

Palladium Catalysis Horizontal-Flow Treatment Wells: Field-Scale Design and Laboratory Study

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PALLADIUM CATALYSIS IN HORIZONTAL-FLOW TREATMENT WELLS: FIELD-SCALE DESIGN AND LABORATORY STUDY

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ABSTRACT: This paper discusses the field-scale design and associated laboratory experiments for a new groundwater remediation system that combines palladium-catalyzed hydrodehalogenation with the use of dual horizontal-flow treatment wells (HFTWs). Palladium (Pd) catalysts can treat a wide range of halogenated compounds, often completely and rapidly dehalogenating them. The HFTW system recirculates water within the treatment zone and provides the opportunity for multiple treatment passes, thereby enhancing contaminant removal. The combined Pd/HFTW system is scheduled to go on line in mid-2002 at Edwards Air Force Base in southeastern California, with groundwater contaminated with 0.5 to 1.5 mg/L of trichloroethylene (TCE). Laboratory work, performed in conjunction with the field-scale design, provided reaction rates for field-scale design and information on long-term catalyst behavior. The apparent first-order reaction rate constant for TCE was 0.43/min, corresponding to a half-life of 1.6 min. Over the long term (1 to 2 months), the reaction rate decreased, indicating catalyst deactivation. The data show three distinct deactivation rates: a slow rate of 0.03/day over approximately the first month, followed by faster deactivation at 0.16 to 0.19/day. The final, fastest deactivation (0.55/day) was attributed to an artifact of the laboratory setup, which caused unnaturally high sulfide concentrations through bacterial reduction of sulfate to sulfide, a known catalyst poison. Sodium hypochlorite recovered the catalyst activity, and is expected to maintain activity in the field with periodic pulses to regenerate the catalyst and control growth of sulfate-reducing bacteria.

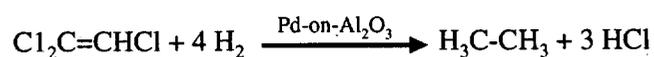
INTRODUCTION

Groundwater contamination is a significant problem at thousands of Department of Defense (DoD) installations and former defense sites. The U.S. Environmental Protection Agency (U.S. EPA) estimated in 1996 that of 8,336 DoD sites needing cleanup, approximately 70% had contaminated groundwater (U.S. EPA, 1997). Volatile organic compounds (VOCs) are the most common groundwater contaminants and are found at approximately 75% of contaminated groundwater sites; the most commonly encountered VOCs are chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (also called perchloroethylene, or PCE). Based on the U.S. EPA estimates, TCE and PCE contaminate the groundwater at over 2,000 DoD installations. The TCE and PCE tend to be mobile and, in aerobic environments, refractory.

This project explores a new remediation strategy for chlorinated hydrocarbons by combining two technologies: Pd-catalyzed hydrodehalogenation and horizontal-flow treatment wells (HFTWs). Palladium (Pd) catalysis is an effective means of removing halogenated contaminants, and the HFTW system creates a zone in which contaminated

water is captured and recirculated. This recirculation leads to higher contaminant removal efficiencies than might otherwise be achieved.

Pd-Catalyzed Hydrodehalogenation. The Pd catalysts are capable of rapidly transforming a wide range of hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs), PCBs, and halogenated methanes, ethylenes, ethanes, benzenes and pesticides (Munakata and Reinhard, 2001). Chlorinated ethylenes react with half-lives of minutes in the presence of dissolved hydrogen gas and a Pd catalyst, even at ambient temperature (Schreier and Reinhard, 1995; Siantar et al., 1996; Lowry and Reinhard, 1999). In the presence of excess hydrogen, dechlorination is complete and is followed by saturation of the double bond, forming ethane and hydrochloric acid (Lowry and Reinhard, 1999).



The formation of hydrochloric acid as a reaction product should not generally represent an obstacle to applying this technology to contaminated groundwater, because reactant TCE concentrations are normally low (less than 30 mg/L), and because groundwaters usually have some natural buffering capacity.

Pd-catalyzed hydrodehalogenation was recently tested in the field (though not in conjunction with HFTWs). A Pd-catalyzed *in situ* groundwater treatment system was used for more than one year at Lawrence Livermore National Laboratory (LLNL) in Livermore, California, beginning in October 1998 (McNab et al., 2000). Two in-well Pd reactors were placed in series, with residence times of 5 minutes in the lower reactor and 6 minutes in the upper reactor. The system was plumbed such that water could enter through the lower reactor (upflow mode) or the upper reactor (downflow mode). In practice, the system was operated for a total of 8 to 10 hours per day: 4 to 5 hours per day in upflow mode followed by 4 to 5 hours per day in downflow mode. During the remaining time, the columns were drained and exposed to air. If the total operating time were increased past 10 hours per day, catalyst deactivation was observed and contaminant removal efficiencies declined. Subsequent experiments by Lowry and Reinhard (2000) show that this behavior is consistent with catalyst deactivation from sulfide produced by sulfate-reducing bacteria; periodic oxygen exposure would inhibit growth of these bacteria. The 14 to 16 hours of daily air exposure were sufficient to maintain catalyst activity for more than one year (the duration of the field test). During this time, the system removed greater than 99% of PCE and TCE, and greater than 98% of carbon tetrachloride (initial concentrations of 0.3 to 0.4 mg/L, 3 to 4 mg/L, and 18 to 21 µg/L, respectively).

The Pd technology offers several potential advantages over currently available treatment alternatives such as conventional pump-and-treat with granular activated carbon (GAC), reactive iron walls, and biological degradation.

- Reaction rates for contaminants can be fast enough for in-well treatment.
- The TCE, PCE, and other chlorinated compounds are destroyed, not merely transferred from the groundwater to another medium (e.g., activated carbon).
- The technology is applicable in deep aquifers.

- The technology is applicable even at high contaminant concentrations, where other treatment technologies might not be feasible.
- There is little or no formation of hazardous by-products such as dichloroethylene (DCE) or vinyl chloride (VC), which can be formed during biological reductive dechlorination.
- Catalytic reductive dehalogenation can be used in groundwater where dissolved oxygen is present, where biological reductive dehalogenation is not feasible.
- The technology can destroy PCE, unlike biological cometabolic oxidation.

Horizontal-Flow Treatment Well (HFTW) Technology. The HFTW system consists of two treatment wells installed in an aquifer. Each well is screened over an upper interval and a lower interval. One well pumps in an upflow mode, extracting water through the lower screen and injecting it through the upper screen. The other well pumps in a downflow mode, extracting water through the upper screen and injecting it through the lower screen. In this field project, a Pd reactor will be placed between the upper and lower screens in each well and will treat the contaminated water as it travels between the screened sections in the well. Using this combination of upflow and downflow modes, the two wells create a region of groundwater recirculation within the aquifer (Figure 1).

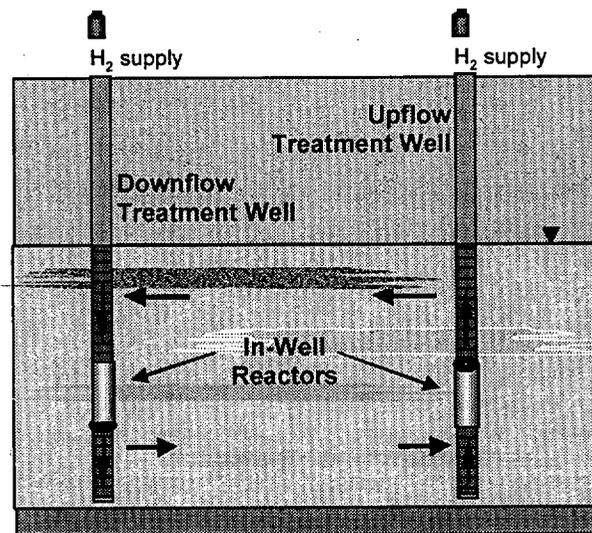


FIGURE 1. Horizontal flow treatment well (HFTW) system.

With this system, groundwater flow is captured by the HFTWs, recirculated through the aquifer, and then released to continue traveling downgradient. If the pump rate is high, relative to the regional groundwater flow rate, then some fraction of the captured groundwater will be recirculated by the wells multiple times, and will pass through the in-well Pd reactors multiple times. Recirculation is improved by the presence of an aquitard or confining layer between the upper and lower screens, i.e., if the aquifer is divided into distinct upper and lower zones. This prevents a “short-circuit” flow of the water between the upper and lower screens of the same well. Modeling studies (Christ et

al., 1999) have shown that the HFTW technology is also applicable to a single-zone aquifer, provided that the aquifer has a horizontal-to-vertical hydraulic conductivity anisotropy ratio of at least 10:1, which is relatively common. Modeling studies also indicate that the plume width captured can easily be several times the distance between the two wells. In this way, HFTWs can provide many of the same advantages as "funnel-and-gate" technologies, often at a substantially lower capital installation cost.

FIELD PROJECT

Site Description. This project will be conducted at Edwards Air Force Base (EAFB), which is located in the Mojave Desert in southern California, approximately 60 miles (100 km) north-northeast of Los Angeles. Measured TCE concentrations at the field site range from 0.5 to 1.5 mg/L. The site was previously used for another demonstration project (McCarty et al., 1998); use of this site is advantageous because treatment and monitoring wells have already been installed and the hydrogeology is relatively well characterized.

The geology in the plume consists of unconsolidated alluvial sediments overlying granitic bedrock. The alluvial sediments are primarily fine- to medium-sized sand, with some silt and clay. The fraction of organic carbon is low, about 0.01 to 0.4%. At the project site, the depth to the water table is approximately 9 m and the depth to the underlying weathered bedrock is about 24 m. The aquifer consists of two zones separated by an aquitard. Estimated thicknesses range from 5.7 to 8 m for the upper unconfined aquifer, approximately 2 m for the aquitard, and from 5 to 9 m for the lower confined aquifer (McCarty et al., 1998; Gandhi et al., 2002). There is a head difference of approximately 0.25 m between the two zones, with the upper zone having higher head. The hydraulic gradient is towards the east-southeast, with the magnitude of the gradient between 0.004 and 0.007 (McCarty et al., 1998; Gandhi et al., 2002). Hydraulic conductivity ranges from about 10^{-3} cm/s to 10^{-2} cm/s in both the upper and lower aquifer zones (McCarty et al., 1998; Gandhi et al., 2002). Assuming a hydraulic conductivity of 3.4×10^{-3} cm/s, a gradient of 0.007, and a porosity of 0.30, the regional groundwater velocity is estimated to be about 6.9 cm/day. However, the regional velocity may differ between the upper and lower aquifer zones.

System Design. The system is comprised of three basic components: the well configuration, the reactors, and the operating conditions. The previous project at the site installed two treatment wells, 10 m apart, and 20 monitoring locations. It is economically impractical to monitor all of the wells, so a subset of 10 monitoring locations was selected, based on modeling results (Gandhi et al., 2002). The monitoring locations were chosen such that there are four wells in the HFTW recirculation zone, and one to three wells each, upstream and downstream of the treatment area, in both the upper and lower aquifer.

The reactor design is modeled on the successful Pd reactors installed at LLNL (McNab et al., 2000), but has been altered based on the conditions at the site and results from laboratory studies. The reactor dimensions are constrained by the well diameter, which is 8 in. (20 cm); the reactor diameter will be 6 in. (15 cm). The reactor length will be 54 in. (137 cm), yielding a single reactor empty bed volume of 6.5 gal (25 L); based on laboratory predictions of TCE removal rates, two reactors in series will be used. The

reactors will be filled with a dispersed Pd/alumina catalyst (an alumina support onto which Pd clusters are dispersed).

The main operating conditions for the field system are the flow rate and the regeneration method. Operational flow rates will be based on reaction rates determined in laboratory results. Regeneration/biogrowth control will either use sodium hypochlorite (shown to be an effective regenerant in laboratory tests) or hydrogen peroxide. The regeneration method will examine the effects of the regenerant concentration, the frequency of regeneration, and the duration of each regeneration pulse.

LABORATORY STUDY

Materials and Methods. The catalyst used in the laboratory study is supplied by Precious Metals Corporation (PMC, Sevierville, TN) and is a dispersed Pd metal on an alumina support, 1/16 in. (1.6 mm) in diameter, with a metal loading of 1% Pd by weight. The catalyst was used in a column reactor experiment, in which catalyst was exposed to a continuous flow of EAFB groundwater. The reactor consisted of a stainless steel column, 1.27 cm in diameter and 9.8 cm in length, with an empty bed volume of 10.5 mL. The bottom of the column held 8.0 g of inert 2 mm diameter borosilicate beads, topped with 1.0 g of catalyst; the remaining space was filled with glass wool. The water supply was hydrogen saturated and amended with 1 to 3 mg/L of TCE. The flow rate was held constant at 0.5 mL/min, which yielded a residence time of 1.7 min in the catalyst section of the reactor. This residence time was chosen such that the initial TCE removals would be approximately 50 to 80%; this range provides the maximum sensitivity to changes in the catalyst activity, which allows optimal observation of catalyst deactivation and regeneration. Aqueous samples were taken at the inlet and outlet of the reactor, extracted in hexane, and measured on an HP5890 Series II Gas Chromatograph equipped with an electron capture detector. Regeneration was performed using a sodium hypochlorite solution (Clorox™), diluted as 2 mL or 20 mL in 700 mL of deionized (DI) water (concentrations of ~150 mg/L and ~1500 mg/L, respectively, as free chlorine). In total, regeneration was carried out three times, under the conditions shown in Table 1.

TABLE 1. Regeneration conditions.

Regeneration Number	1	2	3
Run Time (days)	40	42	62
Duration (min)	1000	240	1200
Regenerant Conc. (as mg/L free chlorine)	150	1500	1500

Results and Discussion. The results from the operation of the EAFB column are shown in Figure 2. As expected, the system initially removed 50 to 80% of the influent TCE. With no regenerative treatment, activity declined over 40 days; however, regeneration using the sodium hypochlorite solutions restored catalyst activity to original levels (R1 and R2 in Figure 2). Although the third regeneration (R3) appears less effective, this is attributed to an increase in sulfide concentration, rather than to any inherent change in the catalyst itself. The EAFB groundwater has extremely high sulfate concentrations (~700 mg/L) and was stored for over a month under hydrogen pressure, which would

allow sulfate-reducing bacteria to grow and produce sulfide; in fact, sulfide was smelled when the EAFB groundwater reservoir was opened at day 67. This result is an artifact of the laboratory setup and should not be seen in the field. Under field conditions, hydrogen is added just before the reactor, so the water will not remain under hydrogen pressure for long periods of time. In response to these results, the laboratory setup was modified so that the source water is stored under nitrogen pressure and hydrogen is added to the water just before flowing through the reactor.

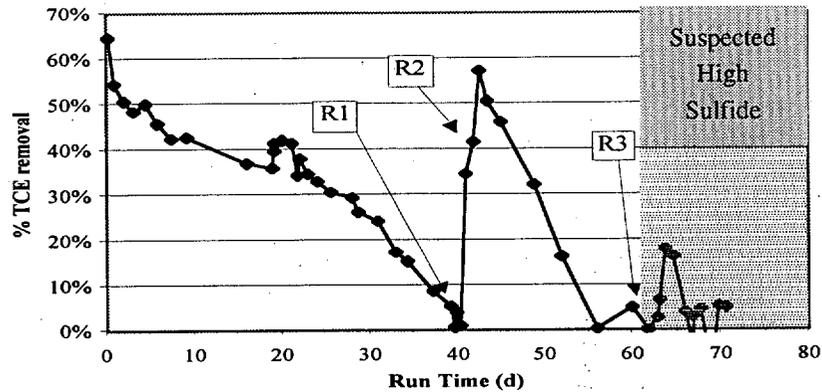


FIGURE 2. TCE removals with EAFB groundwater, residence time of 1.7 min. "R" indicates regeneration using a sodium hypochlorite solution.

Modeling of the data was also performed, to determine the reaction rate and deactivation rate constants. As derived by Levenspiel (1993), the model assumes plug flow, first-order reaction, and first-order deactivation:

$$\ln \ln \frac{C_i}{C_e} = \ln(k\tau) - k_d t$$

where C_e is the effluent concentration (mg/L), C_i is the influent concentration (mg/L), k is the first order reaction rate constant (min^{-1}), k_d is the deactivation rate constant (days^{-1}), τ is the average residence time in the reactor (min), and t is the total run time (days). Based on this model, the EAFB data was analyzed (Figure 3).

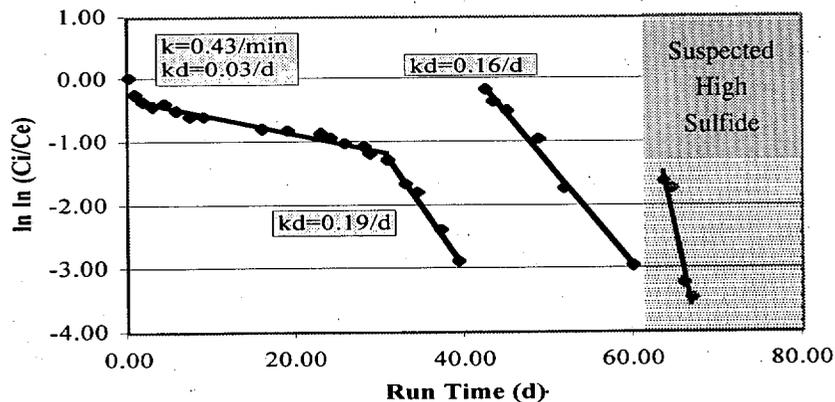


FIGURE 3. Reaction and deactivation kinetics, EAFB groundwater.

The reaction rate constant k is 0.43 min^{-1} , which is comparable to the k of $\sim 0.5 \text{ min}^{-1}$ seen with groundwater from Moffett Federal Airfield (Lowry and Reinhard, 2000). It is interesting to note that the reaction rate for TCE is similar in both groundwaters, despite the fact that they come from different sources. The reaction rate constant of $0.43/\text{min}$ can be used to estimate the residence times needed for a given amount of TCE conversion (Table 2). The shown conversions were selected for the following reasons:

- 99.7%: lowers concentrations to the maximum contaminant level (MCL) of $5 \mu\text{g/L}$, assuming the maximum influent concentration (1.5 mg/L).
- 99%: meets the design criteria of 99% removal
- 90%: meets the design criteria of 99% overall removal, assuming recirculation and two passes through each well, on average.

TABLE 2. Required residence times for TCE conversions in a single pass through the reactor.

Conversion	90%	99%	99.7%
Residence Time (min)	4.9	9.8	12

Also similar to the Moffett Federal Airfield (MFA) groundwater data, the deactivation in the EAFB groundwater appears to have an initial slower rate, followed by a faster rate. Lowry and Reinhard (2000) attribute the second, faster rate to bacterial sulfate reduction, which produces the catalyst poison sulfide (measured at a concentration of $\sim 0.1 \text{ mg/L}$ in the Lowry/Reinhard experiment). With the EAFB groundwater, the initial deactivation rate constant was 0.03 days^{-1} during the first 30 days, and the second rate was 0.19 days^{-1} . After R1/R2, deactivation reoccurred at a very similar rate (0.16 days^{-1}). After R3, with the suspected high sulfide concentrations, the deactivation rate was higher (0.55 days^{-1}); this is consistent with the k_d of 0.42 days^{-1} , seen in Lowry and Reinhard (2000) at a sulfide concentration of 0.4 mg/L . Overall, these deactivation rate results are consistent with sulfide poisoning. It should be noted that the source water in the field (an aerobic aquifer) is expected to be free of sulfide, unlike the laboratory source water, which was stored under hydrogen pressure. It is therefore expected that the deactivation rates will also be relatively low; Lowry and Reinhard (2000) showed that catalyst activity could be maintained in MFA groundwater near the initial high levels, by periodically regenerating the catalyst with sodium hypochlorite. Given the similar behavior of the catalyst in the two groundwaters, it is expected that catalyst activity can be maintained in EAFB groundwater with periodic regeneration.

Implications of the Laboratory Study. Overall, the laboratory results imply that

- 1) Palladium catalysts can successfully remove TCE from the EAFB groundwater.
- 2) The TCE reaction rates are similar in groundwaters from MFA and EAFB.
- 3) The catalyst deactivation behavior is similar between the EAFB and previously studied MFA groundwaters, and is consistent with sulfide poisoning.
- 4) Sodium hypochlorite can regenerate a fully deactivated catalyst. It is expected to be able to maintain catalyst activity with periodic regeneration in the field.

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