Thermal Treatment Technologies: Lessons Learned
**Thermal Treatment Technologies: Lessons Learned**

**Performing Organization Name(s) and Address(es):**
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<table>
<thead>
<tr>
<th>a. REPORT</th>
<th>b. ABSTRACT</th>
<th>c. THIS PAGE</th>
</tr>
</thead>
<tbody>
<tr>
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</tbody>
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# THERMAL TREATMENT TECHNOLOGIES: LESSONS LEARNED

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<th>Topic</th>
</tr>
</thead>
<tbody>
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<td>10:35 AM</td>
<td>Welcome &amp; Introduction <em>(Dr. Hans Stroo)</em></td>
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<tr>
<td>10:35 AM</td>
<td>11:00 AM</td>
<td>Overview and State of the Practice Summary <em>(Dr. Paul Johnson)</em></td>
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<tr>
<td>11:00 AM</td>
<td>11:25 AM</td>
<td>Measuring and Modeling Thermal Treatment at Naval Air Warfare Center <em>(Dr. Bernie Kueper)</em></td>
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<tr>
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<td>12:05 PM</td>
<td>Simulating Thermal Treatment of Fractured Rock <em>(Dr. Ronald Falta)</em></td>
</tr>
<tr>
<td>12:05 PM</td>
<td>12:20 PM</td>
<td>Effects of Thermal Treatment on the Microbial Reductive Dechlorination Process <em>(Dr. Frank Löffler)</em></td>
</tr>
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<tr>
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<td>Adjourn</td>
</tr>
</tbody>
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# THERMAL TREATMENT TECHNOLOGIES: LESSONS LEARNED

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<tr>
<td>12:30 PM</td>
<td></td>
<td>Adjourn</td>
</tr>
</tbody>
</table>
Critical Evaluation of State-of-the-Art In Situ Thermal Treatment Technologies for DNAPL Source Zone Treatment

ER-200314

Jennifer Kingston¹,², Paul Dahlen¹, Paul Johnson¹

¹ - Arizona State University
² – Haley & Aldrich
Project Team

- **Principal Investigators**
  - Paul C. Johnson – Arizona State University
  - Eric Foote - Battelle

- **Others**
  - Jennifer Triplett Kingston – Arizona State University / Haley & Aldrich
  - Paul R. Dahlen – Arizona State University
  - Shane Williams - Battelle
Technical Objective

Develop a tool that can be used by practitioners, regulators, and site owners to anticipate the likely design and performance of thermal-based DNAPL treatment technologies at their sites, including:

- how the technology has been applied in that type of setting,
- the designs employed,
- the operating conditions,
- the performance monitoring that results are based on,
- the performance observed,
- indicators of success at other sites, and
- reasonable bounds on expected performance.

In this project, the performance metrics focus on improvement to groundwater quality and reduction in mass discharge (flux).
### Final Product/Tech-Transfer Concept

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Technology</th>
<th># of Sites</th>
<th># of Pilot Tests</th>
<th># of Full-Scale Systems</th>
<th># of Systems Since 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Generalized Scenario A:</strong> relatively homogeneous and permeable unconsolidated</td>
<td>Steam Heating</td>
<td>7</td>
<td>5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>4</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>9</td>
<td>7</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Generalized Scenario C:</strong> largely permeable sediments with interbedded lenses of low</td>
<td>Steam Heating</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>12</td>
<td>3</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>7</td>
<td>2</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td><strong>Generalized Scenario D:</strong> largely impermeable sediments with interbedded layers of higher</td>
<td>Steam Heating</td>
<td>17</td>
<td>6</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>15</td>
<td>4</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>15</td>
<td>5</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td><strong>Generalized Scenario E:</strong> competent, but fractured bedrock</td>
<td>Steam Heating</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Generalized Scenario F:</strong> karst and/or weathered bedrock</td>
<td>Steam Heating</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Generalized Scenario G:</strong> unknown</td>
<td>Steam Heating</td>
<td>15</td>
<td>2</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Resistance Heating</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>7</td>
<td>3</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

This table and others summarize key design and performance attributes, including numbers of energy delivery points, treatment times, temperatures reached, etc.
Technical Approach

Step 1: Collect, review, and compile historical performance data; then, using professional judgment, decide how best to capture the information in user-friendly performance summary tables linked to idealized conceptual models.

Step 2: Conduct supplemental post-treatment field investigations at four to six sites identified in Task 1. Sites to be chosen to best augment the information compiled in Task 1.

Step 3: Synthesize results – Utilize results from this study, other SERDP/ESTCP projects, etc. to identify performance bounds on improvements to groundwater quality and contaminant mass discharge (a.k.a. “mass flux”).
Summary of Applications Identified

<table>
<thead>
<tr>
<th>Technology</th>
<th>Number of Applications</th>
<th>Pilot-Scale*</th>
<th>Full-Scale*</th>
<th>Number Since Year 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam-Based</td>
<td>46</td>
<td>26</td>
<td>19</td>
<td>15</td>
</tr>
<tr>
<td>Electrical Resistance Heating</td>
<td>87</td>
<td>23</td>
<td>56</td>
<td>48</td>
</tr>
<tr>
<td>Conduction</td>
<td>26</td>
<td>12</td>
<td>14</td>
<td>17</td>
</tr>
<tr>
<td>Other/Radio-Frequency</td>
<td>23</td>
<td>14</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>182</strong></td>
<td><strong>75</strong></td>
<td><strong>98</strong></td>
<td><strong>84</strong></td>
</tr>
</tbody>
</table>

*Some sites have unknown application sizes and thus are not included in the Pilot- and Full-scale counts.*
### Characterization of Documentation

<table>
<thead>
<tr>
<th>Level of Data Quantity</th>
<th>Description</th>
<th>Number of Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>Application in progress</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>No documentation available at the time of this study</td>
<td>26</td>
</tr>
<tr>
<td>1</td>
<td>Insufficient data to assess performance of technology, but some design information</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>Limited performance data; some soils and/or groundwater concentration data and some operating data (e.g., temperature information)</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>Good performance data record, but insufficient for estimating differences between pre- and post mass discharge from source zone</td>
<td>26</td>
</tr>
<tr>
<td>4</td>
<td>Data sufficient for full assessment of performance (groundwater concentrations and mass discharge)</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td><strong>182</strong></td>
</tr>
</tbody>
</table>
## Basic Design Information

<table>
<thead>
<tr>
<th>Technology</th>
<th>Number of Sites With Target Treatment Zones With Sizes In This Range [ft²]</th>
<th>Number of Sites With Density of Energy Delivery Points (electrodes or wells) In this Range [# per 100 ft²]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;10⁴</td>
<td>10⁴ - 4x10⁴</td>
</tr>
<tr>
<td>Steam-Based Heating</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td>Resistance Heating</td>
<td>36</td>
<td>24</td>
</tr>
<tr>
<td>Conductive Heating</td>
<td>19</td>
<td>6</td>
</tr>
<tr>
<td>Other (including Mixing/Heating)</td>
<td>8</td>
<td>2</td>
</tr>
</tbody>
</table>

* For the three steam auger sites, the density is one energy point per cell. This does not fit into the number calculation so it is classified as <0.5.

<1/4 acre

<15 ft spacing
## Basic Operating Conditions

<table>
<thead>
<tr>
<th>Technology</th>
<th>Number of Sites With Temperatures in Target Treatment Zone in These Ranges [C]</th>
<th>Number of Sites With Active Heating Durations in These Ranges [y]</th>
<th>Number of Sites With Post-Treatment Monitoring in These Ranges [y]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;80</td>
<td>80 - 110</td>
<td>&gt;110</td>
</tr>
<tr>
<td>Steam-Based Heating</td>
<td>7</td>
<td>13</td>
<td>1</td>
</tr>
<tr>
<td>Resistance Heating</td>
<td>9</td>
<td>37</td>
<td>0</td>
</tr>
<tr>
<td>Conductive Heating</td>
<td>0</td>
<td>11*</td>
<td>12*</td>
</tr>
<tr>
<td>Other (including Mixing/Heating)</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

* One site had two different temperature values. The 80-110°C temperature was for the saturated zone and the >110°C temperature for the vadose zone.

Reflection of technology capabilities

↑ Durations often decided *a priori*
Geologic Scenarios

- **Scenario A**: relatively homogeneous and permeable unconsolidated sediments (mixtures of sands, gravels and silts, etc.)
- **Scenario B**: largely impermeable sediments with interbedded layers of higher permeability material
- **Scenario C**: largely permeable sediments with interbedded lenses of low permeability material
- **Scenario D**: competent, but fractured bedrock (i.e. crystalline rock)
- **Scenario E**: weathered bedrock, limestone, sandstone
Thermal Geologic Settings

- The majority of recent thermal applications were conducted in settings matching Generalized Scenario B and C.

- Scenario B accounts for 43% (36 of 84) of thermal treatments, two-thirds of which are ERH applications.

- Scenario C accounts for roughly another one-third (29%) of all applications.
Supplemental Field Investigations

Selection Criteria:

1. The hydrogeology of the site was reasonably well-characterized;
2. The aerial extent of the source zone was reasonably defined prior to treatment;
3. The depth to groundwater was <20 ft;
4. The total depth to impacted groundwater was <40 ft;
5. There was access immediately down-gradient of the treatment zone for drilling;
6. Direct-push technology could be used; and,
7. Local site personnel were present to facilitate the logistics associated with the sampling events.
Supplemental data collection emphasizes *post-treatment groundwater quality* and quantification of mass discharge to the aquifer.
## Site Characteristics

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Technology</th>
<th>Geology at This Site is Most Like This Conceptual Scenario&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Number of Permanent Monitoring Wells</th>
<th>Type of Chemicals Treated (C-chlorinated solvents, P-petroleum hydrocarbons, O-others)</th>
<th>Size of Target Treatment Area [ft&lt;sup&gt;2&lt;/sup&gt;]</th>
<th>Thickness of Target Treatment Interval [ft]</th>
<th>Depth to Water [ft]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hunter Army Airfield</td>
<td>ERH</td>
<td>A</td>
<td>12</td>
<td>P, O</td>
<td>30,000</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>Former Pumphouse #2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air Force Plant 4</td>
<td>ERH</td>
<td>B</td>
<td>21</td>
<td>C</td>
<td>21,780</td>
<td>37</td>
<td>30</td>
</tr>
<tr>
<td>Bldg. 181</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAS Building 5, Site 5-1</td>
<td>ERH</td>
<td>C</td>
<td>15</td>
<td>C</td>
<td>14,520</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>EDGY Area 3</td>
<td>ERH</td>
<td>C</td>
<td>17</td>
<td>C, P</td>
<td>18,200</td>
<td>30</td>
<td>N/A</td>
</tr>
<tr>
<td>Site 89</td>
<td>ERH</td>
<td>C</td>
<td>26</td>
<td>C</td>
<td>15,873</td>
<td>21</td>
<td>5</td>
</tr>
</tbody>
</table>

<sup>1</sup>Scenario Descriptors (for the target treatment zone)
- A - relatively homogeneous and permeable unconsolidated sediments (sands, etc.)
- B - largely impermeable sediments with interbedded layers of higher permeable material
- C - largely permeable sediments with interbedded lenses of low permeable material
- D - Competent, but fractured bedrock
- E - Weathered Bedrock

ERH - Electrical resistance heating

N/A - Not Available
### Mass Discharge Sampling

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Number of Transect Sampling Locations</th>
<th>Transect Length (ft)</th>
<th>Vertical Sampling Interval (ft bgs)</th>
<th>Number of Depth-Specific GW Samples</th>
<th>Number of Aquifer Specific-Capacity Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hunter Army Airfield Former Pumphouse #2</td>
<td>10</td>
<td>400</td>
<td>12 - 22</td>
<td>48</td>
<td>47</td>
</tr>
<tr>
<td>Air Force Plant 4 Bldg 181</td>
<td>10</td>
<td>170</td>
<td>29 - 35</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>NAS Site 5-1, Bldg. 5</td>
<td>7</td>
<td>115</td>
<td>6.5 - 21</td>
<td>39</td>
<td>39</td>
</tr>
<tr>
<td>Site 89</td>
<td>7</td>
<td>255</td>
<td>3 - 40</td>
<td>78</td>
<td>62</td>
</tr>
<tr>
<td>EGDY Area 3*</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**Note:** All analysis were performed via groundwater samples from permanent monitoring wells collected by the Corp of Engineers and were sent directly to ASU for analysis. Analyses were performed pre-, during, and post-treatment to gauge how contaminant flux changed while treatment was occurring.

- ft - Feet
- bgs – Below ground surface
- N/A – Not applicable to this site
Example 1

Camp Lejeune

- ERH Treatment 9/03 - 5/04
- DNAPL source
- 43 deep/48 shallow electrodes
Example 1: Sampling Locations

Supplemental data collection emphasizes post-treatment groundwater quality and quantification of mass discharge to the aquifer.
Example 1 – Field Work

Activities at Camp Lejeune:

- Generic Demo Plan submitted Sept. 2005
- Site-specific Demo Plan Feb. 2006
- Field Activities 2/23/06 - 3/3/06
- 60+ hydraulic conductivity tests performed in 14 wells at 8 locations
- Continuous soil core collected at transect location
- 26 groundwater samples collected from 26 wells at 16 locations
- 78 depth-specific groundwater samples collected from 7 direct-push locations; aquifer characterization mini-pump tests performed at each depth
- pH, EC, Temp., DO, ORP, PCA, TCA, PCE, TCE, DCE isomers, VC
Concentration Transect

**Camp Lejeune:** TCE concentrations measured along the transect perpendicular to groundwater flow on the down-gradient edge of the source zone.

![Concentration Transect Diagram](image)

Shadow of treatment zone with respect to GW flow direction
Estimating Mass Discharge

Data Presentation: hydraulic conductivities [cm/s] posted on top of TCE concentration contours [ug/L] along the transect perpendicular to groundwater flow on the down-gradient edge of the source zone

Mass Discharge Calculation: estimated to be about 30 kg/y using the ESTCP-sponsored Mass Flux Toolkit Software from GSI
Example 1 - Conclusion

It is difficult to determine treatment effectiveness at this site because impacts from DNAPL residuals outside of the treatment zone (that were not fully-delineated prior to the ERH design and application) are masking the treatment effect.
Example 2

NAS Alameda

- ERH Treatment 7/04 - 11/04
- DNAPL source
- 35 Energy delivery points with 4 sheet piles making-up an electrode
NAS Alameda ERH System Layout

Mass discharge transect

GW Flow
Example 2 – Field Work

Activities at NAS Alameda:

• Generic Demo Plan submitted Sept. 2005
• Site-specific Demo Plan May 2006
• Field Activities 6/1/06 – 6/9/06
• 40+ hydraulic conductivity tests performed in
• 2 continuous soil core collected at transect location
• 11 groundwater samples collected from 11 wells at 7 locations
• 29 depth-specific groundwater samples collected from 7 direct-push locations; aquifer characterization mini-pump tests performed at each depth
• pH, EC, Temp., DO, ORP, TCA, PCE, TCE, DCA, DCE isomers, VC
Concentration Transect

**NAS Alameda:** TCE concentrations measured along the transect perpendicular to groundwater flow on the down-gradient edge of the source zone.

![Concentration Transect Diagram](image-url)
Estimating Mass Discharge

Data Presentation: hydraulic conductivities [cm/s] posted on top of TCE concentration contours [ug/L] as measured along the transect perpendicular to groundwater flow on the down-gradient edge of the source zone.

Mass Discharge Calculation: estimated to be about 5.72E-03 kg/y using the ESTCP-sponsored Mass Flux Toolkit Software from GSI.
Example 2 - Conclusion

ERH treatment resulted in a significant reduction in contaminant concentrations throughout the 20 ft depth of treatment. Monitoring well concentrations for TCE ranged from 80 to 1 ug/L, while the direct push concentrations for TCE ranged from 49 ug/L to non-detect. Pre-treatment concentrations were in the range of 1,000 – 10,000 ug/L before full-scale treatment.
## Summary of Mass Discharge Results

<table>
<thead>
<tr>
<th>Site</th>
<th>Contaminant</th>
<th>Pre-treatment Discharge (kg/y)¹</th>
<th>Post-treatment Mass Discharge (kg/y)²</th>
<th>Post-treatment Mass Discharge per Linear Foot (kg/y/ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hunter Army Airfield</td>
<td>Total</td>
<td>$5.2 \times 10^1$</td>
<td>$1.9 \times 10^{-1}$</td>
<td>$1.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Former Pumphouse 2*</td>
<td>Contaminant</td>
<td>$6.0 \times 10^1$</td>
<td>$2.1 \times 10^1$</td>
<td>$1.4 \times 10^{-1}$</td>
</tr>
<tr>
<td>Air Force Plant 4 Bldg 181**</td>
<td>Flux</td>
<td>$4.9 \times 10^1$</td>
<td>$1.3 \times 10^{-1}$</td>
<td>$9.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>NAS Alameda Site 5-1, Bldg. 5*</td>
<td></td>
<td>$4.9 \times 10^1$</td>
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<td>$9.6 \times 10^{-4}$</td>
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<tr>
<td>Camp LeJeune Site 89*</td>
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<tr>
<td>Ft. Lewis EGDY Area 3***</td>
<td></td>
<td>$3.2 \times 10^1$</td>
<td>$2.1$</td>
<td>$1.9 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Notes:
1. Mass discharge calculations were based on monitoring well data from the documentation.
2. Mass discharge calculations were based on discrete-depth sampling data, or a combination of discrete-depth sampling data and monitoring well data.
3. Mass discharge calculations were base on discrete-depth sampling data only.
4. Mass discharge calculations were performed for discrete-depth sampling data only and discrete-depth sampling data with monitoring well data.
5. Mass discharge calculations were based on monitoring well data analyzed by ASU personnel.
## Post-Treatment Reductions

<table>
<thead>
<tr>
<th>Site No.</th>
<th>Heating Technology</th>
<th>Generalized Scenario/Site</th>
<th>Dissolved Groundwater Concentration Reduction</th>
<th>Mass Discharge Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>&lt;10x</td>
<td>10x</td>
</tr>
<tr>
<td>1</td>
<td>ERH</td>
<td>Generalized Scenario A (SDC)</td>
<td>10x</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>ERH</td>
<td>Generalized Scenario B+ (SDC)</td>
<td>&lt;10x</td>
<td>x</td>
</tr>
<tr>
<td>3</td>
<td>ERH</td>
<td>Generalized Scenario C</td>
<td>10x</td>
<td></td>
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<tr>
<td>4</td>
<td>ERH</td>
<td>Generalized Scenario C* (SDC)</td>
<td>&gt;10x to &lt;100x</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>ERH</td>
<td>Generalized Scenario C ^</td>
<td>&lt;10x</td>
<td>x</td>
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<tr>
<td>6</td>
<td>ERH</td>
<td>Generalized Scenario C ^</td>
<td>&lt;10x</td>
<td>x</td>
</tr>
<tr>
<td>7</td>
<td>ERH</td>
<td>Generalized Scenario C</td>
<td>&lt;10x</td>
<td></td>
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<tr>
<td>8</td>
<td>ERH</td>
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<td>Generalized Scenario C (SDC)</td>
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<td>10</td>
<td>ERH</td>
<td>Generalized Scenario C</td>
<td>100x</td>
<td></td>
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<tr>
<td>11</td>
<td>SEE</td>
<td>Generalized Scenario C</td>
<td>100x</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>SEE</td>
<td>Generalized Scenario C</td>
<td>10x</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>SEE</td>
<td>Generalized Scenario C ^</td>
<td>1000x</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>SEE</td>
<td>Generalized Scenario D*</td>
<td>&lt;10x</td>
<td>x</td>
</tr>
</tbody>
</table>

* Pilot application appeared to encompass the entire source zone based on documentation reviewed.

+ Mass discharge assessment involved two calculations using first only the post-treatment field investigation data and then the post-treatment field investigation data supplemented with data from a set of monitoring wells that were directly in line with the field investigation transect.

^ Site used two different vertical intervals to calculate mass discharge: 1) Only shallow geology and 2) shallow and deep geology.

SDC – supplemental data collection site for this project
# Mass Discharge Summary – All Sites

<table>
<thead>
<tr>
<th>Site No.</th>
<th>Heating Technology</th>
<th>Site</th>
<th>Contaminant</th>
<th>Pre-treatment Discharge (kg/y)</th>
<th>Post-treatment Discharge (kg/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ERH</td>
<td>Generalized Scenario A</td>
<td></td>
<td>5.2 x 10^1</td>
<td>1.9 x 10^-1</td>
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<tr>
<td>2</td>
<td>ERH</td>
<td>Generalized Scenario B</td>
<td></td>
<td>6.0 x 10^1</td>
<td>2.1 x 10^-1</td>
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<tr>
<td>3</td>
<td>ERH</td>
<td>Generalized Scenario C</td>
<td></td>
<td>4.0 x 10^-1</td>
<td>3.1 x 10^-2</td>
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<tr>
<td>4</td>
<td>ERH</td>
<td>Generalized Scenario C</td>
<td>Total Contaminant Mass Discharge (sum of all components)</td>
<td>6.8 x 10^2</td>
<td>8.2 x 10^-1</td>
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<tr>
<td>5</td>
<td>ERH</td>
<td>Generalized Scenario C</td>
<td></td>
<td>1.7</td>
<td>6.0 x 10^-1</td>
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<tr>
<td>6</td>
<td>ERH</td>
<td>Generalized Scenario C</td>
<td></td>
<td>2.4</td>
<td>9.7 x 10^-1</td>
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<td>ERH</td>
<td>Generalized Scenario C</td>
<td></td>
<td>9.4</td>
<td>2.7 x 10^-2</td>
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<td></td>
<td>4.9</td>
<td>1.6</td>
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<td></td>
<td></td>
<td></td>
<td>9.3</td>
<td>1.7 x 10^-2</td>
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<td></td>
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## Mass Discharge Summary – All Sites

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<td>8</td>
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<tr>
<td>9</td>
<td>ERH</td>
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<td>4.9 x 10¹</td>
<td>1.3 x 10⁻¹</td>
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<td>7.3 x 10⁻²</td>
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<td>SEE</td>
<td>Generalized Scenario C</td>
<td>1.3</td>
<td>2.8</td>
</tr>
<tr>
<td>13</td>
<td>SEE</td>
<td>Generalized Scenario C</td>
<td>1.9 x 10⁻²</td>
<td>1.8 x 10⁻⁷</td>
</tr>
<tr>
<td>14</td>
<td>SEE</td>
<td>Generalized Scenario D</td>
<td>2.9 x 10⁻⁴</td>
<td>1.1 x 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total Contaminant Mass Discharge (sum of all components)</td>
<td>9.7 x 10⁻²</td>
</tr>
</tbody>
</table>
Key Observations

● Data Collection:
  ♦ 182 applications conducted between 1988 and 2007 were identified and reviewed, including
    ▪ 87 electrical resistance heating,
    ▪ 46 steam-based heating,
    ▪ 26 conductive heating, and
    ▪ 23 other heating technology applications.
  ♦ This information indicates that a significant number of applications have occurred and it reflects the acceptance of in situ thermal technologies as viable source zone treatment options.
Key Observations

- Trends in Current Applications

- Approximately half of the 182 applications have been implemented since 2000 and over half of those have been ERH systems.

- ERH applications outnumber all other applications since 2000 by about a factor of three.

- There appears to be a recent trend in the increasing use of conductive heating and decreasing use of steam-based heating.
Key Observations

- Operating Conditions
  - Steam and ERH systems are inherently limited to operating temperatures at about the atmospheric boiling point of water (100 °C) or lower, and most systems operate close to that range.
  - Conductive heating is the only option for achieving significantly higher temperatures than that.
Key Observations

- Energy Delivery Design
  - There appears convergence towards relatively closely-spaced energy delivery points in the design of ERH and conductive heating systems.
    - Spacing for most ERH and conductive energy delivery points was less than 20 ft (6 m).
    - Steam application well spacing was usually greater than 20 ft (6 m).
Key Observations

- Treatment Zone Size
  - 117 of 121 treated areas were $<4 \times 10^4$ ft$^2$ ($<4000$ m$^2$ or an acre) and two-thirds of those were $<10^4$ ft$^2$ ($<1000$ m$^2$ or one-quarter acre treatment areas)
  - It is also apparent that the spatial extents of many source zones are likely ill-defined prior to treatment.
  - This results in under-sized target treatment zones, untreated source zone areas, and minimal beneficial impact to groundwater quality and mass discharge.
Key Observations

- Geologic Setting Effects
  - The effect of geologic setting on performance is difficult to discern in this data set.
    - Most treatment systems were installed in layered settings, characterized as either primarily fine-grained materials with higher permeability lenses (Generalized Scenario B) or primarily permeable materials with finer-grained lenses (Generalized Scenario C).
Key Observations

• Application Operating Times

♦ Most applications (independent of specific technology) lasted less than 6 months
  - There was little documentation as to the criteria or rationale used to determine the duration of operation.
  - There was little indication that the duration of operation was linked to mass removal-, groundwater quality-, or soil concentration-based criteria.
Performance Expectations

- Supplemental data collection indicated that a 100x reduction was achievable if the source zone was adequately delineated and fully encompassed during treatment and if the system was operated for a sufficient period of time.
  - Reductions of less than 100x were seen if the system was not operated for a sufficient period of time, and at sites where the source zone was not fully encompassed a reduction of <10x was typical.

- For sites with a concentration reduction of 100x or more, the final groundwater concentrations could be less than 100 mg/L for individual constituents which then could correspond to a mass discharge of 1E-01 kg/y or less.
Correlations

- Mass discharge reduction to temperature

  - Available data suggests that achieving a target temperature is insufficient to achieve good clean-up, and that application duration, in combination with the treatment zone temperature and treatment zone size likely control the performance.
Combined results from this project and vendor-authored/ASU-edited state-of-the-practice write-ups for key thermal treatment technologies in a users guide targeting program manager, consultant, and regulator audiences.

Thermal tech-transfer meeting in WA in early stages of the project.

Articles in press and under review in GWMR.

May 2009

1 Now with Haley and Aldrich, Lenexa, Kansas
Acknowledgements

The ASU and Battelle team would like to thank the following vendors and companies for their help with this project:

- TerraTherm (R. Baker, G. Heron)
- Shaw Environmental
- URS
- CES
- TRS
- Haley and Aldrich (M. Basel)
- ERM
- Army Corps of Engineers
- McMillian-McGee
- EPA
- Department of Defense – Military branches
- Department of Energy
- And the numerous consulting firms involved in thermal applications that helped us with documentation

The ASU and Battelle team would like to thank the following people for their help in accessing field sites:

- Ron Kenyon (Shaw)
- Daniel Hood (Navy)
- Bob Lowder (Marines)
- Steven Peck (Navy)
- Doug Delong (Navy)
- John McGuire (Shaw)
- Rick Wice (Shaw)
- George Walters (AF)
- Randall McDaniel (Shaw)
- Algeana Stevenson (AF)
- Phil La Mori (BEM Systems)
- Mark Kershner (AF)
- Emile Pitre (USACE)
- Kira Lynch (USACE)
## THERMAL TREATMENT TECHNOLOGIES: LESSONS LEARNED

<table>
<thead>
<tr>
<th>Start</th>
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<th>Topic</th>
</tr>
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<tbody>
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<tr>
<td>12:30 PM</td>
<td></td>
<td>Adjourn</td>
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</tbody>
</table>
Measuring and Modeling Thermal Treatment at Naval Air Warfare Center

Project # ER-200715

Professor Bernie Kueper
Department of Civil Engineering, Queen’s University

C. Lebron, G. Heron, J. Lachance, D. Rodriguez, D. Baston, A. Wemp, P. Lacombe, others...
Thermal Conductive Heating (TCH) in Fractured Rock

- Introduction to TCH
- TOPIC #1 - Influence of inflowing cold groundwater in fractures
- TOPIC #2 - Ability to observe boiling in rock matrix
- TOPIC #3 – NAWC Site pilot test results
- TOPIC #4 - Field parameters to measure
Thermal Conductive Heating

Compliments of Terratherm
Technology Description - Field

Compliments of Terratherm
TCH Heaters

Protected by U.S. and International Patents

Compliments of Terratherm
TOPIC #1 - Assess influence of inflowing cold groundwater on ability to reach boiling in rock


Temperature Between Thermal Wells

\( (q = 33.7 \text{ L/m}^2\cdot\text{day}) \)

\[ K_b = \frac{e^2 \rho g}{12 \mu} \left( \frac{e}{s} \right) \]

Increasing fracture aperture & spacing \((K_b\ \text{fixed})\)
TOPIC #1 - Conclusions

- Inflowing cold groundwater can prolong time required to reach boiling in rock
- Site characterization should focus on
  - Bulk K of rock (hydraulic testing),
  - Fracture spacing (e.g., downhole televsioner),
  - Hydraulic gradient
TOPIC #2 - Assess influence of rock properties on ability to reach boiling in rock matrix

- Heater wells (6)
- Heater-extraction well (1)
- Symmetry boundary
- Flow
- Treatment Zone
- 3 m well spacing
- $T = T_0$
- $P = P_0$
- $\theta = 30^\circ$
Boiling in fracture and matrix

- Start of boiling in fracture
- End of boiling in matrix
- End of boiling in matrix
- Start of boiling in matrix

Temperature (°C) vs. Heating Time (days)
Pressure spike in matrix corresponding to boiling

increasing porosity

Pressure (bar)

Heating Time (days)

φ = 0.005
φ = 0.01
φ = 0.03
φ = 0.05
φ = 0.10
TOPIC #2 - Conclusions

- It may be difficult to monitor progress of heating in bedrock because of:
  
  (i) Variability of boiling point in the rock matrix ($T$ is a function of $P$)
  
  (ii) Lack of well defined temperature plateau indicating boiling in matrix,

- Pressure monitoring may be beneficial

TOPIC #3 – NAWC Pilot Test

- Jet engine testing facility, 1950’s to 1990’s, West Trenton, NJ
- Decommissioned in 1998
- Pump & treat since mid-1990’s
- 2001: NAWC chosen as fractured rock hydrology research site under USGS Toxics Substances Hydrology Program.
- TCE > 20 mg/L
Performance Assessment: Physical Properties

Fraction organic carbon (F_{oc})
Performance Assessment: Physical Properties

Matrix Porosity (%)
Performance Assessment: Field Demo
Well Configuration

- **Sampling location** - Temperature monitoring point
- **Post-remedy sampling location**
- **Groundwater flow**
- **Temperature monitoring point**
- **Heater well**
**Field Demo Rock Temperatures – Averages per depth**

- Good heating from 5-35 ft
- Somewhat cooler 35-50 ft
Fluids Extracted

- Total liquid recovered (m³)
- Water (L/min)
- Steam condensate (L/min)
- Extraction rate (L/min)
- Total extracted volume (m³)

Date (mm/dd):
- 4/10
- 4/25
- 5/10
- 5/25
- 6/9
- 6/24
- 7/9
- 7/24
Performance Assessment

Field Demo VOC mass removal

<table>
<thead>
<tr>
<th>Date</th>
<th>Mass of VOCs (lbs)</th>
<th>VOC mass removed:</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/9</td>
<td>500 lbs</td>
<td>In vapor: 500 lbs</td>
</tr>
<tr>
<td>4/16</td>
<td></td>
<td>In liquid: 33 lbs</td>
</tr>
<tr>
<td>4/23</td>
<td></td>
<td>Total: 530 lbs</td>
</tr>
<tr>
<td>4/30</td>
<td></td>
<td></td>
</tr>
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<td>5/7</td>
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<tr>
<td>7/23</td>
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</tr>
</tbody>
</table>

Est. Total VOCs (TCE based on PID) [lbs] 500 lbs
PID as TCE [ppmV]
Performance Assessment

Collection & Analysis of Rock Samples for Treatment Confirmation
Performance Assessment: Field Demo

- Sampling location - Temperature monitoring point
- Post-remedy sampling location
- Groundwater flow
- Temperature monitoring point
- Heater well
Performance Assessment
Collection & Analysis of Rock Samples for Treatment Confirmation

Rock crusher
(Queen’s University)
Performance Assessment Summary
Collection & Analysis of Rock Samples for Treatment Confirmation

Crushed samples
Performance Assessment

TCE Concentration in Rock Samples

Averages BR-1:
Before: 37 mg/kg
After: 5 mg/kg

Average reduction in TCE:
84% BR-1
69% overall
Example Output
(z = 100 m, S = 5 m, e = 142 um, matrix porosity = 3.3%, matrix f_{oc} = 0.008)
TOPIC #4 – Field parameters to measure
TOPIC #4 – Field parameters to measure in evaluating use of a thermal remedy in bedrock

- Bulk hydraulic conductivity (hydraulic testing)
- Hydraulic gradient
- Fracture spacing (aperture can be calculated)
- Matrix porosity, permeability, and fraction organic carbon
- VOC concentrations in matrix
- Thermal properties of rock matrix
# Thermal Treatment Technologies: Lessons Learned

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<td>Adjourn *</td>
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</tbody>
</table>
Simulating Thermal Treatment of Fractured Rocks

Ron Falta
Clemson University
faltar@clemson.edu
Fractured Porous Media

Unfractured soil layer

Fractured rock
(limestone, sandstone, basalt, volcanic tuff) or unconsolidated material (clay, silt)

Unfractured rock or sediment layer

Shortly after a DNAPL spill

Later time – mostly dissolved
OUTLINE

- Key Processes
  - Energy balance and cost to heat to boiling temperature
  - Energy required to boil off water
  - Steam stripping of dissolved chlorinated solvents

- Numerical Multiphase Flow Models
  - Existing models and capabilities
  - Simulation of Clemson laboratory experiments

- Field Scale Simulations
  - Challenges and approaches
  - Multiple Interacting Continua (MINC)
  - Simulation examples
Energy Balance: heating up to boiling temperature

$$\Delta M^h = (1 - \phi) \rho_R C_R \Delta T + \phi S_w \rho_w C_w \Delta T$$

$$\phi = porosity \ (0.01-0.4)$$

$$\rho_R = rock \ grain \ density \ 2300-2700 \text{ kg/m}^3$$

$$\rho_w = liquid \ water \ density \ 1000 \text{ kg/m}^3$$

$$C_R = rock \ grain \ heat \ capacity \ 800-1200 \text{ J/kg}^\circ \text{C}$$

$$C_w = liquid \ water \ heat \ capacity \ 4200 \text{ J/kg}^\circ \text{C}$$

$$S_w = water \ saturation \ (0-1)$$
Example: cost to heat 1 cubic meter

\[ \Delta M^h = (1 - \phi) \rho_R C_R \Delta T + \phi S_w \rho_w C_w \Delta T \]

\[ = (1-.2)(2650)(1000)(90) + (.2)(1)(1000)(4200)(90) \]

\[ = 191 \text{ MJ/m}^3 + 76 \text{ MJ/m}^3 = 267 \text{ MJ/m}^3 \]

One kW-hr = 3.6 MJ, so 74 kW-hr to heat 1 m³

At $0.10$/kW-hr, this would cost $7.40$/m³
Typical heating pattern with time

Temperature, °C

Time

Dry-out
Boiling
Ambient
Boiling temperature depends on pressure (and dissolved components)

- Under vacuum conditions, the boiling point is lower:
  0.7 atm – boiling at 90°C
  0.5 atm – boiling at 80°C

Dissolved volatile compounds and gases also depress the boiling temperature
Steam stripping of dissolved volatiles: Udell’s 1996 analysis

Assume equilibrium batch conditions in some control volume. Steam vapor is generated by boiling, and leaves the volume, carrying contaminant vapors

\[
\frac{1}{\rho_w} \frac{d(M_w^{H_2O}C_w^c)}{dt} = \frac{1}{\rho_g} \frac{dM_w^{H_2O}}{dt} C_g^c
\]

rate of change of dissolved contaminant mass = rate of volumetric steam generation \( \times \) gas concentration

\[
M_w^{H_2O} = \text{mass of liquid water}
\]

\[
C_w^c = \text{dissolved concentration}
\]

\[
C_g^c = \text{gas concentration}
\]
After some calculus and algebra…

$$\frac{C_{w,c}}{C_{w,0}^{c}} = \left(\frac{M_{w}^{H_{2}O}}{M_{w,0}^{H_{2}O}}\right)\left(\frac{H \rho_{w}}{\rho_{g}} - 1\right)$$

\(H = Henry's\ const.\)

The exponent is huge because liquid water is \(\sim 1600\) times denser than steam vapor. Typical values for \(H\) at steam temperatures are about 0.3 to 7 depending on the chemical
Steam Stripping

- Steam stripping results in geometric reductions in dissolved concentrations of volatiles
- The stripping effect only occurs as liquid water is converted to vapor, and leaves the system
- A system may be at the boiling temperature, with highly variable rates of water phase change – this has tremendous impact on contaminant removal!
Once the rock is hot, boiling starts. Details of the boiling are very important

- Contaminant removal only occurs in the locations where liquid water is being converted to vapor
- The boiling may be well distributed in the rock, or it may be localized around the fractures
1D Simulations (T2VOC)

- 1 m³ block of rock with a single fracture. Fracture and matrix initially saturated with water containing 10 ppm TCE.
- Heat the block with 200 W power.
- Drop pressure in fracture and simulate mass in matrix with time

Consider three conditions:
  a.) steam is mobile in matrix
  b.) steam is immobile in matrix
  c.) intermediate vapor mobility

Add 200 W power uniformly to matrix (simulating electrical resistance heating)
RESULTS: 1-D Simulations

Vapor phase forms as isolated bubbles in matrix, pushing liquid water into fracture where it boils. Heat to sustain fracture boiling comes from thermal conduction.

Vapor forms in matrix and is mobile, flowing freely to fracture. All boiling occurs in matrix, and steam stripping effect is similar to Udell (1996) model.

Initially vapor phase pushes liquid water into fracture where it boils. Later, vapor phase becomes more mobile and flows out to fracture. Boiling moves from fracture to matrix with time.
Energy required to boil away pore water

- The heat of vaporization of water is about 2,260,000 J/kg
- From the previous heating example, there was about 192 kg of liquid water in each cubic meter of rock
- To boil away 50% of this water would require 217 MJ, or about 60 kW-hr. At $0.10/kW-hr, this would cost $6.00/m³ which is comparable to the cost to raise the temperature up to the normal boiling point
- Our laboratory experiments and numerical simulations show excellent contaminant removal with 40-60% liquid water removal during heating.
Numerical Models for Steam Remediation

- There are many existing multiphase flow codes that can be used for modeling thermal remediation in fractured heterogeneous porous media. A partial list:
  - T2VOC (Falta et al., 1992; Falta et al., 1995)
  - NUFT (Nitao, 1993)
  - COMPFLOW (Forsyth, 1994)
  - MUFTE (Helmig et al., 1994)
  - MAGNAS (Panday et al., 1995)
  - STOMP (White and Oostrom, 1996)
  - TMVOC (Pruess and Battistelli, 2002)

These codes have similar numerical formulations and process capability
TMVOC (Pruess and Battistelli, 2002)

- 3D integral finite difference formulation for fractured and heterogeneous media
- Multiphase diffusion with tortuosity effects
- Assumes local (gridblock) chemical equilibrium with linear adsorption isotherms, first order decay of dissolved contaminants
- Includes noncondensible gases (air, etc), and can simulate dry superheated conditions
- Maximum temperature is limited to critical point of water (374 °C)

- 3 phase flow (gas, aqueous, NAPL)
- Full heat transfer and thermodynamics with evaporation, boiling and condensation of water and multicomponent NAPLs
- Temperature dependent vapor pressure, solubility, and Henry’s constants for contaminants
A GUI for TMVOC is available (PetraSim)
Simulation of Laboratory Experiments (SERDP ER-1553)

Field Scale

Fracture-matrix interaction is locally ~ 1-D

Simulated fracture on one end

Unfractured matrix material (silt, clay, limestone, sandstone, etc.)
Experimental Setup

- Data cable
- Fluid in during circulation
- Pressure transducer
- Fluid recovery
- Power
- Power cable
- Ribbon heater wrapped around sample
- Flange with pass-throughs for data, fluids and power
Experimental Results
Chen et al., 2010

Temperature (°C)

Open valve
Turn off heater

Condensate flow rate (ml/h)

Open valve
Turn off heater

Volume of condensate produced (ml)

1,2-DCA
NaBr
**TMVOC model: 2d r-z model. Simulating end effects is critical here**

<table>
<thead>
<tr>
<th>Subdomain</th>
<th>Porosity</th>
<th>Permeability (m²)</th>
<th>Density (kg/m³)</th>
<th>Thermal conductivity (W/m°C)</th>
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<td>100</td>
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Chen et al., 2011
Simulation Results: temperature and condensate production

Chen et al., 2011
Simulation Results: temperature and condensate production

Chen et al., 2011

- Model is predicting a slower transition to vapor flow conditions
- Likely due to fact that we used measured air relative permeability; steam vapor relative permeability is probably higher
- Simulation and experiment both show complete DCA removal at 40% pore volume produced
Field scale simulations of fractured systems

- Numerically challenging due to small size of fractures compared to large size of model
- Large contrasts in permeability and capillary pressure between fractures and rock matrix
- Discretization issues – need to discretize both the fractures (very small) and the matrix (very large), with transitions in size between the two
- Starting from liquid water conditions, gas phase evolution occurs in all boiling gridblocks – possibility of unstable phase transitions
Discrete fracture model

- Normal discretization of fractures and matrix, small elements near fractures
- Most realistic model, but practically limited to simple fracture geometry
- Best for parallel sets of fractures due to computational limits

Wemp et al., 2011
Multiple Interacting Continua (MINC) discretization

Spatial domain is discretized normally into volume elements.

The fracture elements are globally connected in all directions.

Each gridblock is subdivided into a fracture element, and multiple nested matrix elements. The fracture and matrix elements are locally connected to each other in 1-D.

This is similar to a dual porosity formulation, but gradients in the matrix are resolved much more accurately.
Field Simulation Example

Idealized field scale simulation – single element of a repeated 6-phase electrical heating pattern.

3-D orthogonal set of 200 micron fractures with 1m spacing, matrix $k=10^{-15}$ $m^2$; model uses MINC for matrix blocks.

Add 800 kW power for 15 days, then pump vacuum well at 0.5 ATM for 1 year. Re-energize for 3 days and pump vacuum well for another year.
Simulation Result

图表展示了温度、蒸汽提取速率和饱和度随时间变化的模拟结果。图表中包含了温度、蒸汽提取速率和饱和度的折线图，显示了时间（天）与温度（摄氏度）、蒸汽提取速率（升/分钟）和饱和度（微克/升）之间的关系。
Summary

- Experiments and simulations show good removal of volatile contaminants with about 40-50% removal of pore water by thermal treatment.
- Several numerical models are available for simulating thermal remediation. These codes should be able to capture the key heat and mass transfer effects that occur.
- Field scale models of fractured systems are challenging because of scale effects and the strong interaction between the fractures and matrix.
- MINC discretization appears to be the most practical way to setup most large field simulations.
# THERMAL TREATMENT TECHNOLOGIES: LESSONS LEARNED

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Effects of Thermal Treatment on the Microbial Reductive Dechlorination Process

Frank E. Löffler
Microbial Reductive Dechlorination at Elevated T
Key Questions

1. Are reductively dechlorinating (i.e., organohalide-respiring) bacteria active at elevated temperatures?

2. Do reductively dechlorinating bacteria recover activity following exposure to elevated temperatures?

3. Does thermal treatment increase soil organic carbon (i.e., electron donor) bioavailability to sustain the reductive dechlorination process?

4. Does thermal treatment provide opportunities for post-treatment bioremediation to control residual contaminants?
1. Microbial Reductive Dechlorination at Elevated T

- Reductive dechlorination of chlorinated solvents demonstrated at mesophilic temperatures (10-35 °C)

- Occurs in cold (4 °C) aquifers

- A thermophilic PCE-to-cis-DCE-dechlorinating mixed culture containing a Dehalobacter sp. obtained from Rhine River sediment (60-65 °C)
  (Kengen et al. 1999, Appl. Environ. Microbiol. 65:2312-2316)

- Enrichment of PCE dechlorinators from geothermal areas not successful
  (unpubl. results)

- Screening of metagenome libraries established with DNA from geothermal environments did not detect reductive dehalogenase genes (unpubl. results)
An enrichment culture derived from Rhine River sediment dechlorinated PCE to cis-DCE ay 60 °C. A bacterium related to *Dehalobacter* was detected.

Kengen et al. 1999, Appl. Environ. Microbiol. 65:2312-2316
Reductive Dechlorination at Elevated T

Laboratory experiments with the PCE-to-ethene-dechlorinating consortium BDI

Dechlorination to ethene in BDI cultures incubated at 30 °C

Accumulation of VC in BDI cultures incubated at 35 °C

No dechlorination at 40 °C
Potential for VC accumulation

Fletcher et al. 2011, ES&T 45:712-718
1. Microbial Reductive Dechlorination at Elevated T

- A single study reports reductive dechlorination of PCE to cis-DCE at temperatures of 60-65°C. This culture was derived from a “cold” river sediment.

- Search for thermophilic microbes capable of reductive dechlorination has not been successful to date. The efforts to date were limited in scope and the search should continue.

- Metagenome information is currently generated from many environments, including thermophilic habitats. Screening of these data sets for reductive dehalogenase genes will reveal their presence in thermophilic environments and can guide enrichment efforts.
2. Recovery of Reductive Dechlorination Activity

Laboratory experiments with the PCE-to-ethene-dechlorinating consortium BDI

Incubation at 40°C for 24 days prior to cooling to 24°C

Dechlorination of VC to ethene after cooling

Fletcher et al. 2011, ES&T 45:712-718
2. Recovery of Reductive Dechlorination Activity

Laboratory experiments with the PCE-to-ethene-dechlorinating consortium BDI

Incubation at 40°C for 49 days prior to cooling to 24°C

No dechlorination of VC to ethene after cooling

Fletcher et al. 2011, ES&T 45:712-718
2. Recovery of Reductive Dechlorination Activity

*Sulfurospirillum, Desulfobacterium, Dehalobacter, Desulfuromonas, Geobacter, Clostridium*

Isolation and Characterization of a Tetrachloroethylene Dechlorinating Bacterium, *Clostridium bifermentans* DPH-1
Chang et al. 2000, J. Biosci. Bioeng. 89:489-491

Resolution of Culture *Clostridium bifermentans* DPH-1 into Two Populations, a *Clostridium* sp. and Tetrachloroethene-Dechlorinating *Desulfitobacterium hafniense* Strain JH1.

A PCE-dechlorinating spore former would be able to survive high T
No PCE-dechlorinating spore formers have been identified to date
2. Recovery of Reductive Dechlorination Activity

- No reductive dechlorination activity recovered from cultures incubated at temperatures >40°C
- Duration of exposure to elevated temperatures affects recovery of dechlorination activity
- The VC-to-ethene dechlorination step is most susceptible to heat inactivation
  - Increased potential for VC accumulation
- No spore-forming chlorinated solvent dechlorinators have been described
3. Release of ED for Reductive Dechlorination During/Following Thermal Treatment

Microcosm experiments with Ft. Lewis soil

Hydrogen production at different incubation temperatures

H$_2$ concentrations in live and autoclaved Ft. Lewis microcosms after 28 days of incubation

3. Release of ED for Reductive Dechlorination

Microcosms established from Ft. Lewis, WA, and Great Lakes, IL

Depicted is the electron donor (ED) consumption in reductive dechlorination following thermal treatment.

- Prior to bioaugmentation
- ∙ After bioaugmentation
- ∙ After biostimulation I
- ∙ After biostimulation II

⇒ More reducing equivalents directed towards reductive dechlorination in microcosms that had been incubated at lower temperatures
3. Release of ED for Reductive Dechlorination

Microcosms established from Ft. Lewis, WA, and Great Lakes, IL

Depicted is the electron donor (ED) consumption in methane formation following thermal treatment.

- Prior to biostimulation
- After biostimulation I
- After biostimulation II

The majority of reducing equivalents released from the soil matrix during heat treatment are consumed in methanogenesis rather than reductive dechlorination (i.e., <0.1%).
3. Release of ED for Reductive Dechlorination

- Thermal treatment increased the hydrogen flux
- At the two sites investigated, the amount of reducing equivalents consumed in reductive dechlorination negatively correlated with previous incubation temperature (i.e., fewer electrons consumed in microcosms previously incubated at higher temperature)
- At both sites, biostimulation (i.e., the addition of electron donor) was required to sustain reductive dechlorination and ethene formation
- The majority of reducing equivalents was consumed in methanogenesis
4. Opportunities for Enhanced Post-Thermal Treatment Bioremediation

- Bioaugmentation with non-methanogenic consortia can increase the efficiency of the reductive dechlorination process (i.e., a greater fraction of the available reducing equivalents will be consumed in reductive dechlorination).

Before $\Delta T$

Niches Occupied

After $\Delta T$

Open Niches

Bioaugmentation after $\Delta T$

Colonialization of open niches by bacteria in the inoculum
Conclusions

- Residual contamination often remains following thermal treatment.
- Subsequent bioremediation is a promising polishing step to meet remediation goals → Combined Remedy Approach.
- The known bacteria capable of reductive dechlorination cannot tolerate elevated temperatures.
- The VC-to-ethene step is most susceptible to temperature inhibition.
- Thermal treatment increases electron donor (e.g., hydrogen) flux.
- The majority of the hydrogen is consumed by methanogens.
- Thermal treatment may offer unique opportunities for enhanced bioremediation by using bioaugmentation inocula not containing methanogens.
Acknowledgements

- Kelly Fletcher (former PhD student)
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- Kurt Pennell (Tufts University)

SERDP Projects ER-1419 and ER-1586
## Thermal Treatment Technologies: Lessons Learned

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