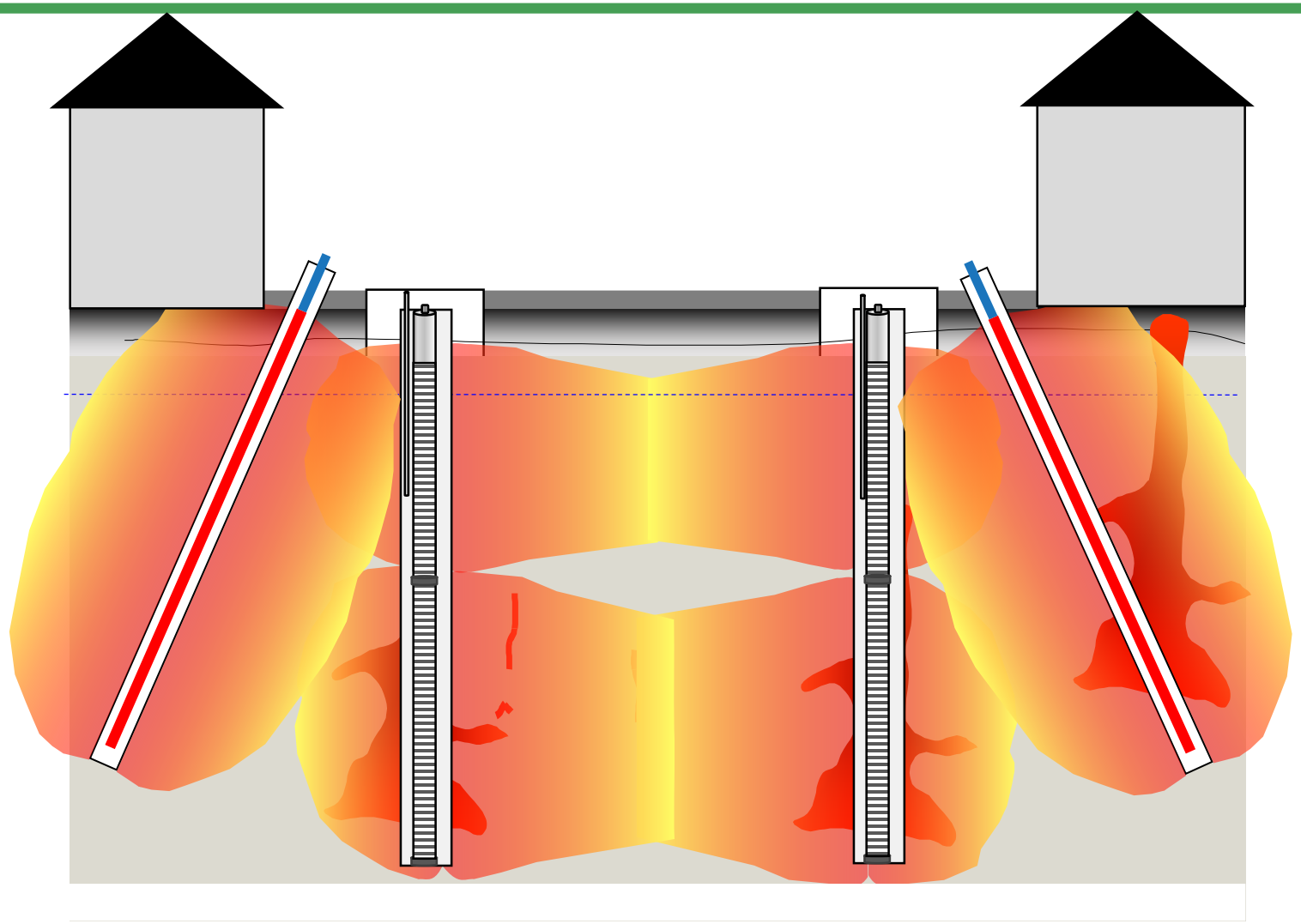
# Combine ISTR Technologies to Match Site Conditions (ERH-TCH)



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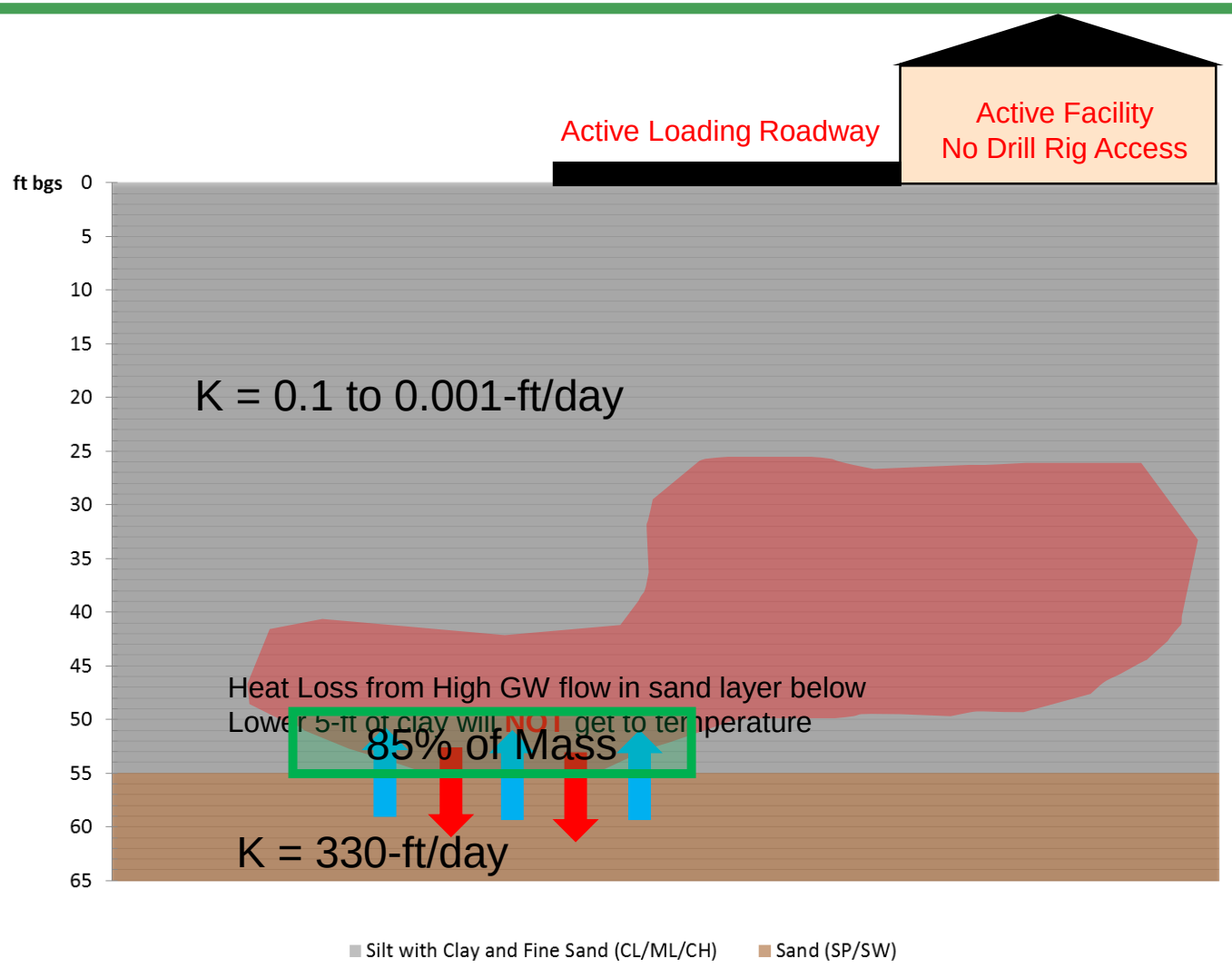
# ERH-TCH-SEE (Yes, Really!)

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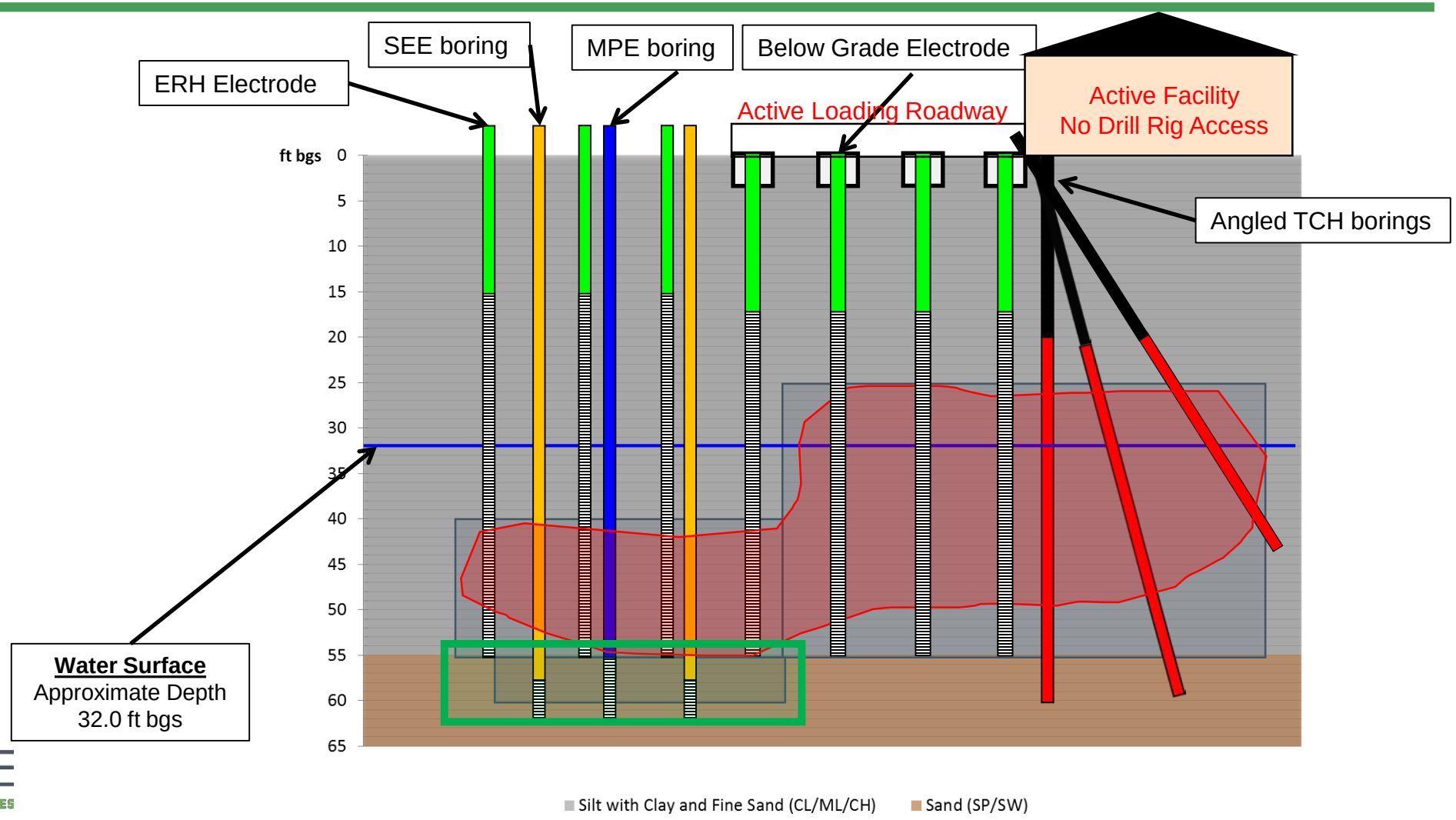
# ERH-TCH-SEE

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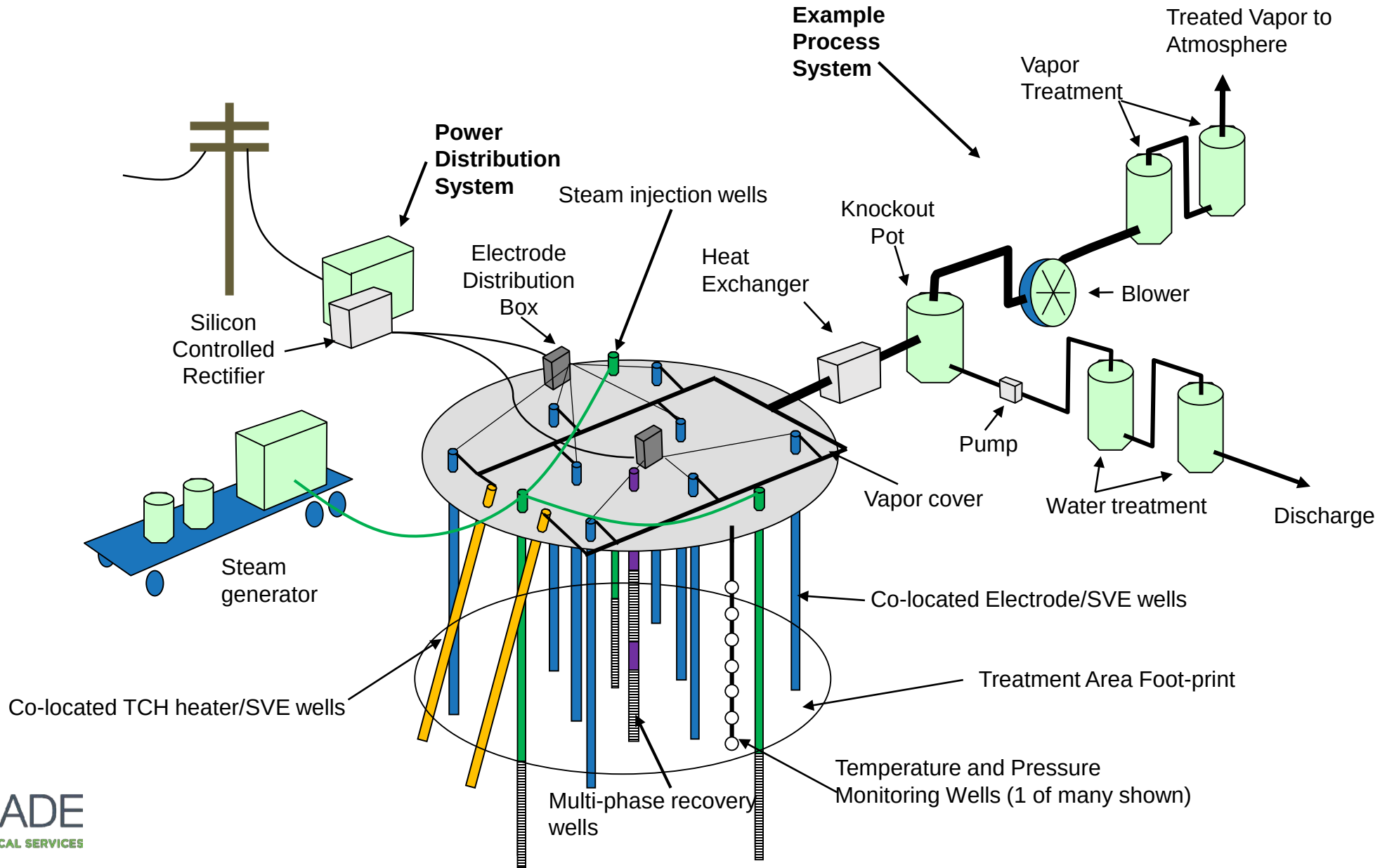
# Schematic of an ERH/TCH/SEE Site

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# How Does Thermal Impact Bio?

At an ISTR Site, heat accelerates dissolution/desorption but also accelerates biodegradation rates of petroleum hydrocarbons and chlorinated solvents.

**Petroleum** - BTEX biodegradation has been shown to triple (3X) from 10 to 20°C and petroleum hydrocarbon biodegradation rates have shown peak degradation rates between 30 and 40°C.

**Chlorinated Solvents** - Up to approximately 40°C, dechlorination rates are expected to double with every 10°C increase in subsurface temperature. Due to:

- Population Growth
- Electron Availability (release from organic material)
- Metabolic Rates/Degradation Rate

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# How Do We Combine the Two?

## Three different “ISTR-Bioremediation” Options

1. **Bio-Polishing**
2. **Low Temperature ISTR– Heat Enhanced Biodegradation**
3. **ISTR Source + Biodegradation of Diffuse GW Plume**


Image Taken From; https://i.pinimg.com/736x/7d/52/e8/7d52e8928a2111dbb93593e34d9959df.jpg

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# Combining ISTR with Bio

**Bio-Polishing** – Utilizing residual heat energy from completed ISTR to “polish” off source area contamination through enhanced biodegradation.

**Low-Temp Heat Enhanced Bio Application** – Deploy an ISTR system with the operational strategy of achieving 30 to 35 $^{0}$C temperatures throughout subsurface, maximizing hydrolysis and biodegradation reaction rates while increasing free product extraction (if exists).

**ISTR Source- Heat Enhanced Biodegradation Diffuse Downgradient Plume** – Deploy an ISTR system with the operational strategy of achieving 100$^{0}$C temperatures in the source area, and allow warm water to move downgradient to aid in the biodegradation of dissolved phase diffuse plume area.

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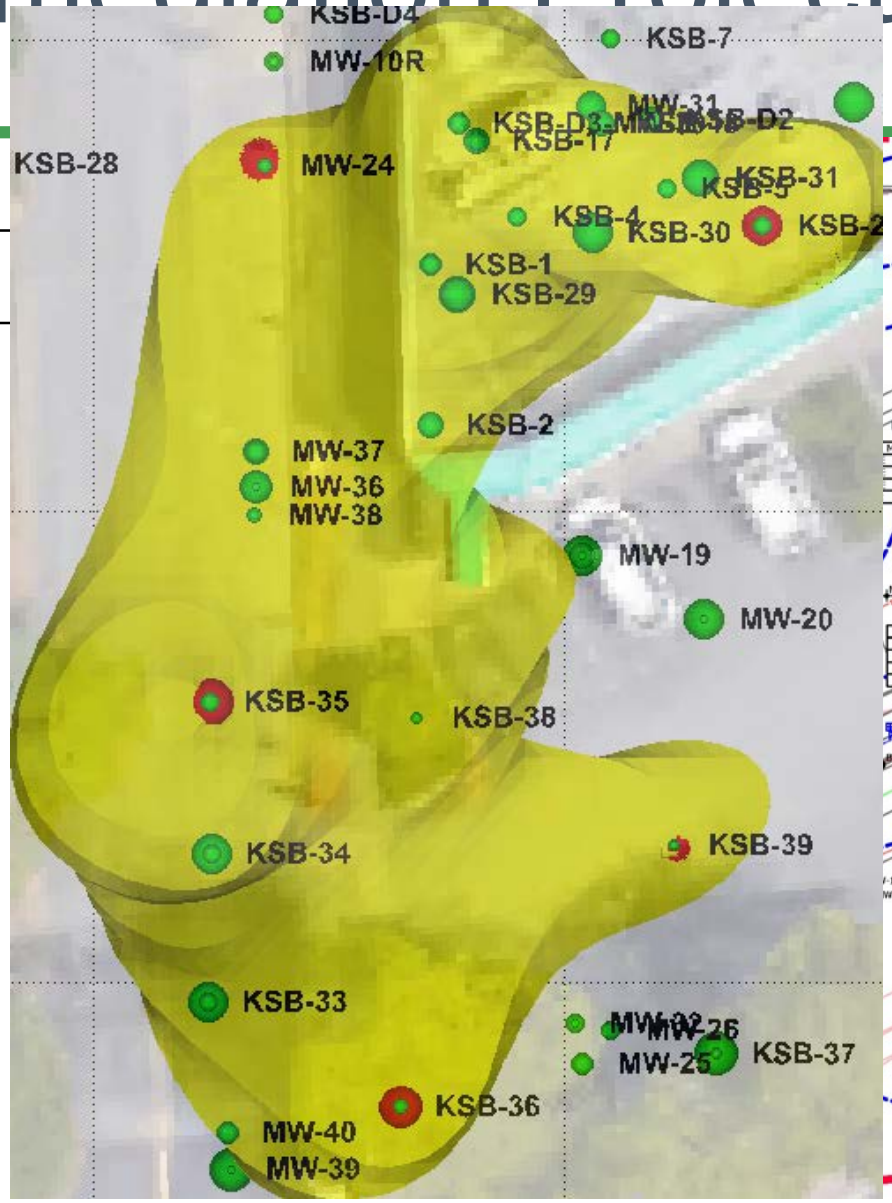
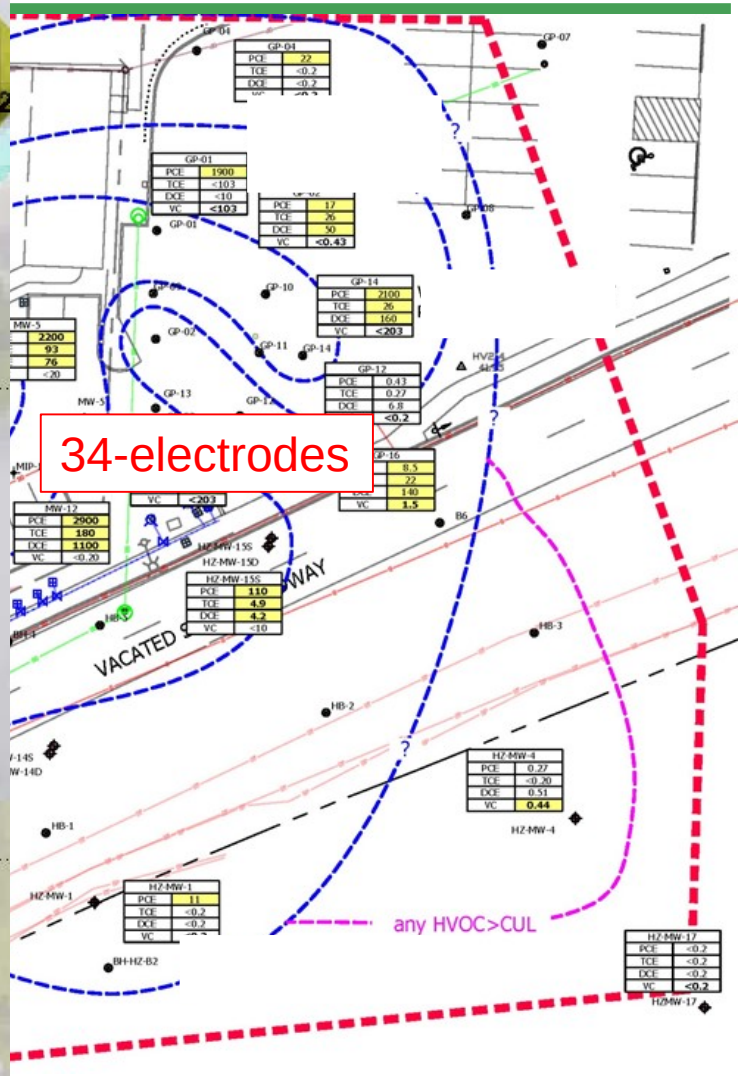
# ERH-Bioremediation Project

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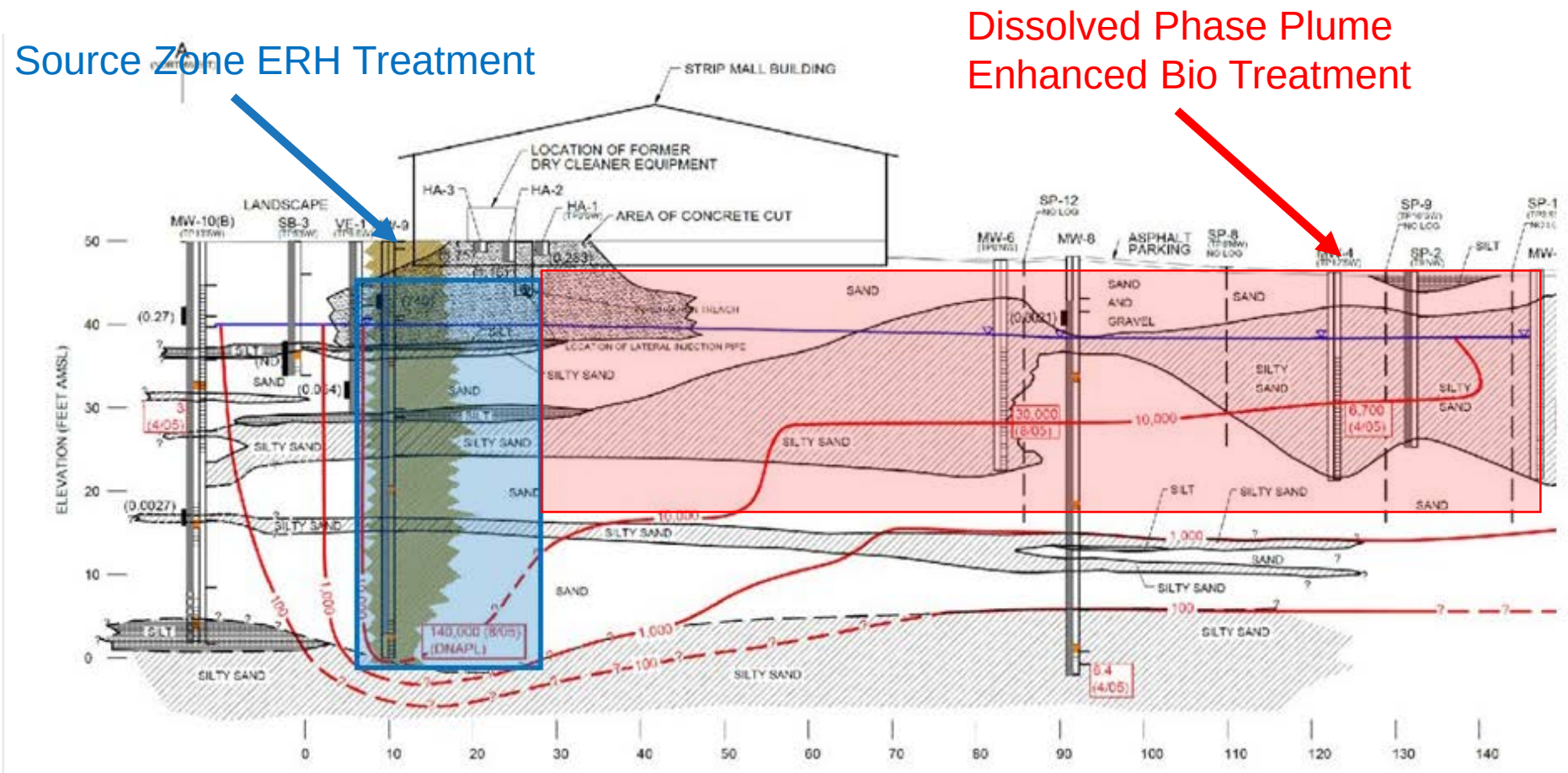
# ERH/Heat Enhanced Bio Project

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# ERH/Heat Enhanced Bio Project

## Seven Figure Savings! Still Treating to Site Clean-up Goals!

The post-ISTR heat enhanced biodegradation phase of the project will combine a series of injections along with a warm water recirculation system to treat the downgradient dissolved phase plume using residual heat from ISTR project.

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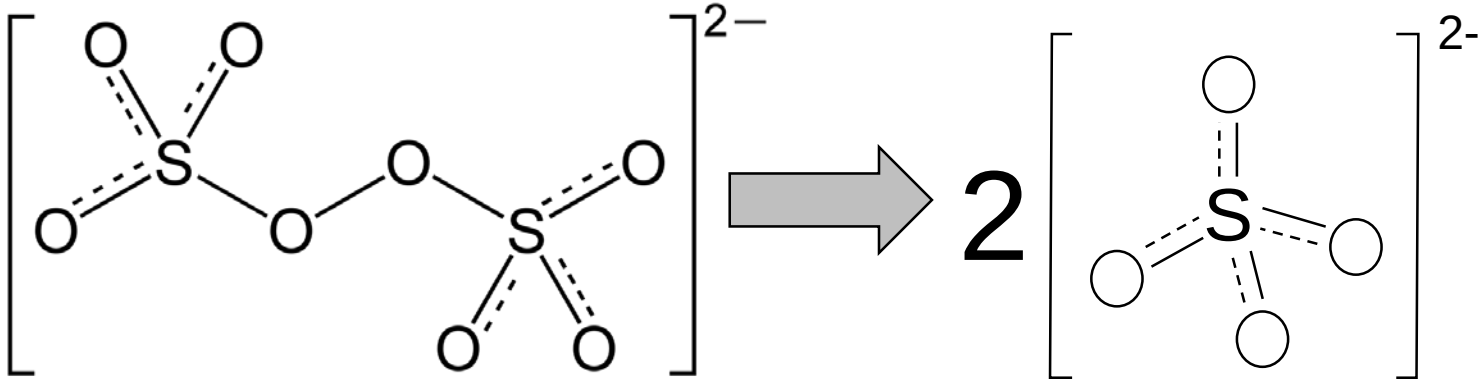
# Thermally Catalyzed Injection (ISCO)

Exposing a solution of sodium persulfate to elevated temperatures causes enhanced activation. The rate of persulfate activation increases with temperature. Thermal activation is thought to proceed where heat decomposes persulfate into two sulfate radicals.




Under thermally activated conditions (i.e., temperature of 40~100°C), there is considerable evidence that the persulfate anion can be converted to a powerful oxidant known as the sulfate free radical which could be used in situ to destroy HVOC contaminants in groundwater and sorbed to the soil matrix.

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*Liang et al., 2003, Liang et al., 2010, Liang & Bruell, 2008, Xiaogang et al, 2011

# Thermally Catalyzed Injection (ISCO)

## Horizontal Integration – ISTR Source ISCO downgradient

ISTR Source Zone Treatment using mass removal approach, combined with ISCO injection to remediate downgradient dissolved phase plume. Taking advantage of warm water effluent out of thermal treatment zone. Could be enhanced with warm water recirculation system.

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# Thermally Catalyzed Injection (ISCO)

## Vertical Integration
## Thermal Followed by Heat Activated Persulfate in Higher Transmissive Zones

- Same classic Site conditions described earlier, Clay - Sand – Clay with high GW in Sand interval.
- Target tight lithology with ISTR
- Once ISTR system turned off, the temperature of the transmissive zone can be closely monitored until it reaches the optimal range for persulfate activation.

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# Thermally Catalyzed Injection (ISCO)

## Temporally

- Prior to reaching asymptote in influent vapor stream concentrations, the average energy requirements are approximately 427 (± 157) kWh/lb of COCs removed.

- Once asymptote is reached, average energy requirements are approximately 3,914 (± 1,741) kWh/lb of contaminant mass removed, a 900% increase in energy demand per unit of contaminant mass removed.

- Continuing ISTR system operations once the asymptote recovery rate has been reached is neither economically nor environmentally responsible

**Turning off power to an ISTR project once these conditions have been reached, and implementing an injection strategy in the treatment area will take advantage of thermal activation while offering the potential for large project cost savings.**

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# Thermally Catalyzed Injection (ISCO)

## Temporally – ISCO followed by ISTR

- ISCO injections reduce mass on Site and shrink the footprint that will necessitate an ISTR approach.
- Net result is a smaller and more targeted thermal footprint and lower overall thermal costs. At the same time, able to meet return on remediation investment (RORI) needs by approaching the project in manageable investment stages.

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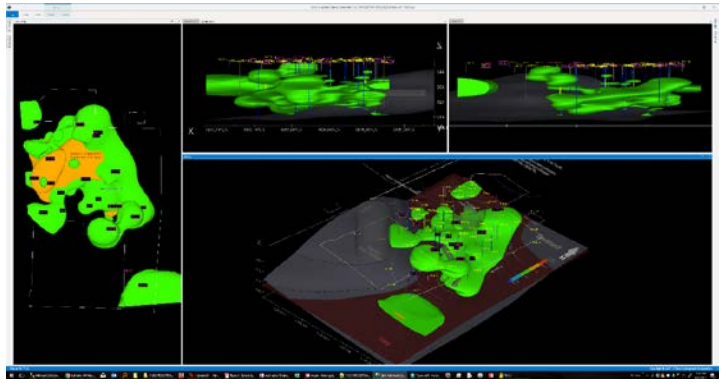
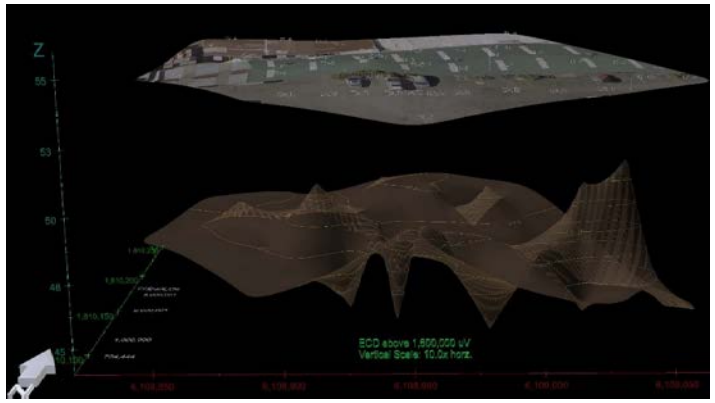
# WHERE DO WE START?

## KNOW YOUR SITE! A SOLID CSM IS THE FIRST STEP & THE MOST IMPORTANT!!!!

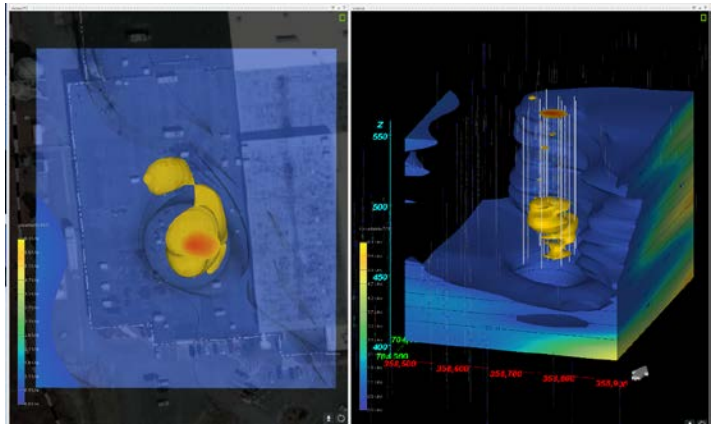


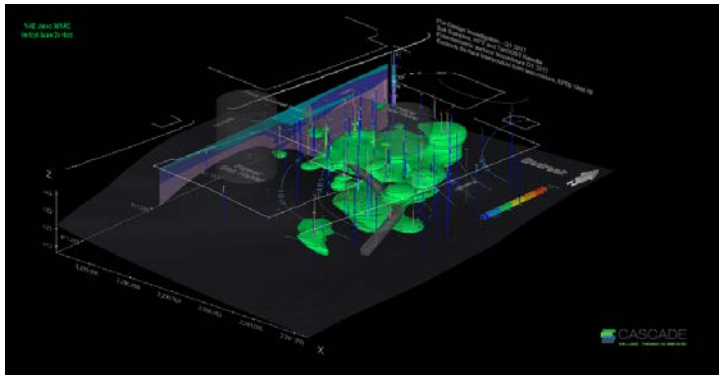


- **HRSC**
  - **Direct Push Technologies**
  - **Targeted Soil Sampling**
  - **Customized data collection (qPCR?)**
- **Data Management/Visualization**

**Define your Site properly – then develop the appropriate remediation strategy!**

**Don’t limit your remedial options to singular technologies!**





# Thank you

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