OPERATION OF AN IN SITU ANAEROBIC BIODEGRADATION SYSTEM FOR A CHLORINATED SOLVENT SOURCE AREA

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ABSTRACT

In situ accelerated anaerobic biodegradation is an innovative remediation technology that addresses common groundwater contaminants such as perchloroethylene (PCE) and trichloroethylene (TCE). One challenge of implementing the technology is controlling the negative effects of biological fouling on system performance. Developing strategies to control biological fouling in these systems increases the viability of this remediation technology.

Successful in situ anaerobic biodegradation of chlorinated solvents requires distributing an organic carbon source (or substrate) throughout the aquifer to accelerate biological activity, which degrades the contaminants. Often, the substrate is delivered through injection wells. Maintaining maximum flow through injection wells is vital for successful remediation and is frequently limited by biological fouling. Conventional biological fouling control techniques used in water treatment and well drilling industries can be applied to in situ bioremediation systems, but must be done without diminishing the system’s anaerobic biological treatment component.

Several biological fouling controls have been used at Dover Air Force Base, Delaware during the operation of a full-scale, in situ anaerobic biodegradation system. The system recirculates groundwater contaminated with TCE through a biological reactive/treatment zone established in the aquifer. Based on a pilot-scale demonstration, the initial biological fouling control plan included “pulsing” organic carbon substrate into the injection wells, physical redevelopment (scrubbing, surging, and pumping), and hydrogen peroxide (H$_2$O$_2$) treatment for severe injection well biological fouling.

Additional strategies implemented during the first three years of system operation improved the control of biological fouling in the system. The improvements included pressurizing the injection wells, using an anaerobic biocide, acid treatments, and adding an iron-sequestering agent to limit the growth of iron-related bacteria.

Hydrogen peroxide and acid treatments have been effective in restoring flow through the system components; however, they are used as a last alternative because they can negatively affect the biological reactive zone. They also can be expensive and are unsafe to handle.

During the first 26 months of system operations, five hydrogen peroxide treatments and one acid treatment were conducted due to severe fouling in the system. As a result of the improvements to the biological fouling control plan, H$_2$O$_2$ or acid treatments have not been required in more than a year and the system recirculation rate has increased from approximately 12 to 18 gallons per minute (gpm) to over 22 gpm.

Through thoughtful application of several biological fouling control techniques, the system’s groundwater recirculation efficiency has been improved without reducing the effectiveness of the biological reactive zone that provides contaminant treatment. The
lessons learned from controlling biological fouling in this system can be applied to other in situ anaerobic biodegradation projects and should promote the use of this technology.

INTRODUCTION
In situ accelerated anaerobic biodegradation (AAB) is successfully employed to treat chlorinated solvents that were historically released into soil and groundwater beneath Building 719, a mission-critical maintenance facility at Dover Air Force Base (DAFB), Delaware. Contaminants are attributed to engine-cleaning activities conducted in the building and include mainly chlorinated ethenes (specifically perchloroethene [PCE], trichloroethene [TCE], cis-1,2-dichloroethene [cis-1,2-DCE], and vinyl chloride). An AAB system was installed to remediate contaminated groundwater in the source area and minimize the continued contribution to the dissolved plume extending approximately one mile downgradient. TCE concentrations as high as 21,000 micrograms per liter (µg/L) have been detected in shallow groundwater at the site. In addition, the enhanced biological activity creates an increase in surfactant compounds associated with metabolic processes in the source area. “Biosurfactants” have been demonstrated to promote solvent partitioning into groundwater from aquifer solids, thereby improving cleanup rates and efficiency (Jennings and Tanner, 2000).

Remediation and characterization of the source area at Building 719 are limited in part by the inaccessible location of source contaminants underneath the building foundation. One critical constraint is that any remedial efforts undertaken must not disrupt operations at this critically active site. Thus, more intrusive remedial methods that might otherwise be appropriate were not considered. Instead, a biological reactive zone is maintained around injection wells through which a carbon substrate and metabolic nutrients are added to the aquifer via recirculated groundwater. Contaminants are reductively dechlorinated via microbial metabolic processes within the reactive zone.

The working conceptual model for the system consists of two interdependent systems: 1) the biological reactive zone provides treatment of the contaminants and 2) the groundwater recirculation system maintains hydraulic control of the contaminants and delivers carbon substrate and nutrients to microbes in the reactive zone.

A previous paper documents the effectiveness of the reactive zone regarding contaminant treatment/destruction (Bloom, et al., 2005). The purpose of this paper is to summarize the operation and maintenance (O&M) strategies employed at the site to ensure efficient operation of the groundwater recirculation system. This paper primarily focuses on strategies for controlling biological fouling and related iron precipitation in the system components, as this has been the primary O&M concern during system operation.

SYSTEM OPERATIONS
Full-scale operation of the AAB system began in February 2002. Four extraction wells located on the downgradient sides of the building capture groundwater contaminated by a shallow source area under the upgradient side of the building. The groundwater is recirculated through 12 injection wells located on the upgradient side of the building near the source area. Figure 1 shows the site with the location of the injection wells, extraction wells, and the source area under the building.
Prior to re-injection of the groundwater, a carbon substrate (lactate) and a metabolic nutrient source (dibasic ammonium phosphate) are added to the recirculated groundwater. This maintains the biological reactive zone established around the injection well field where PCE and TCE are reductively dechlorinated to ethene. Data from shallow and deep monitoring wells within the surficial aquifer are used to assess the effectiveness of the reactive zone.

Operational efficiency of the groundwater recirculation system is measured as total combined flow from the four extraction wells. The designed flow rate for the system was approximately 17 gallons per minute (gpm). A decrease in flow rate indicates an operational difficulty such as excessive biological fouling in one or more of the injection wells, extraction pump failure, or an electrical failure. Flow rates above 17 gpm indicate that the system is operating without any difficulties. Figure 2 shows the total flow rate for the operational history of the system from February 2002 through August 2005. A summary of the system flow rates includes the following observations:

- Flow rates declined steadily during the first 10 months of system operations. The decline is attributed to increasing biological fouling in the injection wells as the biological reactive zone was established.
- In January 2003, system operations were interrupted by severe biological fouling. Flow to the injection wells was restored after treating the wells with H$_2$O$_2$.
- Between March and June 2003, biological fouling and high water table conditions contributed to decreasing injection.
- The system flow rate was restored in June 2003 when 10 of the 12 injection wells were converted from gravity fed to pressurized injection.
Between November 2003 and January 2004, system operations were interrupted on several occasions due to severe biological fouling in the system components. Flow to the injection wells was restored after repeated H$_2$O$_2$ treatments.

Improvements to the O&M strategy result in increased flow rates up to 23 gpm by April 2005. No significant interruptions of system operations were experienced from February 2004 through August 2005.

**ANTI-FOULING STRATEGIES**

Development of successful O&M strategies for the AAB system is complicated by conflicting operational goals. Successful operation of the recirculation system requires minimal biological activity in the system components (injection wells, extraction wells, system plumbing), while the biological reactive zone relies on the enhancement of biological activity in the subsurface around the injection well field. Additionally, the project lifespan is reduced by maximizing system flow rates. Increased flow rates result in shorter recirculation and treatment times for contaminants. Increased flow rates through the source area also maximize the partitioning of sorbed contaminants into groundwater, making them available for reductive dechlorination and decreasing the contaminant mass in the shallow soil under the building. As a result, the efficacy of various O&M strategies are evaluated on the following criteria, listed in order of importance:

1. Strategies must not negatively impact microbial activity associated with reductive dechlorination of contaminants in the reactive zone, either directly or by altering geochemical conditions.

2. Strategies should minimize human contact with hazardous substances (H$_2$O$_2$ for example). Harsh chemical treatments also tend to negatively affect microbial activity in the reactive zone.
3. Strategies must be effective in controlling biological fouling or restoring permeability in the injection wells and other system components in order to sustain maximum flow rates to the injection wells and maintain hydraulic control of dissolved contaminants.

4. Strategies need to be cost effective. Several traditional strategies tend to be labor intensive and therefore cost prohibitive.

5. Strategies with long-term effectiveness tend to result in cost savings.

The following is a summary of the strategies used for the AAB system, including application details, results, advantages, and disadvantages of each.

**Pulsed Substrate and Nutrient Injection**

**Application:** Carbon substrate and metabolic nutrients are injected into injection wells via the recirculated groundwater at high concentrations for short periods of time (approximately 4 to 6 hours per injection event) every 2 to 4 days.

**Advantages:** Pulsed injection reduces the availability of substrate and nutrients in the injection wells, limiting biological activity and fouling.

**Disadvantages:** Bacteria prefer a stable environment. Pulsed injections result in fluctuating concentrations of substrate and nutrients as amendments move through the aquifer in concentration fronts or waves.

**Results:** Based on the results of a pilot study conducted prior to the full-scale system operation, pulsed injection methodology minimizes biological fouling in the injection wells. Contaminant/daughter product mass balances indicate that fluctuating substrate concentrations are not negatively affecting reductive dechlorination (RTDF, 2000).

**Physical Redevelopment**

**Application:** Biomass and precipitates are removed from the injection well screens by scrubbing the well screens with a stiff wire chimney brush, surging the well screens and gravel pack, and purging the wells with a submersible pump.

**Advantages:** Physical redevelopment does not require handling hazardous chemicals. This strategy is effective for removing bulk biological mass and sediments/precipitates.

**Disadvantages:** This strategy is labor intensive with diminishing results as the biological system developed. It also generates purge water with high solids content and chlorinated solvents concentrations, requiring prefiltering and treatment with activated carbon before discharging to industrial sewer.

**Results:** This strategy is effective when applied with H$_2$O$_2$ treatments, but is not effective for sustained maintenance of injection well permeability.

**Hydrogen Peroxide**

**Application:** A 35 percent hydrogen peroxide solution is used to restore injection permeability after the well screens and gravel packs become severely fouled. H$_2$O$_2$ treatment is used in conjunction with physical redevelopment of injection wells to maximize effectiveness.

**Advantages:** H$_2$O$_2$ is a strong oxidizer that dissociates organic matter.
Disadvantages: Oxygen released from H₂O₂ into groundwater is detrimental to the anaerobic environment. H₂O₂ treatments require purging large volumes of oxygenated water from injection wells and treating purged water before discharging it to an industrial sewer, making this strategy labor and cost intensive. Handling a strong oxidizer like H₂O₂ creates health and safety concerns. H₂O₂ may cause precipitation of dissolved metals and off-gassing of degraded organic carbon, which reduce permeability in the aquifer.

Results: Two full-scale treatments effectively restored permeability after injection wells became severely fouled. However, full system treatments are relatively expensive. Additionally, effects of subsequent treatments were shorter lived. No adverse effects to the biological reactive zone, however, have been observed. H₂O₂ treatments are considered a last option for restoring permeability.

Pressure Injection
Application: The 12 injection well heads were sealed to allow injection of recirculated groundwater at well head pressures of less than 3.0 pounds per square inch (psi). The wells were converted from the original gravity feed system in response to decreased head spaces resulting from high water table conditions and reduced permeability.

Advantages: This strategy allows injection of groundwater with minimal headspace and increased injection rates.

Disadvantages: This strategy does not stop or eliminate biological fouling.

Results: Injecting under minimal pressure appears to significantly minimize effects of biological fouling in the injection wells. O&M efforts have been minimized with combined use of pressure injection and anaerobic biocide.

Acid Treatment
Application: Two of the extraction wells and their associated delivery piping were treated with two different acid solutions to remove biological and precipitated iron fouling. The acid solutions were allowed to sit in the system components for extended periods of time and were recovered prior to re-injection.

Advantages: This treatment effectively removes biological mass and precipitated iron from treated components.

Disadvantages: Acid solution and purge water from treated extraction wells requires neutralization and treatment before discharging to industrial sewer.

Results: Acid treatment is effective (at high concentration) for reducing biological and iron fouling in piping. The effects are less obvious for treatment of extraction wells. Acid treatment has not been applied to the injection wells, although future application is possible.

Anaerobic Biocide
Application: Tolcide PS200 is an anaerobic biocide that is applied to injection wells when increased biological fouling is observed. A U.S. Environmental Protection Agency (EPA) Special Local Needs (SLN) permit was obtained prior to Tolcide application at the site. Tolcide is delivered to injection wells and the surrounding gravel pack and was originally applied under normal recirculation conditions.
Starting in April 2003, the AAB system is turned off for extended periods of time (36 hours or longer) following Tolcide injections to increase contact time with biological growth in the injection wells.

**Advantages:** Tolcide is considered a “green” biocide because it degrades relatively rapidly in the subsurface, eliminating purge water that requires treatment. Tolcide is anaerobic and does not oxidize the reductive subsurface environment (as opposed to H\textsubscript{2}O\textsubscript{2}) developed at the site. Since it is pumped directly into recirculated groundwater, handling by site personnel is minimized.

**Disadvantages:** Tolcide can kill the microbes involved in reductive dechlorination if applied incorrectly. The SLN permit for the AAB system requires thorough demonstration that Tolcide will not persist beyond the site and will not discharge into any surface water body. Experience at the site indicates that Tolcide should be applied as a biological fouling preventative, which requires frequent monitoring of biological fouling indicators.

**Results:** Applied to the injection wells as needed to control biological fouling, Tolcide significantly reduces the cost and level of effort required to maintain system flow. After modifying the application method in April 2003, Tolcide has been applied every 1 to 3 months for over 15 months without any significant loss in flow rate due to biological fouling. In fact, the system flow rate has increased approximately 30 percent since Tolcide use began.

**Iron Sequestering Agent**

**Application:** An iron sequestering agent is dripped under gravity into two extraction wells in which dissolved iron is detected. Biological tests at the site indicate that iron related bacteria (IRB) are responsible for most of the biological fouling in the system components.

**Advantages:** Dissolved iron is made unavailable to IRB, limiting the growth of IRB in system components. The iron sequestering agent used at the site is 75 percent hydroxyacetic (glycolic) acid, which is readily biodegradable and can be reinjected into the subsurface.

**Disadvantages:** Hydroxyacetic acid will lower the pH in the reactive zone if not applied appropriately. Mechanical difficulties delivering the iron sequestering agent into the extraction wells have been encountered, due in part to the corrosive nature of the product.

**Results:** Although application has been inconsistent due to delivery problems, the iron sequestering agent appears to minimize biological and precipitated iron fouling in the piping from the extraction wells, as well as biological fouling in the injection wells.

**EFFECTS OF O&M ACTIVITIES ON REACTIVE ZONE EFFICIENCY**

Improvements to the system O&M after the first year of operation have been effective, resulting in a system flow rate 30 percent greater than the designed flow rate. The ability of microbes in the reactive zone to destroy contaminants is measured by the destruction percentage of chlorinated ethenes (PCE, TCE, cis-1,2-DCE, and vinyl chloride) as they travel through the reactive zone. This is done by comparing chlorinated ethene concentrations in the recirculated groundwater prior to re-injection (pre-treatment)
to concentrations measured in wells located directly downgradient of the reactive zone (post-treatment). Destruction percentages for the three deep wells used to monitor conditions in the reactive zone are included in Table 1. Destruction percentages greater than 95 percent are observed in all three wells by May 2003, demonstrating nearly complete degradation of chlorinated ethenes passing through the reactive zone. The sustained efficiency of the reactive zone shows that the O&M strategies employed have not negatively impacted the biological activity associated with contaminant treatment at the site.

**TABLE 1**

**REACTIVE ZONE EFFICIENCY**

<table>
<thead>
<tr>
<th></th>
<th>MW604D</th>
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<th>MW605D</th>
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<th>MW606D</th>
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<tbody>
<tr>
<td></td>
<td>Pre-treatment chlorinated ethenes (µg/L)</td>
<td>Post-treatment chlorinated ethenes (µg/L)</td>
<td>% destruction</td>
<td>Post-treatment chlorinated ethenes (µg/L)</td>
<td>% destruction</td>
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<td>Mar-02</td>
<td>1,248</td>
<td>862</td>
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<td>2,344</td>
<td>2,231</td>
<td>4.8%</td>
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<td>Oct-02</td>
<td>2,993</td>
<td>1,951</td>
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<td>Jan-03</td>
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<td>227</td>
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<td>May-03</td>
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<td>Jul-03</td>
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<td>15.8</td>
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chlorinated ethenes = PCE, TCE, cis-1,2-DCE, and vinyl chloride

**CONCLUSIONS**

Based on observations made during the first 3½ years of system operations, the following conclusions are made regarding the control of fouling in the AAB system:

- Pulsed injections of substrate at high concentrations separated by 2 to 4 days minimizes the impact of biological fouling in the injection wells while still promoting effective reductive dechlorination in the biological reactive zone.

- H$_2$O$_2$ treatments are effective for restoring permeability to severely fouled injection wells. However, they are considered a last resort treatment due to cost of labor, potentially negative impact to the anaerobic biological community, health and safety concerns, and the potential for production of off-gases and precipitation of dissolved metals.

- Injection of groundwater and amendments under low well head pressures (less than 3 psi) extends the period of time required between biological fouling treatments.

- Use of a biodegradable biocide (as needed) and an iron sequestering agent (in extraction wells with measurable dissolved iron) are effective in minimizing O&M effort and costs while allowing for increased recirculation system efficiency.
REFERENCES