Thermal Remediation

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Presentation Overview

1) Introduction

2) Physical Mechanisms

3) Influencing Factors

4) Field Implementation

5) Demonstration Level

6) Applicability and Limiting Factors
Definition

- **Thermal remediation** is a technique where contaminants are removed from a medium by the application of heat to turn the contaminant into a gas. The gaseous contaminant is then removed from the medium.
How does it work?

• Heating the contaminated substance (soil)
• Gas is passed over the top of the substance
• As contaminant heats up it turns into a gas
  • Enter gas stream
• Gas stream leaves thermal desorption chamber
  • Collected for further treatment
Types of Thermal Remediation Strategies

• CROW Method (Contained Recovery of Oily Waste)
• Radiofrequency Heating
• Steam Enhanced Extraction
• Vitrification / Resistance Heating
Why and when do we use it?

• Fast method for cleanup
• Can be used in-situ or ex-situ
• Volatile and semi-volatile chemicals
  • BTEX
  • VOC’s
  • PAH’s
Physical Mechanism for Thermal Remediation

https://www.youtube.com/watch?v=RAMDw9n9AoE&t=13s
Contained Recovery of oily waste: physical mechanism

Primary Mechanisms

- decrease in density to make the NAPL float
- reduce viscosity and increase mobilization (expansion)
  - surface tension will change
- propagation of water front

Secondary mechanisms

- enhance solubility of target NAPL
- in-situ biodegradation enhancement
radiofrequency heating: physical mechanism

Electromagnetic energy → heating

- vaporizes low boiling point liquids (<100°C)
- increases evaporation rate for high boiling point liquids (>100°C)
- displacement by propagating steam front
  - increase permeability
  - decrease viscosity

*analogous to CROW method

Microwaves disrupt physical (molecular) structure of polar compounds (water) → kinetic energy → heating
Steam Enhanced Extraction: physical mechanism

- vaporization of low boiling point liquids (<100°C)
- enhancement of evaporation of liquids (>100°C)
- displacement of contaminants by condensation fronts
- after steam breakthroughs vapors are recovered directly
Vitrification/resistance heating: physical mechanism

- Joule resistance heating → melting → contaminant removal
- Accelerated chemical reactions (melt and pyrolysis zone)
- Organic vapor recovery in vacuum hood
- Pyrolysis of DNAPLs and vapors
Thermal Remediation Influencing Factors

Contaminant & Aquifer
Remediation Techniques to be Discussed

• CROW Method

• Radiofrequency Heating

• In situ “Steam Enhanced Extraction” (SEE)

• Vitrification – Electrical Energy
CROW Method Limiting Factors

• Factors relative to the contaminant:
  o DNAPLs, Semivolatiles removed:
    ▪ Coal Tar, Creosote, Heavy Oils
    • Contaminant density within 10-15% density of water
  o Designed to remove oil wastes denser than water, can work on LNAPLs too

Source: Federal Remediation Technology Roundtable
CROW Method Limiting Factors

• Factors relative to the aquifer:
  • Most suitable aquifer type: fine sands and cobble
  • Hydraulic Conductivity > $10^{-3}$ cm/s
  • High Permeability necessary

Source: Federal Remediation Technology Roundtable
Radiofrequency Heating Limiting Factors

• Factors relative to the contaminant
  • Used on high and low boiling point contaminants
  • Cannot be used on:
    • non-volatile contaminants
    • Heavy metals
    • Inorganic salts

Source: EPA Engineering Bulletin
Radiofrequency Heating Limiting Factors

• Factors Relative to the aquifer:
  • Penetration of radio waves into soils with high dielectric constants
  • Dielectric constant based on porosity and saturation
    • Higher dielectric constants for higher saturated soils
  • Most applicable in unsaturated zones
  • Low permeability soils increase costs and decrease yields
  • Useful in any type of soil

Source: EPA Engineering Bulletin
Steam Enhanced Extraction Limiting Factors

• Factors relative to the contaminant:
  • Used to treat the following contaminants:
    • Petroleum compounds
    • DNAPLs
    • Mixtures of various contaminants
  • Best technique to handle variations in contaminants

Source: EPA Superfund Record Collections
Steam Enhanced Extraction Limiting Factors

• Factors relative to the aquifer:
  • Geologic stratigraphy, surface conditions, chemical characteristics
  • Works effectively in both saturated and unsaturated zones
    • Highly saturated soils less ideal

• Soil type can be a limiting factor
  • Optimal K values > $10^{-3}$ cm/s
  • Less successful in silts and fine clay

Silts and fine clays: Less Successful

< $10^{-3}$ cm/s

Cobbles & Aggregates: Most Successful

Source: EPA Superfund Record Collections
SEE Aquifer and Microorganism effects

• Shallow depth implementation → Low P & T
  • Microorganisms will lie dormant during operation
    • Flourish upon completion of operation
  • “Bioremediation”

• Deep Implementation → High P & T
  • Aquifer will be sterilized during operation
  • Microorganism repopulation required upon completion
Vitrification (Electric Resistance) Limiting Factors

• Factors relative to the contaminant:
  • Utilized to remove VOCs and semi VOCs
  • The following “rule of thumb” contaminant concentrations are as follows:
    • Metal concentrations: 5-16% by weight
    • No continuous metal pollutant extending more than 90% of electrode spacing
    • VOCs < 5-10% by weight

Source: Federal Remediation Technology Roundtable
Vitrification (Electric Resistance) Limiting Factors

• Factors relative to the aquifer:
  • Treatment area and volume:
    • Large area **NOT** favorable due to the necessary **large energy draw**
      • Void space of treatment area should not exceed 150 ft³
  • Effective in any soil permeability
  • Soil must have hydraulic conductivity > 10⁻⁴ to be effective
  • **Vadose zone** soils only (heterogeneous or homogeneous)
  • Buried metal could short circuit treatment system

Source: Federal Remediation Technology Roundtable
Method Comparisons

• Heterogeneous soils: ERH more effective than SEE
• High permeability soils: SEE more effective than ERH
• Highly saturated soils: ERH most effective
• Unsaturated soils: CROW most effective
Field Implementations

• Types
  • Thermal Conductive Heating
  • Steam Air Injections
  • Electric Resistance Heating
Thermal Conductive Heating

• How does it work?
  • Drills are used to place the units into the ground
    • From 2 feet above and below the estimated contaminated zone
  • Series of:
    • electrical powered heaters
      • Spaced between 5-7 feet in distance
    • Vapor extractors

• These can be on different types of contaminants
  • Volatile- Reach temperatures of 100 C
  • Non- Volatile- Reach Temperatures of 150 – 325 C
Thermal Conductive Heating

• How it works in the ground?
  • Soil is heated around the contaminated area
    • Up gradient from a extraction area

• The fluid is then processed and the water and contaminants are separated
Steam Air Injection

• How does it work?
  • Implementation is similar to the Thermal Conductive Heating
    • Main difference is the injection of super heated steam into the ground
  • The placement of these injections can go below the Aquitard
Steam Air Injection

- Working in the ground
  - Steam in injected
  - Pushes contaminant to a Evaporation Extraction Point
  - Same layout of processing as the Thermal Conductive Heating
Electric Resistance Heating

• How does it work?
  • Electric Probes are placed in the ground
    • 14 – 24 FT apart
      • Depending on area of contamination
  • Moisture in the soil is heated to a point of 100 C
    • Allows the NAPL to rise through the ground from the steam produced
  • Collected at a collection point and the processed
Electric Resistance Heating
CROW: Brodhead Creek Superfund Site

Brodhead Creek Superfund Site, Monroe County, Pennsylvania

A coal gasification plant
Coal Tar
Polycyclic Aromatic Hydrocarbons (PAH)
CROW: Brodhead Creek Superfund Site

Free coal tar: 9000 gal  Residual coal tar: 300000 to 4000000 gal

Low yield $\rightarrow$ Overestimation

2008 Site Investigation on 5 ~ 10 feet subsurface:

CROW recover not ideal
SEE: Loring Air Force Base

Limestone, Northeast Maine fractured rock

Contaminants:

- PCE (38mg/L at 21 meters deep)
- TCE, cis-1,2-DCE, vinyl chloride,
- carbon tetrachloride, benzene, toluene

Vaporization
SEE: Loring Air Force Base

Limited funding

Water extracted: 223000 gallons

Steam condensate extracted: 33000 gallons
Lesson Learnt:

• Characterization effort: Fractured rock > Unlithified soils
• Rock thermal expansion not significant
• More injection ➡️ Faster heating
• DNAPL downward movement not observed
RFH: Volk Air National Guard Base, WI

First time

Fire training pit: JP-4 fuels

50000 gallons of hydrocarbon

Homogenous sandy soil → Ideal medium
RFH: Volk Air National Guard Base, WI

![Graph showing Volatile Removal (Purge and Trap Data)]
ISV: Wasatch Chemical In Salt Lake City, UT

Land: 18 acres  Various Industries

Soil: 3600 cubic yard to be treated

Contaminants:

Herbicides, pesticides, dioxins,

VOC and SVOC ~ PCE, TCE, 1,1-DCE and PCD
Figure 6: Concentrations of PCE, TCE, Vinyl Chloride and PCP in Well ES-01, October 2007 to November 2011

Contaminant Concentration (µg/l)

Sampling Date

Oct-06 Feb-08 Jul-09 Nov-10 Apr-12
### Table 10: 2011 Deep Aquifer Groundwater Monitoring Well Results

<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>PCE</td>
<td>5</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>46</td>
</tr>
<tr>
<td>TCE</td>
<td>5</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>31 J</td>
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<tr>
<td>1,1-DCE</td>
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<tr>
<td>Cis-1,2-DCE</td>
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<tr>
<td>Trans-1,2-DCE</td>
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<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>2</td>
<td>&lt;1</td>
<td>&lt;1</td>
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<tr>
<td>PCP</td>
<td>1</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

**Notes:**
- J: Data estimated due to associated quality control data.
- **Bold:** Detected concentration is equal to or exceeds MCL.
Applicability and Limitations
Contained Recovery of Oily Waste (CROW)

Superfund and hazardous waste sites

Aquifer contaminated by oily water

DNAPL

LNAPL

Fine sand to cobble aquifers

hydraulic conductivity $> 10^{-3}$ cm/sec

Can be modified to treat any size

Implemented at almost any site

Limitations to CROW

- Inorganic and VOCs
- High iron content
  - clog injection wells
- Subsurface only
- Contaminant can be pushed down
- Cost
- Not for long-term
Radio Frequency Heating

- Propagates through all media
  - solid, gas, and liquid
- Heats evenly and quickly
- Not limited
  - permeability, heterogeneity, and structural features
- Heats the target
- Directionally focused

Limitations to RF

Only one vendor in the U.S.

Debris

Can’t remediate

- inorganic, and low volatility contaminants

Rate of phase transformation between solid and vapor

Permeability

- tight soil
Steam Enhanced Extraction

- High permeability and groundwater flow
- Above and below water table
  - treats at significant depths
    - >100 ft
- Can treat
  - Volatiles and oils/LNAPLS
- Pressure cycling

[http://www.nap.edu/catalog/2311.html](http://www.nap.edu/catalog/2311.html)
Limitations of SEE

Design

Power

Effectiveness impacted by

- soil type, contaminant characteristics, geology, and hydrogeology
- Shallow contaminants
- Low permeability
- Mobilization and loss of NAPL
Vitrification/ Resistance Heating

EPA recommends for

- Inorganics, heavy metals, and radioactive material
- Durability
- Excellent weathering properties

Soils, sludge or earthen materials

Near surface contamination < 10m

No excavation required

http://www.cpeo.org/techtree/ttdescript/ssvit.htm
Limitations

- Long term
  - performance, stability, and leaching characteristics
- Volatilization/mobilization of contaminants
- Depth of contaminants
- Treatability studies required
- Future use
  - solidified material

Cost and Availability
Contained Recovery of Oily Wastes

Operational Cost: 50-125 $/yd³

available for use in wide variety of soil types

On site availability can take from 4 to 8 months

Radio Frequency Heating

Operational Cost: 65-160 $/yd^3

Table 2. Data Needs for Radio Frequency Heating. [7,8]

<table>
<thead>
<tr>
<th>Data Needs</th>
<th>Possible Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of soil</td>
<td>Low permeability soils increase costs and decrease contaminant recovery;</td>
</tr>
<tr>
<td></td>
<td>dielectric properties of soil determine RF power requirement</td>
</tr>
<tr>
<td>Presence of metal drums or metallic debris</td>
<td>Disrupts current flow; may interfere with electrode placement</td>
</tr>
<tr>
<td>Type of contaminants(s)</td>
<td>Requires supplementation with other treatment methods if nonvolatile contaminants (boiling points &gt;300°C), heavy metals, or inorganic salts are present</td>
</tr>
<tr>
<td>Soil moisture content</td>
<td>High moisture content increases energy requirements and impacts removal efficiency of organic contaminants</td>
</tr>
<tr>
<td>Flow rate and depth of groundwater table</td>
<td>Presence of fast moving groundwater in heated zone acts as an energy sink and negatively impacts process cost; may require diversion of water from heated zone by slurry walls, etc.</td>
</tr>
</tbody>
</table>
Steam Enhanced Extraction

Operational Cost: 50-125 $/yd³

https://clu-in.org/download/techfocus/thermal/ABR09-6-Thermal.pdf
Vitrification

Operational Cost: 400+ $/yd3

Wasatch Chemical plant

- Vitrification operations $375-425/ton
- Ancillary costs: treatability/pilot testing - $50-150K; mobilization - $150-200K; and demobilization - $150-200K

In a full scale operation in Grand Ledge Michigan where 3000 yd3 were treated at $267 per yd3 for mercury contaminated waste
Cost Comparison
Thermal methods

- Site preparation
  - Demobilization
  - Well drilling
- Operation
- Energy supply
  - High voltage connection
  - Fuel source for generator
- Tear down