



NAVFAC
Naval Facilities Engineering Command

ENGINEERING SERVICE CENTER
Port Hueneme, California 93043-4370

CONTRACT REPORT
CR-07-022-ENV

**IN SITU CATALYTIC GROUNDWATER
TREATMENT USING PALLADIUM
CATALYSTS AND HORIZONTAL FLOW
TREATMENT WELLS**

by

Naval Facilities Engineering Service Center
and
Stanford University

June 2007

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

| | | | | | |
|--|------------------------------------|-------------------------------------|----------------------------|--|---------------------------------|
| 1. REPORT DATE JUN 2007 | | 2. REPORT TYPE | | 3. DATES COVERED | |
| 4. TITLE AND SUBTITLE In Situ Calaytic Groundwater Treatment Using Palladium Catalysts and Horizontal Flow Treatment Wells | | | | 5a. CONTRACT NUMBER | |
| | | | | 5b. GRANT NUMBER | |
| | | | | 5c. PROGRAM ELEMENT NUMBER | |
| 6. AUTHOR(S) | | | | 5d. PROJECT NUMBER | |
| | | | | 5e. TASK NUMBER | |
| | | | | 5f. WORK UNIT NUMBER | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Commanding Officer,NAVFAC ESC,1100 23rd Avenue,Port Hueneme,CA,93043-4370 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER CR 07-022-ENV | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | | | | 10. SPONSOR/MONITOR'S ACRONYM(S) | |
| | | | | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) | |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited. | | | | | |
| 13. SUPPLEMENTARY NOTES | | | | | |
| 14. ABSTRACT Environmental Security Technology Certification Program (ESTCP) Cost and Performance Report | | | | | |
| 15. SUBJECT TERMS | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES 39 | 19a. NAME OF RESPONSIBLE PERSON |
| a. REPORT unclassified | b. ABSTRACT unclassified | c. THIS PAGE unclassified | | | |

**Environmental Security Technology Certification Program (ESTCP)
Cost and Performance Report**

**In Situ Catalytic Groundwater Treatment Using Palladium
Catalysts and Horizontal Flow Treatment Wells**



June 2007

Table of Contents

| | |
|---|----|
| Environmental Security Technology Certification Program (ESTCP)..... | i |
| Cost and Performance Report | i |
| 1. Executive Summary | 8 |
| 2. Technology Description..... | 10 |
| 2.1 Pd-Catalyzed Dehalogenation: Development and Application | 10 |
| 2.2 Treatment System and Process for Pd Catalyzed TCE Destruction | 10 |
| 2.3 Mobilization, Installation and Operational Requirements | 13 |
| 2.4 Previous Testing of the Technology | 14 |
| 2.5 Advantages and Limitations of the Technology | 14 |
| 3. Demonstration Design | 15 |
| 3.1 Performance Objectives | 15 |
| 3.2 Selection of Test Site | 16 |
| 3.3 Test Site, Facility History and Characteristics..... | 17 |
| 3.4 Physical Set-up and Operation..... | 18 |
| 3.5 Sampling/Monitoring Procedures | 18 |
| 3.6 Analytical Procedures | 18 |
| 4. Performance Assessment | 19 |
| 4.1. Catalytic TCE Removal: Data and Interpretation..... | 19 |
| 4.2 Performance Criteria and Data Assessment..... | 21 |
| 4.3 Technology Comparison..... | 23 |
| 5. Cost Assessment | 24 |
| 5.1 Cost Reporting | 24 |
| 5.2 Cost Analysis | 25 |
| 5.3 Cost Comparison..... | 29 |
| 5.4 Life Cycle Analysis..... | 30 |
| 6. Implementation Issues | 31 |
| 6.1 Cost Observations with the Demonstration System..... | 31 |

| | |
|--|----|
| 6.2 Performance Observations | 31 |
| 6.3 Scale-up..... | 31 |
| 6.4 Other Significant Observations..... | 31 |
| 6.5 Lessons Learned..... | 31 |
| 6.6 End-User Issues | 34 |
| 6.7 Approach to Regulatory Compliance and Acceptance | 34 |
| 7. References..... | 35 |
| 8. Points of Contact..... | 37 |

List of Figures

| | |
|--|----|
| Figure 2-1. Schematic of treatment system..... | 11 |
| Figure 2-2: Schematic of Hydrogen Feed System. | 11 |
| Figure 2-3: Regeneration After Severe Episodes of Reactor Poisoning During 2004. | 12 |
| Figure 2-4: Regeneration and Reactivation of Reactor After Poisoning Events Due to Insufficient Maintenance Bleaching..... | 13 |
| Figure 4-1. Performance of T1 Pd Catalyst Reactor during Jul-Sept 2005. | 19 |
| Figure 4-2. TCE removal during one day bleaching regime. | 20 |
| Figure 4-3. TCE residual concentration detail under one-day bleaching regime. | 20 |

List of Tables

| | |
|---|----|
| Table 3-1 Performance Objectives..... | 15 |
| Table 4-1: Expected Performance and Performance Confirmation Results | 21 |
| Table 5-1: Cost Elements..... | 24 |
| Table 5-2. Technologies for VOC Remediation. | 25 |
| Table 5-3: Basis for Cost Comparison..... | 26 |
| Table 5-4. Capital Costs..... | 26 |
| Table 5-5. Operation & Maintenance Costs | 27 |
| Table 5-6. Monitoring Costs. | 28 |
| Table 5-7. Examples of Cost Evaluations of Different Competing Technologies | 29 |
| Table 5-8. Present Value Estimates Pd Reactor Operation..... | 30 |

List of Acronyms and Abbreviations

| | |
|-------|--|
| AFB | Air Force Base |
| AFRPL | Air Force Rocket Propulsion Laboratory |
| AFRL | Air Force Research Laboratory |
| DBCP | 1,2-dibromo-3-chloropropane |
| DCE | dichloroethylene |
| DoD | Department of Defense |
| EPA | Environmental Protection Agency |
| ESTCP | Environmental Security Technology Certification Program (sponsored by DoD) |
| FSP | Field Sampling Plan |
| GC | gas chromatography |
| gpm | gallons per minute |
| HASP | Health and Safety Plan |
| HFTW | horizontal flow treatment well |
| LLNL | Lawrence Livermore National Laboratory |
| MCL | maximum contaminant level (established under the Safe Drinking Water Act) |
| NASA | National Aeronautics and Space Administration |
| O&M | operations & maintenance (or operating & maintenance) |
| OSHA | Occupational Safety and Health Administration |
| PCE | perchloroethylene |
| Pd | palladium |
| PID | photo-ionization detector |
| PMC | Precious Metals Corporation (Sevierville, TN) |
| POC | point of contact |
| PRB | permeable reactive barrier |
| QAPP | Quality Assurance Project Plan |
| SEM | scanning electron microscopy |
| TCE | trichloroethylene |
| VC | vinyl chloride |
| VOC | volatile organic compound |
| XPS | X-ray photo-electron spectroscopy |

Acknowledgements

In addition to Environmental Security Technology Certification Program (ESTCP), the following organizations and agencies provided support for this project:

- U.S. Environmental Protection Agency under agreements R-825421 and R-815738-01 through the Western Region Hazardous Substance Research Center, Stanford University under Lew Semprini
- The National Science Foundation Science and Technology Center WaterCAMPWS through agreement CTS-0120978 under Vern Snoeyink
- The Environmental Management Restoration Branch, AFFTC/EMR, Edwards AFB.

1. Executive Summary

1.1 Background

The U.S. Environmental Protection Agency (EPA) estimated in 1996 that of 8,336 DoD sites needing cleanup, approximately 70% had contaminated groundwater, mostly from chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE). Because TCE and PCE are mobile and refractory in aquatic environments, there is significant need for efficient treatment methods. Palladium (Pd) catalyzed reductive dechlorination transforms chlorinated ethylenes and other VOCs into their respective saturated hydrocarbons or lesser chlorinated analogues. With hydrogen gas as the reductant, the process is selective requiring only small quantities of hydrogen to remove contaminants to below regulatory limits. For some VOCs the dechlorination reaction occurs rapidly, even in water under ambient temperature, pressure and pH. The process can be utilized to efficiently treat water contaminated with reactive chlorinated contaminants. A one-pass catalytic process has many advantages, mainly that contaminants are destroyed instead of being transferred to another medium (e.g. air or activated carbon), thus avoiding generation of a secondary waste stream. The technology is particularly favorable for treating water contaminated with high concentrations ($>1 \text{ mg L}^{-1}$) of chlorinated ethylenes and is therefore suited for source control.

1.2 Objectives of the Demonstration

The principal objectives of this evaluation were to:

- (1) Demonstrate the efficacy of catalytic treatment for the destruction of chlorinated ethylenes in groundwater using Pd catalyst.
- (2) Optimize treatment efficiency.
- (3) Develop cost and performance data for full-scale application of the technology.

The demonstration at Edwards AFB was operated in a manner close enough to full-scale that costs were scaled accordingly to represent full-scale application. In the initial proposal, the reactors were expected to be mounted below grade within the horizontal flow treatment wells (HFTWs), thus qualifying as an in situ technology. The selected test site was the Edwards AFB site where the HFTW technology was tested previously in the context of biological treatment (McCarty et al. 1998). Although a dual-column configuration in situ might be possible in principle, its realization was not feasible within the constraints of this pilot-scale demonstration. Once operational issues were resolved and the regeneration protocol was optimized, the catalyst reactor successfully reduced the TCE concentrations in the groundwater by 2-3 orders of magnitude (more than 99%) consistently and without significant loss of catalyst activity.

1.3 Regulatory Drivers

TCE is a known carcinogen, along with other chlorinated ethylenes such as PCE, dichloroethylene (DCE) and vinyl chloride (VC). EPA and the State of California Department of Health Services (DHS) set a maximum contaminant limit (MCL) of $5 \text{ } \mu\text{g L}^{-1}$.

1.4 Demonstration Results

Catalytic TCE destruction was demonstrated for the treatment of contaminated groundwater at Edwards Air Force Base (AFB), California. The process performed as expected, resulting in average effluent concentrations consistently below the MCL ($5 \mu\text{g L}^{-1}$) after one pass through a Pd reactor with contact time of approximately one minute. Influent concentrations ranging from 800 to $1,200 \mu\text{g L}^{-1}$ were reduced by over 99.6% under normal operating conditions. Based on the experience of this project, a capital investment of \$574,000 and annual O&M costs of about \$70,000 (including monitoring & analysis) are sufficient to successfully remediate TCE-contaminated groundwater. The total net present value (NPV) of such a project over a 10 years (y) period is calculated to be \$1.07M. Unique water matrices and the opportunity for multi-contaminant remediation in a single pass make reductive catalysis competitive with and potentially advantageous over other remediation schemes such as air stripping, granular activated carbon (GAC) and permeable reactive barriers (PRB).

1.5 Stakeholder/End-User Issues

Potential end users for this technology are organizations responsible for remediation of groundwater sites contaminated with chlorinated ethylenes (PCE, TCE, DCE isomers and VC). The technology demonstration at Edwards AFB focused on TCE and concluded:

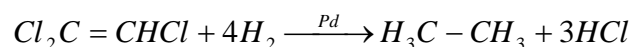
- Pd catalysis consistently destroys TCE, even in anaerobic (but not sulfidic) groundwater.
- The technology can reduce concentrations of TCE to below its MCL.
- Hazardous byproducts are not formed during treatment.
- Operating protocols were determined for above ground systems.
- Experience gained in designing and constructing the reactor system led to significant improvements, lower anticipated costs and more reliable cost estimates for future applications.
- Site specific operating protocols were developed.
- Cost information was developed that demonstrate the technology can be competitive at the scale of the demonstration. From the data provided, it is possible to estimate treatment costs for scaled-up systems. Before scale-up, however, site-specific pilot tests are recommended to assess the fouling potential of the groundwater.

For some frequently found groundwater contaminants such as 1,1,1-trichloroethane, 1,2-dichloroethane and methylene chloride, the process is not effective; and for others (e.g., chloroform) it is slower than for TCE and PCE.

2. Technology Description

2.1 Pd-Catalyzed Dehalogenation: Development and Application

Palladium (Pd) catalysts, in the presence of hydrogen gas, transform many chlorinated VOCs into their respective hydrocarbon compounds. To maximize the specific Pd surface area while minimizing the amount of metal used, a thin layer of Pd is supported on a porous support material such as porous gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$). Pd catalyst transforms chlorinated ethylenes to ethane by replacing all chlorine atoms with hydrogen and hydrogenating the double bond. TCE, for example, reacts with 4 moles of hydrogen gas to form ethane and 3 moles of hydrochloric acid, as shown below:



This reaction is extremely rapid in water (nearly diffusion limited), even at ambient temperature, and proceeds completely to ethane [Lowry and Reinhard, 1999]. In the presence of excess hydrogen, no significant amounts of intermediates (e.g. vinyl chloride) are formed. The formation of hydrochloric acid as a reaction product does not generally represent an obstacle for technology application to contaminated groundwater sites because the reactant TCE concentrations are generally low (less than 30 mg L^{-1}) and groundwater usually has sufficient natural buffer capacity.

The ability of Pd metal to catalyze dehalogenation reactions has been known for decades, but has only recently been applied to treatment of contaminated water. Over the past decade, Reinhard and co-workers have investigated contaminants that are amenable to dechlorination or reduction via Pd catalysis, determined the reaction rates and developed protocols to maintain catalyst activity over time [Schreier and Reinhard, 1995; Siantar et al., 1996; Lowry and Reinhard, 1999, 2000; Munakata, 2005; Davie and Reinhard, 2006; Munakata and Reinhard, 2007].

A column reactor was designed for this demonstration in conjunction with HFTWs. The treatment system design was based on the subsurface reactor system that has been operated since 1999 at the LLNL [McNab et al., 2000]. That system relies on daily venting with air for approximately 12 h to prevent growth of sulfidogenic bacteria and fouling – these operating conditions limit the overall efficiency of the system to about 50% [McNab et al., 2000]. To increase the operating time, the Edwards AFB system was equipped with an automatic bleaching system to allow for more aggressive regeneration and fouling prevention protocols, relying on bleach or hydrogen peroxide as oxidants [Lowry and Reinhard, 2000]. The system was built by a commercial vendor (Bigler and Associates, Lakewood, NJ) and delivered directly to the site. During the start-up phase, numerous components of the system had to be modified to meet the needs and conditions of the Edwards AFB site, significantly delaying operation and augmenting expenses, as discussed below.

2.2 Treatment System and Process for Pd Catalyzed TCE Destruction

The reactor designed for this demonstration is shown in Figure 2-1. The major components include the column reactor, hydrogen feed system, and bleaching system. Because the catalytic

reaction is most efficient for the destruction of TCE, the technology demonstration focused on TCE as the target contaminant and a site was selected where TCE was the only contaminant.

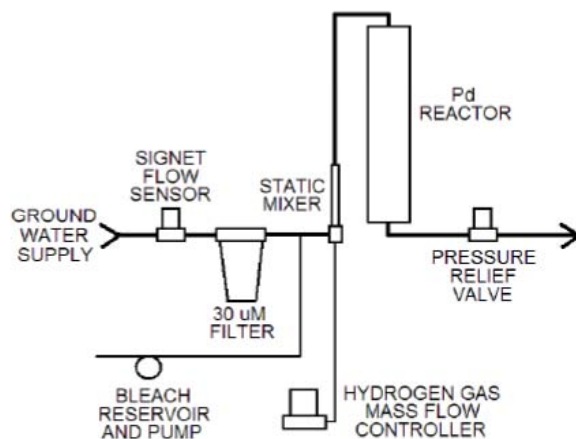


Figure 2-1. Schematic of treatment system

The hydrogen feed system and the protocol for maintaining catalyst activity by bleaching were developed during the course of this demonstration.

2.2.1 Development of a Hydrogen Feed System

According to the original design, the hydrogen feed system consisted of hollow fiber diffusion modules, a 5 L min^{-1} mass flow meter for hydrogen feed and controlled by a hydrogen pressure regulator. To achieve reliable hydrogen feed, mass flow meters were replaced with mass flow controllers; to make the system resistant against biological fouling, gas diffusion modules were replaced with a low-pressure solvent frit and static mixer. The frit produced fine hydrogen bubbles that were dissolved in the static mixer, as shown in the final feed design in Figure 2-2.

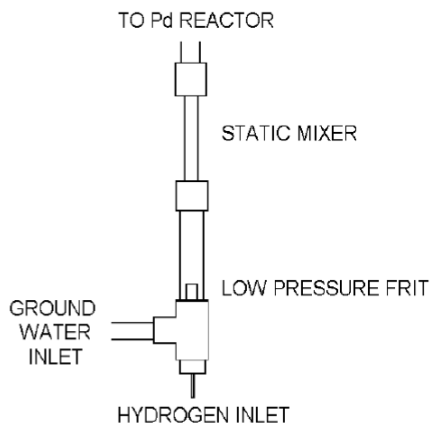


Figure 2-2: Schematic of Hydrogen Feed System.

2.2.2 Hydrogen Demand and Safety

The flammability of hydrogen is a well known risk and prompted health and safety precautions at the Edwards AFB site. For hydrogen/air mixtures, the flammability at standard temperature and pressure is 6.2 to 71.1% by volume [Lange's Handbook of Chemistry] (62 to 711 mL L⁻¹ in air). Considering the low surface area of exposed discharge within the well, the cross sectional area of the well casing and the hydrogen concentration being less than about 20% its solubility, very little hydrogen was expected to volatilize within the well – most would transport into the aquifer as dissolved hydrogen or would rapidly be consumed by sulfate-reducing bacteria.

2.2.3 Optimization of Treatment Conditions, Catalyst Maintenance and Regeneration

The reactor “effluent” sample was actually measured in the discharge well, thus some of the time attributed to catalyst regeneration in this study was actually just mixing time for discharged water within the well to reduce sample TCE concentrations to near or below the detection limit. The discussion of system optimization includes this mixing time in the catalyst regeneration cycle; a more optimized design would sample at the discharge port of the Pd reactor and would likely show a much shorter regeneration cycle time.

Bleaching the Pd catalyst with a dilute solution both prevents the growth of sulfidogenic bacteria and removes inhibitory materials from the catalyst surface. Preventing growth of sulfidogenic bacteria is imperative because once sulfide production starts the catalyst is poisoned, TCE removal decreases rapidly and breakthrough occurs. Loss of activity can be tolerated up to the point where effluent specifications (MCLs) are exceeded, but preventive regeneration with bleach oxidation curtails these operational issues.

Bleaching the catalyst temporarily suspends its activity for TCE reduction because the Pd surface is oxidized in the process. Reactivation of the catalyst is accomplished by contacting the catalyst with hydrogen-saturated water, reducing the oxidized active sites on the Pd surface. Recovery of catalytic activity is shown in Figure 2-3; catalyst that was severely poisoned and subsequently oxidized by bleaching regained activity for TCE reduction as hydrogen-saturated groundwater was passed through the column.

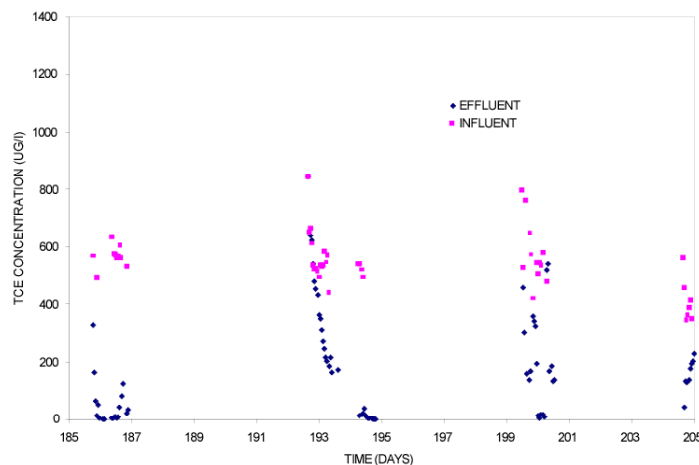


Figure 2-3: Regeneration After Severe Episodes of Reactor Poisoning During 2004.

A sequence of several maintenance bleaching cycles is shown in Figure 2-4. Bleach affects the catalyst surface by creating oxidative conditions within the reactor – eliminating hydrogen from the water oxidizes Pd active sites. When groundwater containing sulfide species is treated in a reductive catalytic reactor, hydrogen sulfide strongly binds to active Pd sites and poisons the catalyst. However, catalyst activity and capacity for TCE reduction may remain high for several days, keeping the effects of sulfide poisoning undetected. After 3-4 days and treatment of approximately 10,000 gal water (at 2 gpm), the number of active Pd sites poisoned by hydrogen sulfide becomes significant and overall TCE removal efficiency decreases. Effluent TCE concentrations eventually exceed the MCL ($5 \mu\text{g L}^{-1}$) and another oxidative treatment (bleach) must be applied to regain catalyst activity.

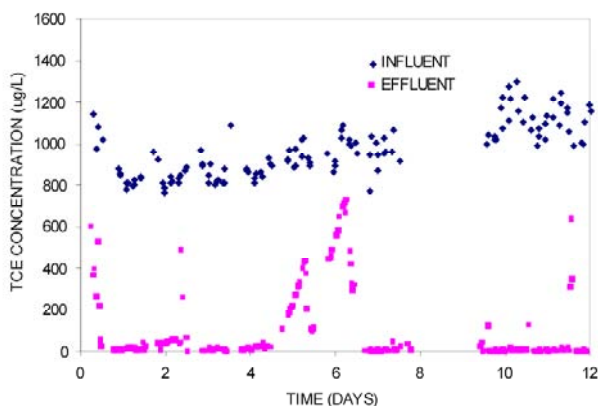


Figure 2-4: Regeneration and Reactivation of Reactor After Poisoning Events Due to Insufficient Maintenance Bleaching.

The effect of omitted daily bleach cycles on reactor performance is also evident from the data shown in Figure 2-4. The expected TCE pulse on Day 4 was not detected, presumably because the bleaching systems malfunctioned and did not deliver the bleach pulse. On Day 5, TCE concentrations began to rise rapidly because after two missed bleach cycles, biological fouling began and caused sulfide poisoning of the Pd catalyst. Fouling was severe enough that the bleach cycle of Day 5 (indicated by the sharp drop in TCE concentration) was not sufficient to regenerate catalyst activity. Catalyst poisoning increased until two manual bleach cycles were applied on Day 6.

2.3 Mobilization, Installation and Operational Requirements

Reactor components, (Pd reactor, hydrogen augmentation, bleach pump and reservoir) should be installed in a secure place near the treatment well. Mass flow controllers, hydrogen supply and computer control systems require housing in a weather-proof and temperature controlled room such as a trailer. Bleach solution usage should be logged regularly. Samples should be collected at a frequency sufficient to detect the onset of fouling and control with maintenance bleaching. If contaminant concentrations exceed expectations (i.e., MCL), more frequent sampling and/or long term regeneration should be performed. Effluent bleach concentrations during regeneration should be monitored on initial startup and periodically thereafter to confirm bleach residual of at least 50 mg L^{-1} . This can be done using a standard pool chlorine test kit.

2.4 Previous Testing of the Technology

McNab et al. [2000] describe the design and performance of the first LLNL system, which has been operated since 1999 in situ with reactor columns mounted in the well bore. The second LLNL system is an above grade system operated since 2002. The first LLNL system operates for 12 h followed by regeneration in air for 12 h. The second system is limited by the yield of the wells and operates only 6 h daily. During the remaining 18 h, the system is drained and catalyst is exposed to air to prevent growth of anaerobic bacteria. Reactor design for the Edwards AFB demonstration was based on the experiences gained through operation of the LLNL systems and laboratory research at Stanford on catalyst fouling. Compared with the LLNL systems, the Edwards AFB project incorporated three major modifications to improve overall efficiency:

- (1) Catalyst regeneration with bleach instead of air venting.
- (2) Treatment of groundwater streams with two catalytic reactors simultaneously in conjunction with HFTWs.

2.5 Advantages and Limitations of the Technology

The potential advantages of the catalytic treatment technology compared to potential alternatives are listed in Table 2-1. Alternatives considered include pump-and-treat, biological cometabolic oxidation [McCarty et al., 1998] and PRB.

Table 2-1: Advantages of Pd/HFTW Technology Relative to Competing Technologies

| Technology | Advantages of Pd/HFTW Technology |
|---|--|
| Pump-and-treat with activated carbon or air stripping | <ol style="list-style-type: none"> 1. No secondary waste stream. 2. Destroys TCE, PCE, DCE, VC and other chlorinated compounds. 3. Rapid transformation, making technology applicable to source control. 2. Pd/HFTW technology destroys TCE, PCE, and other chlorinated compounds, rather than merely transferring them from the groundwater to another medium (e.g., activated carbon) 3. Pd/HFTW technology transforms chlorinated ethylenes compounds very rapidly, so that the Pd/HFTW technology will be less expensive in many cases, and cleanup times are shorter |
| Biological co-metabolic oxidation | <ol style="list-style-type: none"> 1. Applicable at high concentrations, e.g., source control 2. Can destroy contaminants such as PCE that are not amenable to biodegradation. 3. No toxic intermediates formed. 4. Rapid transformation. |
| Permeable reactive barrier (PRB) | <ol style="list-style-type: none"> 1. Cheaper installation, especially at sites with deep contamination. 2. Faster transformation than zerovalent iron, the metal typically used in PRBs |

Advantages of Pd catalysis stem from the technology being destructive, having a small footprint selectivity. Additionally, the process requires only small quantities of a cheap reagent (hydrogen) to complete the reduction. Limitations to the Pd/HFTW technology include the following:

- Sulfide poisons the catalyst, and growth of sulfate-reducing bacteria is encouraged by hydrogen addition to the groundwater as a reagent, requiring biofouling control systems.
- Pd reductive technology is not effective for some common VOCs (e.g., 1,1-dichloroethane, 1,2-dichloroethane and methylene chloride).

3. Demonstration Design

3.1 Performance Objectives

The objective of this project was to demonstrate the feasibility of catalytically destroying TCE in groundwater. The technology is also applicable to high concentrations for control of contaminant sources.

Table 3-1 Performance Objectives

| Performance Objective | Primary Performance Criteria | Expected Performance (Metric) | Actual Performance Objective Met? |
|-----------------------|--------------------------------------|---|---|
| Qualitative | Safety and Reliability | Operation of the technology, including hydrogen addition, can be performed safely Technology gains regulatory acceptance | Yes, with proper routine maintenance, an appropriate treatment and regeneration cycles the system is reliable. Technology is accepted by regulators. |
| | Maintenance | Requires routine maintenance (e.g., changing hydrogen cylinders and preparing bleach solution) for duration of demonstration | Yes, after developing SOP and modifying reactor, two weekly visits were sufficient. With remote control, this might be reduced to one visit in a week or two depending on conditions. Implementation of a regular oxidative regeneration and cleaning schedule was required to maintain catalytic activity |
| | Ease of Use | Routine operation does not require site operator | No, on-site maintenance required biweekly operator visits. |
| Quantitative | Contaminant Reduction | At least 99% TCE destruction | Yes, destruction was greater than 99% under normal operating conditions. |
| | Ability to Meet Regulatory Standards | Final concentration of TCE is below $5 \mu\text{g L}^{-1}$ | Yes, on average concentrations were below $5 \mu\text{g L}^{-1}$ during a 21 h operating cycle. |
| | In situ operation | System is operated in situ with HFTW. | Was not accomplished due to technical challenges |
| | Robustness | Achieves contaminant reduction goals when TCE concentration is $> 1 \text{ mg L}^{-1}$ | Influent concentrations ranged from 0.8 to 1.2 mg L^{-1} and system was still able to reduce concentrations to below MCL. Efficacy is sensitive to sulfide concentration [Lowry and Reinhard, 2000]. |
| | By-Product Formation | MCLs are met for cis-DCE and VC | Yes, ethylene was the only end product. |

3.2 Selection of Test Site

Of the criteria identified as critical, the following were met at Edwards AFB:

- Presence of halogenated contaminants, e.g., TCE and/or PCE, which are amenable to Pd-catalyzed reductive dehalogenation.
- Absence of compounds which are recalcitrant to Pd-catalyzed dehalogenation.
- Shallow water table. Although the Pd/HFTW technology is applicable at sites where the water table is deep, a shallow water table is preferable for the purposes of the technology demonstration because the cost of well installation increases with well depth.
- Presence of at least two hydrogeologic layers of high conductivity, in which the screened sections of the HFTWs can be placed.
- Sufficient hydrogeologic anisotropy to promote groundwater recirculation using HFTWs.
- Site has access to electricity, water, and other required infrastructure.
- Preferably, site has been well characterized in terms of hydrogeology, water quality, and contaminant concentrations.
- Support from the site host and relevant regulatory agencies.

The following conditions were met marginally and resulted in significantly higher development and operational costs and delays:

- Very low concentrations of sulfide ion, which can poison the Pd catalyst. Complete absence of sulfide is preferable; and
- Site location must be such that personnel can travel from Stanford to the demonstration site in a reasonably short amount of time (i.e., less than one day).

The following conditions were not considered but resulted in major complications:

- The site was located in a flood plain causing near catastrophic damage during the winter storms of 2004-2005;
- The site was often times not accessible due to weapons testing in the vicinity of the site causing many unproductive trips; and,
- For security reasons, access was restricted to American citizens, limiting collaboration of foreign students.

The following sites were evaluated as potential demonstration sites for this project: Moffett Federal Airfield (Mountain View, CA), Beale AFB (Marysville, CA), Travis AFB (Fairfax, CA), and Edwards AFB (Lancaster, CA). Of these, Edwards AFB was selected because the site was well characterized, infrastructure was already in place, and the site personnel and local regulators were supportive.

3.3 Test Site, Facility History and Characteristics

Edwards AFB occupies about 470 square miles of high desert area, including all of Rogers and Rosamond dry lakes. The primary mission of the base has been aviation development through experimental and test flight activities. The base presently is operated by the U.S. Air Force Flight Test Center (AFFTC). The base is located about 80 miles northwest from Los Angeles. Site 19 is an open tract of approximately 100 acres situated east of Taxiway E and south of Taxiway D. The site includes buildings 1928, 1931, and adjoining parking areas. These buildings and adjacent concrete pads were constructed in 1958 to house maintenance equipment and test racks for engines used in the X-15 rocket plane.

From 1958 through 1967, approximately one 55-gallon drum of trichloroethylene (TCE) was used per month to clean X-15 rocket engine parts. After 1967, the facility was used for much smaller engines and the TCE use dropped substantially. Testing at the facility ended altogether in 1975. During testing, standard practice was to rinse the spent solvent from the test stands into maintenance shop drains that lead to a concrete basin/holding pond. Wastewater which did not evaporate from the holding pond was periodically pumped and discharged into the desert south of Building 1931. The majority of the wastewater was discharged through a steel pipe leading from the holding pond and terminating approximately 300 feet south.

An additional source of contamination may have resulted from substances disposed into a septic tank and leach field which serviced Building 1931. The septic tank was removed in 1984 but the drain field was left in the ground. The exact location of the leach field is unclear. Two other potential sources for contamination include the original storm water retention pond and the Drainage Area B channel. The original storm water retention pond was located west of the current pond, covering an area approximately 350 feet by 180 feet. Surface runoff from Drainage Area A, which currently flows into the existing pond, previously flowed into the former pond. The unlined drainage channel in the northern portion of the site (discharging onto Rogers Dry Lake) is the terminus for surface runoff from Drainage Area B. Potentially contaminated surface runoff from Drainage Area B may enter the soil, and subsequently the groundwater, along any portion of this unlined channel.

The area south of the buildings has not been developed, although the current storm water retention pond was constructed in the 1960's to prevent drainage from the paved areas west of Site 19 from reaching Rogers Dry Lake. The pond is approximately 1000 feet long, 400 feet wide, and less than 10 feet deep. Historical photographs from Base History Office, Edwards AFB, indicate that parts of Site 19 and parts of Rogers Dry Lake east of Site 19 were periodically flooded prior to construction of the current storm water retention pond in the 1960's. During wet seasons, excess water from the retention pond periodically overflows into low-lying areas north of the pond.

The first evidence of contamination at Site 19 was the detection of TCE in a water sample from a well upgradient of the storm water retention pond. The aquifer containing the TCE is not used as a potable or agricultural water supply near the site. However, base supply wells are withdrawing from similar alluvial materials approximately three miles south of the site. The plume has moved approximately 700 m (2300 ft) from its origin 40 years ago. PCE has not been detected at Site 19 and could not be evaluated.

The demonstration site at Edwards AFB is approximately 400 m east of the storm water retention pond at Site 19. McCarty et al. [1998] and Gandhi et al. [2001] reported TCE concentrations of 1,100–1,400 $\mu\text{g L}^{-1}$ in the groundwater entering the demonstration site in the upper aquifer zone. Recent measurements elsewhere at Site 19 have shown TCE concentrations of 2,300 $\mu\text{g L}^{-1}$ in shallow wells and 4,500 $\mu\text{g L}^{-1}$ in deep wells [internal communication between Stanford University and Edwards AFB personnel].

Site 19 also contains parts of the main fuel transfer (pipeline) system that extends along Taxiway E. Fuel leakage from the pipeline occurred in the 1960's in the northwestern corner of Site 19, and an estimated 250,000 gallons of JP-4 jet fuel were released. Soil was excavated and approximately 100,000 gallons of fuel were recovered during remediation efforts. JP-4 jet fuel was last detected in 1992, and benzene was last detected in 1993.

3.4 Physical Set-up and Operation

The reactor system was mounted on a skid platform and placed on the ground in next to the treatment well. A trailer housing the pump controls systems for the pumps and the computer system, a supply storage and chemicals preparation room and a small workshop was in the vicinity. Hydrogen tanks were stored next to the skid.

3.5 Sampling/Monitoring Procedures

Sampling and analysis was automatic and performed with the ASAP system, which was used at the Seal Beach demonstration and other similar project. Only reactor influent and effluent were monitored.

3.6 Analytical Procedures

Samples processed by the ASAP were analyzed for VOCs by GC and anions by direct reading ion chromatography (IC). In addition, during background sampling, samples were processed by specific ion probe for sulfide (see Appendix of Final Report). For sulfide analysis, a Hach kit was used. TCE was analyzed with a detection limit of approximately 1 $\mu\text{g L}^{-1}$. Biogenic sulfide production within the reactor system was identified by the distinct sulfide odor in the effluent groundwater. The olfactory threshold for sulfide is 29 ng L^{-1} , much lower than analytical detection limits, making odor a more sensitive detection technique.

4. Performance Assessment

4.1. Catalytic TCE Removal: Data and Interpretation

Figure 4-1 represents the data collected from mid-July through the end of November 2005. The gaps in data are due to an interruption in analytical data collection, reactor down time or power failure. Removals exceeded 99% during normal operating conditions and 99.5% immediately after a regeneration cycle. Elevated effluent TCE concentrations during bleaching/regeneration cycles are not seen because they are too short to appear on the timescale of Figure 4-1. Figure 4-2 shows the removal efficiency under normal operating conditions with influent concentrations generally ranging from 800 to 1,230 $\mu\text{g L}^{-1}$ with residual concentrations ranging from 0 to 10 $\mu\text{g L}^{-1}$ during operation cycles and higher during bleaching/regeneration cycles.

TCE spikes occur during maintenance bleach cycles and last for about 3 hours. Long term average removals are 99.6% outside bleaching and 95.5% if concentrations during the bleaching periods are included. Figure 4-2 focuses on the effluent TCE concentrations under standard conditions. There is a trend of increasing TCE concentrations after a bleach pulse and preceding the following bleach pulse. Experience has shown that the effectiveness of the short bleach pulsing decreases with time and long-term or overnight bleaching of the catalyst is then required to restore activity.

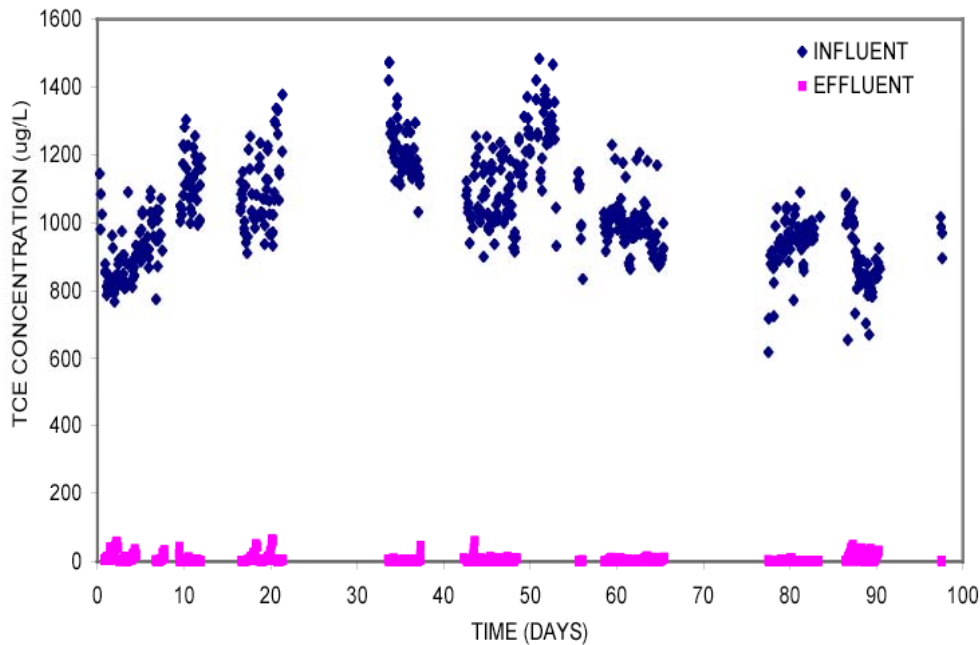


Figure 4-1. Performance of T1 Pd Catalyst Reactor during Jul-Sept 2005.

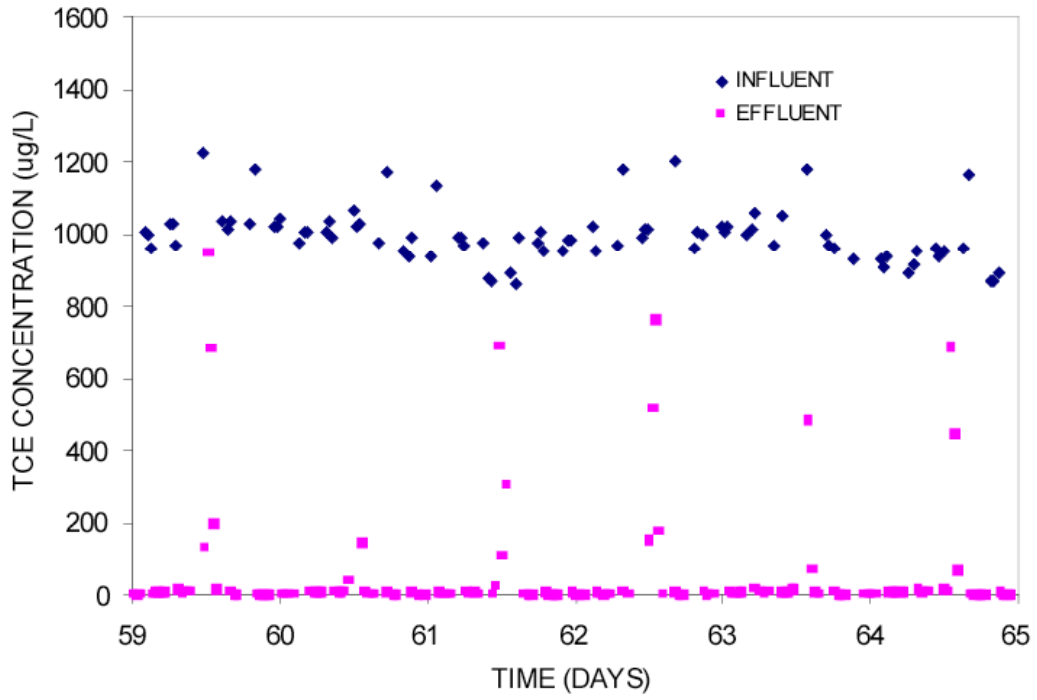


Figure 4-2. TCE removal during one day bleaching regime.

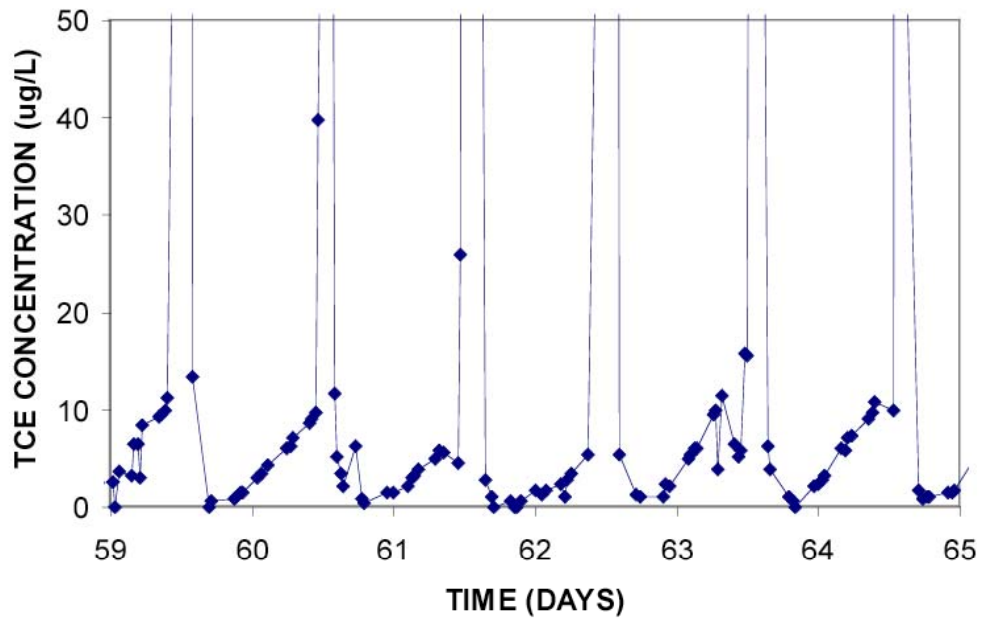


Figure 4-3. TCE residual concentration detail under one-day bleaching regime.

Increasing the frequency of bleach cycles with shorter pulse durations of higher bleach concentrations was tried; unfortunately, this resulted in lower TCE reduction efficiencies, presumably from the shorter pulse durations, but did not decrease the concentrations of the resulting spike in TCE concentrations. Removal of the trace levels of sulfide by precipitation on iron by adding a steel wool scrubber was also evaluated; although this worked, the steel wool dissolved in relatively short time period.

4.2 Performance Criteria and Data Assessment

Table 4-1 summarizes the expected and the actual performance of the process and experience and data gained in this demonstration is summarized in column 4.

Table 4-1: Expected Performance and Performance Confirmation Results

| Performance Criteria | Expected Performance Metric (pre demo) | Performance Confirmation Method | Actual (post demo) |
|--|---|--|---|
| Qualitative Primary Criteria (Performance Objectives) | | | |
| Maintenance | Requires only routine maintenance (e.g., changing hydrogen cylinders) for duration of demonstration | - Experience during technology demonstration - Review of maintenance records | Operation with low maintenance level was possible with improved system design |
| Ease of Use | - Routine operation does not require an operator - Sample collection and changing hydrogen tanks can be performed by personnel with minimum training - System can be operated by personnel with OSHA 24-hour or 40-hour HazWOPER training | - Experience during technology demonstration - Review of maintenance records. | Use was straight forward once standard operating procedures were in place. |
| Qualitative Primary Criteria (Performance Objectives) | | | |
| Contaminant Reduction | At least 99% destruction of TCE and other applicable contaminants | Compare influent, effluent concentrations of Pd reactors | >99% removal; better than expected performance |
| Meeting Regulatory Standards | Final concentration of TCE is below MCL ($5 \mu\text{g L}^{-1}$) | Effluent concentration analysis | Effluent concentration below MCL when calculated as daily average (see comments). |

| | | | |
|--|--|--|--|
| By-Product Formation | MCLs met for cis-DCE ($6 \mu\text{g L}^{-1}$) and VC ($0.5 \mu\text{g L}^{-1}$) | Effluent concentration analysis | By-products below MCL |
| Robustness/ Flexibility | | Effluent concentration histories | System failures result in hydrogen sulfide production |
| Catalyst Activity | Pd catalyst does not need replacement for at least 12 months, likely 5-10 years. | Catalyst was used for the entire project period even though is was poisoned multiple times as a consequence of system failures | Catalyst remained active for longer than 12 months are could be regenerated after prolonged sulfide poisoning. |
| Secondary Performance Criteria | | | |
| Operational Safety | Hydrogen addition can be performed without acceptable safety hazard. | Hydrogen was handled within safety margins | Hydrogen safety concerns need to be appropriately incorporated into the design of the system |
| Versatility | Technology is applicable for a broad range of contaminants | Laboratory studies testing other contaminants. | Technology was tested for TCE only but is applicable for other chlorinated ethylenes. |
| Process Waste | System operates <i>in situ</i> without generation of any secondary waste stream | Experience during technology demonstration | The regenerant bleach solution was discharged to the treatment well. Future designs could easily incorporate neutralization step for bleach. |
| Factors Affecting Technology Performance | Water quality, especially the presence of sulfidic compounds, is the most important determinant affecting technology performance | Experience from this and other sites and laboratory experiments. | The original single column design is not sufficient due to TCE spikes resulting from regeneration with bleach. |

Comparing the actual with the expected performance indicates that the primary objectives of the destruction process were met. Significantly, it was possible to consistently achieve better than 99% TCE removal for 23 h a day and 1 h catalyst regeneration. The regulatory limit of the effluent was met when concentrations are averaged over the 23-h treatment cycle. During a 23-h treatment cycle, concentrations increased from nearly zero to sometimes as high as $10 \mu\text{g L}^{-1}$ exceeding the MCL for approximately half of the time.

These conclusions are based on a relatively small data set, however, because the system performed reliably only towards the end of the demonstration once the reactor was fully developed and the operating procedure was adapted to the site conditions. It is also important to notice that operating conditions had to be maintained within narrow margins. Failure to do so, i.e., missing a bleaching within the specified time intervals resulted in catalyst poisoning and

system upsets. Poisoning causes TCE breakthrough and requires aggressive bleaching for several days. The secondary criteria were met and don't limit application of the technology.

4.3 Technology Comparison

The treatment technology is most appropriately compared with air stripping and activated carbon adsorption. The principle advantages of Pd catalysis are that no byproducts or emissions are produced except bleach solutions and that the technology has a smaller footprint. On the negative side, the technology requires much more sophisticated control mechanisms and detailed attentions to the safety concerns associated with the use of hydrogen. Additionally, Pd catalysis is compared with permeable reactive barriers which have been used for shallow groundwater contamination. A comprehensive efficacy and cost comparison is given in the next section.

5. Cost Assessment

5.1 Cost Reporting

Table 5.1 shows the relevant costs that were tracked and documented during the demonstration in order to estimate the capital and operational costs of the technology with a high degree of veracity.

Table 5-1: Cost Elements

| Cost Category | Sub-Category | Details |
|---|-----------------------------------|---|
| START-UP COSTS | Site Characterization | Characterize the hydrogeology and contaminant distribution of the contaminated site |
| | Bench-Scale Tests | Optimize catalyst performance for specific site conditions |
| | Engineering Design & Modeling | Design well construction, placement of treatment/monitoring wells, etc. |
| CAPITAL COSTS | Mobilization | 1. Permitting, written plans 2. Clearing construction, utilities 3. Set-up of temporary facilities |
| | Pd Catalyst for In-Well Reactors | Purchase commercially-available Pd-on-Alumina catalyst |
| | Reactor Fabrication | Construction of two fixed-bed Pd reactors for installation in treatment wells |
| | Treatment Well Construction | Construct assembly for treatment wells, including reactors, controls, sampling ports, and safeties |
| | Treatment Well Installation | |
| | Monitoring Well Installation | |
| OPERATING COSTS: Direct Environmental Activity Costs | Labor | Cost of an operator/technician to run the system. Does not include labor costs associated with sampling, analysis, or maintenance, which are considered separately. |
| | Consumable Materials | 1. Hydrogen gas 2. Catalyst replacement 3. Catalyst regenerant (e.g., hypochlorite) |
| | Maintenance and Repairs | |
| | Utilities and Fuel | Electricity, fuel, water |
| | Sampling and Analysis | Sample collection by project personnel; sample analysis by project personnel or by commercial laboratory |
| | Long-term Monitoring | Verification of remediation success |
| OPERATING COSTS: Indirect Environmental Activity Costs | Environmental and Safety Training | Includes OSHA 24-hour or 40-hour HazWOpER training |
| | OSHA Ambient Environment Sampling | Required for comparison with alternative technology |
| | Waste Manifesting | Required for comparison with alternative technology |
| OPERATING COSTS: Demobilization | Site Restoration | 1. Removal of equipment and structures 2. Well closure/removal |
| | Decontamination | |
| | Personnel demobilization | |
| | Reporting | |

5.2 Cost Analysis

Costs for Pd catalysis are compared with the costs of other baseline alternative technologies. The baseline alternative technologies chosen for this comparison are air stripping, granulated activated carbon (GAC) and permeable reactive barriers (PRB). Pump and treat technologies such as air stripping and GAC are the most commonly applied groundwater remediation methods. PRB is also referred to as “iron wall” or “iron curtain,” because zerovalent iron is almost always the catalytic material used. PRBs are often used for remediation of groundwater contaminated by chlorinated solvents. These technologies are compared in Table 5-2.

Table 5-2. Technologies for VOC Remediation.

| Technology | PCE | TCE | DCE | VC | Destructive | Notes |
|----------------------------------|-----|-----|-----|----|-------------|--|
| Air Stripping | • | • | • | • | No | <ul style="list-style-type: none"> - Ineffective at high conc. - Generates waste stream - Deep aquifers increase well/pump cost |
| Granular Activated Carbon (GAC) | • | • | | | No | <ul style="list-style-type: none"> - Ineffective at high conc. - Produces secondary waste stream - Deep aquifers increase well/pump cost |
| Permeable Reactive Barrier (PRB) | • | • | • | • | Yes | <ul style="list-style-type: none"> - Can also handle nitrate, nitrite - Only for shallow aquifers |
| Palladium Reductive Catalysis | • | • | • | • | Yes | <ul style="list-style-type: none"> - Can also handle nitrite - Faster kinetics than Fe - Applicable at high conc. - Water quality affects performance - Deep aquifers increase well/pump cost |

In order to compare the costs for these three technologies, it is necessary to specify the operational conditions, such as the scale of the operation, the hydrogeologic setting, the contaminant concentrations and any other relevant site conditions. The values shown in Table 5-3 do not represent estimates of the conditions at Edwards Air Force Base; rather, they are chosen to represent realistic values of a contaminated site, so that the Pd/HFTW technology can be compared to pump and treat (P&T) and PRB technologies. The groundwater TCE concentration of 1 mg L^{-1} is relatively average, as shown by the example field sites in Table 5-7. The acceptable endpoint of $5 \text{ } \mu\text{g L}^{-1}$ is the maximum contaminant level for TCE. Depth to water table will vary significantly by site, but 10 ft depth and 30 ft thickness is standard for a shallow aquifer, amenable to all technologies compared in Table 5-7. Other factors such as hydraulic gradient and conductivity are site specific, and the capture zone, maximum pump rate, inflation and interest are selected during project design. As such, many of the assumptions are site and project

specific and those listed below represent only a starting point for new project design.

Table 5-3: Basis for Cost Comparison

| Factor Affecting Cost | Value |
|---|------------------------------|
| Contaminant Concentrations | 1 mg L ⁻¹ TCE |
| Acceptable Endpoint | 5 µg L ⁻¹ TCE |
| Depth to Water Table | 10 feet below ground surface |
| Aquifer Thickness | 30 feet |
| Hydraulic Gradient | 0.0067 |
| Hydraulic Conductivity (average) | 10 m d ⁻¹ |
| Width of Capture Zone | 600 ft |
| Maximum Allowable Pump Rate through Treatment Wells | 3.5 gpm |
| Annual Inflation Rate | 5% |
| Annual Interest Rate | 8% |

Although budgeted, the Pd catalyst did not need frequent replacement and is expected to last for the life time of the technology. Therefore, catalyst cost is to be a one-time capital investment for a typical groundwater remediation project. The reactor system is budgeted above using PVC instead of stainless steel – in the wake of this pilot study it was determined that stainless steel adds unnecessary expense. Capital and operational costs are shown in Tables 5-4 and 5-5.

Table 5-4. Capital Costs.

| Cost Element | Cost | Subcost |
|--|------------------|----------------|
| Site Characterization | \$118,000 | |
| Hydrogeological characterization | | \$118,000 |
| <i>Wells for estimating hydraulic head and gradient (7 wells, \$10,000 each)</i> | | \$70,000 |
| <i>Pump tests to estimate hydraulic conductivity</i> | | \$24,000 |
| <i>Cores and analysis to estimate hydraulic conductivity</i> | | \$24,000 |
| Technology Mobilization, Set-up, and Demobilization | \$59,000 | |
| Transportation/delivery of equipments, facilities, and personnel | | \$24,000 |
| Set-up of temporary facilities (e.g. trailer) and utilities | | \$24,000 |
| Demobilization | | \$11,000 |
| Planning and Preparation | \$155,000 | |
| Engineering design and modeling | | \$85,000 |
| Permits and licenses, including water discharge | | \$24,000 |
| License fees associated with use of a technology | | \$0 |
| Regulatory interaction | | \$6,000 |
| Written plans | | \$40,000 |
| <i>Work plans</i> | | \$12,000 |
| <i>Sampling and analysis plans</i> | | \$12,000 |
| <i>Health and safety plans</i> | | \$6,000 |
| <i>Community relations plans</i> | | \$5,000 |
| <i>Site management plans</i> | | \$5,000 |
| Site Work | \$72,000 | |

| | | |
|---|------------------|----------|
| Establish physical infrastructure for technology application | | \$18,000 |
| Activities to restore site to pre-remediation conditions | | \$18,000 |
| Activities to meet specifications if site restoration plan | | \$18,000 |
| Preparing specific site of the technology | | \$18,000 |
| <i>Clearing and grubbing</i> | | \$6,000 |
| <i>Earthwork</i> | | \$6,000 |
| <i>Construction of utilities, etc.</i> | | \$6,000 |
| Installation of the Treatment System | \$134,000 | |
| Treatment wells (2 wells, \$20,000 per well) | | \$40,000 |
| Pumps (2 pumps, 2 gpm flowrate, \$5,000 per pump) | | \$10,000 |
| Packet | | \$5,000 |
| Assembly | | \$2,000 |
| Monitoring wells (4 wells, \$4,000 per well) | | \$16,000 |
| Palladium catalyst treatment system | | \$61,000 |
| <i>Palladium catalyst with eggshell coating (20 kg, \$245 per lb)</i> | | \$11,000 |
| <i>Skid-mounted reactor system and gas skid</i> | | \$50,000 |
| Start-up and Testing | \$18,000 | |
| Establishment of operation conditions | | \$6,000 |
| Shakedown | | \$6,000 |
| Training of O&M personal | | \$6,000 |
| Other Costs | \$18,000 | |
| Data processing and computer equipment | | \$6,000 |
| Safety equipment | | \$6,000 |
| Vehicles | | \$6,000 |
| Miscellaneous | | \$0 |
| TOTAL CAPITAL COST | \$574,000 | |

Table 5-5. Operation & Maintenance Costs

| Cost Element | Cost | Subcost |
|--|-----------------|----------------|
| Labor | \$35,000 | |
| Maintenance of technology and associated equipment | | \$25,000 |
| Labor supervision (100 h, \$50 per h) | | \$5,000 |
| Payroll expense (100 h, \$50 per h) | | \$5,000 |
| Materials | \$1,350 | |
| Pd catalyst | | \$0 |
| Chemicals | | \$1,350 |
| <i>Hydrogen gas (6 cyl, \$50 per cyl, \$10 per month rental fee)</i> | | \$720 |
| <i>Bleach (2 gal per column per wk, 2 columns, \$3 per gal)</i> | | \$630 |
| Utilities and Fuel | \$2,000 | |
| Fuel | | \$500 |
| Electricity | | \$1,000 |
| Water | | \$500 |
| Equipment ownership, Rental or Lease | \$0 | |
| Equipment ownership | | \$0 |
| Rental | | \$0 |
| Lease | | \$0 |

| | | |
|---|-----------------|---------|
| Other Costs | \$10,000 | |
| Repair/maintenance of office/administrative equipment | | \$5,000 |
| Health and safety cost | | \$5,000 |
| <i>Personal protective Equipments</i> | | \$2,000 |
| <i>Monitoring of personnel health and safety</i> | | \$3,000 |
| Total Operation and Maintenance Cost (Annual) | \$48,350 | |

Monitoring costs for a Pd/HFTW system are shown in Table 5-6. Early monitoring is monthly and bi-monthly (years 1-3) in anticipation of operational issues that demand attention during start-up; monitoring in subsequent years is quarterly, reflecting the minimal attention needed once the reactor is operational and the early issues are resolved. A few important notes about the table:

- The sampling frequency follows the shown schedule, and costs are based on the assumption of two (2) monitoring wells and a cost of \$1,000 per well per round of sampling and analysis;
- Inflation was assumed 5% annually, with a discount rate of 8%; and,
- The clean-up time for the example site is estimated at 10 years, with a replacement cost of \$11,000 for palladium catalyst at end of year 5 included.

Table 5-6. Monitoring Costs.

| Year | Sample frequency | Monitoring cost | O&M cost | Inflated O&M |
|----------------------------------|------------------|-----------------|----------|------------------|
| 1 | Monthly | \$24,000 | \$72,350 | \$72,000 |
| 2 | Bi-monthly | \$12,000 | \$60,350 | \$63,000 |
| 3 | Bi-monthly | \$12,000 | \$60,350 | \$67,000 |
| 4 | Quarterly | \$8,000 | \$56,350 | \$65,000 |
| 5 | Quarterly | \$8,000 | \$56,350 | \$68,000 |
| 6 | Quarterly | \$8,000 | \$56,350 | \$72,000 |
| 7 | Quarterly | \$8,000 | \$56,350 | \$76,000 |
| 8 | Quarterly | \$8,000 | \$56,350 | \$79,000 |
| 9 | Quarterly | \$8,000 | \$56,350 | \$83,000 |
| 10 | Quarterly | \$8,000 | \$56,350 | \$87,000 |
| O&M cost, NPV | | | | \$482,000 |
| Pd replacement cost ¹ | | | | \$11,000 |
| Total O&M cost | | | | \$493,000 |
| Total O&M cost, NPV | | | | \$493,000 |

The costs of the three technologies must be compared over their entire life cycles. This analysis is based upon a net-present-value approach, using 5% annual inflation and 8% interest rates. The costs considered are start-up costs, capital costs, operations and maintenance (O&M) costs and recurring regulatory or institutional oversight costs. Future liability is not considered for the PRB and the Pd/HFTW technologies because these destroy TCE rather than transferring it to a different medium. Future liability must be considered for evaluation of the P&T technology. The

life cycle period will commensurate with the time period required for each technology to treat the entire contaminant plume. Table 5-7 shows other pilot studies and field sites using alternative technologies. All costs are inflated to June 2006, and the adjusted total cost provides a basis for economic comparison of the competing technologies.

5.3 Cost Comparison

Comparing various field sites where these technologies were implemented, Pd catalysis is cost competitive as an alternative treatment technology for VOC contaminated groundwater. Table 5-7 details the cost comparison. Data for each project was extrapolated to an operation period of 10 years to provide consistent weighting for capital and operating costs.

Table 5-7. Examples of Cost Evaluations of Different Competing Technologies

| Technology | TCE [mg L ⁻¹] | Removal [%] | Cost per 1,000 gal treated ¹ [\$] |
|--|------------------------------|-----------------|---|
| <i>Air Stripping</i> | | | |
| Gold Coast, FL ² | 0.45 | 99 | 7 |
| Des Moines, IA ² | 0.045 | 96 | 1 |
| <i>Granular Activated Carbon (GAC)</i> | | | |
| La Salle, IL ² | 13.3 | 96 | 250 |
| Old Mill, OH ² | 6.1 | 75 | 336 |
| Lawrence Livermore National Lab, CA ³ | 3.0 | 99 | 83 |
| Commencement Bay, WA ² | 0.13 | 98 | 10 |
| <i>Permeable Reactive Barrier (PRB)</i> | | | |
| Moffett, CA ² | 20 | -- ⁴ | 547 |
| Intersil, CA ² | 13 | 98 | 228 |
| <i>Palladium Reductive Catalysis</i> | | | |
| Edwards AFB, CA | 1 | 99.6 | 8 |
| | 10 | 99.9 | 9 ⁵ |

¹ All costs amortized for 10 years operation.

² Data taken from EPA report no. 542-R-99-006 {{127 USEPA 1999; }}.

³ Data taken from McNab et al {{41 McNab,W.W. 2000; }}.

⁴ Data not given.

⁵ Estimated using the economic model for Edwards AFB (2007).

The normalized costs (\$ per 1000 gal) were calculated by dividing the total net present values of capital and O&M costs by the total number of gallons treated during the 10 years project period. At \$8 per 1,000 gal, catalytic technology is cost competitive with GAC and PRB at all field sites listed. Air stripping is more cost effective at low TCE concentrations, but if TCE is present at or above 1 mg L⁻¹, Pd catalysis becomes much more competitive. An estimated cost for remediation of 10 mg L⁻¹ TCE to the MCL of 5 µg L⁻¹ was generated using the economic model developed during this project. As shown, the total cost only increased by \$1 per 1,000 gal treated because

the capital costs are relatively nominal when compared with the O&M costs. There are many compounds, including DCE and VC, that only adsorb weakly on GAC and thus Pd catalysis offers a significant improvement in remediation methods. GAC is not economically viable at elevated contaminant concentrations, as seen in Table 5-7, because the carbon must be replaced or regenerated frequently. If the groundwater is contaminated with multiple chlorinated solvents, GAC and air stripping will increase significantly in price as they become saturated much more quickly. Pd catalysis can handle multiple contaminants, especially chlorinated ethylenes, and elevated concentrations in a single pass, offering a distinct advantage over other technologies.

Given that PRBs need little to no maintenance, the technology costs in Table 5-7 may appear elevated. However, it is important to note that PRBs operate with very slow groundwater velocities at higher capital costs and relatively equal operating costs when compared with pump and treat technologies. Pd catalysis can be used to treat high volumes of water at controllable rates, but PRBs are constrained by groundwater flow rates and the permeability of the reactive wall. Thus, actual treatment costs are not as cheap as one might expect from a relatively passive treatment technology.

5.4 Life Cycle Analysis

For full-scale implementation of Pd catalysis, the life-cycle costs are dependent primarily on the project duration and the establishment of an effective maintenance schedule. By operating a Pd reactor for a longer period of time, the capital costs including the catalyst, pumps and associated plumbing are amortized at a lower rate, thereby lowering overall costs. Another important cost factor is effective maintenance of the catalyst and reactor (mainly periodic disinfection), which maintains high catalyst activity and long-term TCE removal, possibly beyond the five-year budgeted catalyst lifetime.

Operational costs are relatively low given the amount of TCE destroyed in the process – basically having sufficient maintenance personnel time allocated to bleaching and periodic grab sampling ensures the system is effectively collecting and treating the contaminated groundwater. The frequency of grab sampling could decrease over time if the system has consistent TCE removal during the start-up months but would likely depend on the requirements of the overseeing regulatory agency.

Table 5-8 presents the life cycle costs for implementing Pd catalysis at a site contaminated with 1 mg L⁻¹ TCE. For an operational period of 5 years, the total cost of building and operating a catalytic Pd reactor would be \$840,000. If operated for 10 years, assuming Pd replacement after year 5, the total cost is \$1,065,000.

Table 5-8. Present Value Estimates Pd Reactor Operation

| Element | NPV |
|-----------------------------|-------------|
| Capital investment | \$572,000 |
| Pd replacement after 5 y | \$11,000 |
| Annual O&M cost | \$48,000 |
| Annual monitoring cost | \$70,000 |
| Present value over 5 years | \$840,000 |
| Present value over 10 years | \$1,065,000 |

6. Implementation Issues

6.1 Cost Observations with the Demonstration System

The key factors that affected project costs included (1) debugging the control system, (2) redesigning and rebuilding the reactor, (3) developing a site specific operating protocol, (4) developing a detailed understanding of the poisoning process, (5) flooding of the site, (6) travel to the site, (7) extreme variations in temperature, and (8) interlocking of hydrogen system and treatment system in areas that were not needed. Costs that could be avoided in a follow up demonstration are costs for stainless steel reactors, hollow fiber hydrogen feed modules. The most important parameter affecting the costs of operating the technology is monitoring frequency and the impact of water quality on bleaching schedule. For instance anaerobic conditions require more frequent bleaching and therefore reduce the throughput. Significantly, the catalyst turned out to be nearly indestructible and not a cost factor. With proper maintenance, the catalyst life time may last for the duration of a project. The reactor should be developed with robust control and communication system, reliable bleaching and hydrogen feed systems, and should be procured with operational guarantees.

6.2 Performance Observations

Although the site water had a high tendency to turn sulfidic, we were able to meet treatment goals. Operation in conjunction with the HFTW was not possible due to the long and difficult start up phase. Subsurface operation of the reactors (originally planned) would have added costs to the operation that seem out of proportion to the benefits gained.

6.3 Scale-up

The demonstration-scale was perhaps two to four times smaller than an expected a full-scale application at this site. At many sites, water flow may be limited by the capacity of the well to produce water. We recommend extensive testing of a system of this size system before significant up scaling is attempted and systems with multiple treatment pairs are attempted..

6.4 Other Significant Observations

Significant benefits can be gained by implementing this technology. For typical sites the demonstration size was appropriate and cost estimates relatively accurate. Implementation requires a willingness to comply with the safety precautions for using hydrogen, which is not common knowledge for most environmental engineering firms.

6.5 Lessons Learned

Overall, the Edwards Air Force Base (AFB) demonstration project showed that reductive catalytic destruction of TCE is an efficient technology ready for field implementation, provided the lessons learned from this project are applied to future sites. The capability of the technology to handle high TCE concentrations makes it very attractive for source control at many Department of Defense (DoD) and commercial contaminated groundwater sites. This memorandum identifies and explains the major technical, regulatory and management aspects that must be considered in applying catalytic groundwater treatment at other field sites.

6.5.1 In Situ v. Ex Situ

The Edwards AFB demonstration project was planned and designed to operate in situ by installing the reactors inside 6-inch diameter treatment wells, but was only tested ex situ, i.e., with the reactors and the associated plumbing and instrumentation mounted above grade on a rig accessible for maintenance. Mounting the reactor column inside the treatment wells (i.e., operating in situ) would result in higher maintenance costs since lifting the reactors from the wells would require a crane. The reasons to operate this technology in situ are:

- (1) Regulatory compliance
- (2) Site footprint requirements

For the Edwards AFB demonstration project, the regulatory requirement that the treated water was not to be reinjected into the subsurface was waived, allowing evaluation of the technology above in ex situ mode. Considering the technology is still relatively immature, it is recommended that the technology be operated ex situ until all reliability issues are resolved, which will require regulatory approval.

At military and industrial sites, it is not expected that the footprint will be of concern as open space is ample and the footprint of an ex situ system is still relatively small. In urban settings or locations where an extremely small footprint is required, operating in situ will reduce the visible footprint of the site.

6.5.2 Site Selection

Applicability of catalytic technology is determined by two criteria:

- (1) Target contaminant reactivity and site water concentration
- (2) Site water quality

While this demonstration examined groundwater contaminated with TCE, the technology is also applicable to other contaminated aqueous streams such as wastewater, industrial effluent and drinking water as long as water quality does not significantly hinder the catalytic process. For contaminants that are less reactive than TCE and other chlorinated ethylenes, reactors would need to be larger than that used at Edwards AFB, increasing the cost.

Site water quality can significantly impact the efficacy of Pd-catalyzed contaminant reactivity. The most significant groundwater matrix species is sulfide, which is believed to poison Pd catalyst at any concentration, even at or below the odor threshold of $\sim 29 \text{ ng L}^{-1}$. From a practical standpoint, the technology should not be implemented where sulfide is detectable by odor or any other method. Similarly, if sulfide odor is noticed in the reactor effluent but not in the influent, sulfide is biogenically produced within the reactor, indicating the need for bleaching. There was no oxygen in the Edwards AFB groundwater. In laboratory experiments it was shown that dissolved oxygen impacts the process by consuming hydrogen; TCE conversion was reduced from 46.0% to 13.4% by adding 450 μM oxygen to the influent water (oxygen was 67% converted) [Lowry and Reinhard, 2001]. However, these impacts are relatively insignificant and can be overcome increasing the reactor size and adding excess hydrogen. Overall, the presence of oxygen is beneficial because it inhibits sulfide formation.

Sulfate itself does not affect catalyst performance because it is not reduced by Pd and hydrogen, but in the presence of hydrogen and sulfate-reducing bacteria it is readily converted to sulfide which poisons the catalyst. The ideal site for Pd-catalyzed reduction of a target contaminant would have a very reactive contaminant (e.g., TCE) and a low concentration of oxygen to inhibit sulfide formation. Overall, anoxic sites such as the Edwards AFB site with no oxygen but some nitrate are suited for the application Pd catalysis.

6.5.3 System Design, Fabrication, and Procurement

As each field site has different groundwater contaminant and matrix conditions, sites must be evaluated on a case-by-case basis. Once groundwater hydrogeology is understood and contaminant removal levels are established, system sizing and detailed design can follow simple guidelines.

- (1) Systems should be sized based on the optimal design of horizontal flow treatment wells and the hydrogeological conditions
- (2) Components should be extensively tested at the factory under realistic treatment conditions
- (3) Delivery should only be considered complete after on-site testing
- (4) Systems should be equipped for remote control
- (5) For remote systems, local maintenance support should be available on an as needed basis.

Sizing of the system depends on the overall treatment needs and the design of the water extraction and re-injection system. Hydraulic loading several times of what has been tested at the Edwards AFB site should be possible. Scaling to lower flows is also possible.

Component testing requires operating the system with similar groundwater (i.e., similar pH and matrix species). The desired flowrate should be verified and tested for pump and pipe sizing verification. Extreme temperatures should be considered if they will be encountered on-site.

Requiring on-site testing of the system is essential to ensure hydraulic performance on-site is commensurate with that in the lab. Flow control and valve systems must be checked with the integration of automated sampling and analysis mechanical equipment. Also, training of on-site personnel is essential to minimize operation and maintenance costs. Remote control of the system should be tested to ensure technical feasibility of remote operation.

Finally, post-delivery support must be local. System downtime increases significantly when support is distant and/or non-responsive.

6.5.4 Project Management

Managing a demonstration or full-scale field site using catalytic reductive technology requires trained management and operations personnel and well-designed operational and safety plans. The recommended approach is to develop a project management structure as follows:

- (1) Implement a phased approach to all tasks with discrete goals for each phase; and,
- (2) Scrutinize the interdependencies of each task and allow slack for adjustments.

The phased approach creates a much longer anticipated timeline, but better addresses the needs encountered in the field. Having discrete goals focuses efforts on the task at hand and results in

achievable deliverables. Scrutiny of the interdependencies of each task is important because delays in one task will inevitably impact all related tasks. For example, the technology should be contemplated for use only at well-characterized sites.

If the system is to be operated remotely, it is important to have an operational plan that details the interaction between remote operators and site personnel – especially during emergencies, periods of system malfunction or maintenance.

6.6 End-User Issues

To consider implementing the technology, potential end-users need access to relevant expertise technology, which at this point is not yet widely available.

6.7 Approach to Regulatory Compliance and Acceptance

Regulatory acceptance should not be a problem.

7. References

- Air Force Institute of Technology, <http://en.afit.af.mil/env/insitubio.htm>.
- Baker, E.G., L.J. Sealock, R.S. Butner, D.C. Elliott, G.G. Neuenschwander, and N.G. Banns. 1989. *Catalytic destruction of hazardous organics in aqueous wastes: Continuous reactor system experiments*. Hazardous Waste & Hazardous Materials, vol. 6(1), pp. 87–94.
- California Department of Health Services, 2001. <http://www.dhs.ca.gov/ps/ddwem/chemicals/PHGs/TCEMCLreport12-01.pdf>
- Christ, J.A., M.N. Goltz, and J. Huang. 1999. *Development and application of an analytical model to aid design and implementation of in situ remediation technologies*. Journal of Contaminant Hydrology, vol. 37, pp. 295–317.
- Cunningham, J.A., T.P. Hoelen, G.D. Hopkins, C.A. Lebron, and M. Reinhard. 2006. *Bioremediation of cis-DCE at a sulfidogenic site by amendment with propionate*. Groundwater Monitoring & Remediation, in press 26, (2006).
- Ferland, D.R., K.G. Boggs, S. Niekamp, J.A. Christ, A. Agrawal, and M.N. Goltz. 2000. *Chlorinated hydrocarbon treatment using a horizontal flow treatment well system*. Remediation of Chlorinated and Recalcitrant Compounds: Physical and Thermal Technologies. G.B. Wickramanayake and A.R. Gavaskar, editors. Battelle Press, Columbus, OH, vol. C2-5, pp. 253–260.
- Ferland, D.R., and M.N. Goltz. 2000. *Modeling an innovative technology to remediate chlorinated-solvent-contaminated groundwater*. Military Engineer, in review.
- Gandhi, R.K., G.D. Hopkins, M.N. Goltz, S.M. Gorelick, and P.L. McCarty. 2001. *Full-scale demonstration of in situ cometabolic biodegradation of trichloroethylene in groundwater, 1: Dynamics of a recirculating well system*. Water Resources Research, in review.
- Kalnes, T.N., and R.B. James. 1988. *Hydrogenation and recycle of organic waste streams*. Environmental Progress, vol. 7(3), pp. 185–191.
- Kovenklioglu, S., Z. Cao, D. Shah, R.J. Farrauto, and E.N. Balko. 1992. *Direct catalytic hydrodechlorination of toxic organics in wastewater*. American Institute of Chemical Engineers Journal, vol. 38(7), pp. 1003–1012.
- Lowry, G., and M. Reinhard. 1999. *Hydrodehalogenation of 1- to 3-Carbon Halogenated Organic Compounds in Water Using a Palladium Catalyst and Hydrogen Gas*. Environmental Science & Technology, vol. 33(11), pp. 1905–1910.
- Lowry, G., and M. Reinhard. 2000. *Pd-catalyzed TCE dechlorination in groundwater: Solute effects, biological control, and oxidative catalyst regeneration*. Environmental Science & Technology, vol. 34(15), pp. 3217–3223.

- McCarty, P.L., M.N. Goltz, G.D. Hopkins, M.E. Dolan, J.P. Allan, B.T. Kawakami, and T.J. Carrothers. 1998. *Full-scale evaluation of in situ cometabolic degradation of trichloroethylene in groundwater through toluene injection*. Environmental Science & Technology, vol. 32(1), pp. 88–100.
- McNab, W.W., Jr., R. Ruiz, and M. Reinhard. 2000. *In-situ destruction of chlorinated hydrocarbons in groundwater using catalytic reductive dehalogenation in a reactive well: Testing and operational experiences*. Environmental Science & Technology, vol. 34(1), pp. 149–153.
- Munakata, N. 2005. *Palladium Catalyzed Hydrodechlorination for the Treatment of Groundwaters: Sulfide Deactivation Model, Regenerant Comparison, and Chemical Surface Changes*. PhD Thesis, Department of Civil and Environmental Engineering, Stanford, CA.
- Rylander, P.N. 1973. *Organic Syntheses with Noble Metal Catalysts*. Academic Press, New York.
- Schreier, C.G., and M. Reinhard. 1995. *Catalytic Hydrodehalogenation of Chlorinated Ethylenes Using Palladium and Hydrogen for the Treatment of Contaminated Water*. Chemosphere, vol. 31(6), pp. 3475–3487.
- Siantar, D.P., C.G. Schreier, C.-S. Chou, and M. Reinhard. 1996. *Treatment of 1,2-Dibromo-3-Chloropropane and Nitrate-Contaminated Water with Zero-Valent Iron or Hydrogen/Palladium Catalysts*. Water Research, vol. 30, pp. 2315–2322.
- United States Environmental Protection Agency. 1997. *Clean Up the Nation's Waste Sites: Markets and Technology Trends, 1996 Edition*. EPA 542-R-96-005, April 1997.

8. Points of Contact

Table 8-1: Points of Contact

| POINT OF CONTACT Name | ORGANIZATION Name Address | Phone/Fax/email | Role in Project |
|--------------------------|--|---|--------------------------------|
| Carmen LeBron | Naval Facilities Engineering Service Center Restoration Development Branch 1100 23rd Ave., ESC-411 Port Hueneme, CA 93043 | Phone: 805-982-1616 FAX: 805-982-4304 Carmen.lebron@navy.mil | Project Manager |
| Martin Reinhard | Stanford University Dept. of Civil & Environmental Engineering. Stanford, CA 94305-4020 | Phone: 650-723-0308 FAX: 650-723-7058 reinhard@cive.stanford.edu | Principal Investigator |
| Mary Spencer | Edwards Air Force Base Chief, Env. Mgmt. Restoration Branch AFFTC/EMR 5 East Popson Ave, Bldg 2650A Edwards AFB, CA 93524 | Phone: 661-277-1466 FAX: 661-277-6145 mary.spencer@edwards.af.mil | Site Host |
| Richard Russell | U.S. Environmental Protection Agency Region 9, SFD-8-1 75 Hawthorne Street San Francisco, CA 94105 | Phone: 415-744-2406 russell.richard@epa.gov | Remedial Program Manager (RPM) |
| Elizabeth Lafferty | Regional Water Quality Control Board Lahontan Region 6V, Victorville Office 15428 Civic Center Dr., Suite 100 Victorville, CA 92392 | Phone: 760-241-6583 | Remedial Program Manager (RPM) |
| John O’Kane | Department of Toxic Substances Control 8800 Cal Center Drive Sacramento, CA 95826 | | Remedial Program Manager (RPM) |
| Bob Wood | Edwards Air Force Base | Phone: 661-277-1407 | Remedial Program Manager (RPM) |

| | | | |
|--------------------|--|--|--|
| | Chief, Environmental Restoration Division AFFTC/EMR 5 East Popson Ave., Bldg. 2650A Edwards AFB, CA 93524-1130 | FAX: 661-277-6145 robert.wood@edwards.af.mil | |
| Dorothy Coughlin | Computer Sciences Corporation Flight Test Support Center P.O. Box 446 Edwards AFB, CA 93523-0446 | Phone: 661-277-9203 FAX: 661-277-1527 dorothy.coughlin@edwards.af.mil | Community Relations |
| Roberto Ruiz | Lawrence Livermore National Laboratory 7000 East Avenue, L-530 Livermore, CA 94550 | Phone: 925-422-0061 FAX: 925-422-9203 mcnab1@llnl.gov | Reactor design |
| Mark Goltz | Air Force Institute of Technology Dept. of Engineering & Environmental Mgmt. 2950 P Street, Building 640 Wright-Patterson AFB, OH 45433-7765 | Phone: 937-255-6565 FAX: 937-656-4699 mgoltz@afit.af.mil | Model development |
| Jeffrey Cunningham | Jeff Cunningham, Assistant Professor Dept. of Civil & Environmental Engineering University of South Florida 4202 E. Fowler Ave., ENB 118 Tampa, FL 33620 | e-mail: cunning@eng.usf.edu phone: 813-974-9540 fax: 813-974-2957 web: http://www.eng.usf.edu/~cunning | Workplan Development |
| Gary Hopkins | Stanford University Dept. of Civil & Environmental Engrng. Stanford, CA 94305-4020 | Phone: 408-262-2070 FAX: 408-263-8931 hopkins@cive.stanford.edu | Site construction; Site management; Safety Officer |