ENGINEERING SERVICE CENTER
Port Hueneme, California 93043-4370

CONTRACT REPORT
CR-07-022-ENV

ADDENDUM TO CR-07-016-ENV:
IN SITU CATALYTIC GROUNDWATER TREATMENT USING PD-CATALYSTS AND HORIZONTAL FLOW TREATMENT WELLS

ACTION ITEM: LESSONS LEARNED

Submitted by:
Carmen Lebron, Naval Facilities Engineering Service Center
Martin Reinhard, Gary Hopkins, and Matthew Davie, Stanford University

February 2007

Approved for public release; distribution is unlimited.

Environmental Security Technology Certification Program (ESTCP)

In Situ Catalytic Groundwater Treatment Using Pd-Catalysts and Horizontal Flow Treatment Wells
ER-0012

Action Item: Lessons Learned

February 2007

Summary of Lessons Learned

The capability of reductive catalytic destruction was demonstrated during an ex situ pilot scale demonstration at an Edwards Air Force Base (AFB) site where groundwater is contaminated with high concentrations of TCE. This memorandum identifies and explains the major technical, regulatory and management aspects that must be addressed before applying catalytic groundwater treatment at other field sites.

1. Operating In Situ Versus Ex Situ

The Edwards AFB demonstration project was planned and designed to operate in situ by installing the reactors inside 6-inch diameter horizontal flow treatment wells. Motivating factors behind operating this technology in situ include:

(1) Regulatory compliance (no need to extract groundwater above surface for treatment), and
(2) Site footprint requirements (the desire to minimize the visible footprint of the field site therefore gaining the flexibility to operate in situ when there is not enough space on site to have an ex situ system).

The demonstration plan called for initial operation ex-situ, followed by in-situ operation of the reactors once maintenance requirements were identified. Soon after ex-situ operation began, it became obvious that 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. Therefore a decision was made to operate the reactors ex situ only, i.e., with the reactors and the associated plumbing and instrumentation mounted above grade on a rig accessible for maintenance. In this specific case, 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.

A lesson learned during this demonstration is that the technology is relatively immature, therefore, it is recommended that the technology be operated ex situ until all reliability and maintenance issues are addressed.

At military and industrial sites, it is not expected that the footprint (i.e., the amount of open space necessary to host the reactors and associated plumbing) 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.

2. Target Contaminants and Site Water Quality

Applicability of catalytic technology is determined by two criteria:

a) <u>Target contaminant reactivity and site water concentration</u>

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. Table 1 provides a preliminary list of contaminants that are potentially amenable to catalytic reduction using Pd and hydrogen gas and their corresponding reactivities (normalized to TCE). For contaminants that are less reactive than TCE and other chlorinated ethylenes, the contact time would need to be greater than the 0.71 min used at Edwards AFB, requiring either larger reactors or a slower flowrate.

Table 1: Compounds Amenable to Catalytic Destruction Using Pd and Hydrogen Gas

Contaminant	By-products	Relative Reactivity
Trichloroethylene (TCE)		1.00
Dichloroethylene isomers (DCE)		
c-DCE		1.30
t-DCE		1.22
1,1-DCE		1.09
1,2-dibromo-3-chloropropae (DBCP)		0.97
Carbon tetrachloride (CT)	Chloroform	0.91
Vinyl chloride (VC)		0.90
Tetrachloroethylene (PCE)		0.83
1,1,2-trichlorotriflouroethane (Freon-113)		0.23
Nitrite		0.10
Chloroform (CF)		0.06
N-Nitrosodimethylamine (NDMA)		0.01

(b) Site water quality

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 ~ 29 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.

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.

In addition, although there was no oxygen in the Edwards AFB groundwater, laboratory experiments have shown that dissolved oxygen impacts the process by consuming hydrogen. For example, 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 can be overcome increasing the reactor size and adding excess hydrogen. Overall however, the presence of some oxygen is beneficial because it inhibits sulfide formation.

Table 2 lists the effect of groundwater quality parameters on Pd catalyst performance and Catalytic Reductive Dechlorination (CRD).

Table 2. Site Characteristics Affecting CRD Technology Performance.

Site Characteristic	Anticipated Effect on Technology Performance
Dissolved oxygen	No anticipated effect given sufficient hydrogen addition.
Sulfide	Can poison Pd catalyst, even below detection limit of common test kits (0.01 mg L^{-1}). Requires oxidative regeneration (hypochlorite).
Soil microbial population	Possible reduction in activity if sulfate-reducing bacteria form biofilms on Pd catalyst surface and/or generate sulfide. Can be controlled via hypochlorite treatment.
Groundwater buffer capacity	Groundwater must be sufficiently buffered that formation of hydrochloric acid during contaminant dechlorination (if applicable) does not significantly alter groundwater pH. It is expected that most aquifers have this capacity.

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 <u>on-site</u> 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 can be increased several fold more

than the 1.23 m min^{-1} used at Edwards AFB by designing longer, narrower reactors. Contact time is the factor controlling TCE removal. Scaling to lower flows is also possible.

It is recommended that components be tested while operating the system with similar groundwater (i.e., similar pH and matrix species) as the site. The desired flowrate should be verified and tested for pump and pipe sizing verification. Extreme temperatures should be considered if they are expected at the site.

On-site testing of the system is essential to ensure hydraulic performance on-site is commensurate with that estimated 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 system components should be tested to ensure operability of the system.

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 periods of system malfunction or maintenance.

Finally, troubleshooting support must be procured locally as there will be unanticipated problems once the system is installed and operation commences. System downtime increases significantly when support is distant and/or non-responsive.

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 will likely create a longer schedule, but will address the needs encountered in the field better. 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. Furthermore, the technology should be contemplated for use only at well-characterized sites.