

# **Development and Application of an *In Situ* Technology to Treat Various Soil and Groundwater Contaminants**

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**ABSTRACT:** The limitations of conventional soil and groundwater contamination remediation technologies have motivated a search for innovative technologies; particularly *in situ* technologies that do not require extraction of contaminants from the subsurface. All engineered *in situ* remediation systems require that the contaminant be mixed with a remedial compound. Horizontal flow treatment wells (HFTWs), an innovative technology that consists of a pair of dual-screened treatment wells, were used at a trichloroethylene (TCE) contaminated site to efficiently achieve this mixing of contaminant and remedial compound in order to effect *in situ* bioremediation (McCarty *et al.*, 1998). In this paper, the potential of HFTWs to treat chlorinated aliphatic hydrocarbons (CAHs) as well as other soil and groundwater contaminants of concern, such as nitroaromatic compounds (NACs), perchlorate, and methyl-tert-butyl ether (MTBE), is examined. Through a combination of laboratory studies, model analyses, and field evaluations, the effectiveness of this innovative technology to manage these contaminants is investigated.

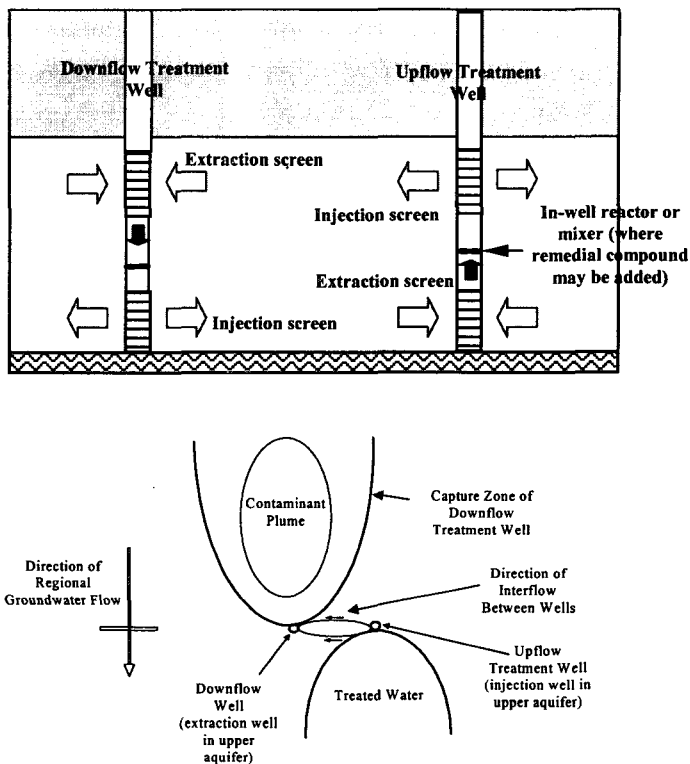
## **1. INTRODUCTION**

The limitations of conventional soil and groundwater contamination remediation technologies have motivated a search for innovative technologies; particularly *in situ* technologies that do not require extraction of contaminant from the subsurface. All engineered *in situ* remediation systems require that a remedial compound be mixed with the contaminant; where the remedial compound might be, for example, a nutrient to stimulate contaminant biodegradation by indigenous or introduced microorganisms, an oxidizing or reducing agent to chemically destroy the contaminant, or a solid catalyst or sorbent. One technology that has recently been

demonstrated to efficiently achieve this *in situ* mixing of contaminant and remedial compound consists of a pair of dual-screened treatment wells (McCarty *et al.*, 1998; Stoppel and Goltz, 2003). As shown in Figure 1, the technology, also known as horizontal flow treatment wells (HFTWs), captures contaminated water flowing from upgradient into the upper screen of a well that is pumping water in a downwards direction (called the downflow well) and the lower screen of a well that is pumping water in an upward direction (the upflow well). Treatment might consist of a remedial compound being mixed into water flowing through the wells to stimulate biodegradation in bioactive zones that are established around the injection screens of the treatment wells (the lower and upper screens of the downflow and upflow wells, respectively), or contaminant destruction in an in-well reactor. Water is also circulated between the wells, flowing from the injection screens to extraction screens, resulting in multiple passes of water through the treatment system. This recycling of water through the treatment system allows the HFTW system designer to control the overall treatment efficiency of the system, where overall treatment efficiency is defined as the fraction of contaminant that is removed by the system, as contaminated groundwater flows from upgradient of the HFTW system to downgradient of the system. One major advantage of the HFTW system is that the contaminant need not be extracted from the subsurface for treatment.

### **1.1 Prior applications of HFTWs**

As far as the authors know, there have been only two field applications of HFTWs that have appeared in the literature (McCarty *et al.*, 1998; Gandhi *et al.*, 2002a; Gandhi *et al.*, 2002b; SERDP, 2003). Both of these applications were conducted at Site 19 of Edwards Air Force Base (AFB), where a trichloroethylene (TCE) contaminated groundwater plume is located. The first technology application used an HFTW system to stimulate indigenous bacteria to biodegrade relatively low concentrations of TCE (<1.5 mg/L) by aerobic cometabolism. The second application used an HFTW system which combined aerobic cometabolic bioremediation with in-well vapor stripping to remediate the source area of TCE contamination at the site, where TCE concentrations were significantly higher than plume concentrations (as high as 8 mg/L). Each of these applications is discussed below.



**Figure 1. Cross-section (top) and plan (bottom) views of HFTW system**

**1.1.1 Aerobic cometabolic bioremediation of Chlorinated Aliphatic Hydrocarbons (CAHs)**

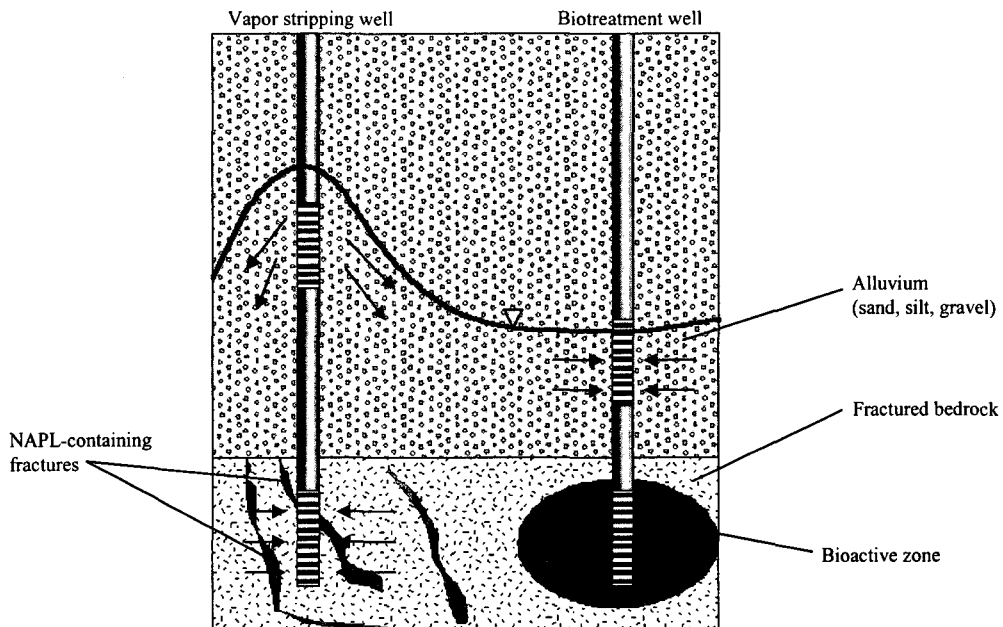
Aerobic cometabolic bioremediation is a remediation technology that takes advantage of the capability of indigenous microorganisms to degrade CAHs, such as TCE, when the microorganisms are provided an electron donor (primary substrate) and an acceptor (oxygen) in the presence of the chlorinated contaminant. The presence of the primary substrate induces a nonspecific enzyme which, fortuitously, cometabolically oxidizes the target contaminant while the microorganisms metabolize the primary substrate for growth and energy (Criddle, 1993). The effectiveness of this technology depends on being able to mix the primary substrate, oxygen, and the target CAH, and then to provide this mixture to the indigenous microorganisms. In the implementation of aerobic cometabolic bioremediation at Edwards AFB, an HFTW system was used to mix a primary substrate (toluene) and oxygen source (oxygen gas and hydrogen peroxide) into TCE-contaminated water flowing through the treatment wells. The water (containing TCE, primary substrate,

and oxygen) was discharged into the aquifer and *in situ* bioactive treatment zones were established around the discharge screen of each treatment well. McCarty *et al.* (1998) reported details of the evaluation of aerobic cometabolic bioremediation at Edwards AFB Site 19. TCE removals with each pass of contaminated water through the bioactive zones were approximately 85%. However, because of recirculation between the two treatment wells, overall TCE removal, comparing upgradient concentrations of about 1 mg/L, with concentrations downgradient of the treatment system of about 20-30 µg/L, was over 97%.

### **1.1.2 Bioenhanced In-well Vapor Stripping (BEHIVS) to remediate CAH-contaminated source zones**

In-well vapor stripping (IWVS) is a method for removing volatile organic compounds (VOCs) from groundwater without removing the water. Air is injected into a well and VOCs are volatilized. The VOC-rich vapor is removed and treated using granular activated carbon. By injecting air into the well, air lift pumping is effected and groundwater in the cleanup zone is recirculated and successively cleaned. Dissolved concentrations can be reduced by 90 to 99 percent within the cleanup zone (Gvirtzman and Gorelick, 1992, 1993).

BEHIVS combines aerobic cometabolic bioremediation with IWVS. These two technologies complement each other in that IWVS is amenable for sites contaminated with high concentrations of volatile CAHs and aerobic cometabolic bioremediation is appropriate as a polishing step. Together these two technologies offer the potential for near complete removal of high levels of a CAH like TCE, such as would be found at a soil and groundwater contamination source area. The treatment system installed at the source area of the Edwards AFB TCE plume consisted of a single IWVS well and two biotreatment wells located downgradient and on either side of the IWVS well (Figure 2). The IWVS well treats the relatively high contaminant levels present near the source, while the cometabolic bioremediation wells "polish" the effluent from the vapor stripping well. The nutrients required for cometabolism, toluene and oxygen, are added at the biotreatment wells.



**Figure 2. BEHIVS Concept**

Operation of the BEHIVS system for 4-1/2 months at the Edwards AFB Site 19 contamination source area resulted in reducing the TCE concentrations in the lower aquifer zone by 91 percent. Average TCE concentrations in the upper aquifer zone were reduced by 56 percent. The total TCE mass removed was 8.8 kg, 7.8 kg of which resulted from in-well vapor stripping and 1.0 kg from biotreatment. Capital and operating costs were estimated at \$30 per 1,000 gallons of water treated, which compares extremely well with competing technologies (SERDP, 2003).

## **2. POTENTIAL APPLICATIONS OF HFTWs**

### **2.1 In-well Palladium (Pd) Catalytic Reactors to Treat Chlorinated Aliphatic Hydrocarbons (CAHs) and Nitroaromatic Compounds (NACs)**

A major disadvantage of the two bioremediation technologies described above to treat CAHs is the need to inject a hazardous substance, toluene, into the subsurface. An alternative technology has been proposed that uses an abiotic process to accomplish in-well destruction of the CAHs (Munakata *et al.*, 2002; Stoppel and Goltz, 2003). The process, Pd-catalyzed CAH reduction, uses molecular hydrogen ( $H_2$ ) as an electron donor and passes the CAH/ $H_2$  mixture

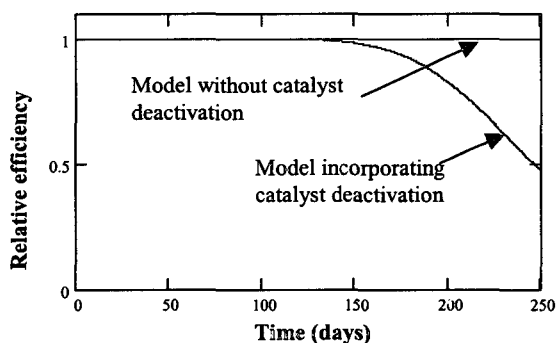
through a palladium (Pd) catalyst reactor installed in each treatment well of an HFTW system. The hydrodechlorination process destroys the contaminant by replacing all chlorine atoms on the CAH with hydrogen and saturating the double bond to produce ethane and hydrochloric acid. This reaction is extremely rapid in water even at ambient temperature and proceeds all the way to ethane (Lowry and Reinhard, 1999). Commercially available catalysts can be used such as alumina spheres coated with 1% palladium metal. Hydrogen can be added safely using microporous hollow fiber membranes.

Although catalytic dehalogenation of CAHs with Pd-catalysts and hydrogen gas (Pd/H<sub>2</sub> catalyst system) has been known for many years, most of the studies were concerned with reactions of non-aqueous solvents and high substrate concentrations. Interest in the Pd-catalyzed dehalogenation of chlorinated contaminants in groundwater and wastewater is relatively recent. Technology maturity has evolved from early batch studies conducted at Stanford University (Schreier and Reinhard, 1995; Siantar *et al.*, 1996; Schüth and Reinhard, 1998) and elsewhere. The laboratory studies demonstrated the complete dehalogenation to ethane of TCE, PCE, cis- and trans-1,2-DCE, and vinyl chloride in water containing hydrogen and small quantities of commercially available Pd catalysts. No intermediates were detected. Hydrogen sulfide was shown to poison (deactivate) the catalyst. Lowry and Reinhard (2000) showed that deactivated catalyst could be regenerated by flushing with a dilute sodium hypochlorite solution.

A field test of Pd/H<sub>2</sub> in-well catalysts was conducted at the Lawrence Livermore National Laboratory (LLNL). In the LLNL test, one treatment well equipped with two reactors connected in series was used. The water table was at 26 m below the ground surface and the contamination treated was 42.5 m deep. Contaminated water was drawn into the well through screens at the lower end of the well, saturated with molecular hydrogen, and then passed through the packed bed catalyst columns. The column effluent was discharged into the upper hydrostratigraphic unit. Influent TCE concentrations ranged from 3-4 mg/L. After two months of operation, removal efficiencies ranged from 93 to 99 % depending on the hours of operation per day. Catalyst activity could be maintained for a prolonged time by exposing the reactors every day to non-hydrogenated water after approximately 6 hours of operation (McNab *et al.*, 2000).

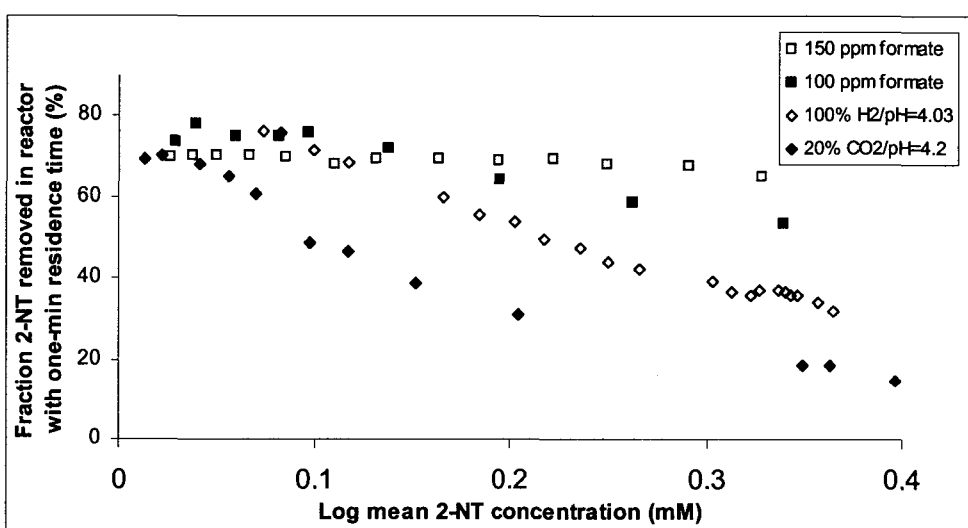
A field demonstration of Pd/H<sub>2</sub> in-well catalysts as part of an HFTW system is planned for the same part of the Edwards AFB TCE plume previously used for the aerobic cometabolic bioremediation study discussed earlier (Munakata *et al.*, 2002). The treatment wells used for the bioremediation study will be modified by installing in-well Pd reactors and hydrogen gas feed lines. Experimental (Munakata *et al.*, 2002) and modeling (Stoppel and Goltz, 2003) results showed that catalyst deactivation could be managed so that the in-well system could effectively contain TCE-contaminated groundwater. Figure 3 presents the results of a modeling study which shows that for the chemical and hydrological parameters at the Edwards AFB TCE-contaminated site, only after several months would catalyst deactivation impact system performance. It was also shown in the laboratory that after deactivation of the catalyst begins to impact system performance, the catalyst may be cost effectively regenerated using a sodium hypochlorite solution (Munakata *et al.*, 2002).

In-well application of Pd catalysis as part of an HFTW system is also being investigated to treat NAC-contaminated groundwater. NACs such as 2,4,6-trinitrotoluene (TNT) are important soil and groundwater contaminants at explosives manufacturing facilities and Department of Defense ranges. In addition, NACs similar to those used in explosives can be found in insecticides, herbicides, pharmaceuticals, dyes, plastics, and many other commonly used products. The natural breakdown of these contaminants creates byproducts such as amines, which are known neurotoxins and carcinogens.



**Figure 3. Comparison of HFTW models with and without catalyst deactivation for remediation scenario based on Edwards AFB Site 19 (Stoppel and Goltz, 2003)**

Phillips (2003) experimentally investigated the kinetics of Pd-catalyzed NAC reduction in a column reactor using both molecular hydrogen and formate as electron donors. In the laboratory experiments, 2-nitrotoluene (2-NT) was used as a model NAC. As can be seen in Figure 4, which plots the fraction of 2-NT destroyed in a Pd reactor with a one-minute residence time versus the log mean of 2-NT concentration in the reactor, when formate is used as an electron donor, reduction kinetics are faster and there is less catalyst deactivation as NAC loading increases. Based on these experimental results, the potential of using an in-well Pd catalytic reactor with formate as an electron donor to manage subsurface NAC-contamination is being investigated.



**Figure 4. Comparison of formate and molecular hydrogen as electron donors for Pd-catalyzed reduction of 2-nitrotoluene (2-NT) (Phillips, 2003)**

## **2.2 In Situ Bioremediation to Treat Methyl-tert-Butyl Ether (MTBE)**

Methyl tert-Butyl Ether (MTBE) is a gasoline oxygenate used to improve combustion efficiency and reduce air pollution. Having been added to gasoline for over 20 years as an octane boosting agent, MTBE more recently has been added to reformulated gasoline in National Ambient Air Quality Standards non-attainment areas (Moyer and Kostecki, 2003). The Clean Air Act Amendments of 1990 require the use of gasoline oxygenates to reduce ozone and carbon monoxide emissions. MTBE is



added to some degree in approximately 30 to 50 percent of all gasoline sold in the United States (OFA, 2003).

MTBE finds its way into drinking water generally due to releases of MTBE-containing gasoline from leaking underground storage tanks, gasoline spills, and gasoline use in watercraft (Moyer and Kostecki, 2003). Results of the U.S. Geological Survey's National Water Quality Assessment program from 1993-1994 show MTBE is the second most common volatile organic compound found in drinking water sources (Squillace *et al.*, 1996). Along with concerns about the ubiquity of MTBE contamination are the persistence and mobility of MTBE in groundwater. Due to its low octanol-water partition coefficient ( $\log K_{ow} = 0.94-1.16$ ) and high aqueous solubility (23.2 - 54.4 g/L at 25 °C) (MacKay *et al.*, 1993) MTBE does not sorb well to aquifer solids and thus migrates in the dissolved phase along with the flowing groundwater.

In 1997 the United States Environmental Protection Agency (EPA) initiated a drinking water advisory for MTBE establishing safe limits at 20 to 40 µg/L (EPA, 1997). Seeking to maximize consumer safety and acceptability, the EPA advisory limits are established at or below the most common thresholds for detection of unpleasant odor and taste in water (EPA, 1997).

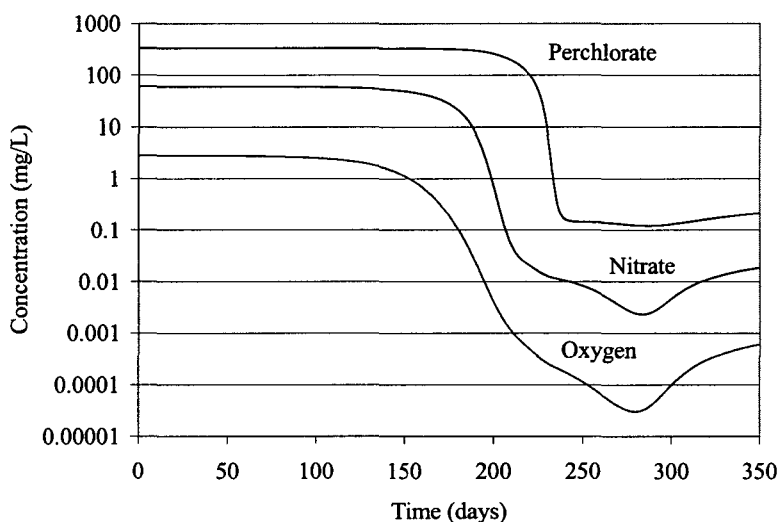
Field and laboratory studies have demonstrated that MTBE can be degraded *in situ* through both abiotic and biotic processes. The potential for *in situ* bioremediation of MTBE in groundwater is currently being studied at the Department of Defense (DoD) National Environmental Technology Test Site at Port Hueneme, California (Environmental Security Technology Certification Program, 2003) as well as Vandenberg Air Force Base, California (Wilson *et al.*, 2002). These studies have shown that addition of oxygen can potentially stimulate indigenous microorganisms to biodegrade MTBE. Addition of oxygen to promote MTBE biodegradation has been effected using a permeable wall at Port Hueneme and oxygen diffusers at Vandenberg AFB (ESTCP, 2003; Wilson *et al.*, 2002). However, these two "mixing" technologies have the inherent limitations of passive systems; that is, contaminated groundwater can bypass them due to changes in groundwater flow over time. Model studies are underway to evaluate the viability of using an HFTW system to mix oxygen into MTBE-contaminated groundwater in order to achieve plume remediation (Goltz and Mackay, 2002).

### **2.3 *In Situ* Bioremediation to Treat Perchlorate**

Perchlorate, an oxyanion extensively used by the aerospace industry in the production of solid rocket fuel, potentially contaminates the drinking water of 15 million people in the United States (Logan, 2001). In addition to their use in rocket fuels, perchlorate salts are used in nuclear reactors, electronic tubes, finishing of leather products, explosives, fireworks, and matches. Chilean caliche, a nitrate salt found in Chile, is the only confirmed natural source of perchlorate. Even at concentrations in the low part per billion range, perchlorate is suspected of affecting hormone production in humans (Urbansky, 1998). Perchlorate is a health concern because it obstructs the production of thyroid hormone by hindering the uptake of iodide into the thyroid gland (Wolf, 1998). There also is concern about unknown developmental effects of perchlorate ingestion on neonates and children. Specifically, there have been reports on the potential for perchlorate to cause congenital hypothyroidism, a cause of mental retardation in unborn babies (Lamm and Doemland, 1999). Perchlorate is very mobile in groundwater and can persist for decades under typical groundwater conditions (Urbansky, 1998). Conventional methods of remediating perchlorate-contaminated groundwater involve extracting the groundwater and treating it above ground; for example in ion exchange or fluidized-bed reactors (Logan, 2001).

It has been shown in the laboratory and the field that when an electron donor such as acetate is mixed into perchlorate-contaminated water, naturally occurring bacteria can reduce the perchlorate (Envirogen, 2002; Cox and Neville, 2003). Due to competition for electrons, perchlorate reduction occurs after the reduction of other electron acceptors such as oxygen and nitrate, which may also be present. To investigate the potential for using an HFTW system to mix electron donor into perchlorate-contaminated groundwater, in order to contain a perchlorate plume, Parr *et al.* (2003) developed and applied a numerical model that incorporated the relevant physical and biochemical processes that affect perchlorate transport and fate in the subsurface. The numerical model coupled a three-dimensional fate and transport model, which simulates advective/dispersive transport of solutes induced by regional groundwater flow and operation of the HFTWs, with a biodegradation model that simulates perchlorate reduction, and the reduction of competing electron acceptors, by indigenous microorganisms. The model was applied to an example site to demonstrate how *in situ* perchlorate biotreatment might be implemented in the field. Figure 5 presents model simulations of perchlorate and

two competing electron acceptors (oxygen and nitrate) concentrations downgradient of an HFTW system being used to mix acetate as an electron donor into groundwater at a hypothetical site. Biochemical parameters used for the simulations are based upon literature values and laboratory results. Note from the figure that perchlorate concentrations are reduced only after reduction of the more preferred acceptors. Also note from the simulations that the system appears capable of reducing perchlorate concentrations by over three orders of magnitude. A sensitivity analysis using the model was also conducted to evaluate which engineered and environmental parameters most affect technology performance. In Table 1 we see that the distance between the HFTW treatment wells is an important parameter affecting system performance. Interflow is a measure of the percentage of water entering an extraction screen of a treatment well that originated in the injection screen of a treatment well. From the table, we see that as the distance between the treatment wells decreases, interflow increases, and downgradient perchlorate concentration decreases. This is expected, since the greater the interflow, the more times is water recycled through the treatment system. Conversely, we also see that as distance between the treatment wells increases, interflow decreases. The decreased interflow means that more highly contaminated water goes through the treatment wells, resulting in higher mass removals (and higher downgradient concentrations).



**Figure 5. Breakthrough of electron acceptors at a downgradient observation well**

Well Spacing	Mass Degraded	Interflow	Downgradient Concentration
9 m	8,100 kg	0.68	0.197 mg/L
15 m	10,100 kg	0.59	0.212 mg/L
39 m	15,000 kg	0.30	0.350 mg/L
57 m	17,200 kg	0.11	0.530 mg/L

**Table 1. Cumulative perchlorate mass degraded and downgradient concentration after 350 days of HFTW operation at a site initially contaminated with 330 mg/L perchlorate**

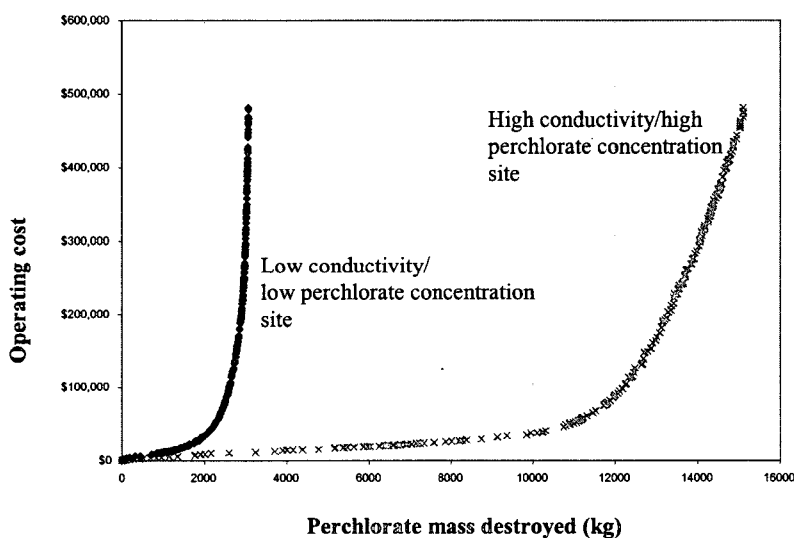
### **3. TECHNOLOGY OPTIMIZATION USING GENETIC ALGORITHMS (GAs)**

Implementation of the HFTW system at a contaminated site requires a number of engineering decisions. Particularly when the HFTWs are used to mix an electron donor or acceptor into contaminated water in order to effect *in situ* bioremediation (such as might be the case for remediation of MTBE-, perchlorate-, or TCE-contaminated groundwater), a designer must decide upon treatment well pumping rate, treatment well separation distance, the amount of electron donor or acceptor injected into the groundwater, and the donor/acceptor injection schedule, in order to attain desired remedial objectives. Note that there may be several competing remedial objectives. Three common objectives are: (1) minimize system cost, (2) maximize contaminant mass destroyed, and (3) minimize downgradient contaminant concentrations. As an example of how optimization techniques could be applied to solve this complex problem, Knarr *et al.* (2003) used a multiobjective evolutionary algorithm (MOEA) to help design an HFTW remediation system at a perchlorate-contaminated site.

Knarr *et al.* (2003) coupled the technology model of Parr *et al.* (2003) discussed in the previous section with the GENERAL Multi-Objective Program (GENMOP) MOEA. GENMOP is a Pareto-based, multi-objective, genetic algorithm with real-valued crossover and mutation operators, fitness sharing, and parallel computation capability. Details of GENMOP may be found in Knarr *et al.* (2003). GENMOP was applied to two actual perchlorate-contaminated sites in order to determine the Pareto front, which is the set of solutions that perform better across all objectives (known as non-dominated solutions). For simplicity, only two objectives were used: (1) minimize system operating cost, and (2) maximize contaminant mass destruction. Two very different sites were selected for analysis. One site had a high

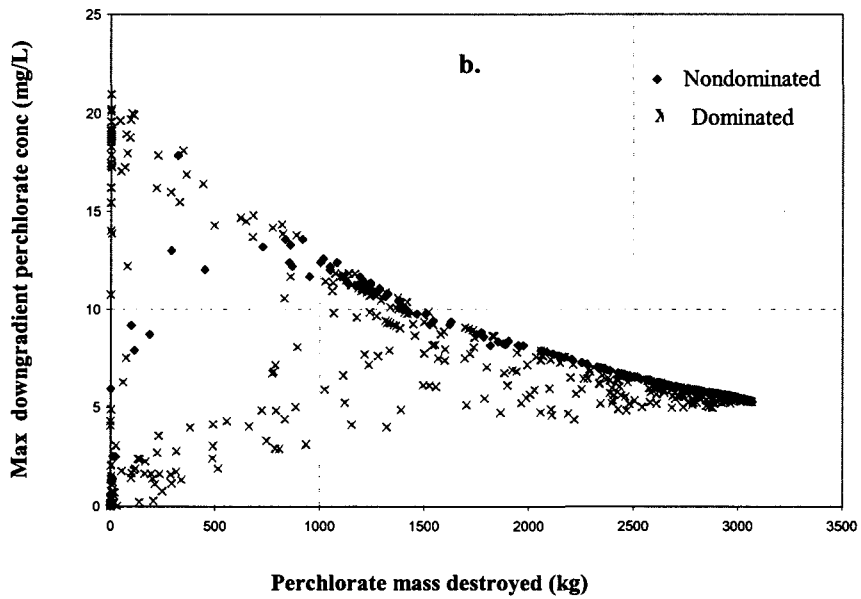
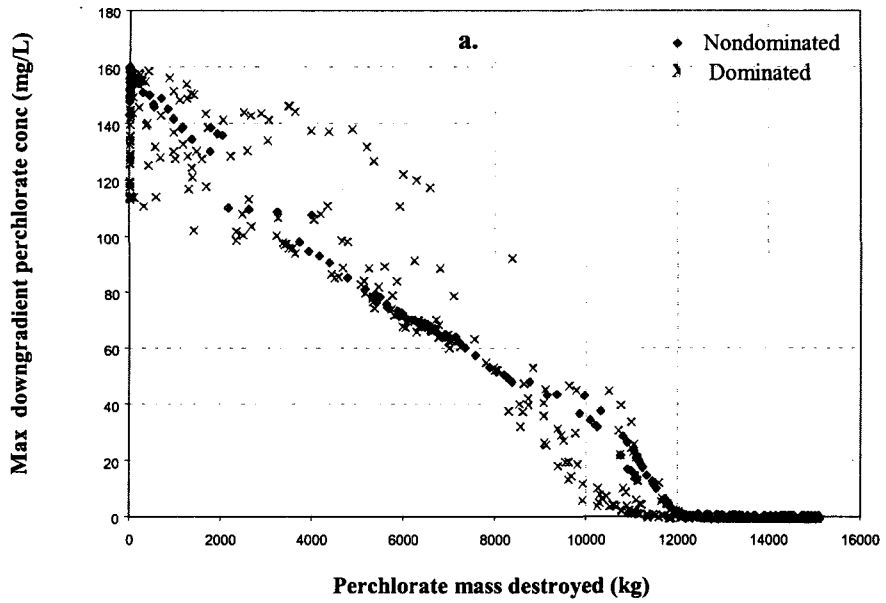
hydraulic conductivity and relatively high initial perchlorate concentrations while the other site had relatively low conductivity and perchlorate concentrations.

The Pareto fronts for the two sites are shown in Figure 6. The first objective (operating cost) is plotted on the y-axis while the second objective (perchlorate mass destroyed) is plotted on the x-axis. We see from the figure that for the same cost, much more perchlorate mass can be removed at the site with high hydraulic conductivity and contaminant concentrations. We also see that for both sites, the incremental cost of perchlorate removal increases nonlinearly as mass removed increases.



**Figure 6. Pareto fronts for the high and low conductivity/perchlorate concentration sites (600 day simulations)**

Figure 7 plots perchlorate concentration downgradient of the treatment wells versus perchlorate mass removed for both dominated and non-dominated solutions at the two sites. Recall that downgradient perchlorate concentration was not one of the objectives of the optimization, although it is an important parameter, as regulations typically would specify the allowable downgradient concentration. Figure 7a shows that for the high conductivity/high perchlorate concentration site, as might be expected, downgradient concentration decreases as more perchlorate mass is removed by the treatment system. It should also be noted that the very low downgradient concentrations correspond to high cost solutions; that is, pumping rates and the quantities of electron donor that must be added are high.



**Figure 7. Maximum perchlorate concentration downgradient of HFTWs vs. perchlorate mass removed at the (a) high and (b) low conductivity sites (600 day simulations)**

Interestingly, Figure 7b, which plots perchlorate concentration downgradient of the treatment wells versus perchlorate mass removed at the low conductivity/low perchlorate concentration site, behaves differently and presents some unexpected results. Here we see that there are a number of solutions that simultaneously have low mass removed and low downgradient concentrations. These solutions correspond to low cost solutions; that is, pumping rates and the quantities of electron donor that must be added are low. The reason for this apparent contradiction (low cost, low mass removal solutions that result in very low downgradient concentrations) is that in these solutions, the treatment wells are located very close to each other and due to the low hydraulic conductivity at the site, regional groundwater flow velocities are small. Due to this small separation between the treatment wells and slow regional groundwater flow, water pumped by the HFTWs recycles through the treatment system many times and very low concentrations are attained, although very little mass is being treated. Otherwise, results for the two sites are similar, with downgradient concentrations generally decreasing as perchlorate mass removed increases, though due to the difficulty with which water flows at the low conductivity site, the magnitude of mass removed and the downgradient concentrations that may be attained are less than at the high conductivity site.

#### **4. SUMMARY**

The potential of the HFTW system to treat a number of groundwater contaminants by mixing remedial compounds into the water without the need to extract the contaminant from the subsurface has been investigated over the past several years in a series of laboratory investigations, modeling studies, and field evaluations. This series of investigations has enabled the technology to progress to its present point, where it is on the verge of widespread commercial application to manage a number of subsurface contaminants. The investigations have been crucial in providing remedial system designers and site managers with the understanding and tools needed to implement the technology.

#### **5. ACKNOWLEDGEMENTS**

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## 국문요약

최근 현장(In situ)에서의 토양 및 지하수 오염정화는 오염물질을 현장에서 추출해 지상에서 처리하는 것이 아니라, 직접 현장에서 미생물 혹은 화학물질과 오염물질의 혼합을 통한 분해기작을 이용해, 오염물질을 제거하는 과정을 의미한다. 이러한 현장오염정화 기법 중 하나가 Figure 1에 도시한 수직흐름처리정(Horizontal Flow Treatment Wells, HFTWs)으로 2개의 정(well) 중간지점에 반응물질을 설치한 후 각각의 정에서 상향 및 하향흐름을 발생시켜 주위의 지하수를 순환시키면서 정화하는 기법이다.

### 1.1 Prior application of HFTWs(수직흐름처리정의 과거 적용 사례)

TCE로 오염된 Edwards 공군기지 Site 19에서 HFTWs와 BEHIVs(미생물에 의한 분해[생분해] 효율을 높인 공기분무법)의 오염물질의 정화효율을 비교한다.

#### 1.1.1 Aerobic cometabolic bioremediation of Chlorinated Aliphatic Hydrocarbons (지방족 염화탄화수소(CAHs)의 호기성 생분해(HFTWs 적용))

TCE로 오염된 지역에 HFTWs 시스템을 적용하며, 반응물질로 생분해를 촉진하기 위해 toluene을 매개체로 한 산소공급원(산소가스, 과산화수소)을 활용하였다. 2개의 정에서 지속되는 지하수의 재순환을 통해 97%의 TCE 물질이 제거됨을 확인하였다.

#### 1.1.2 Bioenhanced In-well Vapor Stripping(BEHIVs) to remediate CAH-contaminated source zones (CAHs 오염원의 제거를 위한 BEHIVs 기법 적용)

Figure 2에 나타나는 BEHIVs 기법은 기존의 공기분무법(IWVS)의 역할인 공기주입을 통한 휘발성유기오염물(VOCs)의 제거기작에 산소의 주입을 통한 생분해 활성화기작을 동시에 발생시키는 방법이다. 반응물질에는 1.1.1과 동일한 물질이 사용되었으며, 정화 후 대수층 상부에서는 91%, 하부에서는 56%의 TCE가 제거되었으며, 다른 정화법에 비해 매우 경제적으로 평가되었다.

## 2. Potential Applications of HFTWs (HFTWs의 가능한 적용기법)

### 2.1 In-well Palladium(Pd) Catalytic Reactors to Treat CAHs and NACs (Palladium (Pd)의 촉매반응을 통한 CAHs 및 방향족 질소화합물(NACs)의 정화)

1장의 생분해 방법은 위해물질인 toluene을 사용하기 때문에, Pd의 촉매반응을 통해 CAH의 염소원자를 치환하여 ethane 등으로 정화하는 연구가 최근 이루어지고 있다.

Stanford 대학에서의 연구결과를 통해 CAHs 물질은 소량의 Pd 촉매와 물에 함유된 수소가 존재하면 중간 산물의 생성 없이 빠르게 ethane 으로 변환됨과 황화수소의 존재 시 촉매에 미치는 영향을 확인하였다. 또한, Pd/H<sub>2</sub> 반응에 대한 현장 실험이 수행되었으며, 93~99%의 TCE 제거효율을 보였다.

Figure 3 은 Pd 의 촉매반응 실험 및 모델링에서 시간이 경과함에 따라 촉매의 효율은 떨어지는 양상을 나타낸다. 이렇게 낮아진 촉매의 효율을 높이기 위해서 차아염소산염 용액을 이용해 촉매를 재생하는 방법을 이용한다.

Pd 의 촉매반응을 통한 토양 및 지하수에 다량 존재하는 TNT 와 같은 NACs 를 정화하는 방법도 조사되었다. 그렇지만, 반응 후 신경유해 및 발암물질인 amine 과 같은 중간산물이 발생하기 때문에 포름산염을 이용한 방법이 연구되었다.

Figure 4 는 2-NT 의 농도와 1 분 동안 제거된 2-NT 의 비율과의 관계를 통해 NAC 의 농도가 높아질수록 촉매효율의 낮아짐 현상이 줄어드는 양상을 보여준다.

## **2.2 In Situ Bioremediation to Treat Methyl-Tert-Butyl Ether (MTBE 의 정화를 위한 현장에서의 생분해)**

연비향상과 매연감소를 위한 연료첨가제로 이용되는 MTBE 는 미국의 식수원에서 2 번째로 많이 발견되는 휘발성유기화합물(VOC)이며, 높은 용해도로 인해 대수층에 흡착되지 않고 지하수를 따라 이동한다. 현재 미국의 여러 지역에서 진행 중인 연구는 오염된 지하수의 흐름이 발생하는 길목에 산소를 함유한 투수성 벽체를 설치하여 MTBE 를 제거하는 내용이지만, 시간에 따라 지하수의 이동경로가 변하기 때문에 향후 지속적인 실험이 진행되어야 한다.

## **2.3 In Situ Bioremediation to Treat Perchlorate (과염소산염의 정화를 위한 현장에서의 생분해)**

항공우주산업에서 연료첨가제로 사용되는 과염소산염(perchlorate)은 갑상선 기능저하 및 태아의 정신지체를 유발할 수 있는 오염물질로, 매우 이동성이 높으며 난분해성이다. 전통적으로는 오염된 지하수를 지상으로 추출해 처리했지만, HFTW 시스템에서 초산염(acetate) 등의 전자제공물질을 오염물과 혼합한 후 자연적으로 생성되는 박테리아를 이용해 과염소산을 제거하는 연구가 수행 중이다.

Figure 5 에서는 전자수여물질(산소, 질소)의 농도 감소 직후 과염소산염의 농도가 감소하며, 오염정화 시 과염소산염은 3 차(3 orders) 이상 농도 저감이 이루어짐을 나타낸다.

Table 1에서는 정화정(treatment well)에서 나온 물이 다시 다른 정화정으로 들어가는 비율을 interflow로 정의하여, 정화정 사이의 간격, interflow, 과염소산염의 농도저감효과와의 관계를 통한 정화 효율을 보여준다. 간격이 넓을수록 interflow는 작아지며 처리되는 양은 많아지지만 농도 또한 높아짐을 확인할 수 있다.

### 3. Technology Optimization Using Genetic Algorithms (유전자 연산방식을 이용한 기술 최적화)

각각의 토양 및 지하수 오염지역에 대해 (1) 시스템의 비용을 최소화하고, (2) 분해되는 오염물질의 양을 최대화 하며, (3) 처리 후 오염농도를 최소화하기 위해, 다목적 진화적 연산방식(MultiObjective Evolutionary Algorithm, MOEA)을 이용하여, 최적의 정화방법을 구한다. Knarr는 일반 다목적 MOEA 프로그램(GENMOP)을 사용하여, 비용의 최소화와 처리오염물질의 최대화의 관계를 도출하였다(Pareto fronts, Figure 6). 처리비용이 동일할 경우, 투수성과 오염물의 농도가 높을수록 많은 양의 오염물질이 제거되며, 비용과 처리오염물질량의 관계가 비선형임을 확인할 수 있다.

Figure 7에서는 투수계수 및 과염소산염 농도에 따라 분해되는 과염소산염의 양에 대한 HFTWs에서의 농도 변화를 보여준다. 이와 같은 관계를 통해 HFTWs의 가동율, 반응물질의 양 등을 결정할 수 있다.

### 4. Summary

본 연구는 HFTW 시스템의 현장 적용 가능성을 살펴보기 위한 것으로, 지난 수년간의 실내실험, 수치해석 및 현장조사의 수행을 통해 최적의 정화법을 도출하는 방법을 설명한다. 지반오염 정화의 광범위한 상용화 적용에 대해 아직 시작단계에 있는 현재의 기술수준을 보다 발전시킬 수 있도록 본 연구는 수행되어왔다. 본 조사는 토양 및 지하수 오염정화법을 수행하는데 필요한 지식에 대해 오염정화시설의 설계자 및 공사관계자 등에 제공하는 것에 주안점을 두었다.