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NATO/CCMS Pilot Study

Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)

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SPECIAL SESSION

Treatment Walls and Permeable Reactive Barriers

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NORTH ATLANTIC TREATY ORGANIZATION

NATO/CCMS Pilot Study

Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater — Phase III

SPECIAL SESSION ON

Treatment Walls and Rermeable Reactive Barriers

Harald Burmeier, Chairman

University of Vienna
Vienna, Austria

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NOTICE

This report was prepared under the auspices of the North Atlantic Treaty Organization's Committee on the Challenges of Modern Society (NATO/CCMS) as a service to the technical community by the United States Environmental Protection Agency (U.S. EPA). The document was funded by U.S. EPA's Technology Innovation Office under the direction of Dr. Michael Kosakowski. The Annual Report was edited and produced by Environmental Management Support, Inc., of Silver Spring, Maryland, under U.S. EPA contract 68-W6-0014. Mention of trade names or specific applications does not imply endorsement or acceptance by U.S. EPA.

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Introduction

The Council of the North Atlantic Treaty Organization (NATO) established the Committee on the Challenges of Modern Society (CCMS) in 1969. CCMS was charged with developing meaningful programs to share information among countries on environmental and societal issues that complement other international endeavors and to provide leadership in solving specific problems of the human environment. A fundamental precept of CCMS involves the transfer of technological and scientific solutions among nations with similar environmental challenges.

The management of contaminated land and groundwater is a universal problem among industrialized countries, requiring the use of existing, emerging, innovative, and cost-effective technologies. This document provides a report from the first meeting of the Phase III Pilot Study and is designed to share information among countries on innovative treatment technologies. The United States is the lead country for the Pilot Study, and Germany and The Netherlands are the Co-Pilot countries. The first phase successfully concluded in 1991, and the results were published in three volumes. The second phase, which expanded to include newly emerging technologies, concluded in 1997; final reports documenting 52 completed projects and the participation of 14 countries will be published in 1998. Through these pilot studies, critical technical information has been made available to participating countries and the world community.

Phase III focuses on the technical approaches for addressing the treatment of contaminated land and groundwater. This includes issues of sustainability, environmental merit, and cost-effectiveness in addition to continuing to draw on the merits of emerging remediation technologies. The objectives of the study are to critically evaluate technologies, promote the appropriate use of technologies, use information technology systems to disseminate the products, and to foster innovative thinking in the area of contaminated land. The first meeting of the Phase III Pilot Study on the Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater convened in Vienna, Austria, on February 22-27, 1998, with representatives of 20 countries attending. Each participating country presents case studies or projects to the Pilot Study for discussion.

Also at this first Phase III meeting, the first special technical session was convened on treatment walls and related permeable reactive barrier technologies, under the chairmanship of Prof. Dipl.-Ing. Harald Burmeier of the University of Northeast Lower Saxony. This report contains the proceedings of that special session. A companion publication, the first Annual Report of the Phase III studies, contains abstracts of the first 15 demonstration projects selected, reports on the legislative, regulatory, programmatic, and research issues related to contaminated land in each participating country, and the statement of purpose for the Phase III Pilot Study. General information on the NATO/CCMS Pilot Study may be obtained from the Country Representatives listed at the end of this report, or—for each paper—from the authors themselves.

Stephen C. James
Walter W. Kovalick, Jr., Ph.D.
Co-Directors

General Overview

Harald Burmeier[1]

Remediation of groundwater is most commonly performed by “pump-and-treat” methods: the contaminated groundwater is extracted from the aquifer and subjected to above-ground-treatment before being reinjected or discharged. Multi-component systems are designed according to the particular contamination by taking physical, chemical, and biological treatment processes into consideration.

Pump-and-treat methods require continuous energy for pumping water from the extraction wells and operating the water treatment systems. Besides that, periodic maintenance and monitoring has to be performed. Generally, these systems have to be operated for a long time. As a consequence, remediation costs are substantial. Despite the wide spectrum of technologies available for above-ground treatment, residual contaminants frequently remain at undesirably high levels in the subsurface.

Alternatives to these methods are passive working systems that depend on the usage of the groundwater’s natural hydraulics. There is a wide spectrum of possible solutions ranging from intrinsic remediation to permeable reactive or adsorptive barriers.

As early as 1982, the idea to treat contaminated groundwater by installing a permeable reactive barrier was shown in a figure in a remediation handbook issued by the U.S. EPA. But the 1980s were not the time for further development of such innovative in-situ clean-up methods.

In 1989, the potential of Permeable Reactive Barriers (PRB) was recognized more clearly and was developed further by the University of Waterloo, Canada. Since that time a lot of laboratory- and bench-scale investigations led to the first full-scale *in situ* demonstration at Borden, Ontario, Canada.

Now, in 1998, over 500 project studies world-wide reflect the interest in this technology. The small number of so far only 20 commercial applications shows that it is a long way from the pilot study to the field application.

Today, a lot of experts in North America and Europe are working on several research issues concerning the PRB technology, as there are:

- processes in the media and aquifers (hydraulics, geochemistry, *etc*.),
- suitable materials for reactive walls,
- design and construction,
- long-term effectiveness,
- treatment of contaminant-mixtures, and
- standards for construction, monitoring, *etc.*

Although many questions remain to be answered, a significant cost reduction potential of more than 30 percent is expected when PRBs are used instead of pump-and-treat methods.

In this Special Session of the *Phase III Pilot Study on the Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater (Phase III)*, a dozen

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papers are presented on the international state-of-the-art concerning technical construction issues, reactor materials, and full-scale projects. This report summarizes those proceedings and the discussions following them, research and development needs, and recommendations for further action items.

I would like to extend my special thanks to all experts for preparing reports and giving presentations during this Pilot Study Meeting in Vienna. Last-but-not-least, I would like to gratefully acknowledge the input and substantial support provided by Steve James, John Moerlins, and Volker Franzius during the preparation and coordination of this session.

Permeable Reactive Barrier Research at the National Risk Management Research Laboratory, U.S. Environmental Protection Agency

Robert W. Puls[1]

Much of the current research on ground-water remediation has focused on the removal of contaminated water from the subsurface and treating it at the surface. While the removal of the contaminants is desirable, the costs are often prohibitive and rarely are contaminant concentrations lowered to the required regulatory levels. This has been particularly evident for standard “pump-and-treat” approaches. *In situ* chemically reactive permeable walls are being considered as a low-cost and effective alternative for the treatment of contaminated waste sites. The chemical form of the contaminant in question is transformed via oxidation, reduction or precipitation reactions to an immobilized or non-toxic form. The application of *in situ* approaches to subsurface remediation will increase the emphasis on adequate site characterization and thorough understanding of the subsurface system targeted for remediation as well as the geochemical mechanisms controlling contaminant transformations.

Background

Research into the use of zero-valent metals to remediate ground-water contaminated with mixed wastes (inorganic and organic) has been ongoing at the U.S. Environmental Protection Agency’s National Risk Management Research Laboratory (NRMRL) in Ada, Oklahoma since 1991. The primary emphasis has been on inorganic constituents such as chromate, arsenic, nitrate and sulfate and chlorinated organic compounds (e.g., trichloroethylene, cis-dichloroethylene, and vinyl chloride). Laboratory research conducted by scientists at the NRMRL conclusively demonstrated the effectiveness of using zero-valent metals to remediate chromate and chlorinated organic compounds in groundwater and this research was scaled up to a pilot-scale demonstration in September 1994, near an old chrome plating facility on the U.S. Coast Guard (USCG) Support Center near Elizabeth City, North Carolina. Results indicated that complete treatment of chromium and the chlorinated organic compounds in the groundwater was possible using this technology. Chromium concentrations were reduced to less than 0.01 mg/l, much less than drinking water limits. The chromate was reduced via corrosion of the elemental iron to the nontoxic and insoluble chromic ion (Cr^{3+}), which forms an insoluble mixed chromium-iron hydroxide phase. The chlorinated organic compounds were similarly degraded to below maximum contaminant levels set for groundwater by the U.S. EPA.

Full-Scale Systems

A full-scale demonstration of a permeable reactive barrier to remediate groundwater contaminated with chromate and chlorinated organic compounds was initiated at the USCG site by researchers from NRMRL and the University of Waterloo in 1995. A continuous wall composed of 100% zero-valent iron was installed in June, 1996, using a trencher that was capable of installing the granular iron to a depth of 8 m. The trenched wall was approximately 0.6 m thick and about 60 m long. The wall begins about 3 feet below the ground surface and consists of about 450 tons of granular iron. The installation of the wall was completed in less than a day. The total installation cost was $500,000, with the cost of iron representing approximately 35% of the total. Total installation, site investigation, design feasibility tests, general contracting, and post-installation monitoring costs have been less than $1 million. Savings compared to traditional pump-and-treat

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exceed $5 million over a 10-year period primarily due to reduced operation and maintenance costs due to the passive nature of this technology.

The continuous trenching equipment used for the installation was similar to a large "Ditch Witch." It uses a large cutting chain excavator system combined with a trench box and loading hopper. As the trenching machine moved along, the cutting chain excavation removed the native soil, while a front end loader filled the hopper of the trench box. The granular iron flowed through the hopper and out the back of the trench box into the just-excavated trench. The walls of the trench box extended to the width and depth of the trench maintaining the opening until the iron was emplaced.

The system was designed to meet lower concentrations of contaminants below maximum concentration limits (MCLs) for groundwater set by U.S. EPA of 0.05 mg/l Cr(VI), 5 µg/l TCE, 70 µg/l DCE and 2 µg/l VC.

Results

To-date, there has been two years of post-installation performance monitoring performed by these same researchers. For all but one quarterly sampling event, 15 multilevel samplers (7 to 11 sample ports per sampler) and 9 to 10 compliance (5-cm PVC) wells have been sampled. In addition to on-site sampling of the full suite of geochemical indicator parameters listed in the site work plan, samples have been collected for laboratory analysis of the following constituents: TCE, cis-DCE, vinyl chloride, ethane, ethene, methane, major anions, and metals. In addition, numerous vertical and angle cores have been collected to examine changes to the iron surface over time and to evaluate the formation of secondary precipitates which may affect wall performance over time. Coring was done vertically (perpendicular to ground surface) and on an angle (30°). The former method provided continuous vertical iron cores, while the latter provided a transverse core through the wall with the aquifer-iron interfaces intact (front and back of the wall). These cores continue to be under study. Inorganic carbon contents increase dramatically at the up-gradient aquifer sediment-iron interface and decrease within the wall moving down gradient, reaching background levels within 10 cm down gradient from the down gradient iron-aquifer sediment interface. Total inorganic carbon content has increased over time within the wall.

Results of geochemical sampling on site indicate that iron corrosion is proceeding within the wall. There are significant reductions in Eh (to >-400 mv), increase in pH (to >10), absence of DO, and decrease in alkalinity. Down gradient of the wall (1.5 m), pH returns to near neutral and Eh is quite variable with depth. Over time there have been indications that a redox front is slowly migrating down gradient within the first few meters of the wall. Water levels indicate little difference (<0.1 m) between wells completed and screened at similar depths up gradient and down gradient of the wall, indicating that the wall continues to effectively function as a "permeable" reactive barrier.

Sampling results for chromate indicate that all chromate was removed from the groundwater within the first 15 cm of the wall as expected. No chromate is detected down gradient of the wall either in the multilayer samplers or in the 5-cm compliance wells located immediately behind the wall.

The vast majority of the multi-layer sampling ports show reduction of the chlorinated compound concentrations to less than regulatory target levels. Only one port (ML25-1) continues to show levels above target concentrations. This is the deepest port in the middle of the wall where the organic solvent compound concentrations are highest.

Other Inorganic Contaminants

Other inorganic contaminants currently under study include nitrate and arsenic. These inorganic contaminants are transformed via oxidation-reduction reactions to less mobile and/or less toxic forms and immobilized as insoluble precipitates or through essentially irreversible adsorption reactions. Zero-valent iron can effectively transform nitrate to reduced forms as confirmed with mass balance determinations. The use of different organic materials also further reduces the nitrate and experiments are in progress to account for all nitrogen forms produced. Experiments have also explored the use of iron-organic material mixtures. Experiments with arsenic are currently underway and we are exploring conversion to reduced and oxidized forms for immobilization in a reactive barrier.

Disclaimer

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency, it has not been subjected to the Agency’s peer and administrative review and therefore may not necessarily reflect the views of the Agency and no official endorsement may be inferred.

Discussion

Zero-valent iron walls can affect the pH of chlorinated solvent plumes. The pH of a plume can increase to 10 to 11 after passing through a 100% iron wall. This change is always observed due to the nature of the corrosion reaction that takes place and occurs regardless of whether the plume contains chlorinated solvents or chromium. However, the iron can be mixed with pyrite or native aquifer sediments (*e.g.*, 50% iron and 50% sediment) to buffer the pH in the walls to less than 7.5. The buffered walls exhibit an environment favorable for microbial activity, so there is a lot of sulfide is produced. Additionally, hydrogen is produced during the corrosion reaction at the iron surface. The production of hydrogen is significant—up to 1,000 nM of dissolved hydrogen has been measured at the Elizabeth City site.

Puls’s data documented a buildup of chromium (2% by weight after one year) in the PRB installed at Elizabeth City, and Puls expects it to increase in the future. This expectation is based on two-year column tests in which over 3,000 pore volumes were pumped through under accelerated conditions. Although a buildup occurred that reduced the permeability of the column, it did not impact the reduction of chromate in the groundwater. The pressure buildup caused by the precipitate occurred after pumping approximately 500 pore volumes. It is difficult to extrapolate these laboratory results to field-scale tests, and Puls said that they will continue to monitor for long-term reactivity in the wall.

The residence time for pore water in the fastest part of the barrier is two days. The hydraulic conductivity of the aquifer varies over its 24-foot thickness, and the highest hydraulic conductivity occurs within a 2-meter interval. This interval contains the highest concentrations of Cr^{6+}, but most of the TCE is found in deeper zones. The reduction of chromium causes no inhibitory or competitive effect on the degradation of TCE, because the chromium and TCE are present in different intervals. While the hydraulic conductivity of the aquifer ranges from 2-5 inches/day, the hydraulic conductivity of the wall is 10-12 inches/day.

Permeable Treatment Walls—Design, Construction, and Cost

Eberhard Beitinger[1]

Abstract

The Design of Permeable Reactive Barriers (PRB) is discussed with reference to preventing effects such as inflow of fine soil particles, precipitation of carbonates, iron and manganese, and loss of effectiveness by uncontrolled growth of biomass.

Several construction methods are presented and evaluated in terms of design objectives, installation methods, implementation, effectiveness and cost.

1. *In Situ* Groundwater Remediation with Permeable Reactive Barriers

According to EPA, "...a permeable reactive barrier (PRB) is a passive *in situ* treatment zone of reactive material that degrades or immobilizes contaminants as groundwater flows through it. Natural gradients transport contaminants through strategically placed treatment media. The media degrade, sorb, precipitate, or remove dissolved organics, metals, radionuclides, and other pollutants. These barriers may contain reactants for degrading volatile organics, chelators for immobilizing metals, nutrients and oxygen for microorganisms to enhance bioremediation, or other agents." [1]

The following report is focused on construction methods that prevent negative effects that may reduce the effectiveness of the treatment media, negatively change the hydraulic conditions, or reduce the long-term PRB performance. This includes the application of knowledge and experience from groundwater well design and the evaluation of innovative technologies to remove and/or reactivate the treatment media *in situ*.

Permeable Reactive Barriers have commonly been, or are designed to be, installed through excavation and replacement. This method is limited to approximately 8 m in depth, and the costs becomes prohibitive at greater depths. Alternative installation methods for greater depths include slurry wall construction, high pressure jetting, deep soil mixing, and hydro fracturing in the United States [2]. In Germany large diameter vertical borings, slurry methods and a modified deep wall construction are under evaluation or investigation, but have not yet been tested in the field.

2. Design Objectives for Permeable Treatment Walls

The hydraulic behaviors of the two major permeable treatment wall design types—funnel and gate systems or continuous reactive walls—are based on the hydraulic permeability of the whole construction system, including permeability of filter layers, screens and the treatment media itself. The system permeability of the wall construction should be at least twice the permeability of the aquifer. It might be better to choose a factor of 10 times higher permeability for the wall system because of to all the limiting parameters that will reduce permeability with time. The major limiting factors are expected to be as follows:

- inflow and settling of fine-grained soil particles, which will block the pore spaces and reduce the permeability;

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- precipitation of carbonates such as calcium or magnesium carbonates, iron oxides/hydroxides, and ferrous carbonate or other metal precipitates in the filter layer or treatment media;
- uncontrolled growth of microorganism, such as bio-clogging; and
- other, mainly long-term and unknown effects, which may reduce the permeability.

The following design objectives are focused mainly on the use of activated carbon as the treatment media. But most of these design objectives may also be useful if zero-valent iron (ZVI) or other media are chosen as reactive filling materials.

Major design objectives are to:

- Prevent the inflow of fine-grained soil particles by installing a filter layer between the adjacent soil and the treatment media according to the well-known filter criteria;

- Prevent changes to the physical and chemical properties of the groundwater such as temperature, pressure, pH, oxygen content (redox potential), nutrients, or be aware that these changes will result in precipitation or microorganism activity that might be of advantage in specific cases;
- Design a wall-system that allows the removal and replacement of the treatment media after a period of several years or decades;
- Design a pipe-system in the wall to allow the injection of water or air for flushing to eliminate precipitates or sludges or to remix the media by turbulence; and
- Design openings for inspection, removal or sampling of the treatment media.

The above list of design objectives may not be applicable in every case. Based on the specific site conditions, the nature of contamination and the remediation goals, additional design objectives have to be considered.

3. Design Criteria

The design of Permeable Reactive Barriers needs to carefully address the following design criteria. In general, investigations to obtain design data should be planned with reference to the specific design parameters for a long-term performance of the underground treatment wall.
Design criteria are:

- Geology
- Hydrology
- Depth to groundwater
- Thickness of the aquifer
- Groundwater flow direction and gradient
- Permeability
- Grain-size distribution
- Pore volume
- Groundwater chemistry, such as pH-value, redox-potential, electrical conductivity, oxygen content, temperature, hardness, iron and manganese concentration, sulfates, and nutrients
- Biological activity (microorganisms)
- Pollutants (concentration, spread, transfer conditions)
- Site conditions, topography, and access
- Sensitivity of aquifer regarding potential users
- Damage to existing buildings regarding settling problems
- Available time for remediation
- Effectiveness of treatment

- Costs
- Monitoring.

4. Construction Methods

During the last five years, a variety of construction methods have been developed in Canada, the United States and in Europe. Some of these construction methods have been implemented or tested in field scale. Others are proposed for implementation but have not yet been adapted.

4.1 Peat-Filled Trench

The University of South Carolina [1] obtained a patent October 15, 1991, for a method for *in situ* removal of hydrocarbon contaminants from groundwater using a permeable barrier comprising a peat material or, an immobilized nutrient layer and peat material layer in series.

As shown in Figure 1, it is assumed that an open trench would be excavated and filled with the reactive media. The construction method is simple and inexpensive.

The specific costs for open trenches are mainly the costs for excavation and disposal, including costs for lowering groundwater and, if necessary, stabilizing the open ditch.

The actual costs, without stabilization, may range between US\$10-100/m². Costs for stabilization will vary within US\$50-100/m².

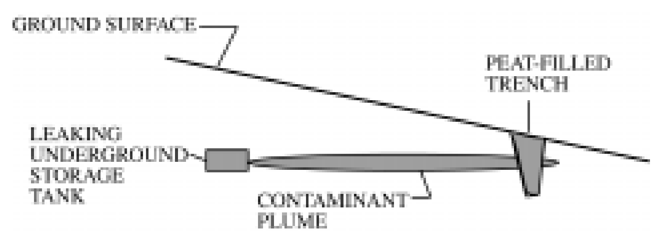

Figure 1. Peat-filled trench [1]

4.2 Solid-Free Trench

In February 1992, a German patent [2] was granted to Dr. Haldenwang and Dr. Eichhorn for a solid-free trench construction in which the walls of an open trench are permeable and stabilized and the groundwater flows through it (Figure 2). Additionally, piping for aeration or circulation of water within the open trench was proposed including measures for capping and emission control.

For field testing, a 6 m deep, 1.4 m wide and approximately 10 m long trench was established on a refinery site and tested for several years.

No solid media is used as reactive media but according to its function as an underground permeable barrier this technology is mentioned as an alternative within the group of permeable reactive barriers. To stabilise the wall, permeable sheet piles have been proposed. The specific costs are estimated to range between US\$200-400/m² not including any preparation or other aeration/de-aeration installations.

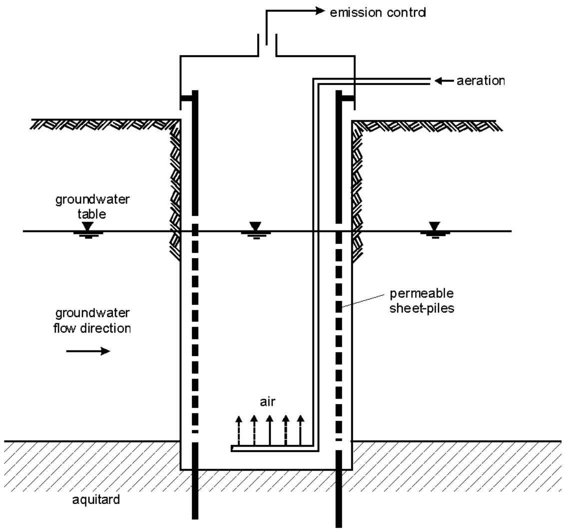

Figure 2: Solid-free trench [2]

Figure 2. Solid free trench [2]

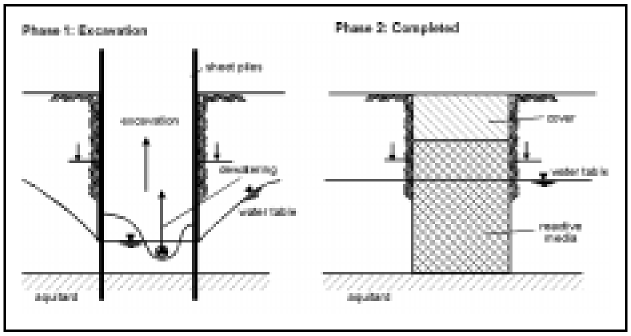

Figure 3. Open trench construction of Permeable Reactive Barriers

4.3 Open Trench Construction

In several cases, open trenches filled with reactive media have been planned or executed. Vertical sheet piling was used to stabilise the open excavation ditch and pulled after filling of reactive media was completed. The maximum width of the reactive wall is dependent on the distance that the sheet pile walls are driven into the ground (Figure 3).

One of the major disadvantages is that there is no filtration layer between the adjacent soils and the reactive media to help avoid inflow of fine-grained soil particles. Also recovering the filling material (reactive media) is not possible without destroying the structure itself. The specific construction costs will vary (without reactive media) in the range of US$100-200/m².

4.4 Treatment Wall Construction by WCI-Umwelttechnik GmbH

WCI Umwelttechnik GmbH has developed a special method of wall construction that allows the adsorbing or other reactive media to be recovered without the need to demolish and rebuild the wall structure [3]. The patented system includes filtration layers to prevent inflow of fine soil particles and measures to avoid precipitation by oxidation of iron and manganese. As shown in Figure 4, the main design components are:

- a filter layer, consisting of gravel or sand pack, located between the trenched aquifer and the interior wall elements;
- interior wall elements, made of specially designed brick elements or pre-cast concrete shells to define an interior filling space for the treatment media, including openings for the groundwater through-flow and horizontal elements to stabilise the earth pressure;
- a clay seal to prevent inflow of stormwater and contact with atmospheric oxygen;
- a cover plate as an opening device for the recovery and replacement of the treatment media —additionally these covers can be made waterproof and airtight.

Some typical dimensions are shown for the cross section of the wall construction in Figure 5.

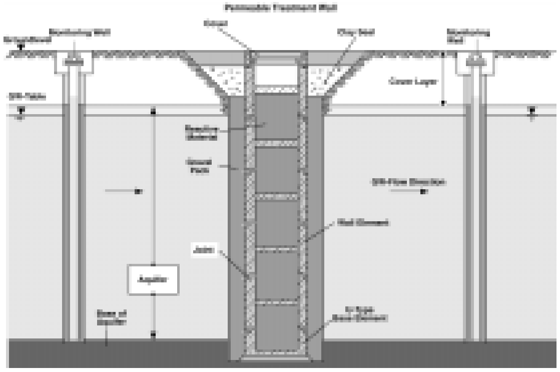

Figure 4. Permeable Treatment Wall Construction

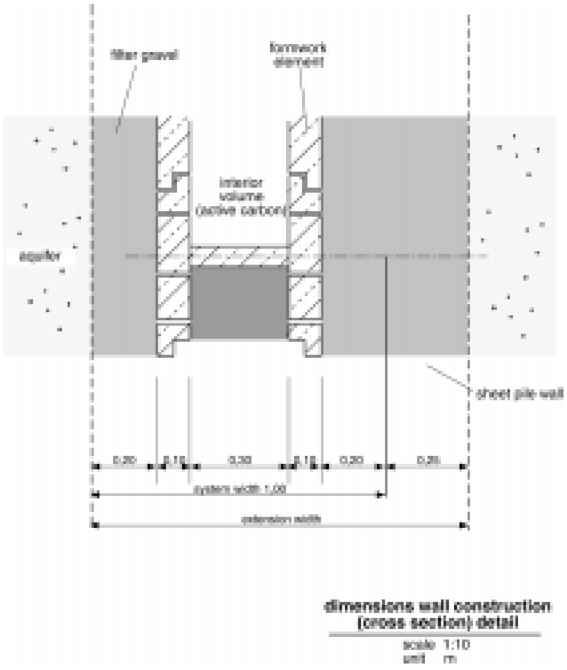

Figure 5. Cross-Section—Treatment Wall

Depending on the usually low groundwater flow velocity, the retention time of groundwater in a 0.30 m thick treatment media layer is between several hours and one or two days.

In order to dimension the retention time and media thickness, new approaches must be developed based on test results in the field. In particular for the use of activated carbon, the retention time, surface capacity and the height or width (thickness) of media layers in the permeable treatment walls will differ widely from those dimensioning criteria used in conventional aboveground activated carbon filters (Table 1).

Table 1: Dimensioning Criteria

Dimensioning Criteria	PRB-adsorbing	Conventional Activated Carbon Filter
Retention time	5 - 30 hrs	1 - 2 hrs
Surface load capacity	0.02 - 0.06 m/h	10 - 15 m/h
Height/width filter layer	0.3 - 0.5 m	2 m

Installation methods

The installation methods are described in detail in Figures 6 to 11.

In phase 1 (Figure 6) sheet pile walls will be driven into the earth. The distance between the piles will be 1 m or more, according to the chosen system width. The sheet piles will be installed 2 m into the bottom layer of the aquifer.

In phase 2 (Figure 7) excavation will commence within the two sheet pile walls. An open ditch will be used to lower the groundwater table below the excavation level.

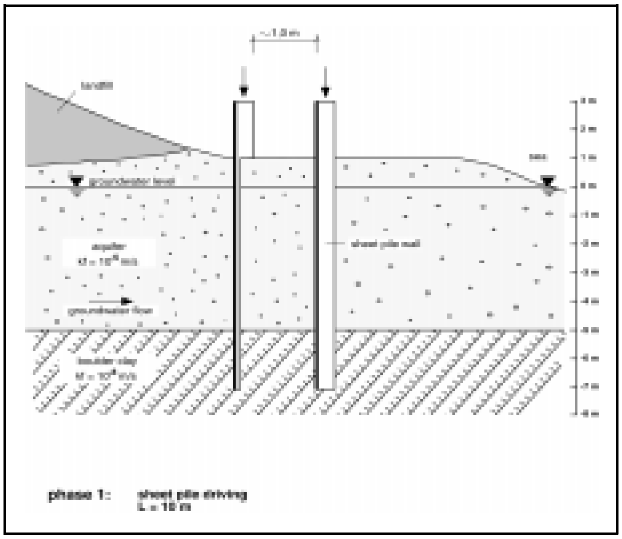

Figure 6. Construction Phase 1

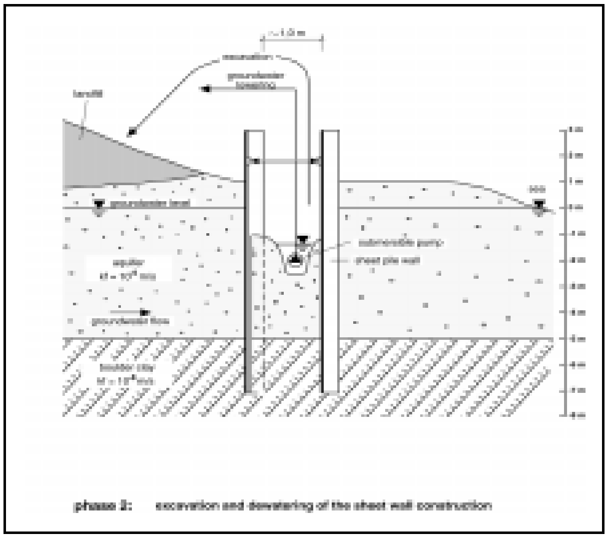

Figure 7. Construction Phase 2

After completion of the excavation (Figure 8), a concrete base layer will be cast in situ and dewatering will be continued. The horizontal earth pressure will be supported with beams.

Now the installation of the forms and placing the filter gravel can begin on the concrete layer (Figure 9). As the construction grows, groundwater level can be allowed to rise again.

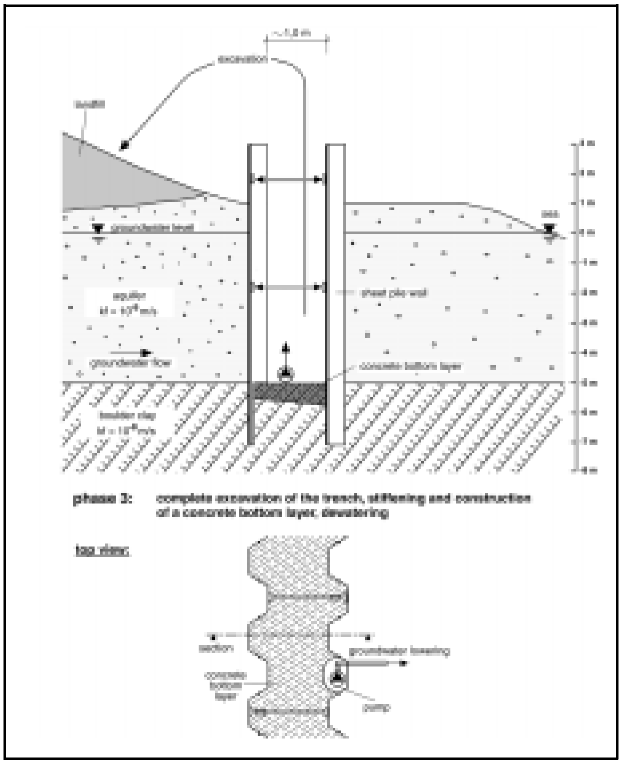

Figure 8. Construction Phase 3

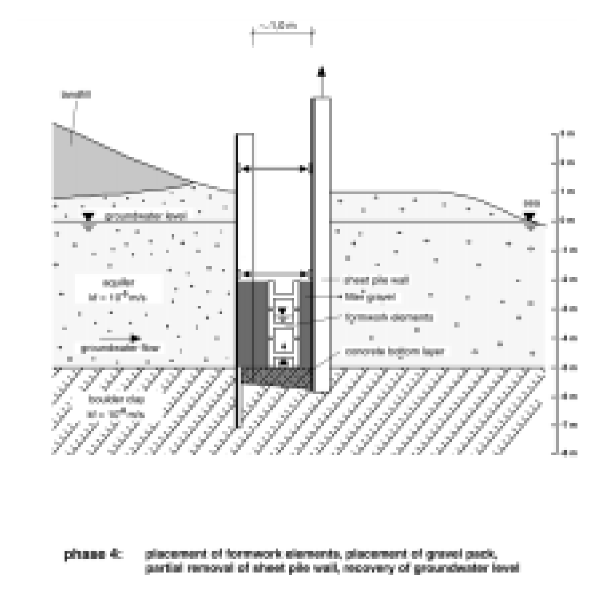

Figure 9. Construction Phase 4

As the wall construction continues (Fig. 10), sheet piles can be raised accordingly and the treatment media will be filled into the interior space of the forms.

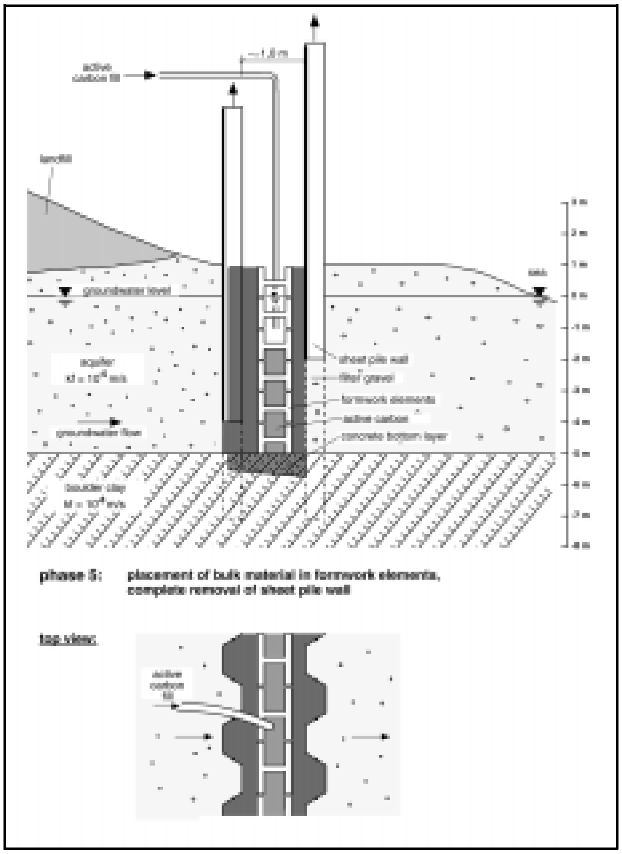

Figure 10. Construction Phase 6

Finally, the wall cover, the clay seal and some other measures can be installed to complete the construction (Figure 11). In addition, bank protection (if located near a shore as in the given example), monitoring wells and a roadway for the tank trucks (to remove and replace the treatment media) may be installed.

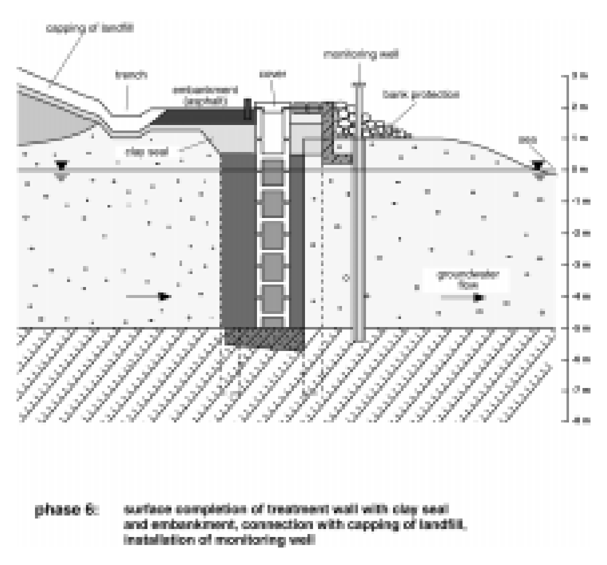

Figure 11. Construction Phase 6

Figure 12 shows an approximately 30-m long constructed longitudinal section. All the necessary installation phases from excavation to covering the completed wall are illustrated. For longer walls, several construction sections may be useful.

The construction costs for permeable treatment walls with a depth of 8 m are estimated to range from DM 850 to 1400 per square meter (US$500-900/m²) without the treatment media (an additional DM 300/m² [US$180/m²] for an activated carbon layer of 0.3 m thickness).

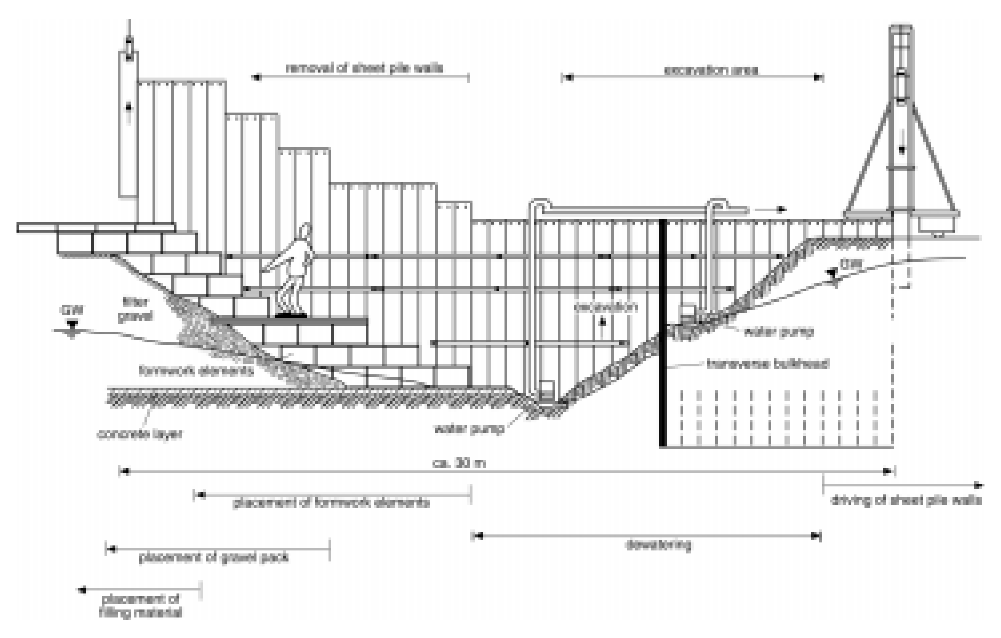

Figure 12. Construction Progress in Longitudinal Direction

4.5 Construction Patented by Dr. Steffen Ingenieurgesellschaft

Another construction method based on a slurry wall technology was patented (June 27, 1992) by a German consultant, Dr.-Ing. Steffen Ingenieurgesellschaft mbH, Essen [4]. The patented idea is to press a sheet pile or a double-T-formed steel beam down into the ground and to inject activated carbon by pulling the beam out again (Figure 13). The overlapping process of pressing and injection will form a continuous wall of reactive media with a width of approximately 0.10-0.15 m. Depending on geology, depths to 20 m or more can be reached. When the adsorbent capacity has been exhausted, a second wall is planned upstream.

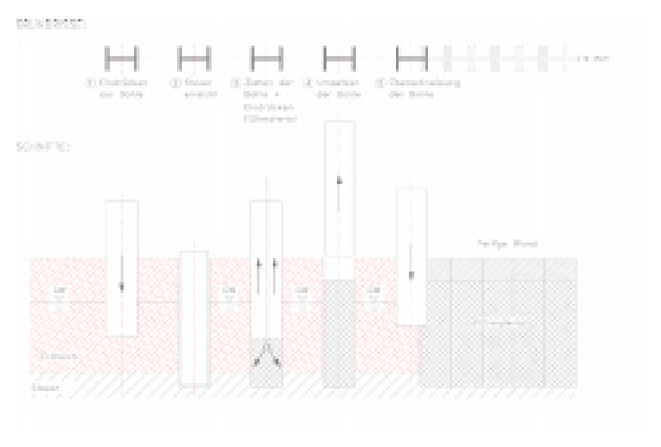

Figure 13. Dr.-Ing. Steffen—Barrier Construction Phases

There is no filter layer and the recovery of the media is not anticipated. Such a wall construction may be blocked easily by inflow of fine soil particles or by precipitation effects. The cost range is estimated to be US$200/m² without the media itself.

4.6 Large Diameter Borehole Construction Method

This construction method is used in the U.S. as well as in Germany. Mull und Partner, Hannover, Germany, has proposed a continuous overlapping iron-filled wall in Nordrhein-Westfalen to prevent downstream contamination of chlorinated hydrocarbons emitted by a laundry.

Usually, borehole diameters from 0.8-1.6 m are chosen. Individually located bore holes, established in several lines are known as an "iron-fence." The method is applicable for continuous walls, if the bore holes overlap, or for gate constructions. Depths to 20-25 m may be reached with no problems. By overlapping the bore holes, a loss of approximately 15-20 % of the filling material has to be allowed. Depending on the geology, in most cases steel pipes have to be used for stability of the borehole during excavation. This construction method is shown in Figure 14.

The costs for this method are US$300-500/m², excluding filling materials.

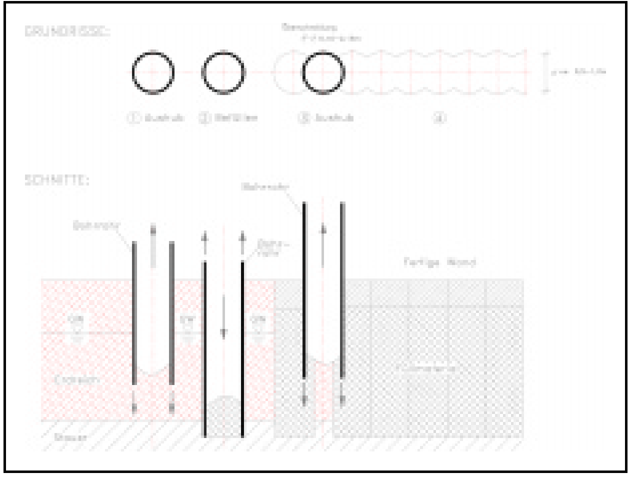

Figure 14. Large Diameter Borehole Construction Method

4.7 Method developed by Sax+Klee, Germany

The German construction company, Sax+Klee GmbH, Mannheim, has developed a modified large diameter borehole construction method for a funnel-and-gate PRB system. The innovative approach includes using bore holes filled with impermeable clay to connect the funnel sheet pile walls with the gate structure. Also new is the proposed installation of an interior well screen with four wings to create a filler zone between the surrounding soils and the reactive media (Figure 15).

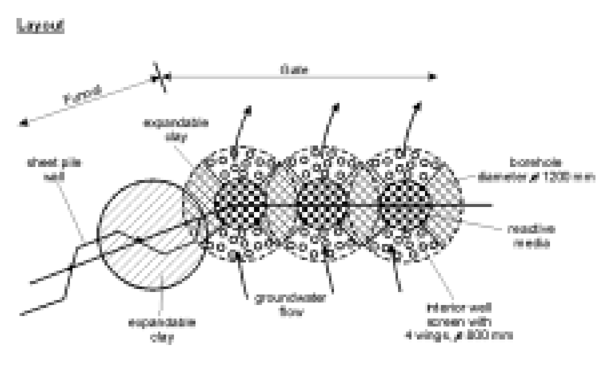

Figure 15. Sax+Klee GmbH, Germany

The costs for a 40 m wide and 19 m deep gate construction are estimated to be approximately US$1,400/m².

A filling material of petroleum activated carbon is proposed for a site with groundwater contaminated with petroleum hydrocarbons and aromatics (BTEX). The site is a former U.S. Army tank farm.

4.8 "Funnel and Gate" Patented by University of Waterloo

The funnel and gate method (Figure 16) has been patented worldwide since April 23, 1992, for the University of Waterloo, Canada [5].

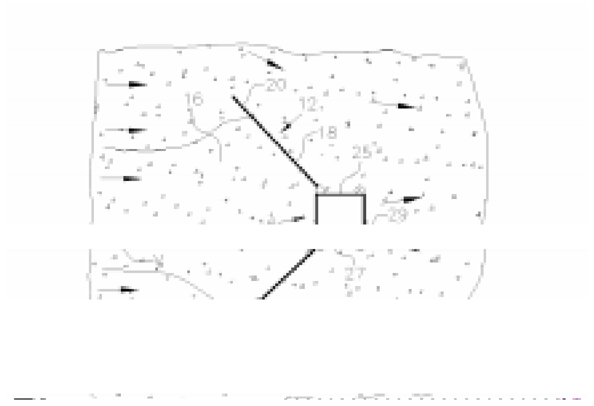

Figure 16. Funnel and Gate System, University of Waterloo

"Contaminated groundwater is treated *in situ*, by funnelling the water through a gate or gates in a watertight in-ground wall. Treatment material in the gate breaks down the contaminant, or otherwise removes the contaminants from the flowing water. A removable caisson is first driven into the ground, excavated, and then a receptacle, for the treatment material, is lowered into the hollow interior."

The patent itself shows a wide variety of construction elements, such as caissons made of steel (receptacles), slurry and sheet pile waterproof walls, removable baskets in the receptacle, removable caissons, *etc*.

Costs for the construction methods proposed by the University of Waterloo may vary in the range of US$200-1,000/m².

4.9 Bio-Polymer Slurry Trenching Technique

Geo-Con, a subsidiary of Woodward-Clyde, reported (December 23, 1997) the performance of a funnel-and-gate project for the U.S. Department of Energy, Oak Ridge, as follows:

> *Geo-Con recently completed what we believe to be the first permeable reactive wall installed using the bio-polymer slurry trenching technique. The reactive gate consists of a 30-foot (900 cm) iron filing "gate," with two 100-foot (30 m) wings composed of pea gravel. The system is 2 feet (60 cm) wide and extends down to bedrock, which is approximately 26 feet (780 cm) below ground surface.*

The purpose of the permeable reactive wall is to collect a plume of groundwater contaminated with volatile organic compounds (VOCs). The trench intercepts the groundwater, funneling it through the pea gravel to the iron filing gate. As the groundwater passes through the filing gate, the VOCs are removed.

This project was originally contracted to another company, to be built by excavating dry and backfilling with the filings and pea gravel. Upon nearing completion of the first cut-approximately 20 feet (600 cm) deep, the trench collapsed. Geo-Con proposed to complete the project using a bio-polymer slurry to maintain trench stability during gravel and iron filling installation. Geo-Con was able to complete the project in three days, expediting the project schedule and providing a considerable cost saving over other installation methods. [6]

The author estimates costs for this technique to be in the range of US$300-500/m², not including the filling materials.

4.10 Other Construction Methods

The following listing of other construction methods under discussion or developed for the installation of Permeable Reactive Barriers is not complete; it reflects the knowledge of the author about actual information.

- Enviro Wall is a trademark of Barrier Member Containment Co. Ltd. and Argonne National Laboratory. By help of a guide box installation, an HDPE geomembrane will be installed, and a groundwater collection and redistribution system will guide groundwater to a pass through module. The open trench will be refilled with site soil and capped with bentonite after installation of membranes and horizontal collection systems.

- The PRB Action Team reports studies using high pressure jet grouting systems to create either permeable grout diaphragms or columns [7]. Overlapping these structures creates longer, continuous barriers. In a field study, two grout formulas have been tried: a resin/granular cast iron slurry and a kaolinite clay/iron slurry. Also, deep soil mixing and hydrofracturing (horizontal and vertical) are under discussion in the U.S. as alternative installation methods.

- Envirotreat Ltd., UK, is currently working on the development of active containment systems using special clay materials. Addition of reactive materials to clay barriers is also under investigation. Overlapping large diameter bore holes are one of the construction methods is considered to be applicable.
- Several German engineering companies have proposed the installation of gates in the form of concrete structures for horizontal or vertical through-flow (Peschla und Rochmes, Edenkoben, and WCI Umwelttechnik, Essen). These are conventional underground concrete structures, caissons, or chambers that contain removable reactive media. These buildings are expensive and limited to use as single gate structures.
- WCI-Umwelttechnik GmbH is working on a deep wall construction method using modified slurry wall techniques with additional caissons as containment for the reactive media.

Finally, the injection of reactive material into the unsaturated or saturated zone, not forming a defined structure, is a potential method, but not discussed in this report.

5. Costs

Table 2 presents a rough overview to costs for the several construction techniques mentioned. They do not include the filling material. They also depend on national markets and on actual/future experience and developments. Some of the actually methods may disappear in the near future, and others may show economical advantages. Generally, we need more field testing and full-scale experience than we now have.

Table 2: Cost Overview

Construction method		Max Depth [m]	Cost Range [US$/m²]
4.1	Peat-filled trench	5	10 -100
4.2	Solid-free trench	10	200 - 400
4.3	Open trench construction	10	100 - 200
4.4	WCI-treatment wall	12	500 - 900
4.5	Dr. Steffen’s patent	20	200
4.6	Large diameter borehole	20-25	200 - 500
4.7	Sax+Klee system	20	1000 - 1500
4.8	Funnel and Gate	20	200 - 1000
4.9	Bio-polymer slurry	30	300 - 500
4.10	Other construction methods	10	100 - 300
		20	200 - 1000
		30	500 - 1500

6. Conclusions

In our estimation, it is too early to evaluate construction methods in general. They strongly depend on the required depth, hydrogeology, contaminants, remediation targets, *etc.* Most of the construction methods discussed are unproven in relation to PRBs, or are under testing.

A wide variety of construction elements are available. The future will show which systems are most applicable to shallow and deep aquifers and that are economically sound.

Full-scale applications and field tests will be helpful in establishing the innovative PRB technology as a proven and available remediation alternative. Besides the research and development activities regarding effective reactive media, we have to deliver inexpensive, durable construction techniques to install (recoverable) reactive media in the contaminated groundwater plume.

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[2] Patentschrift DE 41 05 987 C2, Haldenwang, Eichhorn, February 26, 1991 “Vorrichtung und Verfahren zur *in situ*-Behandlung verunreinigter Grundwässer”.

[3] Patentschrift DE 44 25 061 C1, WCI-Umwelttechnik GmbH, July 15, 1994 “Permeables Behandlungsbett zur Reinigung kontaminierter Grundwasserströme *in situ*”.

[4] Patentschrift DE 4221 198 C2, Dr.-Ing. Steffen Ingenieurgesellschaft mbH, June 27, 1992 “Verfahren zum Entfernen von wasserlöslichen sorbierbaren Schadstoffen aus einem abströmenden Grundwasser in der Umgebung eines Kontaminationsherdes”.

[5] International Patent W093/22241, Cherry, Vales, Gillham, University of Waterloo, Canada, April 23, 1992 “System for Treating Polluted Groundwater”.

[6] Geo-Con, internal company information, not published, December 1997.

[7] Permeable Reactive Barrier Action Team, Summary of the Remediation Technologies Development Forum, Virginia Beach, Virginia September 18-19, 1997.

Discussion

It was suggested that treatment walls may not need to intercept *all* of the contaminated groundwater, due to the expense of constructing the walls, and could be designed to treat (for example) only 90% of the groundwater flow. This would make the technology cheaper and more appealing. Beitinger agreed that such walls can be constructed (*e.g.*, an iron fence or non-overlapping borehole reactors), but the decision is usually based on whether the regulating authority would permit continued flow of untreated water.

Development of Iron-Based Reactive Barrier Technologies for Remediation of Chlorinated Organic Contaminants in Groundwater[1]

Robert W. Gillham[2]

Abstract

Granular iron was not recognized as an effective reductant for promoting the dechlorination of halocarbons in aqueous solution until the late 1980s. Furthermore, the suggestion that granular iron be used, for *in situ* remediation of groundwater containing halocarbons was initially met with a high degree of skepticism. In the intervening years, the use of granular iron for groundwater remediation has emerged as a new and significant environmental technology. This paper outlines some of the major contributions that have led to the growing scientific and market acceptance of the technology.

Introduction

Recognizing the limitations of pump-and-treat methods for groundwater remediation (NAS, 1994), considerable attention has now turned to the use of *in situ* permeable reaction barriers (PRBs). An early review of this topic (prepared in 1992) is given in Gillham and Burris (1997). In this concept, a permeable "wall" containing the appropriate reactants is constructed across the path of a contaminant plume. As the contaminants pass through the reactive material under passive groundwater flow, they are removed by chemical and/or physical processes. Proponents of PRBs cite reduced capital cost, low operating and maintenance costs, and conservation of water and energy among the potential advantages over pump-and-treat systems.

The use of granular iron for removal of chlorinated organic contaminants has led the interest in PRBs. With initial recognition in 1989, this concept is now emerging as a significant technology for groundwater remediation. This paper summarizes the major steps in both the scientific understanding and acceptance, and in the commercial development of the technology.

Scientific Development

In studies of the effect of sampling-well materials on sample integrity, (Reynolds et al., 1990) it was observed that the concentration in aqueous solution of several chlorinated organic contaminants declined when in contact with certain metals. Though this observation was made in 1984, it was not until 1989 that the potential significance with respect to groundwater remediation was recognized. Further testing confirmed the earlier results and revealed various aspects of the process. In particular, based on our early understanding of the reactions, the passive *in situ* use of granular iron was proposed as an alternative for remediation of groundwater containing halocarbons. Response to publication of the early experimental results and concepts (Gillham and O'Hannesin, 1992) generally varied from skepticism to disbelief.

A degree of credibility and the attention of the scientific community was gained through two papers published in 1994. Gillham and O'Hannesin (1994) showed a wide range of contaminants to degrade, in the presence of granular iron, at rates that are several orders of magnitude greater than natural abiotic degradation rates reported in the literature. Evidence was presented to indicate that the reaction was abiotic

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[1] Submitted for publication in: *Proceedings,* American Society of Civil Engineers, 1998.

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reductive dechlorination and followed pseudo-first order kinetics. Matheson and Tratnyek (1994), from detailed studies of the degradation of carbon tetrachloride, showed results consistent with those of Gillham and O'Hannesin (1994), and further proposed three possible reaction mechanisms. All involved sequential dechlorination through one-electron transfer. Both Matheson and Tratnyek (1994) and Gillham and O'Hannesin (1994) proposed two simultaneous redox reactions 1) oxidation of the iron coupled with reduction of water and 2) oxidation of iron coupled with reduction of the chlorinated organic compound. Reaction (1) results in the production of H_2 and Fe^{2+} and an increase in pH as a consequence of the production of OH^-. Reaction (2) causes a further release of Fe^{2+}, the release of Cl^- and production of a less chlorinated organic compound. Based on generally low concentrations of dissolved iron observed in batch and column tests, it was proposed that iron precipitates as $Fe(OH)_2$, limiting the pH increase to values in the range of about 9 to 10.

The scientific aspects of the technology “came of age” through an American Chemical Society symposium “Contaminant Remediation with Zero-Valent Metals” organized by Drs. Paul Tratnyek and Martine Reinhard (209th ACS National Meeting, Anaheim, California, April 2-7, 1995). As an indication of the increasing interest, over 40 abstracts were submitted for presentation. Information was presented indicating that the reactions occur on the solid surfaces rather than in free solution (Weber, 1995 and Totten and Roberts, 1995); based on relatively low production of intermediate degradation products, the one-electron sequential degradation pathway was brought into question (Sivavec and Homey, 1995 and Orth and Gillham, 1995). Totten and Roberts (1995) showed that two-electron transfers can occur, and through this and subsequent work by Roberts et al. (1996) and others, it is now widely accepted that at least for the chlorinated ethenes, trichloroethene and tetrachlorothene, there are two competing pathways, single- electron transfer with DCE isomers and vinyl chloride as intermediate products and two-electron transfer where chloroacetylene is the intermediate. Though both pathways are followed simultaneously, in most situations it appears that the latter is dominant. This is favorable of course since chloroacetylene is highly unstable, while the DCE isomers and vinyl chloride generally degrade more slowly than their parent compounds (TCE and PCE).

Other important contributions concern the affects of inorganic constituents (other than Fe°). Sivavec and Horney (1995) noted that the iron surfaces are generally covered with an iron oxyhydroxide coating, suggesting a two-step degradation process, sorption onto the surface followed by electron transfer. Noting that electron transfer must occur through the surface coatings, the nature of the coatings and their ability to conduct electrons becomes an important issue. Precipitation of $Fe(OH)_2$, a consequence of both reactions (1) and (2) as presented previously, could form a protective coating thus resulting in a loss of activity over time. In subsequent studies, however, (Odziemkowski et al., 1998) it has been shown that $Fe(OH)_2$ is converted to magnetite, which is conducting to electrons, thus maintaining the activity of the iron surfaces.

It is also recognized that the increase in pH caused by the reduction of water can have a profound influence on the inorganic chemistry of natural waters. In particular, in response to increasing pH, bicarbonate in solution is converted to carbonate, which can result in the precipitation of carbonate minerals such as siderite and calcium carbonate. These have the potential to form surface coatings that could reduce activity and ultimately clog pores, resulting in loss of permeability. In pilot-scale laboratory tests reported by Mackenzie et al. (1995), there was no apparent loss of reactivity of the iron, though pore blockage was identified as an issue requiring further investigation. A further contribution of the 1995 ACS symposium was the identification of materials with much higher reaction rates than iron. For example, Korte et al. (1995), and later Liang et al. (1997), showed that a bimetallic consisting of palladium plated onto the iron surface could increase reaction rates, by up to two orders of magnitude.

Current areas of active investigation include fundamental studies of reaction mechanisms and pathways, and degradation rates and pathways for a wider range of organic contaminants. Work continues to identity effective bimetal couples and concerns remain regarding the long-term integrity of the catalytic enhancement. Certainly the most pressing practical issue is the long-term performance of zero-valent iron in natural subsurface environments. Various research groups are continuing to investigate the changes over time in the surface characteristics of iron in contact with various types of groundwater, and the nature and consequences of precipitates that may form.

Commercial Development

As discussed in NAS (1997) and summarized in Macdonald (1997), many companies developed for the purpose of marketing new environmental technologies have had a remarkably poor record of success. In particular, the requirement for regulatory acceptance of new technologies and the fact that the incentives for site owners generally encourage the delay of remedial action are significant contributors to a sluggish environmental market. The *in situ* iron technology is marketed by EnviroMetal Technologies Inc. (ETI) under a licensing agreement with the University of Waterloo. ETI was incorporated in 1992, at a time when there was a high degree of skepticism. In addition, because capital costs of installing an *in situ* iron treatment system are not particularly advantageous, the main financial incentive is in greatly reduced long-term operating and maintenance costs. Clearly, in 1992, it was not possible to demonstrate these savings.

The first important contribution to market access was the development, in 1992, of an *in situ* demonstration at Canadian Forces Base Borden. The early results of that test showed that the dechlorination reaction would indeed proceed *in situ*, and each passing year of consistent performance, raised the level of confidence in the efficacy of the technology. As reported in O'Hannesin and Gillham (1998) this facility performed consistently and effectively over the five- year duration of the test. The second major contribution to market development was the first *in situ* treatment system at a commercial site Yamane et al., 1995). This occurred in late 1994 and early 1995, at a time when general knowledge of the technology was at a low level and long-term *in situ* performance remained as a significant unresolved question. The interest of the client in new technologies, and willingness to support the testing required to develop the design was critical to this initial application, and a significant contribution to market development.

Another important development was the identification of large quantities of granular iron available at reasonable cost. Currently there are three major suppliers, all of whom recover cuttings from metal machining and fabrication operations, treat and grade the materials and resell the product for a variety of commercial uses. These materials have proven to be highly effective as the reductant in the dechlorination process.

While regulatory concerns can slow technology implementation, regulators, particularly the EPA, have contributed in a major way to the growing acceptance of the iron technology. In addition to favorable results reported by EPA researchers, an above-ground demonstration installed in New Jersey in 1995 was monitored under the EPA SITE program, resulting in a favorable report (US EPA, 1997). Similarly, an *in situ* demonstration in New York State promises to result in a favorable report under the SITE program (anticipated in 1998). Inclusion of PRBs, as a Working Group under the Remediation **Technology**

Development Forum has also played an important role in disseminating information concerning PRBs generally and the use of granular iron in particular.

ETI currently reports the installation of ten demonstration facilities and twelve full-scale treatment facilities. While the numbers remain small, the trends suggest a growing awareness and acceptance of the technology. In particular, all recent installations have been full-scale, the time between initial contact and implementation is decreasing and the number of inquiries continues to increase.

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Discussion

Cores collected from two commercial sites showed little change in bacterial activity over the upgradient interface; however, no information was collected for the downgradient side of the treatment wall.

Although there were numerous monitoring wells situated throughout the Borden site, there was no noticeable affect on the hydrologic flow regime. Most are small-diameter shallow wells that were installed for another purpose prior to constructing the wall.

Treatment walls can be used in low-permeability or fractured-bedrock aquifers if there is a measurable gradient. Fractured bedrock is more difficult, although Gillham mentioned a treatment wall currently being installed at a site with fractured bedrock. The fractures are being sealed by jet grouting, and reactive treatment materials are being jetted into the fractures. Hydrofracturing can be used to widen fractures before injecting materials.

There is a sharp pH gradient within the iron wall. The pH-neutral groundwater typically increased to pH 9-10 within the first 10-15 cm of the upgradient side of the wall.

Practical Solutions for the Treatment of Polluted Groundwater

Gérard Evers[1]

The remediation of polluted sites and its treatment constitute a complex problem, and every case is special. Many solutions are proposed to clean or to isolate pollutants, such as biological treatment, soil washing or flushing, electrochemical treatment, vacuum extraction, stabilization, or containment.

Matching a site and a remediation technique depends on many parameters. Design studies for the improvement of these sites take into account not only the chemical context, but also the geology and hydrogeology as well. In many cases, it is necessary to preserve the groundwater flow.

Soletanche Bachy developed several innovative solutions in this field. Drainage trenches, used either alone or in combination with cut-off walls, allow controlling and extracting pollutants while the local groundwater regime is maintained.

Extensive research over the last ten years about the behavior of dissolved pollutants, organic and mineral, ended up with a variety of materials able to trap pollutants in drainage conditions (ECOSOL and IRIS materials), and in a process of underground water seepage control and treatment called the “drain panel process.”

Trapping mechanisms

Several physical and chemical mechanisms are involved to trap pollutants in groundwater. Precipitation, adsorption, and ionic exchange are the most important.

Precipitation

Chemical precipitation is mainly used to eliminate dissolved heavy metals, such as iron, nickel, copper, lead, trivalent chromium, and hexavalent chromium.

These cations are often precipitated in the form of metallic hydroxides in chemical reactions controlled by the pH. In cement-based materials, lime solubility dictates a pH of 12-12.5. However, this reserve of alkali in cements, although large, is not infinite, and alkaline buffers may be incorporated in trapping materials to extend their precipitation ability with time. In some cases, specific reagents are employed to react with pollutants and to precipitate into a insoluble mineral forms.

Adsorption

Adsorption is a physical mechanism based on the properties of some porous materials to fix molecules on their surface. Specific surface governs this mechanism. Attractive forces have different origins:

- physical bonds by pores of similar sizes to the target molecules;
- Van der Waals forces (electrical trapping) is applicable to polarized molecules;
- surface affinity—hydrophobic organic molecules have affinities for sites on activated carbon.

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Adsorption on activated carbon is a widely used method for removing organic pollutants dissolved in waste water. Adsorption capacity values vary depending on the compounds to be removed. For instance, adsorption capacity of chlorophenol is six times higher than that of butylacetate in same conditions. Some clays are able to adsorb cations such as cadmium, strontium, mercury, nickel, and zinc.

Ion exchange

This process is employed for removing dissolved anions in polluted groundwater. Removal method can be percolation through specific resins or clays. This mechanism is well adapted to eliminating cyanides. Two processes are described here to implement these pollutant trapping drainage materials: the drain panel and the drainage trench.

The Drain Panel Process[2]

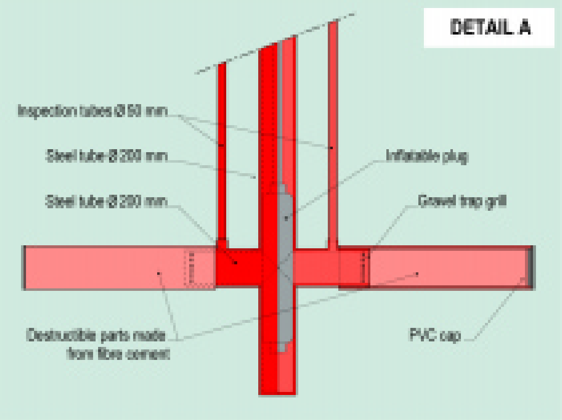
In order to avoid spreading an industrial or accidental pollutant, watertight confinement barriers are often installed together with a pumping system, to keep the water table within the confined area below the outside water table. A water treatment installation will clean the pumped water before returning it to the ambient groundwater. But this classical concept has several inconveniences, which can be solved by the drain panel process.

The drain panel process consists of drainage panels separated by watertight cement slurry panels. A conduit, at the bottom of the watertight panel, establishes the hydraulic continuity between the two drainage panels on either side. A valve, operated from the surface, can be installed to regulate this hydraulic continuity.

The drain panel can be built in combination with the classical confinement barrier, or in combination with a partial barrier, which will then form the so-called “funnel-and-gate” solution. The drain panel system can be used to considerable depths (30 meters or more).

Construction Method

The watertight cement slurry panel is excavated first. When the excavation is completed, a horizontal conduit (200 to 400 mm diameter), linked to a vertical standpipe, is installed at the base of the panel. This conduit has destructible parts closed off with caps at both ends. A temporary inflatable plug avoids any flow through the conduit.



When the slurry has set, the adjacent drainage panels can be excavated using a biodegradable drilling mud. The sealing slurry, vertically covering the destructible parts located at the ends of the conduit, is excavated, and the destructible parts are cut, either by the excavation tool or by another suitable method.

When the excavation of the drainage panel is completed, it is filled with appropriate drainage material, and conductivity between drainage panels is established by withdrawal of the temporary inflatable plug (next three figures).

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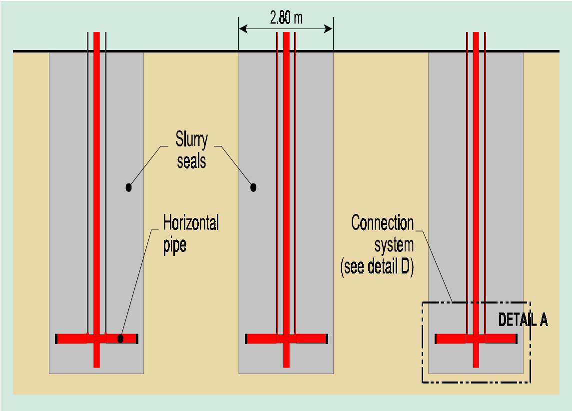
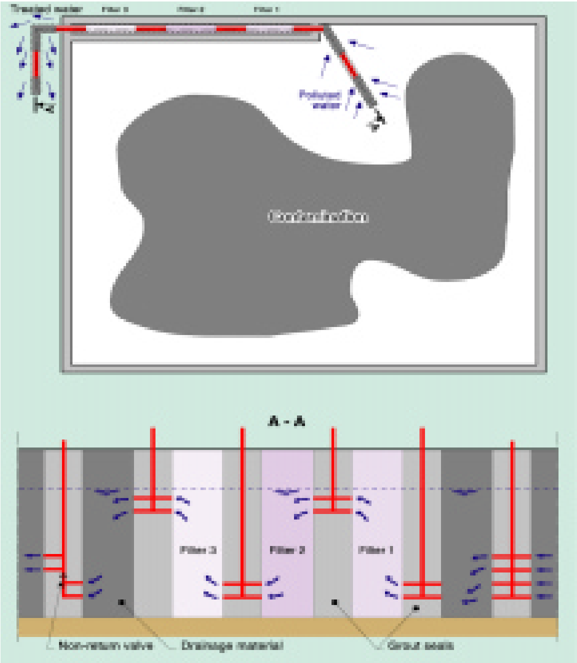
[2] ECOSOL and DRAIN PANEL are patented.

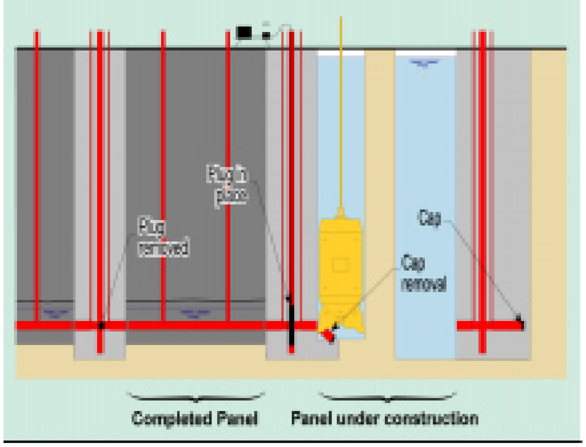


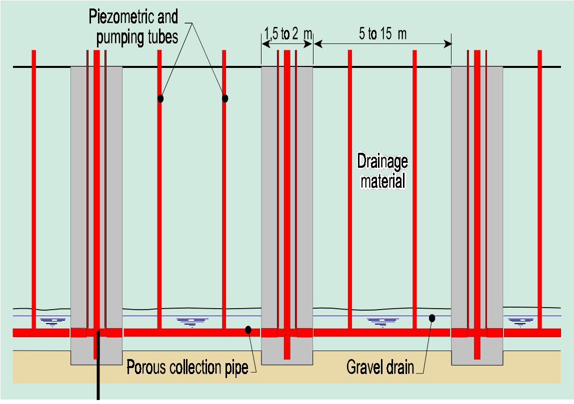
Drainage Material

Drainage panels can be filled with trapping materials adapted to the nature and content of organic or mineral pollutants (figure below).

If required, successive drainage panels with different retention filters can be installed to clean the groundwater. In this case, appropriate positioning of the conduits in the slurry panel may regulate the flow and create an efficient volume for the active barrier.



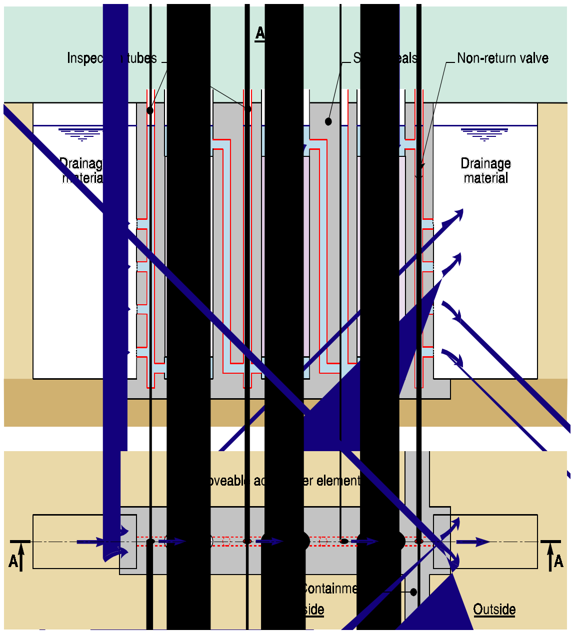




Filter Cartridges

In this case, the whole treatment system, with conduits, filter retention tanks and monitoring equipment, is installed in the cement slurry (see figure at right).

Upstream, intermediate, and downstream piezometers allow permanent monitoring of the pollutant concentration at each point of the treatment system. The filter retention tanks are designed for an easy exchange of the filter cartridges when they are saturated.



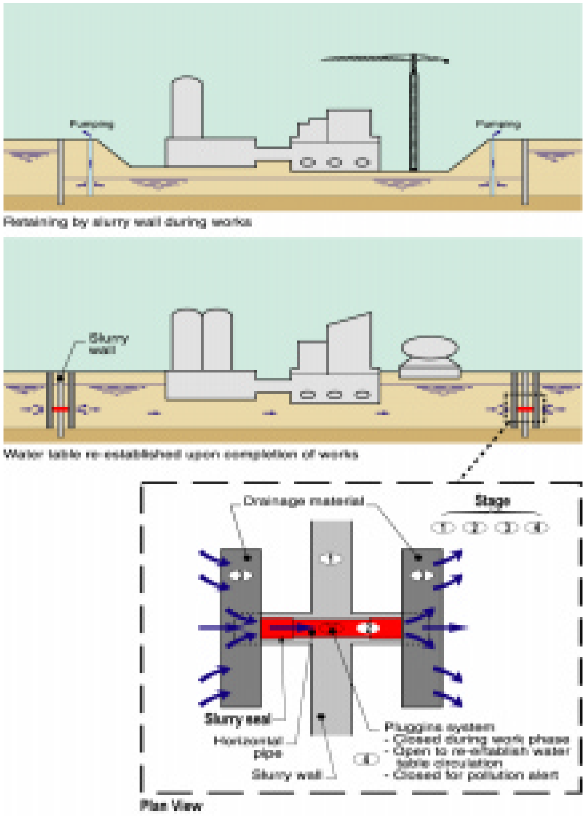
Other Applications for Drain Panels

Underground construction often requires temporary, watertight, cut-off walls around the excavation pit. But without precautions, such cut-off walls will create a permanent perturbation in the groundwater flow, and consequently will have a lasting influence on the hydraulic environment.

The drain panel system will probably reestablish the hydraulic continuity between the upstream and downstream aquifers.

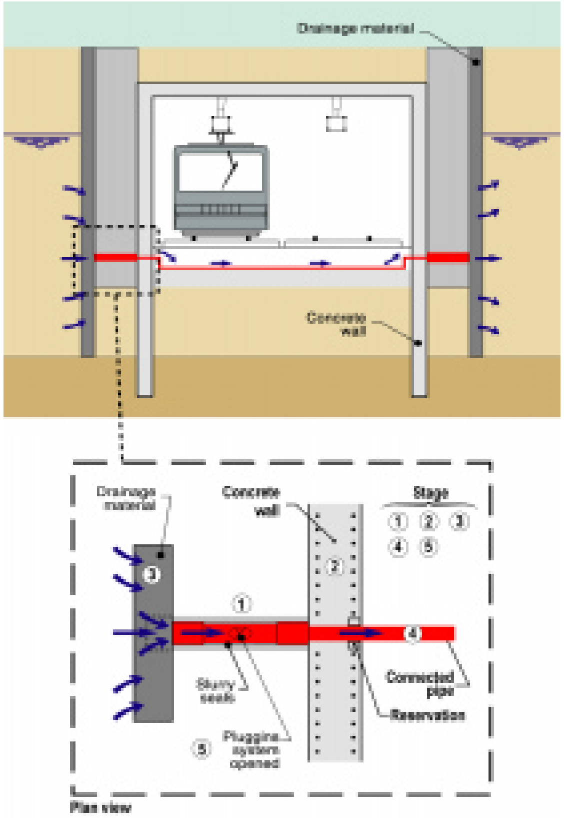
For a temporary cut-off wall, drain panels can be installed at different points along the perimeter. Each drain panel is composed of a central watertight cement slurry panel and two drainage panels (one at each side of the cut-off wall). While lowering the water in the excavation pit, hydraulic connectivity through the drain panel is avoided by temporarily plugging the conduit. When construction is completed, the hydraulic connectivity between upstream and downstream can be reinstated by withdrawing the plug (figures at right).

A possible solution for permanent works is shown on the figure below. Drain panels are installed at each part of the work, and the hydraulic continuity is reinstated, by installing a drainage pipe at slab level and connection with the drainage panels.



Retaining by slurry wall during works

Water table re-established upon completion of works



Treatment of Chrome Pollution by Pollutant-Trapping Drainage Trench

The purpose of the pollutant-trapping drainage trench is to intercept polluted groundwater and treat it *in situ*. The trench does this without maintenance, staff, or energy input. The example given here after was applied to solve a chromate-polluted groundwater problem.

Pollution Source and Type

The pollution was caused by materials containing hexavalent chrome being used in the construction of the A22 motorway in northern France, near Lille.

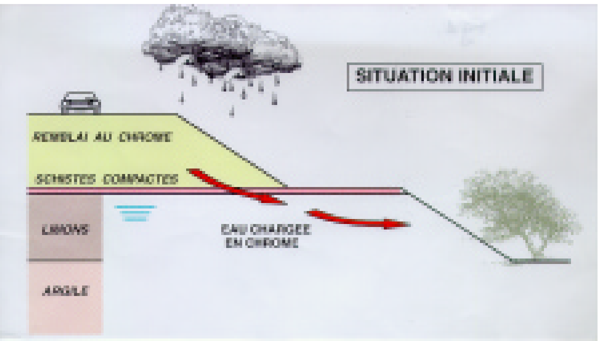
The toxicity of the material, which was known at the time of construction, prompted engineered safeguards in the fill. Unfortunately, the design of the central platform did not completely control seepage. Soon after the road was opened, there were indications of chrome (VI) in the seepage water at some spots.

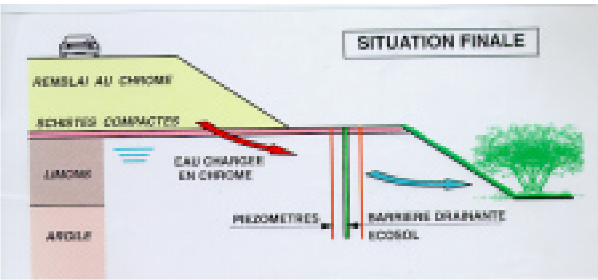
In 1987, a company located below the motorway (downgradient of groundwater flow) reported chrome (VI) in its drainage water, and this pollution was accompanied by bare patches in the vegetation of the motorway bank.

Site Characteristics

The ground under the road embankment consists of 4-5 meters of sandy silt overlying Flanders clay. The water in this silt flows gently towards a banked slope some 10 m downgradient of the fill, directly overlooking the company car park.

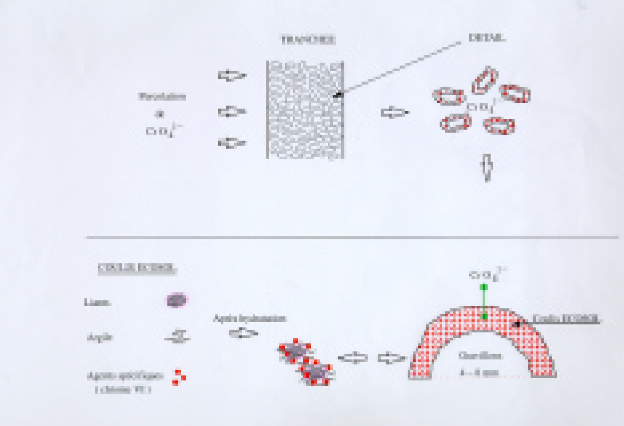
Over time, rain infiltrating into the fill leached into the soil. This water, contaminated with chrome (VI), percolated into the aquifer despite the layer of rolled shale at the base of the fill. Water in the toe ditch below the bank had the characteristic lemon yellow coloring of chromate pollution. In dry weather, patches of yellowish efflorescence appeared on the slope. Seeps of polluted water that killed off the vegetation could be seen on the slope above the company car park.





The site was surveyed to explore the extent of the pollution. Auger holes were sunk for soil samples. Chemical analysis revealed serious soil pollution, with chrome (VI) present in concentrations of up to 1,000 mg/kg, but disappearing beyond a depth of 5-6m because of the impervious Flanders clay bed. Groundwater samples taken from piezometers yielded very high chrome (VI) contents, practically up to 2,000 mg/l. Chrome (VI) is soluble and highly toxic, and the maximum permitted level in drinking water is 0.05 mg/l.

Engineering Design



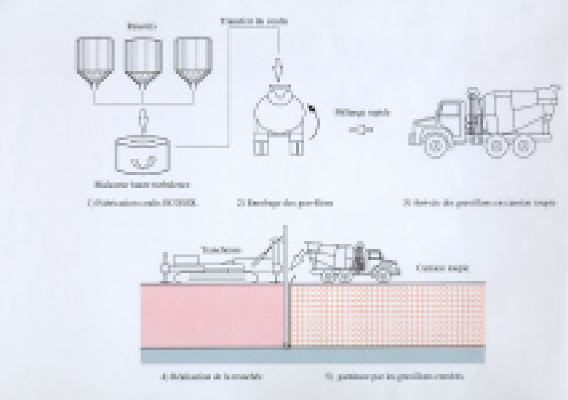
The proposed solution consists of intercepting the polluted groundwater with an Ecosol drainage trench designed to trap chrome (VI). More precisely, a trench is dug and backfilled with a pervious, porous, pollutant-trapping material (figure at right).

The required material is obtained by mixing sorted gravel with a special slurry from the Ecosol range. These slurries are special formulations developed and patented by Soletanche Bachy to suit the exact nature of the pollutants in question: radioactive elements, heavy metals, or organic compounds.

The gravel grains coated with pollutant-trapping slurry bond together so when the mix hardens, they form a rigid, porous structure through which water readily circulates. As the water seeps through, the chemical pollutants are trapped on the film of hardened Ecosol formulation adhering to the grains of gravel.

Preparation of Ecosol Material

Several crucial parameters must be controlled when preparing the Ecosol material (see figure at right):



- *Slurry/gravel weight ratio*. This ratio must not be too high, or the structure will not be sufficiently porous. Nor must it be too low, or the gravel grains will not be completely coated.

- *Gravel size*. For any given ratio between a unit volume of slurry and the weight of gravel, a finer gravel size will increase the active surface area of the structure and reduce the thickness of the hardened slurry coating the gravel grains. This speeds up the trapping reactions. On the other hand, it reduces the permeability of the structure, with the attendant risk of the pores becoming clogged.

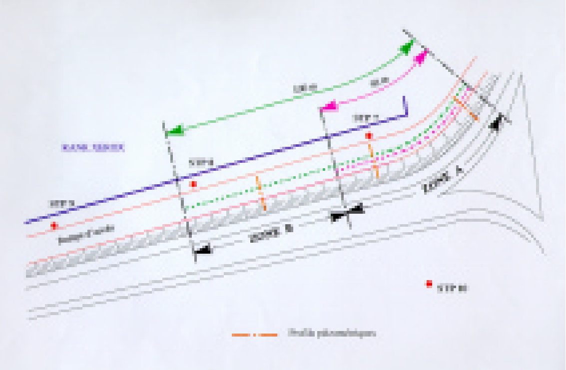
- *Selection of gravel and slurry*. The bond between the film of hardened slurry and the gravel skeleton must be sound and durable. The use of cement slurry and compatible gravels ensures durability, provided the same precautions are used as when designing standard concrete mixes.

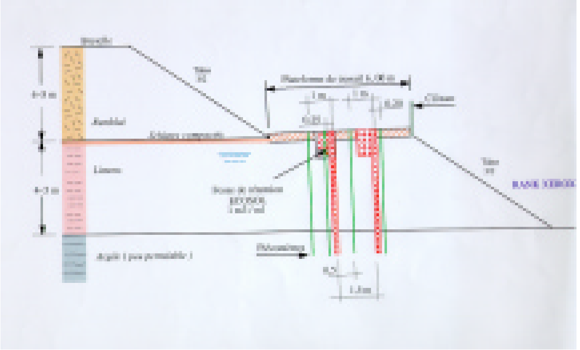
- *Rheological properties of slurry*. The rheology of the freshly-mixed slurry paste must be designed to form a stable film coating the gravel. Therefore, apart from the specific pollutant-trapping substances, the mix must be designed so that the initial stiffness of the paste when the gravel is incorporated is not too great, nor too low.

- *Slurry formulation*. All types of Ecosol slurry can be used, provided their rheological properties are suitable. The exact formulation of the slurry depends on pollutant types and concentrations and required trapping capacity. The mix design is done in the laboratory. In this instance, the cumulative quantity of chrome (VI) trapped per cubic meter of material could be determined. The Ecosol material is prepared by adding the various reagents in the composition at the mixer. This slurry is then used for coating the gravel. This is done in a truck mixer, so that the sorted gravel is delivered, the slurry added, the mix blended and the material delivered to the point of use all in one vehicle.

Trenching

On site, the trench is dug by a machine capable of digging to a depth of six meters. The mobile frame carries a chain and square-sided chute to guide the backfill material from the top hopper into the trench. The Ecosol-coated gravel is brought in by the truck mixer to the trench hopper, and the blended material flows like concrete. The result is a trench backfilled with Ecosol-coated gravel.





There were two zones: (A), where groundwater is intercepted by two trenches, because this area has the highest chrome (VI) concentrations; and (B), where the flow is intercepted by a single trench.

The 0.25-m wide drainage trenches were widened at the top. This extra thickness of trap potential deals with surface water contaminated with chrome (VI) liable to seep into the aquifer.

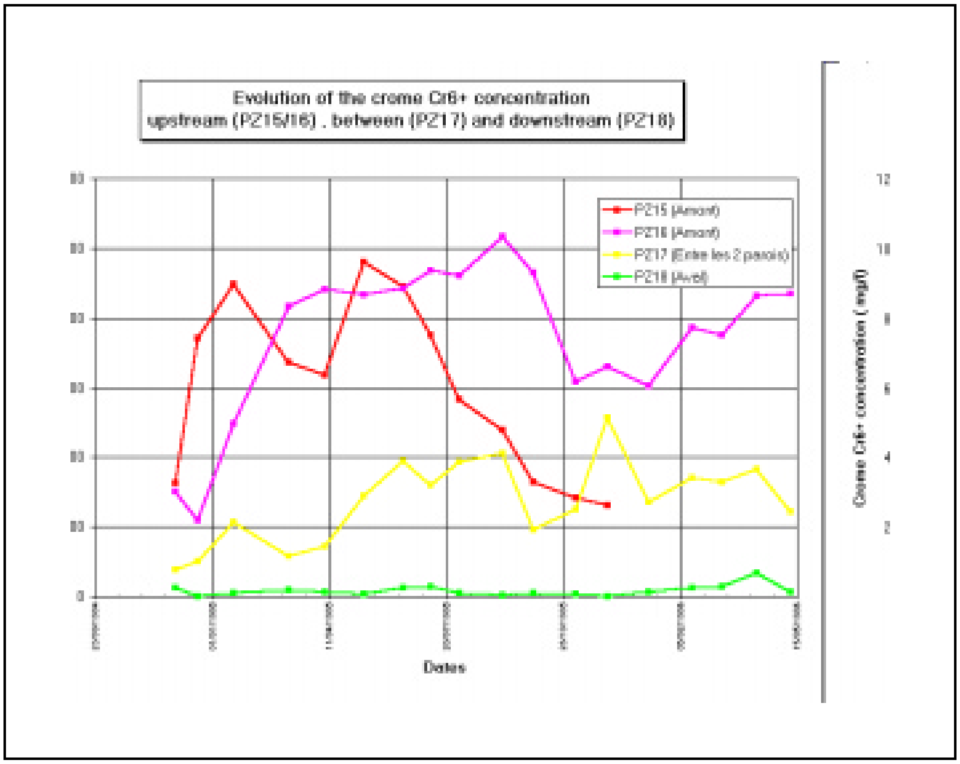
Trench Performance Monitoring

Three piezometer profiles perpendicular to the trench monitor the trend in chrome (VI) concentration up- and downgradient of the of the trench. In total, 11 piezometers were installed, and each month, their water levels are recorded and water samples taken for laboratory analyses.

Analysis of these data confirm the existence of an hydraulic gradient, perpendicular to the trenches, from the embankment downwards to the car park location.

The following figure shows the chrome concentration upstream and downstream of the barrier, during the 18-month observation period following the completion of the construction. The figure shows the good performance of the curtain: the chrome concentration remains at a high—but variable—level upstream of the curtain, while negligible concentrations are recorded downstream.

The measurements are still going on, and they confirm these findings. The Ecosol material confers a high trap potential, around 15 kg of chrome (VI) per linear meter of trench.



Discussion

In response to a question, Evers explained that the treatment wall was excavated using a trenching machine capable of excavating only to a depth of 10 m. The overall problem with the permeable treatment wall is that the reactive material is expensive (US$800/m^3), but not all of it is receiving contaminated groundwater. Because the soil is not uniform, there are preferential flow pathways, and approximately 10% of the wall handles 90% of the contaminated groundwater. The advantage of the funnel-and-gate system is having successive reactive materials that receive contaminated groundwater flow.

There are at least three options for constructing a treatment wall to optimize cost-efficiency: (1) construct one continuous trench and fill it with a mixture of iron and sand; (2) use pea gravel screens upgradient to average the flow rate through the wall; or (3) construct a wall of varying thickness to account for variations in groundwater flow. As long as substantial information on groundwater flow was available, plans can be made for treatment walls having variable thicknesses. Generally, however, funnel-and-gate technology has an advantage in evening out flow through the wall, but may magnify uncertainties.

There was some concern that if the hydrology of a site is not understood, use of a funnel-and-gate system can retard normal groundwater flow, causing an increase in upgradient thickness of the water. The hydrology of a site must be modeled carefully prior to constructing a treatment wall. Modeling and the design of a funnel-and-gate system can be very expensive, perhaps accounting for up to 20% of the overall construction costs (compared to only 10% for slurry walls).

Degradation of TCE at Zero-Valent Iron: Chemical Processes Effecting the Design and Performance of Permeable, Reactive Fe(0) Walls

Wolfgang Wüst, O. Schlicker, and A. Dahmke[1]

Permeable reactive walls present a cost-effective alternative to classical pump-and-treat technologies for the removal of dissolved contaminants from groundwater plumes, provided that a fairly passive long-term performance can be guaranteed. Many materials are under research for use in such reactors, but zero-valent iron has been studied most intensely, since it is commercially available at low costs, and a variety of contaminants can be immobilized by reduction reactions (Dahmke *et al.*, 1997). Based mainly on the results of our own studies, we describe the degradation of chlorinated aliphatic hydrocarbons, the most important application of Fe(0) reactors, and in this context, we discuss the chemical processes effecting the design and performance of permeable reactive Fe(0) walls.

Degradation of chlorinated hydrocarbons with zero-valent iron is known to be a heterogeneous surface reaction, and thus dechlorination can only take place after the chlorinated compound has been associated at the iron surface (Matheson and Tratnyek, 1994). Kinetics is described as pseudo-first-order (k_{obs} [1/h]) with respect to dissolved concentrations, and k_{obs} is reported to be proportional to the iron surface (BET) concentration (Gillham and O´Hannesin, 1994; Sivavec and Horney, 1995). Different commercially available irons show a broad variety in costs as well as physical properties (Figure 1).

Figure 1. Comparison of different irons

Iron source	*Spec. surface area [m^2/g]*	*Porosity [%]*	*Costs [DM/t]*	*Costs [DM/m^3]*
A	0.12	37	800	3,400
B	0.5	58	450	1,400
C	0.032	39	500	2,300
D	0.63	0.74	300	600

Testing iron from different producers, we found considerable differences in reactivity with respect to TCE degradation. Differences in iron surface area concentrations could not sufficiently account for it, since we normalized k_{obs} to this parameter (Figure 2). The normalized first-order rate constants were in the same range as reported for different iron sources in North America (Johnson *et al.*, 1996).There a various other parameters like foreign elements and grain geometry that may affect reactivity. Even iron from the same source showed differences in reactivity.

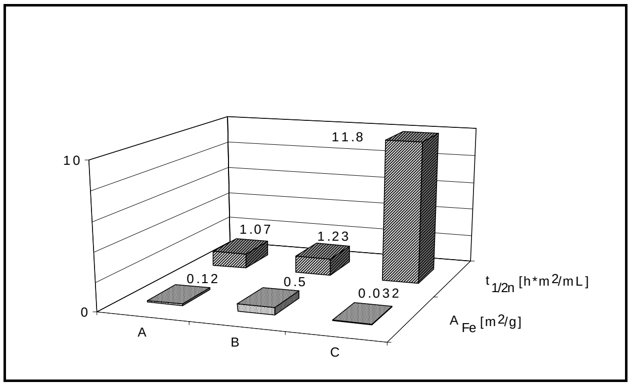


Figure 2.

In low mineralized waters competitive, cathodic reactions may occur that can affect the performance of permeable, reactive Fe(0) walls. Oxygen

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consumption was found to be fast in our column experiments, leading to a zone of Fe(III) precipitates at the column inlet, where hydraulic conductivity was reduced considerably (Dahmke *et al.* 1997). Effects on the degradation kinetics in Fe(0) reactors were not detected, since only a few centimeters are affected by aerobic corrosion. Formation of hydrogen by anaerobic corrosion is thermodynamically favorable, but it depends strongly on the voltage differential. For different irons, we found dependence of reactivity on the iron source, and pH at the inflow ranging from no anaerobic corrosion to a strong gas production (Figure 3), which affects hydraulic conductivity and discharge of gaseous TCE from the column. Hydrogen is the dominating compound in the gas phase, and low-weight aliphatic hydrocarbons (total HC) consisting exclusively of saturated HC account for less than 1 % mol gas, fairly independent of the iron source (Figure 4, Figure 5). TCE, at a concentration of 1 mMol in the column feed, increases the molar fraction of the total HC to 1-3 %, and short-chain unsaturated compounds (ethene, propene) appear in the HC pattern, accounting for TCE degradation. Further column experiments discussed below were performed with iron from a source that was found to have the highest voltage differential with respect to anaerobic corrosion, and a fairly high normalized k_{obs}.

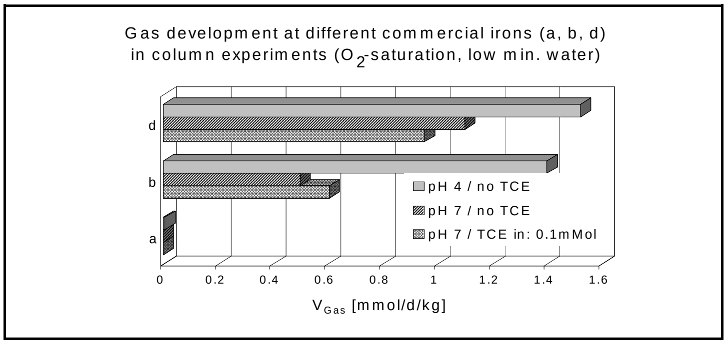


Figure 3.

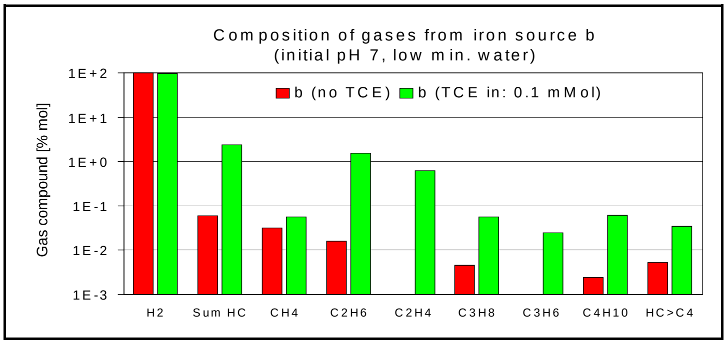


Figure 4.

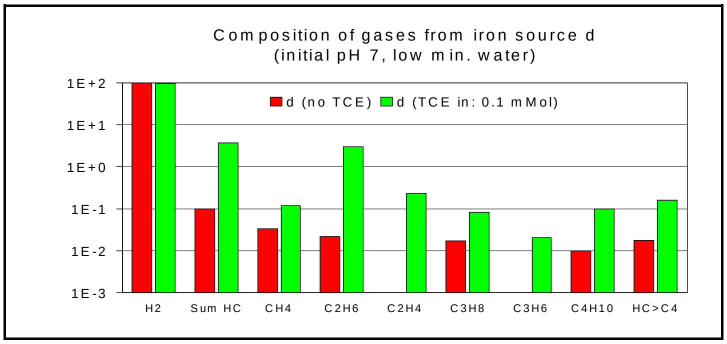


Figure 5.

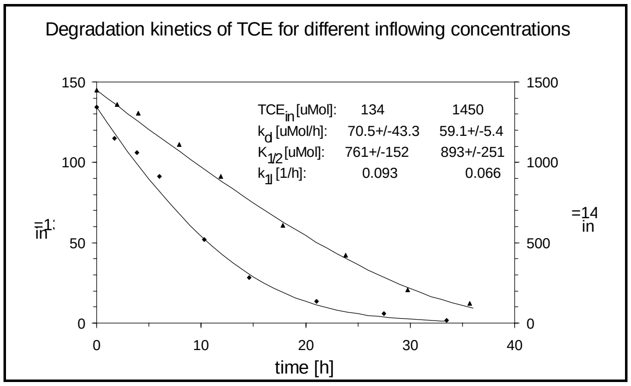
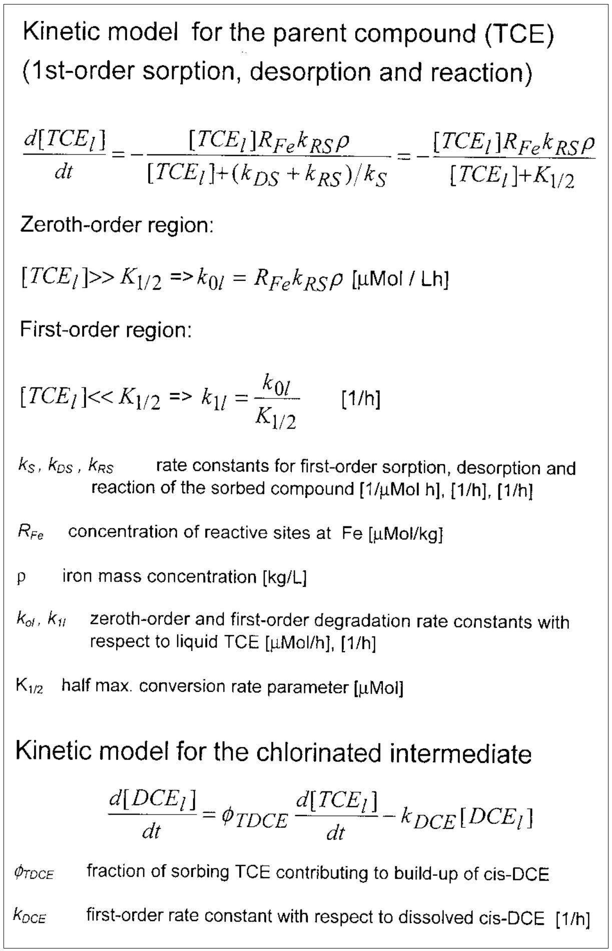


Figure 6.

Looking at the dechlorination kinetics in more detail, we found that the degradation rate was levelling off at a higher concentration due to saturation of reactive sites at the iron surface. An enhanced model accounting for first-order sorption, desorption, and reaction of sorbed TCE (Figure 6, Figure 7) was fitted to the data with good success by the AQUASIM model. Parameters for zeroth- and first-order kinetics with respect to dissolved TCE-concentration are estimated. Since the dominant chlorinated intermediate, cis-DCE, did not exceed 1% of the initial TCE concentration, first-order build-up and degradation was found to be sufficient to fit the measured data. Neither the intermediate cis-DCE nor the kinetics of parent TCE were significantly affected by a 5-fold increase in flow velocity (Figure 8). Cis-DCE as parent compound was degraded faster than TCE both in the zeroth-order and first-order region (Figure 9) in the column experiments. This is the



Kinetic model for the parent compound (TCE) (1st-order sorption, desorption and reaction)

$$\frac{d[TCE_l]}{dt} = -\frac{[TCE_l]R_{Fe}k_{RS}\rho}{[TCE_l]+(k_{DS}+k_{RS})/k_S} = -\frac{[TCE_l]R_{Fe}k_{RS}\rho}{[TCE_l]+K_{1/2}}$$

Zeroth-order region:

$$[TCE_l] >> K_{1/2} \Rightarrow k_{0l} = R_{Fe}k_{RS}\rho \ [\mu\text{Mol / Lh}]$$

First-order region:

$$[TCE_l] << K_{1/2} \Rightarrow k_{1l} = \frac{k_{0l}}{K_{1/2}} \quad [1/h]$$

k_S, k_{DS}, k_{RS} rate constants for first-order sorption, desorption and reaction of the sorbed compound [1/µMol h], [1/h], [1/h]

R_{Fe} concentration of reactive sites at Fe [µMol/kg]

ρ iron mass concentration [kg/L]

k_{0l}, k_{1l} zeroth-order and first-order degradation rate constants with respect to liquid TCE [µMol/h], [1/h]

$K_{1/2}$ half max. conversion rate parameter [µMol]

Kinetic model for the chlorinated intermediate

$$\frac{d[DCE_l]}{dt} = \phi_{TDCE}\frac{d[TCE_l]}{dt} - k_{DCE}[DCE_l]$$

ϕ_{TDCE} fraction of sorbing TCE contributing to build-up of cis-DCE

k_{DCE} first-order rate constant with respect to dissolved cis-DCE [1/h]

Figure 7.

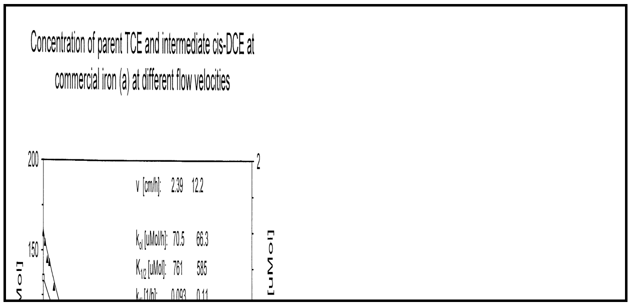


Figure 8.

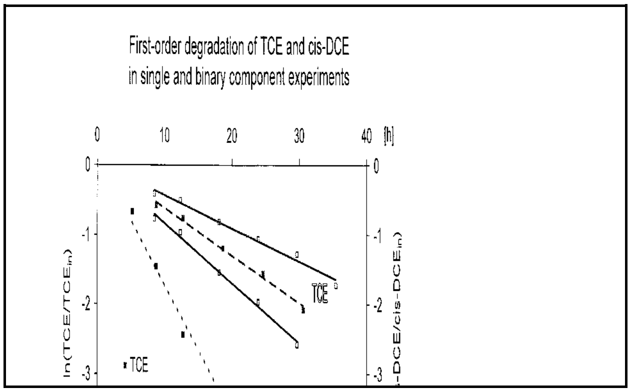


Figure 9.

reverse of the kinetics reported for these compounds (Johnson *et al.*, 1996). In the binary component experiment, degradation rates of both compounds were reduced and competition between TCE and cis-DCE will be discussed in more detail (Wüst *et al.*, in preparation). Since groundwater plumes contaminated by chlorinated hydrocarbons usually contain a variety of compounds, competition between these single compounds has to be considered.

We were also testing the effect of different groundwater constituents (chloride, phosphate, sulfate, chromate, nitrate) on the degradation of TCE in column experiments, where the dissolved concentration of the respective groundwater constituent is gradually increased.

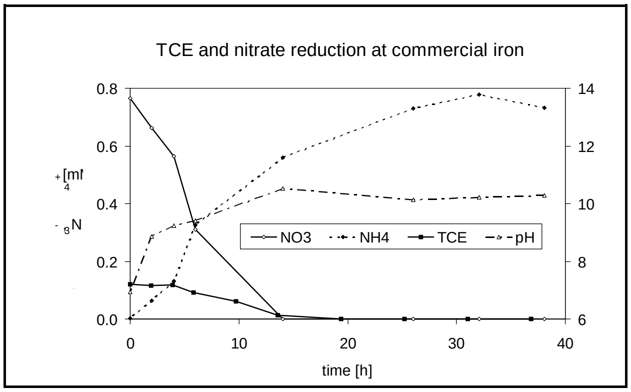


Figure 10.

Abiotic nitrate (Figure 10) and chromate (data not shown) reduction at zero-valent iron were found to be faster than the degradation of TCE. Nitrite as an intermediate could be detected only in traces, and all nitrate-N was reduced to the terminal N(-III). Reduction of 50 mg/l nitrate (German drinking water standard) can result in 13.3 mg/l ammonium entering the aquifer. Since pH is driven up to values greater than 10, ammonia is likely to form. High inflowing nitrate concentration leads to inhibition of both the reduction of nitrate and TCE by zero-valent iron. Consequently, the TCE concentration front is passing through the iron column ahead of the nitrate front (Figure 11). Passivation is due to the formation of a considerable amount of iron precipitates (dissolved iron <0.01 mg/l). They are possibly more oxic due to the higher redox potential both in solution and at the iron surface, and thus less conductive.

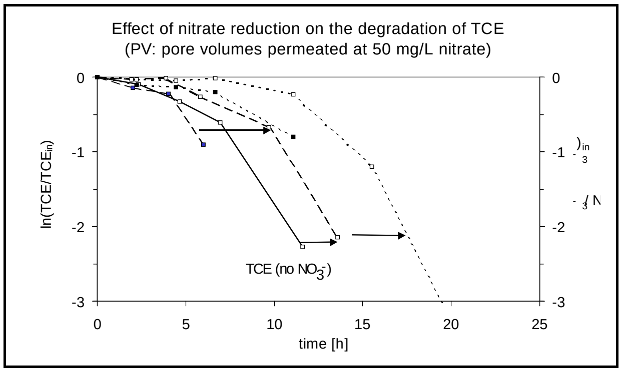


Figure 11.

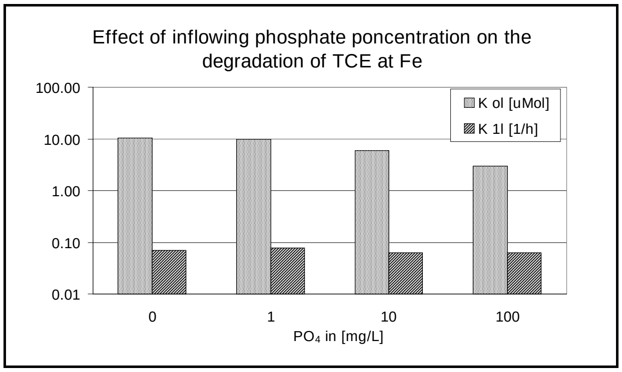


Figure 12.

Phosphate can affect the performance of iron walls only at higher inflowing concentrations (>1 mg/l phosphate). At 10 mg/l, we observed a decrease in both, zeroth- and first-order rate constant (Figure 12). 100-mg/l phosphate in the feed further reduced zeroth-order degradation but so far did not effect first-order degradation in the back part of the column. Phosphate is sorbing, and forms vivianite, which was detected by XRD in addition to magnetite. Formation of these precipitates could be predicted by the geochemical equilibrium program PHREEQEC. In contrast to phosphate, loss of sulfate from solution could not be observed. Considerable decrease in the degradation of TCE, however, was found at a concentration of 500 mg/l sulfate (Figure 13). Higher sulfate concentration (1,000 mg/l) did not enhance the passivation of iron.

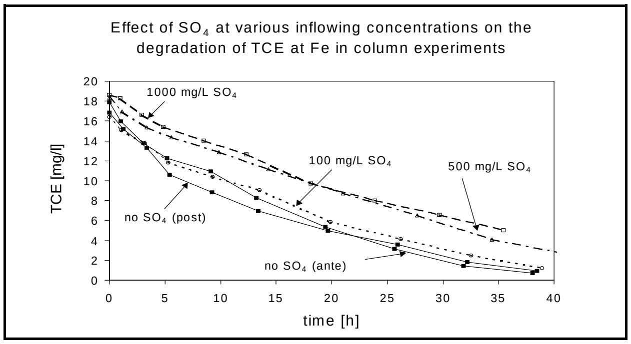


Figure 13.

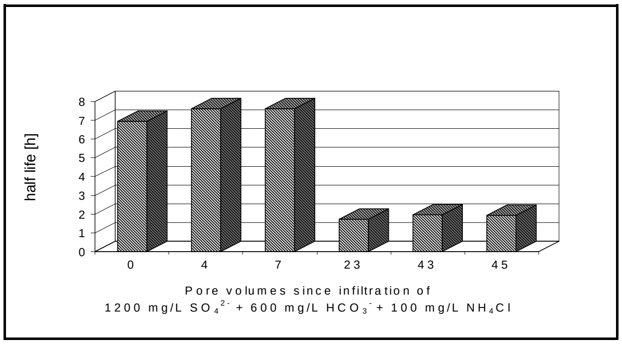


Figure 14.

Sorption of sulfate was found to be reversible, and the column fully recovered after its desorption from the iron surface.

Abiotic sulfate reduction was not observed, but microbiological transformation to sulfide took place in one of our columns to some extent. There we found degradation rates to increase (Figure 14), which we attribute either to the enhancement of abiotic degradation because of sulfide formation (high electric conductivity) or to co-metabolic TCE degradation. Enhancement of reactivity was also attained by palladizing zero-valent iron. First-order kinetics was stable over a wide range of flow velocities and no maximum degradation rate (zeroth-order kinetics) could be detected even at high inflowing TCE concentrations (Figure 15). Increasing chloride concentrations confirmed the results known from aerobic anaerobic corrosion studies: the first-order rate constant increased by 2 in the range of 0-100 mg/l chloride (Figure 16).

In a low-mineralized groundwater environment, we expect long-term stability of dechlorination rates in permeable, reactive Fe(0) walls and hydrocarbons as final products enter the aquifer. Description of the degradation kinetics by a pseudo-first order model was not sufficient at higher TCE concentrations, where zeroth-order kinetics was observed. We succeeded in fitting the data by a Monod-type model. Competition

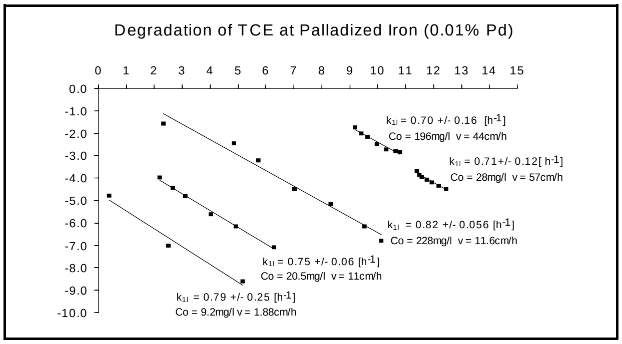


Figure 15.

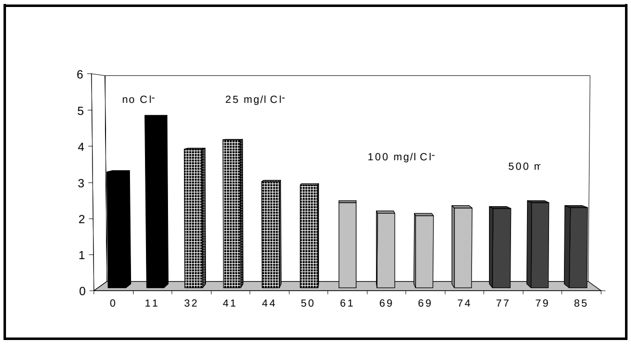


Figure 16.

among different chlorinated compounds has to be expected as shown in the case of TCE and cis-DCE, and has to be considered in the reactor design.

Redox-competitive inorganic groundwater constituents (oxygen, water, nitrate, chromate) can affect the design and performance of reactive iron walls considerably. Products like hydrogen gas and ammonia can be formed and enter the aquifer. Iron precipitates can reduce permeability and reactivity. Under certain conditions, the concentration front of the chlorinated compounds is passing through the reactor due to passivation of zero-valent iron. These reactions may limit the scope of permeable reactive Fe(0) walls.

Inhibition observed by phosphate and sulfate seems to be of minor importance. At ambient groundwater concentrations, phosphate did not effect degradation kinetics of TCE, since it was precipitated at the front of the column. No abiotic reduction was observed for sulfate (as for nitrate and chromate), but degradation rates were enhanced by microbiological sulfate reduction.

We expect that microbiological reduction of nitrate and chromate in the groundwater plume can reduce the impact of these anions on the performance of reactive iron walls. Passivated walls can possibly be regenerated by chloride, which is known to break down passive films on zero-valent iron, and which we found enhanced degradation rates in our experiments. We further assume that ascorbic acid will recover degradation rates due to its reducing and complexing properties.

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Discussion

Paul Bardos asked for an explanation of Figures 3, 4, and 5, which show a system with just oxygenated water and iron producing trace amounts of short-chained hydrocarbons. Wüst said that the iron contained 3 percent carbon, which may have been the source of the hydrocarbons. Alternatively, there may have been organics in the gas phase that were reduced.

Hermann Schad also asked for an explanation of the apparent conversion of 100% of the nitrate to ammonia, while column experiments using site groundwater showed that much less nitrate had been converted. Wüst responded that the difference is probably due to microbiological reactions that reduce more of the nitrate.

The Treatment of Groundwater with Mixed-Wastes:
Reductive Dechlorination of TCE and Reductive Precipitation of Uranium

Liyuan Liang[1] and B. Gu[2]

Abstract

The overall goal of this project was to perform a pilot-scale field evaluation of the reactive barrier technology at the Bear Creek Valley, Tennessee. The groundwater plume at the site contains mixed wastes of uranium (U), technetium, organic solvents and a high concentration of nitrates. This study was undertaken to determine the effectiveness of zero-valent iron (Fe°) and several adsorbent materials for the removal of radionuclides, nitrates and chlorinated volatile organic compounds from the contaminated groundwater. Several types of reductive and adsorbent materials were evaluated, including Fe° filings, peat materials, ferric oxides, and Cercona™ Bone-Char. Results indicate that Fe° is a promising barrier material to extract U from contaminated groundwater and is more effective than the adsorbents, particularly at high U concentration. A combination of Fe° and peat materials was effective in removing both nitrate and U from the contaminated groundwater. Organic solvents, such as trichloroethylene (TCE), trichloroethane and tetrachloroethylene, were all effectively degraded in the contaminated groundwater with Fe°.

For uranium, almost 100% was removed through reactions with Fe° at an initial concentration of up to 84 mM (or 20,000 mg U/l). Results from the adsorption and desorption kinetic studies and spectroscopic studies demonstrate that a reductive precipitation of U with Fe° is the major reaction mechanism. Only a small percentage (<4%) of uranyl appeared to be adsorbed on the corrosion products of Fe°. Experiments showed that the reduced U(IV) species on Fe° surfaces could be reoxidized and potentially remobilized if re-exposed to atmospheric oxygen. However, the remobilization may not occur if the U is sequestered by co-precipitation with ferric oxyhydroxides. Results of this study demonstrate that Fe° can be an effective medium for U removal from mixed waste in passive groundwater treatment systems.

INTRODUCTION

In situ permeable reactive barrier technology (based primarily on zero-valence iron, Fe°) has been identified as a potentially cost-effective, passive treatment technology for contaminated groundwater [1-2]. Interest in the technology by both private industries and federal agencies has generated extensive research activities in the last few years. Initial laboratory research has been carried out to determine the rates of the reactions for both the destruction of chlorinated solvents, such as trichloroethylene (TCE) and the immobilization of metals (*e.g.*, Cr(VI), Tc(VII), and U(IV)) by Fe° [3-7]. The understanding of the kinetics of contaminant removal is necessary for designing the residence time and sizing the reactive barrier.

Following the kinetic work, mechanistic studies have mushroomed in an attempt to understand the pathways for dehalogenation and to identify daughter products [8-9]. Although detailed reaction pathways and mechanisms have not been determined unequivocally, the reaction is believed to be a heterogeneous surface reaction [7-10]. Reduction of halogenated compounds is known via hydrogenolysis, in which a halogen ion is exchanged for a hydrogen ion, consuming 2 electrons [11]. From the known partially dehalogenated daughter products (such as dichloroethylene (DCE) and vinyl chloride (VC) from TCE), laboratory studies show that the stepwise dehalogenation via hydrogenolysis indeed takes place on the metal surface [10, 12-13]. Further study has indicated that a reaction pathway via reductive beta-elimination

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occurs with Fe°, producing acetylene [14-15]. With a series of chlorinated ethene or methane, results show that the less chlorinated compounds, such as DCE and VC, are more difficult to dehalogenate than are the more highly chlorinated compounds [7]. Alternative bimetallic systems (*e.g.*, plating of small amounts of Ni, Cu, Zn, and Pd onto Fe°) have been found to accelerate the dehalogenation rates for various volatile organic compounds. In some cases, the bimetallic systems dehalogenate the compounds that are ineffective with Fe° alone [16-18].

While numerous studies have been conducted in the laboratory and field to determine the degradation mechanisms and kinetics for organic contaminants by Fe°, relatively few studies have examined the potential for using Fe° to remove radionuclides and heavy metals from contaminated groundwater. It is believed that reductive precipitation is a major pathway for the removal of Cr(VI) and Tc(VII) [5, 19-20]. However, for uranium (U) it is still unclear whether the removal of uranyl results from reductive precipitation or from adsorption onto the corrosion products of Fe° [4, 21-23]. Knowing which of these two mechanisms dominates the reaction is necessary because they largely determine the mobility and fate of these contaminants in a given geochemical environment. For example, if uranyl is largely adsorbed onto the hydrous iron oxides or the corrosion products of Fe°, the adsorbed U would be readily desorbed by the presence of competing ions and complexing agents such as CO_3^{2-} and dissolved organic matter in groundwater. Furthermore, a change in the groundwater pH would profoundly influence the adsorption and desorption behavior of U on ferric oxide surfaces. Alternatively, if U is primarily removed by reductive precipitation, the precipitated U would not be remobilized unless the groundwater redox conditions are changed and the reduced U(IV) species are reoxidized.

At Bear Creek Valley, Tennessee, the groundwater is contaminated with uranium, technetium, organic solvents (such as tetrachloroethylene, TCE, and trichloroehtane) and a high concentration of nitrates. The overall goal of this project was to perform a pilot-scale field evaluation for treating the mixed contaminant plume with the reactive barrier technology at the site.

The objectives of this study were to determine the effectiveness of zero-valent iron and several adsorbent materials in removing radionuclides, nitrates and chlorinated volatile organic compounds from the contaminated groundwater. Results for organic solvent removal have been discussed elsewhere [33], and in this paper, we report on the reaction kinetics and mechanisms for the reduction or removal of uranyl [as $UO_2(NO_3)_2$] with various iron filings and adsorbent materials. The work was part of the remedial actions using the permeable reactive barrier technology to intercept and treat U, nitrate, and other contaminants migrating to the tributaries of Bear Creek at the U.S. Department of Energy's Y-12 Plant located in Oak Ridge, Tennessee. In particular, there is a desire to remove U from the groundwater because it is a major contributor to risk down-gradient of the Bear Creek.

EVALUATION OF REACTIVE MEDIA FOR U REMOVAL

Uranium Reaction Kinetics

The reaction rates for uranyl removal by Fe° filings were studied in batch experiments by mixing 2 g of iron filings with 10-ml U solution as [$UO_2(NO_3)_2$] at an initial concentration of 4.2 mM (1,000 mg U/l). Four sources of iron filings were evaluated: (1) Master-Builder iron filings (0.4–1 mm) (Master-Builders, OH), (2) Cercona cast iron foam (Cercona of America, OH), (3) Peerless iron filings (0.5–1 mm) (Peerless Metal Powers and Abrasives, MI), and (4) coarse Peerless iron filings (3–12 mm). Aqueous samples were withdrawn, filtered and U activity was then analyzed by a Liquid Scintillation Analyzer [24].

All four types of Fe° filings studied were effective in removing uranyl from the aqueous solution (Figure 1). Over 97% U were removed within 30 min by all types of Fe° filings and no detectable amounts of U were left in the solution phase after about 1 hour of reaction. However, ferric oxide was not as effective as iron filings in removing uranyl in solution; only about 15% of the added uranyl was removed by the ferric oxide. The reaction rate for uranyl removal by ferric oxide appeared to be fast, reaching equilibrium in less than 1 min (only one data point could be collected).

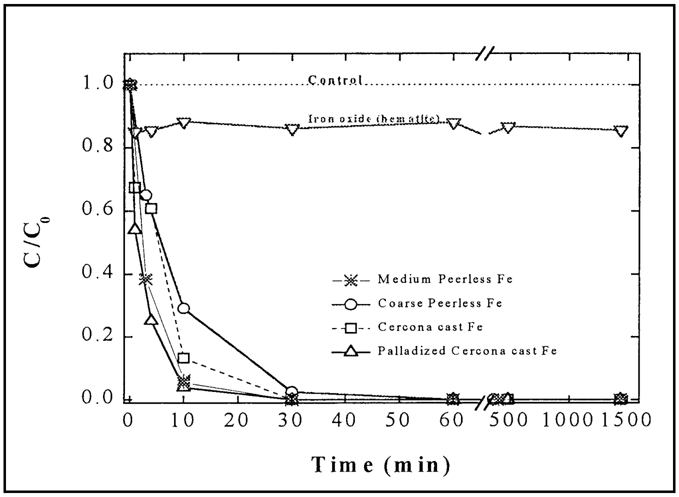

Figure 1. Reaction kinetics between uranyl and zero-valent iron filings or iron oxide powder in aqueous solution.

These observations indicate that U was removed by ferric oxide largely through surface adsorption, which often exhibits fast reaction kinetics. In contrast, the reductive precipitation process usually takes longer because it involves the corrosion of Fe° and an electron transfer process from Fe° to uranyl. Because the U solution was not deoxygenated before the experiment, a time-lag would be required to establish a low redox potential. The partial U removal by the ferric oxide could be attributed to the limited availability of surface sites; the adsorption process reached its maximum when an excess amount of uranyl was added in the solution. Although the Fe° filings have a relatively low specific surface area (about 1 m^2/g) in comparison with ferric oxide powder (10.1 m^2/g), the filings removed almost 100% of uranyl in the aqueous solution after approximately 30 min. The relatively slow reaction rates and the relatively high U removal efficiency by Fe° compared to ferric oxide suggest that reductive precipitation of uranyl is the dominant mechanism for U removal by Fe°.

U Removal Efficiency and Capacity

Because Fe° filings corrode in water, uranyl is expected to adsorb onto Fe°-corrosion products such as ferric oxyhydroxides. To evaluate the partitioning of U in Fe° and its corrosion products, the following experiments were performed. A 10-ml uranyl solution (42 mM or 10,000 mg/l) was equilibrated with 2 g of Fe° for approximately 3 weeks on a shaker. The solid and solution mixture was then removed from the shaker, and the supernatant was immediately decanted. The iron filings were thus separated from the corrosion products (*i.e.*, particulates) in the supernatant. The amount of U associated with the filterable particles was then estimated by analyzing U concentrations in solution before and after samples were filtered through a 5 µm filter.

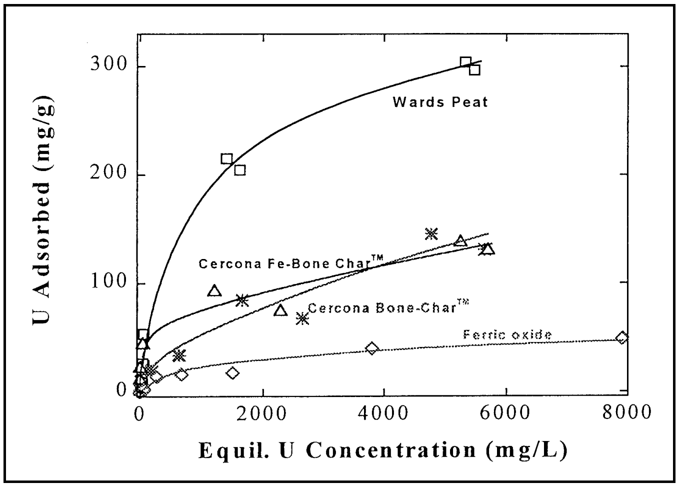

Figure 2. Uranyl adsorption by adsorbent materials (Wards peat, ferric iron oxide, and Cercona™ bone Char)

The U removal efficiency and capacity through the reductive precipitation and adsorption by Fe° and several adsorbent materials (ferric oxide, peat, and Cercona™ bone-char) were further evaluated in batch studies. Figure 2 shows the typical adsorption isotherms of uranyl on these adsorbent materials. The initial slope and the plateau of the adsorption isotherms define the adsorption affinity (or efficiency) and capacity [25]. It is evident that all these adsorbent materials were effective at removing U at a relatively low solution concentration (<50 mg U/l). The initial slopes (*i.e.*, the initial partitioning coefficients) ranged from about 40 to > 10,000 ml/g, with the Cercona™ Fe-bone-char being the most effective at a low initial concentration. However, the Wards peat exhibited an adsorption capacity that was 2-3 times higher than that of Cercona™ Fe-bone-char and about 5-6 times higher than that of the ferric oxides on a weight basis. As the solution U concentration increased, a relatively large percentage of U was left in the solution because of the limited sorption capacity of the solid materials.

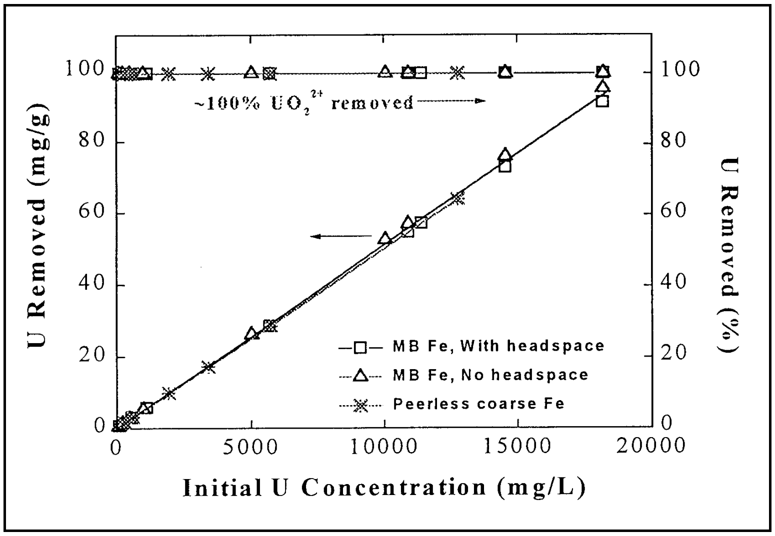

Figure 3. U removal by various zero-valent iron filings: Master-Builder (MB) with headspace, MB without headspace, and Peerless coarse iron filings

In contrast, reactions between uranyl and Fe° resulted in almost 100% removal of U in solution as shown in Figure 3. Regardless of the initial U concentration in solution (up to 84 mM or 20,000 mg/l), no detectable amounts of U were found in solution after reaction with Fe°. Note that Figure 2 is plotted against the equilibrium concentration of uranyl in solution, whereas Figure 3 is plotted against the initial U concentration added because no detectable amounts of U could be found in the equilibrium solution. Analysis by the phosphorescence-lifetime instrument gave not only a high sensitivity for detecting uranyl (on the order of parts per trillion) but also the valence states of U because U(IV) does not phosphoresce [26]. In order to determine if the reduced U(IV) species were present in the equilibrium solution phase, some selected aqueous samples were also exposed to the air and treated with peroxide (H_2O_2) and HNO_3 and re-analyzed by the phosphorescence-lifetime instrument. Again, no detectable amount of U was found in the solution after the treatment. These results are therefore indicative of a reductive precipitation of U by Fe° rather than an adsorption process because adsorption would have resulted in a partitioning of U in the solution phase. No maximum loading capacity may be defined for U removal as long as sufficient amounts of Fe° are present in the system to maintain a favorable reducing environment. The adsorption process may dominate only when Fe° is consumed and the corrosion products (Fe-oxyhydroxides) are formed in the system.

We further evaluated the percentage distribution of U in the Fe° and its corrosion products in suspension because, if U was largely adsorbed on the corrosion products of Fe°, the adsorbed U may be desorbed and/or co-transported with the suspended colloidal particles. Results (Table 1) indicated that only a small percentage of U was associated with these suspended particles (or the corrosion products) after shaking for ~3 weeks in the batch experiments. The majority of added uranyl was precipitated on the Fe°. Additionally, a desorption experiment with 0.1M Na_2CO_3 indicated that U associated with suspended particles *(i.e.*, the corrosion products) was readily desorbed (>64%). However, only small amounts of U (<0.21%) in Fe° could be washed out with the carbonate solution (Table 1). It is known that CO_3^{2-} complexes with uranyl to form negatively charged U species such as $UO_2(CO_3)_2^{2-}$, which does not adsorb on the negatively charged ferric oxyhydroxide surfaces at the given pH conditions (pH > 10) [27-28]. The zero point of charge of common ferric oxyhydroxides is in the range of 6-8.5 [29]. Therefore, these results suggest that uranyl, which was in the initial solution, was converted to less soluble U(IV) species by the Fe°. The large percentage of extracted U from the suspended particulates implies that U was primarily adsorbed in its VI-oxidation state by the corrosion products, although these corrosion products only constituted a small percentage of the Fe° mass. These observations are consistent with that of Grambow *et al.* [21], who found that a large percentage of uranyl was adsorbed on the corrosion products of Fe° and that uranyl was only partially reduced to U(IV) species. It is important to note, however, that we obtained these suspended particles of iron corrosion products by vigorously shaking the Fe° solution and then immediately decanting the suspension. Under static column flow-through conditions, no suspended particles could be observed by means of turbidity measurements; this suggests that iron corrosion products may be cemented within the Fe° mass or precipitated downgradient in the column. This cementation of iron corrosion products is desirable for sequestering U or other contaminants in *in situ* groundwater treatment systems.

Table 1. Uranium partitioning in the Fe° and the suspended particles (*i.e.*, the corrosion products of Fe°) before and after washing with 0.1M Na_2CO_3

	Peerless Iron Filings			Master-Builder Iron Filings		
	Before wash (mg)	After wash (mg)	U desorbed (%)	Before wash (mg)	After wash (mg)	U desorbed (%)
U in Fe°	96.09	95.89	0.21	97.23	97.16	0.07
U in suspended particles	3.91	1.39	64.5	2.77	0.18	93.6

Identification of Reaction Products by Spectroscopic Studies

Reductive precipitation of uranyl to U(IV) by Fe° is thermodynamically favorable according to the following reactions:

(1) $Fe^{2+} + 2e^- \Leftrightarrow Fe(0)$ $E^o = -0.440$ V
(2) $UO_2^{2+} + 4H^+ + 2e^- \Leftrightarrow U(IV) + 2H_2O$ $E = -0.07$ V at pH 8.

The reduced U(IV) readily forms oxyhydroxide precipitates in solution [30-31] or precipitates on Fe° surfaces. The fluorescence spectroscopic technique was employed in an attempt to identify the valence state of U on Fe° surfaces and in solution. The analytical technique was also employed to evaluate the possible re-oxidation processes of the reduced U(IV) on Fe° surfaces. It is known that only the oxidized U(VI) gives strong fluorescence whereas the reduced U(IV) does not. In Figure 4, the fluorescence spectra are plotted for (1) a uranyl aqueous solution, (2) a uranyl suspension containing ferric oxide powder (hematite), (3) a uranyl solution in the presence of Fe°, and (4) a background aqueous solution without uranyl. The uranyl aqueous solution itself showed strong intensity in fluorescence. In the presence of hematite, the intensity was decreased, but no fluorescence spectra were observed after uranyl reacted with Fe°. These results are consistent with the batch kinetic and equilibrium studies, which showed that uranyl was reduced to U(IV) by Fe°. However, because uranyl is only adsorbed onto ferric oxide and not reduced, a strong fluorescence spectra was observed in the ferric oxide systems as a result of the adsorbed uranyl species and the uranyl remaining in solution.

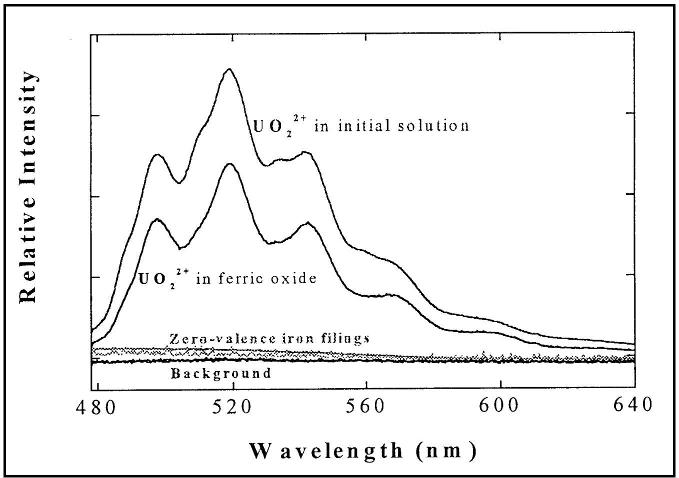

Figure 4. Fluorescence spectra of uranyl before and after reactions with ferric iron oxide (hematite) or zero-valent iron filings in solution

Several lines of evidence presented above have demonstrated that, in the presence of Fe°, uranyl was primarily reduced to U(IV), which was precipitated on the iron surface. This work has addressed how persistent these reduced U species are on the iron surface, especially if they are exposed to atmospheric oxygen. Figure 5 shows the fluorescence spectra of a few solid Fe° samples at different exposure to air after reacting with uranyl solutions. A strong fluorescence spectrum was observed after uranyl was reacted with a rusted Fe° and then dried in the air for 2 days. By comparison, a much weaker fluorescence spectrum was observed when uranyl reacted with Fe° and was then dried in a Speed-Vac for 4 h. No fluorescence signal could be identified for the freshly prepared U- Fe° specimen. These results demonstrate that the reduced U(IV) species on Fe° surfaces could be re-oxidized. Furthermore, the re-oxidation rate appeared to be relatively slow (on the order of days) in comparison with its reduction process (on the order of minutes, Figure 1).

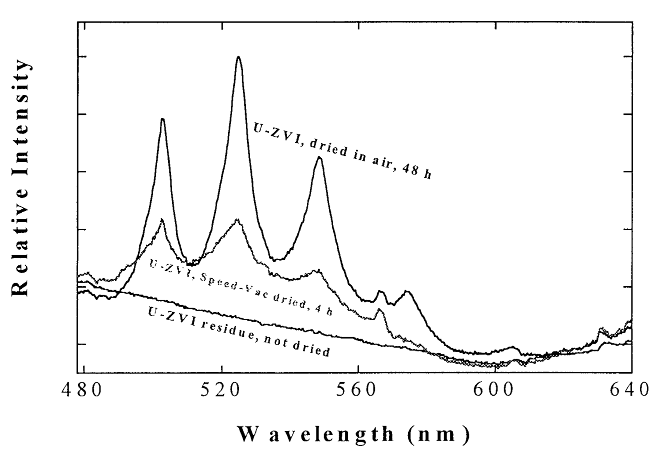

Figure 5. Fluorescence spectra of U on zero-valent iron surfaces, showing the adsorbed uranyl or the reoxidation of precipitated U(IV) to U(VI) species

Implications for groundwater remediation

Both batch experiments and spectroscopic studies showed that Fe° is effective in removing U from water under reducing conditions. The major reaction pathway is via reduction of uranyl by Fe° to form insoluble U(IV) surface species. Adsorption of uranyl by corrosion products accounts for a small percentage of total uranyl removal. The overall removal rates are fairly fast, and the half-life of the reaction is on the order of a few minutes, assuming a pseudo-first order kinetic reaction. Experiments also show that re-oxidation can occur when reduced U(IV) is exposed to atmospheric oxygen.

These results imply that using iron in a permeable reactive barrier to remove U is feasible for groundwater remediation. However, U retained by Fe° may be reoxidized and remobilized when the precipitated U(IV) on Fe° is exposed to atmospheric oxygen. The effect of dissolved oxygen in water on the rate of re-oxidation has not been determined in this study, but will be included in future work. As long as a reducing condition is maintained in the permeable reactive barrier by Fe°, it is likely that the reduced U(IV) is coprecipitated and eventually cemented with the Fe° corrosion products. Both laboratory and field-scale experiments are underway to determine the removal efficiency *in situ*, and to gauge the geochemical influence to such technology. The long-term performance of Fe° reactive barriers with respect to its efficiency, byproduct formation, and clogging is still a matter of debate [32]. Results of this work have demonstrated that Fe° is an effective medium that can be used to remove certain redox-sensitive radionuclides and metals, in addition to its ability to degrade many chlorinated organic compounds.

ACKNOWLEDGMENTS

Cercona™ Bone-Char materials were supplied by R. Helferich at Cercona of America, Inc. Technical assistance by Dr. M. Dickey, X. Yin and assistance on SEM and XRD analyses by Y. Roh and S. Y. Lee are gratefully acknowledged. We thank D. Watson for his helpful comments on the manuscript. This work was supported by the Subsurface Contaminants Focus Area of Office of Environmental Management, U.S. Department of Energy. Travel support for L. Liang through the UK Environment Agency is gratefully acknowledged.

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Discussion

Wolfgang Wüst asked whether Liang observed a maximum capacity for sorption of uranium. He noted that he did not see a problem with leaving uranium in an iron reactor because it is very anoxic and uranium will remain reduced unless conditions become oxidizing and mobilize the uranium. Liang indicated that leaving uranium in the reactor is a different issue from leaving iron *in situ* when used for treating organic solvents because of the environmental implications. She said that the experiments that were conducted examined the worst-case scenario. In column flow-through experiments, no suspended solids were noted.

Timothy Vogel asked whether nitrate was transformed mainly to ammonia or whether it was converted to nitrogen gas as well. Liang responded that the nitrate was mainly transformed to nitrite because reduction to nitrogen takes longer. Wüst added that he did not find nitrite in his experiments. We all agree that the reactive media determine the by-products of the reaction.

Bioprocesses in Treatment Walls: Bioscreens

Huub H. M. Rijnaarts[1]

Abstract

The feasibility of intrinsic and enhanced bioremediation approaches for 16 contaminated sites in the Netherlands are discussed. At least five out of 10 chlorinated solvent sites, natural attenuation can be used as one of the tools to prevent further dispersion of the plume. At two sites stimulation of the intrinsic dechlorination processes in a bioactive zone is required, and pilot field tests are currently under way. In three sulphate-reducing/methanogenic aquifers contaminated with aromatic compounds, natural anaerobic degradation of the risk-determining benzene was demonstrated not to occur spontaneously by microcosm studies. Benzene biodegradation could be initiated by feeding small amounts of oxygen (in all samples) or nitrate (only in one sample). Investigations at two locations contaminated with hexachlorocyclohexanes (HCHs) indicated significant intrinsic bioattenuation of HCHs under very low field-redox conditions, and of the HCH-degradation products chlorophenol and benzene under sulphate/iron reducing conditions. Biostimulated zones remain required to complete the degradation of HCH and the degradation product monochlorobenzene.

INTRODUCTION

The ideas concerning best approaches for remediation of polluted soil and groundwater are rapidly changing. A few years ago many engineers and regulators considered contaminated aquifers as biologically inactive systems that could only be remediated by very drastic and expensive methods like soil vapor extraction or large scale pump-and-treat. Nowadays, one has become aware that the natural microbial population in soil and groundwater react actively when confronted with pollution, and thus offer new and better ways to protect groundwater resources at acceptable costs.

Often, natural biodegradation processes can convert large amounts of contaminants without any external stimulus. Sometimes, the natural processes can completely degrade or immobilize pollutants during their down-gradient transport. When sufficient time and space is available, an intrinsic remediation approach can in principal be completely protective for man and surrounding ecosystems. At other sites, the natural biodegradation processes need to be enhanced in order to obtain a sufficient risk reduction and groundwater protection. Such a stimulation can be performed in a bioactive zone or bioscreen. In such a zone, the autochthonous bacteria are supplied with the appropriate electron donors, acceptors or nutrients. At some sites, the microbial population is not yet fully adapted to the most optimal biodegradation process. In such a case bioaugmentation of the bioscreen may be a solution. Intrinsic remediation, when necessary combined with bioscreens, is becoming the new approach to deal with large and complex contaminated sites.

Natural and enhanced attenuation as a risk based solution for contaminated soil and aquifers is currently being investigated at various sites in the Netherlands. A number of the 16 cases investigated by TNO will be discussed below.

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RESULTS AND DISCUSSION

Chlorinated Solvents

At the Rademarkt site (Groningen, The Netherlands) contaminated with perchloroethylene (PCE) and trichloroethylene (TCE), mixed redox conditions control the intrinsic biodegradation processes. In a methanogenic/sulfate reducing zone a complete reductive dechlorination reaction via vinyl chloride to ethene and ethane occurs. However, the transformation rates of vinyl chloride observed in the field (and in the laboratory) are too slow to prevent migration of this hazardous compound to areas to be protected. The low amounts of DOC (< 10 mg/l) indicate a lack of sufficient amounts of electron donor naturally present. Laboratory experiments identified that a mixture of electron-donors is most suitable to enhance the in situ reductive dechlorination. An *in situ* pilot test with an anaerobic activated zone designed for complete reductive dechlorination is planned this fall. In another flow direction in the field, the redox condition changes from methanogenic/sulfate reducing to oxic conditions. In the reduced part, PCE and TCE are transformed to cis-1,2-dichloroethylene (DCE) and vinyl chloride (VC), which both disappear after entering the oxic zone. Probably, these compounds are removed by intrinsic oxidation. Hence, in this flow direction, a complete sequential degradation of the chlorinated compounds is achieved.

At another PCE/TCE site in Maassluis, the contaminated aquifer contains high concentrations of organic carbon (up to 700 mg/l DOC). Here, complete reductive dechlorination is observed. Most likely, this is a result of the high amounts of intrinsic electron donors and a well-adapted autochthonous microbial population.

The results of the characterization of redox conditions and intrinsic biodegradation at 10 chlorinated solvent sites will be presented. For at least five of these sites studied, intrinsic remediation is an important part in an approach to effectively control the risks. At two sites at least, *in situ* biodegradation needs to be stimulated in *in situ* activated zones to protect down stream areas.

Intrinsic chlorinated solvent remediation is further investigated by testing electron donors and measuring *in situ* hydrogen pressures in the field and in laboratory microcosms. Thus a further insight into mechanisms involved will be obtained.

At present, new technologies are being developed by TNO for application in bioscreens and remediating chlorinated solvent hot spots and chlorinated solvents in low-permeable soils and subsurface layers. Combination of electro-reclamation techniques and biological methods appear to bring new solutions in the near future.

Aromatic and Oil-Related Hydrocarbons

Aromatic compounds are often the risk-controlling compounds at oil and gas production sites, and at sites of coating and nutrition industries. At three sites in the north part of The Netherlands, deep anaerobic aquifers contaminated with benzene, toluene, ethylbenzene or xylenes (BTEX) have been investigated. Under the existing sulfate-reducing conditions, the intrinsic biodegradation of toluene and ethylbenzene could be demonstrated in the field and in microcosm studies. Benzene biodegradation could not be evidenced with the field data. Laboratory microcosm studies with five different sediment samples were performed. For each sample a series of comparable triplicate microcosms were incubated; in total about 300 microcosms were used. The results demonstrate thus far (200 days of incubation) that spontaneous intrinsic anaerobic benzene biodegradation does not occur in these sediment and groundwater samples.

Microcosm method development studies indicated that special care is required to prevent artifacts: “apparent intrinsic anaerobic” benzene biodegradation could be demonstrated to originate from low (often not measurable) amounts of oxygen introduced into the systems, when inappropriate materials and techniques were used.

Microcosms were also used to investigate possibilities to stimulate biodegradation of benzene and BTEX compounds. Especially, addition of nitrate and low amounts of oxygen to the anaerobic samples was studied. In one out of the five series of sediment-microcosms, nitrate-reducing benzene biodegradation appeared to occur after lag-times greater than 100 days. In addition, anaerobic benzene degradation could be initiated in all samples by spiking low amounts of oxygen. Further investigations are underway to elucidate mechanisms and quantify remediation process parameters. The results are used for designing pilot demonstration tests to be performed this spring/summer.

At an oil refinery site in the Rotterdam Harbor area, an aerobic reactive-trench bioscreen is tested for managing a plume of the dissolved fraction of a mineral oil contamination (80% of the compounds belong to the C6 - C12 fraction). Bench scale experiments are currently performed to establish: i) optimal grain-size and packing density for the porous media used in the trench; and ii) optimal oxygen supply rates to sufficiently initiate aliphatic hydrocarbon biodegradation and to minimize clogging with iron(III)oxides.

Chlorinated Pesticides

HCH isomers are important pollutants introduced by the production of lindane (gamma HCH). At two sites, intrinsic anaerobic biodegradation of HCH and corresponding degradation-intermediates (benzene and monochlorobenzene) is currently being investigated. At one site, natural biodegradation processes appear to completely degrade all compounds except the monochlorobenzene; possibly some biostimulation may be required at the downstream end of the plume. At the other site, interception of the HCH/chlorobenzene/benzene plume is required. A bioactivated zone as an alternative to conventional large scale pump-and-treat is currently being investigated. At present, laboratory process research aimed at developing a combination of anaerobic-microaerophilic *in situ* stimulation in such a bioactivated zone is being performed. The results indicate good prospects for further development and pilot scale demonstration.

Guidelines for Application of Natural Attenuation or Bioscreens

Dutch and Nicole-supported guidelines for assessing the feasibility of natural attenuation approaches for various contaminant situations are currently under development, making use of already existing protocols (USA) and taking Dutch/European specific conditions, knowledge and regulatory constraints into account. These guidelines are to become tiered decision tools. In the first steps, a minimum of data is required for an initial feasibility screening, thus saving costs. At higher tiers, data requirements are designed to address natural degradation under various redox-situations (including sequential redox conditions) that often occur in European sedimentary regions.

CONCLUSION

Intrinsic and enhanced *in situ* bioremediation approaches become more and more accepted as appropriate cost-effective solutions for aquifers and soils contaminated with organic chemicals. These techniques still need to be further developed and demonstrated and could also be expanded to control and remediate mixtures of organic and inorganic (heavy metal) pollutants.

Discussion

Hexachlorocyclohexanes can be degraded using zero-valent iron and without producing benzene as a by-product. Zero-valent iron may be an appropriate reactive material for these types of compounds as long as the mass-balance considers monochlorinated benzene.

Because there is no natural nitrate at the site, anaerobic benzene degradation was stimulated by introducing nitrate. Even though The Netherlands has a 50 mg/l nitrate drinking water standard, the introduction of nitrate did not pose a problem because concentrations in the stimulated system ranged from only 10-20 mg/l.

Novel Catalyses for Reactive Barriers[1]

Timothy M. Vogel[2]

The presentation that we will make today is a combination of several different presentations, not necessarily those planned for today. But the point is simply to talk about different types of material that might be able to catalyze or to react with compounds of interest in barriers and in wall systems, so we can target a number of different reactions (Figure 1), and we'll use some information that has been collected in other laboratories and with participants, including Nada Assaf-Anid at the University of Manhattan, Pedro Alvarez from the University of Iowa, and Larry Nies at Purdue University, who all have contributed in some or the other to the data that we will present today.

There are basically two different concepts for the remediation of groundwater contamination: (1) Methods based on transfer and concentration of the contaminants based on activated carbon —activated carbon even in a wall is not a reactive wall but an adsorption wall—and more innovative methods such as mobilization of contaminants with surfactants or in situ absorption barriers—but these methods all produce secondary waste streams that have to be treated separately. (2) Destructive methods—such as thermal, oxidative, biological, or catalytic dehalogenation—that are shown in the laboratory to work effectively.

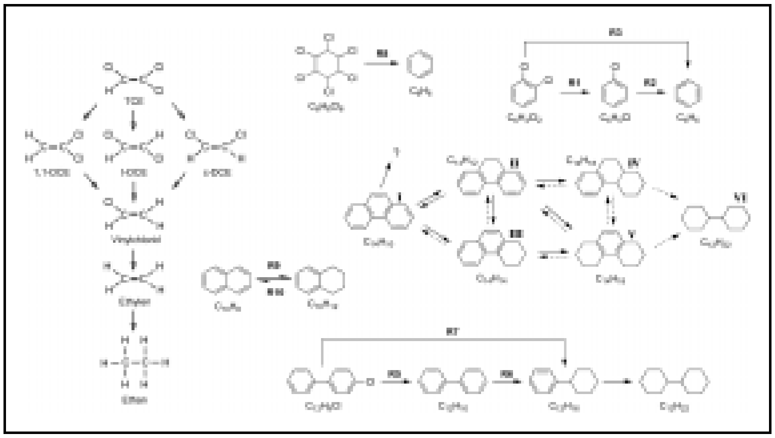

Figure 1. Reactions

What we'd like to do is to talk about these reactive systems from two points of view: what kind of reactions we would like to observe, and what reactions we would not like to observe. The example is with the chlorinated alkenes, where a lot of individuals do not like to see the presence of vinyl chloride. What we'll talk about is ways to catalyze some of these reactions and to avoid certain by-products.

Our approach is to look at the different problems that have been associated with literature reports on catalyzed reactions and to try to identify ways to answer these questions. Today one of our goals is to, in a sense, initiate some discussion, because we are going to talk about some things that have not necessarily been brought to a scientific, critical review, nor applied in full-scale processes, so any comments that you have would be gratefully received.

We looked at reaction rates (Figure 2), and the question often asked is, how we can do reactions faster. In a talk presented yesterday, there was a

Reaction rates	Activation energy, steric hinderance, diffusion limits
Compounds degraded	Electrophilicity, hydrogenation
Corrosion of material	Selective reactivity, protection, pretreatment
Metal inactivation	Chemical reactivity, redox changes — electron sources

Figure 2. Problems and Solutions

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[1] This paper was prepared from a transcript of Dr. Vogel's presentation.

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comparison between zero-valent iron and biological reactions, where the rates were much faster with the zero valent. And then just recently, we had another on the use of bio-screens, so there is a question about reaction rate that has to be considered with cost—we're not going to talk about cost—we're going to talk about what we can to increase reaction rates. So either we try to change the activation energy of the system, or in the case where there is some kind of steric hindrance—where the molecules cannot come in contact with the reactive surface—or in the same respect diffusion limits between the molecules in the bulk solution and the site of reactivity. These are ways to address the reaction rates and maybe improve them.

Other questions are related to the compounds that are degraded. Many compounds are degraded by existing systems, but are degraded at rates that are not acceptable, therefore some people say these compounds are not degraded by a particular system. For example, some people say iron cannot degrade a certain chlorinated compound, when in fact it's more the rate that is not acceptable, not whether it can degrade or not degrade. We'd like to separate the issue of the possibility of a degradation occurring from an unacceptable rate. Thus, we want to examine the kinds of mechanisms and how they affect these dechlorinations or reductions. And finally, there are issues about the lifetime of the material, and how it's affected, and how you can engineer support material and different catalyst systems, such that the lifetime is long enough for the application.

In addition, we will discuss some biological aspects and using organisms coupled with other systems like iron to deal with problems that result from the applications of catalysts.

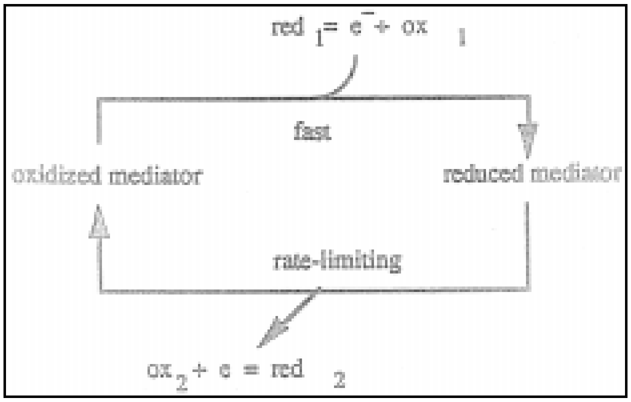

Figure 3. Simplified electron flow

The general schematic is a cyclic system (Figure 3) in which an electron comes from some source, is transferred to the molecule that is the pollutant, the pollutant is reduced by that reaction, and the source is then regenerated (or maybe not) (Assaf-Anid *et al.*). There are two ways of looking at this: One is based on thermodynamics, and thermodynamics are (for those who are not aware of these systems) the pressures pushing the system around—the force. But then, there is also the question about the kinetics, the rates. You can have a large force, but if you have a small rate, it will be slow. Take a hydraulic dam. You can have a lot of water behind a hydraulic dam, but if the hole is small, not much water will go through it, so we need to separate conceptually thermodynamic data from kinetic data. The thermodynamic possibility is necessary, but it doesn't provide you with a real process that you can apply if the kinetics are unacceptably slow.

If we look at the thermodynamics of different systems, we can see in Table 1 (taken from several literature studies) that there are measures of different redox couples that are used to determine whether the thermodynamics of a system is favorable not. This is the redox couple between the oxidized and reduced phases of these compounds. Some of the data are pretty standard, for example water—the oxygen/water couple. This provides you with some information about the potential energy—how high the water is behind the dam—but it does not tell you anything about the rate at which these reactions will go. These are just potential electron donors in systems, and those in Figure 4 are ones from biological systems based on a 1987 review (Vogel *et al.*, ES&T) concerning these types of catalysts.

Table 1. Standard potentials (E°) of biologically relevant electron donors or reductants

Reductants	E° (volts)
Vitamin B_{12}	-0.59 to -0.8
Co(I) tetraphenylporphin	-0.56

Reductants	E° (volts)
Ferrodoxin (reduced)	-0.43
H_2	-0.42
Cr(III)	-0.41
NADH + H^+	-0.32
Cytochrome P450 (unactivated)	-0.30
Glutathione (reduced)	-0.23
Cytochrome P450 (activated)	-0.17
Fe (II) deuteroporphin IX	0.00
Ubiquinone (reduced)	0.10
Cytochrome c (+2)	0.22
Fe(II)	0.77
H_2O	0.82

What is of interest is the effect that the complex has on the metal. If you talk about iron, or oxidized iron, and there is some work with iron porphyrins, the important aspect is that the term, “iron reactive barriers,” for example, is uninformative because it’s necessary to consider whether it’s zero valent iron; whether the iron is complexed in some form or the other; or what the iron is doing.

Table 2 shows redox couples between Fe^{3+} and Fe^{2+} in different complexes or the different ligands. Redox energy varies for the same iron couple, based upon the way that it’s complexed by the organic: the potential for reduction or oxidation in these systems varies with the ligand. There is also some cobalt data in the table. A metal is not in an isolated situation, but has certain complexes associated with it that may have an effect on the thermodynamics.

Table 2. Standard reduction potential of Fe^{3+} and Co^{3+} to the respective bivalent ions

Ligand	E° Fe (+3/+2), V	E° Co (+3/+2), V
1,10 phenanthroline	+1.20	
3 bipyridin	+0.95	+0.31
water	+0.77	+1.88
glycine	~+0.4	+0.15
6 NH_3	+0.37	+0.11
6 $(CN)^-$	+0.36	-0.80
cytochrome c	+0.25	
meso-tetrakis (N-methyl-pyridil) porphin	+0.17	
$EDTA^{4-}$	+0.13	+0.37
rubredoxin	-0.05	

Ligand	E° Fe (+3/+2), V	E° Co (+3/+2), V
iron protoporphyrin	-0.12	
8-hydroxyquinoline	-0.15	

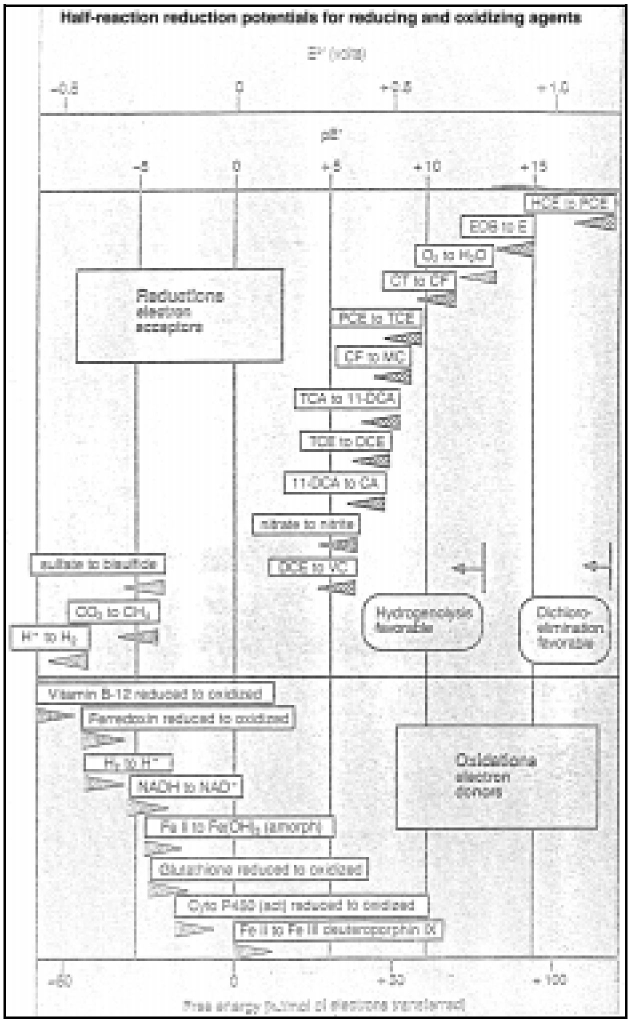

Figure 4. Thermodynamic potentials

The redox potential of your chlorinated or non-chlorinated organic that you want to reduce needs to be examined in order to determine (based upon your electron donor and your electron acceptor) whether you have a potential energy production. And again, borrowing from a review (Vogel *et al.*, 1987, ES&T), Figure 4 shows data where, by classic chemical methods, you can determine the energy that would be derived, and the thermodynamic potentials for coupling different reactions, electron donors, and acceptors.

For example, one reductive dechlorination is from tetrachloroethylene (PCE) to trichloroethylene (TCE). That is one-half of the couple, and if you coupled it then with vitamin B_{12}, for example, which is a cobalt-containing porphyrin, you would have a favorable reaction. The distance would be the amount of energy, the potential energy from that reaction is about one volt. In other words, it is a thermodynamically favorable reaction to use vitamin B_{12} to dechlorinate PCE to TCE. This is just a simple figure that has two couples, an electronic donor and an acceptor. These types of tables and calculations are useful because they allow you to determine what the thermodynamic potentials are in your system, assuming you calculate this accurately for the concentrations in your actual system and not for standard-state calculations that is typical in the literature. Then you can determine in your system whether you have a gap here, and whether you have the potential to cause the reaction that you want. Note that as you get less chlorine on some of these chlorinated aliphatics, the redox potential decreases.

In summary, this concept of coupling these different kinds of complexes with reductive dechlorination or with reductions of molecules has been studied and discussed extensively in the literature. This is all in published review articles, but it's enough to give you an idea. Table 3 shows some of the chlorinated compounds that have been observed to degrade and the complexes that have been reported to be responsible. The diversity of potential catalysts for chlorinated compounds is relatively high, and from a thermodynamic point of view, there is considerable interest.

Table 3. Reduction of halogenated aliphatic compounds by transition metal complexes

Compound	Products	Reductant
Methanes		
Chloromethane	Alkylated co-complex	Co(I) chelates

Compound	**Products**	**Reductant**
Dichloromethane	Methane Cl-alkylated B_{12}	Cr(II) SO_4 B_{12}-Co(III) (methylcobalamine)
Trichloromethane	Methane Dichloromethane Dichloromethane Cl-alkylated B_{12}	Cr(II)SO_4 Fe(II)P Fe(II)P B_{12}-Co(III)
Tetrachloromethane	Methane Chloroform Cl-alkylated B_{12}	Cr(II)SO_4 Fe(II)P B_{12}-Co(III)
Bromomethane	Methane Alkylated co-complex	Cr(II)SO_4 Co(I)-complex
Dibromomethane	Methane, ethene	Fe(II)P
Tribromomethane	Br_2-alkylated B_{12}	B_{12}-Co(III)
Ethanes		
Chloroethane	Alkylated co-complex	Co(I)-complex
1,1-Dichloroethane	Ethane, ethanol	Cr(II)SO_4
1,1,1-Trichloroethane	Ethane, ethanol, ethene, chloroethane 1,1-Dichloroethane 1,1-Dichloroethane	Cr(II)SO_4 Fe(II) Fe(II)P
Hexachloroethane	Tetrachloroethene Tetrachloroethene	Fe(II)P Cr(II)SO_4
Bromoethane	Ethane	Ni(I)
1,1-Dibromoethane	Ethane, ethanol	Cr(II)SO_4
1,2-Dibromoethane	Ethene Ethene	Fe(II) Fe(II)P
Propanes		
1-Chloropropane	Alkylated co-complex	Co(I)-complex
1,1-Dichloropropane	Propane, propanol, propene	Cr(II)SO_4
1-Bromopropane	Alkylated co-complex	Co(I)-complex
1,2-Dibromo-3-chloropropane	Propene, allyl chloride	Cr(II)SO_4

Note: The homolytic cleavage of cobalt-carbon bonds requires 15-30 kcal/mol and can occur at relatively low temperatures.

Figure 5 shows an example where a carbon tetrachloride (CT) is dechlorinated by cobalt in solution to chloroform (CF) over a period of about eight hours. When that cobalt was placed into a porphyrin (Figure 6), you see that the reaction rate changes drastically and you have dechlorination within about an hour (Figure 7 is an example of a porphyrin).

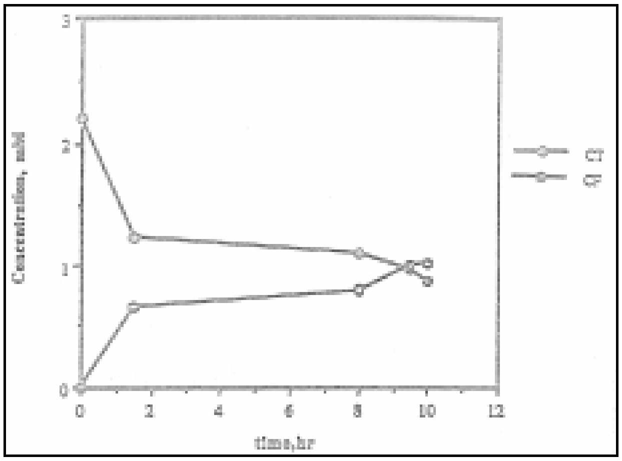

Figure 5. Carbon tetrachloride (CT) dechlorinated to Carbon fluoride (CF).

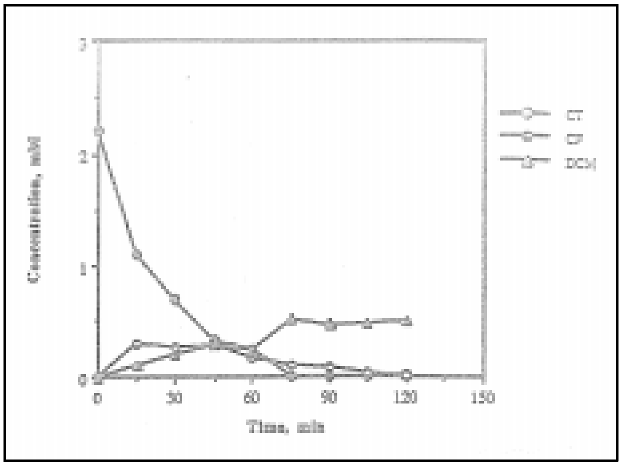

Figure 6. Carbon tetrachloride dechlorinated to carbon fluoride in the presence of vitamin B_{12}

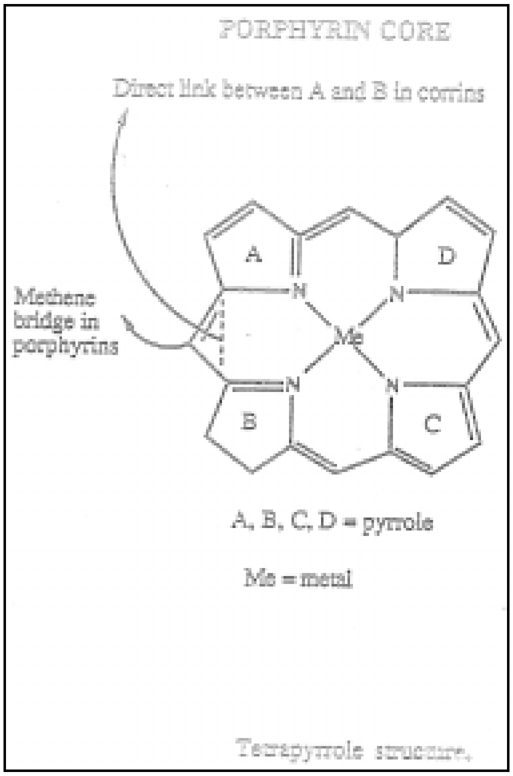

Figure 7. Porphyrin Core

The same kind of process is observed with a large range of metals, thus, the practical question becomes where can the metals be placed: on what kind of surface, or in what kind of complex in which good thermodynamics and a high kinetic rate are possible. In other words, what we want is a lot of water behind the dam and a large hole in the dam, so that the reaction flows.

Another example is with zinc (Figure 8): by itself; with carbon tetrachloride again; and zinc with vitamin B_{12}, which goes much faster. So using that concept of thermodynamics and that aspect of kinetics, you can engineer systems where your catalyst is potentially active from an energetic point of view, and where the system has physical characteristics and chemical characteristics such that the kinetics will be quite rapid.

Another proposed use of iron is with a microorganism for the conversion of nitrates to N_2 to avoid ammonia (Alvarez *et al.*). Figure 8 is a schematic of the process: an organism that would use hydrogen gas and would be responsible for this reaction. The thought was that it would provide some synergy between the iron and the microorganism. This synergy would allow for some benefits in terms of the hydrogen production, in terms of possible effects on the iron, and also possibly reducing the competition of nitrate with other compounds like chlorinated solvents on the iron (Figure 9). In addition, it might cause a higher reactivity for certain compounds that don't react very rapidly with iron, like dichloromethane. That's the basis for the synergy between the two. Figure 10 shows a mass balance in different tests: iron powder, steel wool, iron with this organism, *Pseudomonas*, *Pseudomonas* and steel wool, and with hydrogen. The "Unrecovered NO_3^-" in the figure is the lack of the mass balance. With iron powder alone, mostly ammonia was produced. With steel wool alone, there

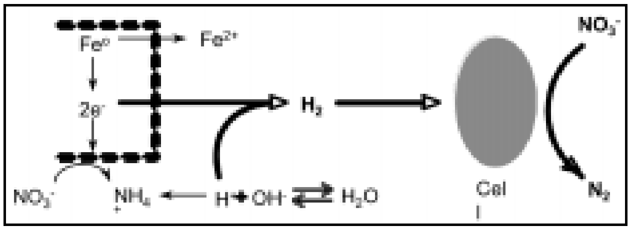

Figure 8. Nitrate removal can be enhanced by combining Fe° with hydrogeonotrphic denitrifiers. Bacteria will use cathodic H_2 as electron donor to produce harmless N_2 instead of objectionable NH_4^+.

was considerable un-reacted nitrate and ammonia. And in the presence of the microorganism, considerable amounts of the N_2O were measured in these mass balances.

- e° corrosion rapidly induces anoxic conditions.
- Bacteria may remove passivating H_2 layer from Fe° surface, increasing Fe° reactivity. Use of H_2 increases e^- flow from Fe° (cathodic depolarization).
- Removal of inhibitory products by Fe° enhances bacterial participation in cleanup process *(e.g.*, NO_2^- reduction by Fe°; metals precipitation due to high pH caused by Fe° corrosion).
- Bacteria could remove pollutants that Fe° cannot (*e.g.*, dichloromethane).

Figure 9. Basis of Synergism for Fe° + Bacteria

Figure 10. Mass balances

Discussion

In response to a question from Resat Apak, Vogel indicated that some metal chelates used as catalysts are inside membranes. They are trapped in a system that allows the transfer of the chlorinated compound, but keeps the solubilized porphyrins in membrane systems. Vogel indicated that there are several techniques documented in the literature to re-oxidize the cobalt(II)EDTA to cobalt(III)EDTA, including the use of electron donors, solid catalysts, and chemical reductants.

Wolfgang Wüst asked whether any column experiments were done before conducting the field work, because his experience has shown that if catalysts are used, iron hydroxides or other precipitates inhibit the diffusion (and thus reactivity) of EDTA. Schüth said that he was currently running laboratory experiments in which several thousand pore volumes have been exchanged with groundwater. He has not observed much precipitation in these experiments because the pH was lowered, not raised. However, microbial growth did pose a problem for mass transfer due to diffusion.

Liyuan Liang asked whether and how much hydrogen was introduced into the system. Vogel indicated that hydrogen had been introduced in the laboratory, and the amount was calculated by stoichiometry. In the column and laboratory experiments, hydrogen gas was bubbled through the water to create hydrogen-saturated water. However, Vogel cautioned that this approach may not work in the field.

Paul Bardos observed that many of the projects that were discussed in the treatment wall session involved highly engineered solutions in terms of emplacing walls and improving the reactive matrix. He asked if the advantages of these improvements were actually worth the increased costs, given that a trench with iron filings treats groundwater reasonably well. Vogel responded that iron filings cannot treat all contaminants, nor is there any other existing PRB suited for all contaminants and subsurface environments. Co-contaminants can cause problems, and some contaminants are less reactive than others. The contaminants that cannot be treated by iron walls must be determined, and inexpensive reactive materials must be found to treat them.

Noting that the cost of iron filings for an iron wall accounts for a significant proportion of the construction costs, Bob Siegrist asked how the use of a more expensive catalyzed metal such as palladium could be cost-effective when compared to pump-and-treat methods. Vogel responded that although palladium costs more than iron, the reactivity of palladium is also greater, so it could still be more cost effective because you do not need as much material. Wüst noted that his tests have indicated that the cost of using 0.1 percent palladium (the optimum amount) was approximately the same as iron, but the reactivity of the palladium was much greater. He expressed concern, however, that the palladium could be mobilized under certain conditions and contaminate the groundwater.

Harry Whittaker noted that there has been a lot of discussion thus far on reductive dehalogenation barriers and asked whether oxidative dehalogenation barriers are being developed. Vogel indicated that techniques for oxidative dehalogenation barriers have been patented recently, including systems involving Fenton's agent.

Funnel-and-Gate Systems for *In Situ* Treatment of Contaminated Groundwater at Former Manufactured Gas Plant Sites

Hermann Schad[1] and Peter Grathwohl[2]

Introduction

Groundwater contamination by polycyclic and monocyclic aromatic hydrocarbons (PAH and BTEX) is typical for many former manufactured gas plant sites. Most of the PAHs are very persistent in the subsurface environment—they are still present in high concentrations many decades after the contamination occurred, and they cannot be removed from the subsurface within a reasonable time period by pump-and-treat. This persistence above all is caused by slow dissolution kinetics of the compounds from non-aqueous phase liquids, slow diffusion of the contaminants from low permeability zones (that have accumulated the pollutants over decades) or resistant adsorption of the contaminants by the aquifer material.

Fast remediation of such contaminations is only possible by excavating the contaminated soil. This, however, can only be applied at shallow sites and is still expensive because of the high disposal or treatment costs of the contaminated material. Also the location and extent of the subsurface contamination has to be known in detail, which is not feasible at large and abandoned industrial sites. Thus, new alternative approaches for *in situ* groundwater remediation have to be developed. Since the goal of remediation in general is the protection of groundwater resources downgradient from a contaminated area, *in situ* treatment may be focused on the plume rather than on the source. This can be achieved using the concept of *in situ* passive treatment systems, which in general are built perpendicular to the flow direction (*e.g.*, Teutsch *et al.*, 1996). The technical implementation is either in the form of a continuous permeable wall or as a funnel-and-gate system. In both cases no active pumping is required to move the groundwater through the treatment zone. Within the reactive zone the pollutants are either degraded, sorbed or precipitated through biotic or abiotic processes.

In this paper, we present an example for a funnel-and-gate system, which is currently being planned for the long-term remediation of the former manufactured gas plant site of the city of Karlsruhe in southern Germany.

Site Characterization

The site is located within the municipal area of the city of Karlsruhe and covers approximately 100,000 m^2. Site investigation programs were completed in 1996 (Trischler and Partner, 1996) with the recommendation for funnel-and-gate as the most favorable remediation technique for that site. The latter was based on a feasibility study (IMES, 1996), in which the general and site specific advantages of passive *in situ* treatment were discussed and evaluated technically and economically.

The geological and hydrogeological situation at the site may be classified as typical for the upper Rhine valley. The aquifer has a mean thickness of about 12 m and consists of mostly sandy gravel, which is

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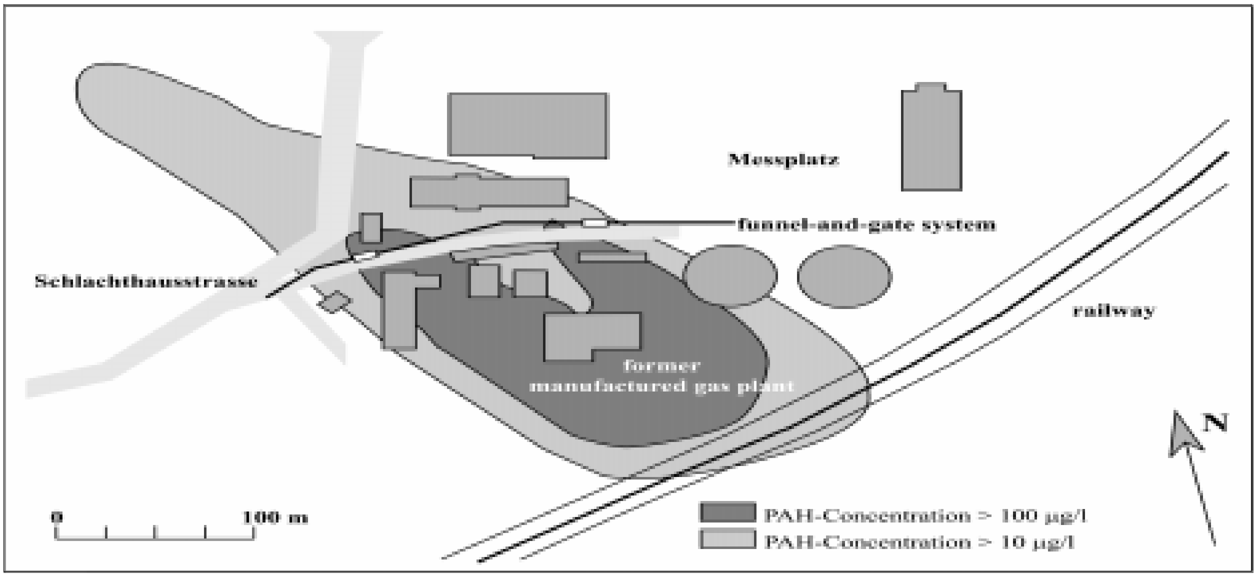

Figure 1. Site map showing the PAH plume and the location of the funnel-and-gate system

underlain by a clay layer at a depth of 15 m below surface. Groundwater drainage is dominated by the Rhine river northwest of the site. The mean groundwater flow direction therefore is from southeast to northwest (Figure 1). The contamination of the site is dominated by PAHs with acenaphthene being the highest concentrated compound of the plume extending about 400 m down gradient from the site. Several infiltration hot spots of non-aqueous phase (NAPLs) liquids were located within the saturated zone at the site. PAH concentrations of the soil at many places exceed 10 g/kg. Altogether approximately 55,000 m^3 or 100,000 tons of soil (within the saturated zone) are highly contaminated.

The hydraulic conductivity of the aquifer was estimated to 1.4 x 10^{-3}m/s and the hydraulic gradient is approximately 0.1%. The groundwater flow rate from the contaminated site under natural conditions is about 2.7 l/s.

Based on the environmental regulations to be applied, the groundwater contamination at the site has to be remediated. For several remediation techniques the investment and running costs were estimated prior to the final evaluation of the site investigation results (Table 1).

Table 1. Summary of estimated costs in DM for 50 years operation for different remediation techniques (Trischler and Partner, 1996)

Technique	Investment Costs	Running Costs	Unforeseeable Costs	Total Costs
Thermal Treatment	34,900,000	200,000	3,500,000	38,600,000
Containment	11,600,000	4,000,060	3,100,000	18,700,000
Pump-and-Treat	5,600,000	8,300,000	1,400,000	15,300,000
In Situ Immobilization	15,600,000	600,000	3,200,000	9,400,000
Funnel-and-Gate	7,500,000	4,100,000	1,700,000	13,300,000

With a feasibility study (IMES, 1996) it was shown, that a funnel-and-gate can be installed at the site. The main components of such a system will be a slurry wall of approximately 240 m in length and two gate buildings with a total volume of about 400 m^3. The principal questions with regard to the system design are related to the decontamination process within the gates and to the hydraulics of the entire system.

Decontamination within the gates will be based on adsorption of the PAHs on activated carbon. In order to determine the design parameters for the gates the processes relevant for operating the gates have to be identified and parameterized. In order to answer the questions related to the hydraulic behavior of the funnel-and-gate a numerical model will be necessary. Based on these experimental and numerical investigations the technical construction details have to be designed.

In the following sections the key questions related to sorption, hydraulic behavior and technical construction will be discussed based on the results of the feasibility study.

Sorption/Retardation

The adsorption of hydrophobic organic contaminants from the aqueous phase generally increases with decreasing solubility of the compound (or increasing octanol/water partition coefficient, K_{ow}) and increasing organic carbon content of the aquifer solids. Natural materials with high organic carbon content such as coals or bituminous shales cause significant retardation of organic contaminants from groundwater. Such materials with high sorption capacities may be used for passive removal of strongly hydrophobic contaminants in groundwater (such as PAHs), which are the key problem at many former manufactured gas plant sites). Much more efficient is adsorption onto activated carbon, which is already a well-established technology for *ex situ* treatment of drinking water, polluted groundwater or waste water. For successful use in a permeable wall or in a funnel-and-gate system permeability and sorptive properties of the adsorptive wall material (adsorbent) must be optimized. Both the permeability and the sorption rates depend on the grain size of the adsorbent, the permeability increasing with increasing grain size, and the sorption rates decreasing with increasing grain size squared.

In general, an economically efficient *in situ* groundwater treatment system that relies on adsorption of the contaminants must fulfill the following requirements:

1. Long regeneration cycles (3-10 years). Thus, high sorption capacities or adsorption combined with biological or abiotic degradation of less sorbing compounds are required.

2. Relatively high permeability in comparison to that of the aquifer in order to prevent steep hydraulic gradients.

3. Fast sorption kinetics in order to achieve high retardation factors even at high groundwater flow velocities (short contact times in funnel-and-gate applications).

4. No decrease in permeability or “chemo-biofouling” of the adsorbent due to competitive adsorption of dissolved organic matter or the growth of a biofilm that may plug adsorbent pores (although biodegradation of contaminants would be highly desirable for a sorptive plus reactive wall).

The retardation of contaminants, such as in a sorptive permeable wall, can be calculated based on the sorption coefficient, K_d:

$$R_d = 1 + K_d \cdot \frac{\rho}{n}$$

where ρ denotes the bulk density and n the porosity of the filter (in packed beds both values lie within a narrow range). R_d may be interpreted as the number of pore volumes that can be displaced before break-through of the contaminant occurs. K_d denotes the ratio between the sorbed and aqueous concentrations of the contaminant. If sorption is nonlinear (which is often the case for strongly hydrophobic contaminants and strong adsorbents such as granular activated carbon, GAC), K_d can be calculated in a first approximation from the commonly-used Freundlich type adsorption isotherm:

$$K_d = \frac{C_s}{C_w} = K_{Fr}\, C_w^{1/n-1}$$

where C_s, C_w, and K_{Fr} denote the equilibrium solid and aqueous concentrations of the solute and the Freundlich sorption coefficient, respectively. The Freundlich exponent 1/n is usually smaller than 1, resulting in decreasing K_d values with increasing concentration of the contaminant.

Activated Carbon Adsorption

Adsorption capacities for organic compounds using activated carbons are much higher than in naturally occurring organic sorbents. Figure 2 shows literature data on adsorption of a variety of organic compounds onto activated carbon (F300). Distribution coefficients (K_d) were calculated based on the Freundlich sorption isotherms (K_{Fr}, $1/n$) for an aqueous concentration of 10% of the pure compound's water solubility. For compounds with high water solubilities (S > 1 mg/l), an almost linear inverse relationship between K_d and S is observed (solid line in Figure 2). Since bulk density and porosity in a packed bed of granular activated carbon are both close to 0.5, K_d in a GAC passive treatment wall is approximately equal to the retardation factor R_d.

Sorption Kinetics and Permeability

The data shown in Figure 2 are valid for equilibrium sorption, which is not always applicable since the mean residence times (contact times) in a permeable sorptive wall may be too short for complete equilibration. Sorptive uptake of solutes by a porous adsorbent particle is diffusion limited. This results in K_d values that increase with the square root of time for short-term sorptive uptake (less than 50% of sorption equilibrium reached). Fast equilibration would be achieved for small particles with high surface to volume ratios. Small particles, however, result in low permeabilities. In a funnel-and-gate system the permeability of the gate has to be as least as high as in the aquifer. In a first approximation the permeability (K) increases with the grain radius of the adsorbent particle squared and the intergranular porosity. Since the porosity in loose packed beds will generally lie within a relatively narrow range, between 0.4 and 0.6, the main factor influencing the permeability is the size of the adsorbent particles. For typical groundwater flow velocities and a thickness of the sorptive wall of about 1-2 m, the mean residence time of contaminated groundwater will range from less than a day to a few days. If the mean residence time is too short for equilibration, the K_d values will be much smaller than expected for equilibrium conditions, which would in turn result in an early breakthrough of the contaminant through the sorptive wall.

Column Tests with Contaminated Groundwater From the Site

A natural bituminous shale sample and three different GACs were used in laboratory column tests in order to investigate the transport of PAHs within the gates. Breakthrough of PAHs in the bituminous shale column was already observed after approximately 10 displaced pore volumes, indicating that the equilibrium sorption capacity was not reached (by far). In the GAO columns, no breakthrough was observed, and PAHs were concentrated in the first few centimeters of the packed bed (Table 2), as determined by methanol extraction of thin GAO layers after the column test.

The results obtained for the GAO indicate that sorption at these relatively slow flow velocities is reasonably close to equilibrium (typical flow velocities in drinking water treatment are much higher) and the retardation factors to be expected are higher than 3,000.

Table 2. Column tests for removal of PAHs (16 EPA PAHs) from contaminated groundwater (PAH concentration approximately 2500 µg/l, predominantly naphthalene and acenaphthene)

Adsorbent (GAC)	**F100**	**D15/1**	**C40/4 (pellets)**	**Bit. Shale**
Origin	Chemviron	Lurgi	Carbo Tech	Lias & (Aalen)
Grain Size [mm]	0.5-3	1.25	4.2	2-4
BET-Surface Area m^2/g	770	1,102	1,281	16
Column Length [cm]	14	12	13	21
Porosity (intergranular)	0.52	0.68	0.61	0.48
Run Time (days)	23	23	23	112
Pore Volumes Displaced	885	731	814	1,097
Flow Velocity [m/day]	5.3	4.0	4.6	2.1
Mean Residence Time [h]	0.6	0.76	0.68	2.6
PAH Penetration Depth	<1.5 cm	<1.5 cm	<4 cm	breakthrough

Batch Experiments on Sorption of PAHs onto GAC

Batch experiments were performed in order determine the equilibrium adsorption isotherms and the sorption kinetics of selected PAHs (acenaphthene, fluorene, phenanthrene, fluoranthene, and benz(a)anthracene) for three different GACs and a O_{18}-modified silica gel used as reference sorbent (Table 3).

Table 3. Properties of GACs Used in Batch Experiments.

Property/GAC	**F100**	**C40/4**	**TE143**	**C_{18}**
Origin	Bituminous Coal	Bituminous Coal	Coconut	Silica Gel
Manufacturer	Chemviron	Carbo Tech	Pica	IST
BET Surface Area [m^2/g]	770	1280	993	$F_{oc} = 0.19$
Total Pore Volume [cm^3/g]	0.422	0.630	0.483	-
Average Pore Radius [Å]	10.95	9.87	9.71	-
Radius [mm]	0.8-1.0	1.0-2.0	0.4-0.5	20-35µm

K_d and K_{Fr}, determined in the equilibrium sorption experiments (Table 4) agree reasonably well with literature data shown in Figure 2. The K_d values measured in the sorption kinetic experiments were much lower than expected from the equilibrium values (Table 4). The sorption kinetic data agreed very well with the numerical solution of Fick's second law for intraparticle diffusion (Figure 3). The apparent diffusion coefficients were between 1 x 10^{-12} and 1 x $l0^{-13}$ $m^2 s^{-1}$.

Table 4. Freundlich coefficients (K_{Fr}, 1/n), equilibrium K_d and K_d values measured in the batch kinetic experiments after 24 h, 3 days and 7 days (K_d *).

	F 100			C 40/4			TE 143			C_{18} Silica		
	Ace	Fln	Phe	Ace	Fln	Phe	Ace	Fln	Phe	Ace	Fln	Phe
Log K_{Fr}	6.2	6.1	5.9	6.0	5.9	5.7	5.2	5.6	5.7	4.8	5.0	5.2
-1/n	0.59	0.81	0.56	0.87	0.99	0.70	0.92	0.67	0.56	0.81	0.82	0.79
Log Kd at 10% S	5.2	5.6	5.0	5.6	5.8	5.1	5.0	4.9	4.7	4.3	4.6	4.8
Log Kd* 24 h	3.4	3.7	4.1	3.2	3.2	3.3	3.3	3.3	3.4	4.6	4.9	5.1
Log Kd* 3 days	4.0	4.3	4.4	3.6	3.7	3.7	4.5	4.4	4.2	4.6	4.9	5.1

	F 100			C 40/4			TE 143			C_{18} Silica		
Log Kd* 7 day5	4.0	4.5	4.7	3.9	3.9	3.9	4.8	4.8	4.6	4.7	5.0	5.3

Hydraulic Aspects of Funnel-and-Gate Systems

There is a basic difference between the hydraulic design of a funnel-and-gate system and a continuous permeable wall. For the continuous permeable wall, the only essential hydraulic design criterion is the hydraulic conductivity of the wall material, which should be more permeable than the aquifer material. In the case of a funnel-and-gate system, the hydraulic design depends on a number of factors, including the number, position, and size of the gates, the length and angle of the funnel, and the hydraulic conductivity of the reactive material within the gates. Starr and Cherry (1994) provided the basic functional relationships for one-gate systems. From a practical perspective, the major design criterion is the width of the capture zone (treatment zone) achieved for a given length of the funnel and the gate(s). The width of the capture zone can be approximated from the total flow rate through the gate(s). In Table 5, the numerical results obtained from the feasibility study (IMES, 1996) are summarized. It is obvious that the number of gates (equally distributed over the length of the funnel) is of much greater influence for the width of the capture zone than the total length of the gates.

Table 5. Dependence of the total flow rate through the gate(s) on the number of gates and the total length of the gate(s)

Number of gates	Total length of gates [m]	Total flow rate [1/s]
1	12	1.04
1	36	1.55
2	12	1.58
2	24	2.01
3	18	2.09
3	24	2.22

Another aspect that needs to be considered in the design of funnel-and-gate systems is the heterogeneity of the aquifer. The location of the capture zone can be affected by low and high permeability zones in the subsurface. Figure 4 shows results from the 3-dimensional stochastic groundwater flow model. The three examples (one homogeneous case and two stochastic realizations) show that the size of the capture zone does not change even though the parameters vary considerably. However, the position of the capture zone (little elongated box) is different for every case. The stochastic model study showed that the length of the funnel had to be increased by a 20% safety factor in order to compensate the uncertainty related to the heterogeneity of the aquifer.

It is also interesting to note that a tenfold increase of the conductivity of the gate only resulted in a less than 10% increase of the flow rate through the gates for a given funnel-and-gate configuration. This finding was found to be true for gate permeabilities exceeding the aquifer permeability.

Technical Construction of the Funnel-and-Gate System at the Site

For constructing the funnel several different possibilities, *e.g.*, slurry wall or sheet pile wall etc. are readily available. These techniques are state-of-art and have been applied in the construction business many times. The innovative part of the funnel-and-gate system is the construction of the gate(s) and the connection between the funnel and the gate(s). Since it is anticipated that the sorptive activated carbon fill of the gate(s) has to be exchanged from time to time, the gate(s) will be reinforced concrete buildings, which can be

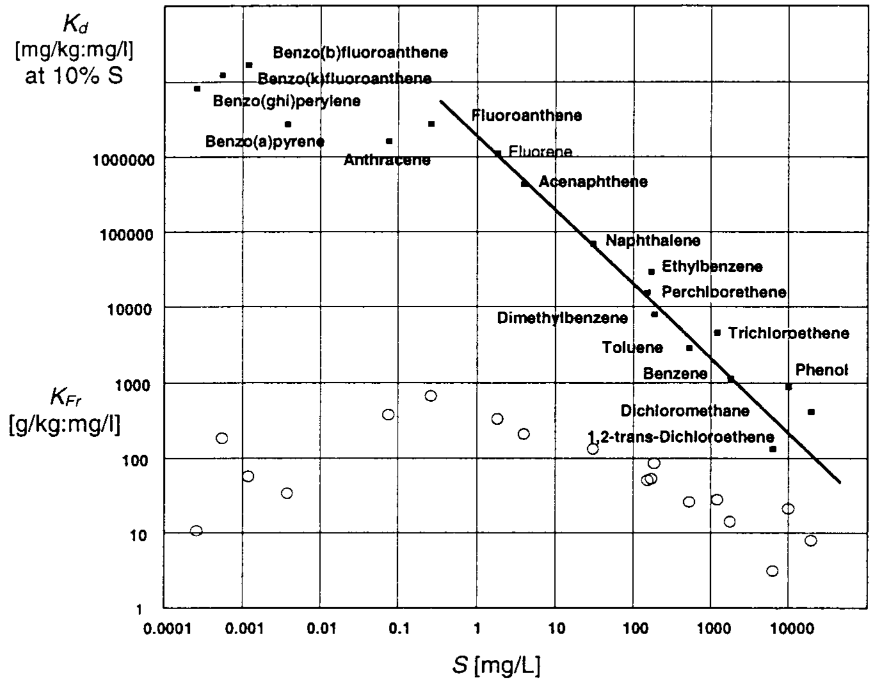

Fig. 2: Freundlich sorption coefficients K_{Fr} (open symbols) as reported in the literature (American Water Works Association, 1990; Sontheimer et al., 1985) for GAC (F300) and distribution coefficients (K_d : filled, labeled squares) were calculated for a concentration of 10% of the water solubility S [mg/L] of the respective compounds.

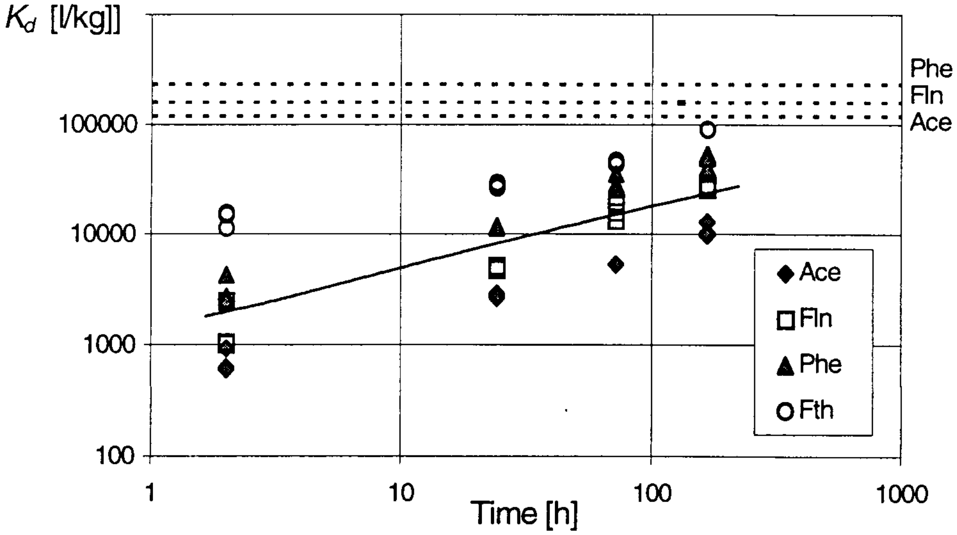

Fig. 3: Sorption kinetics of Acenaphthene (Ace), Fluorene (Fln), Phenanthrene (Phe) and Fluoranthene (Fth) onto GAC (F100). The solid line was calculated using a numerical model (Crank-Nicolson implicit/explicit scheme) for sorptive uptake of Fln in a bath of limited volume. Dashed, horizontal lines denote the equilibrium K_d (Ace, Fln, Phe).

emptied. In Figure 5 the conceptual design of the gate construction is illustrated In a horizontal (A) and two vertical sections (B) and (C). The pit will be excavated after installing a stiffened sheet pile caisson. The concrete building will be constructed either in place of will be prefabricated. Simultaneous to the construction of the gate(s), a gravel pack will be filled between the gate building and the sheet piles at the inflow and outflow sides of the gate(s). After completion of the gate, construction the sheet piles will be pulled out, allowing the contaminated groundwater to flow through.

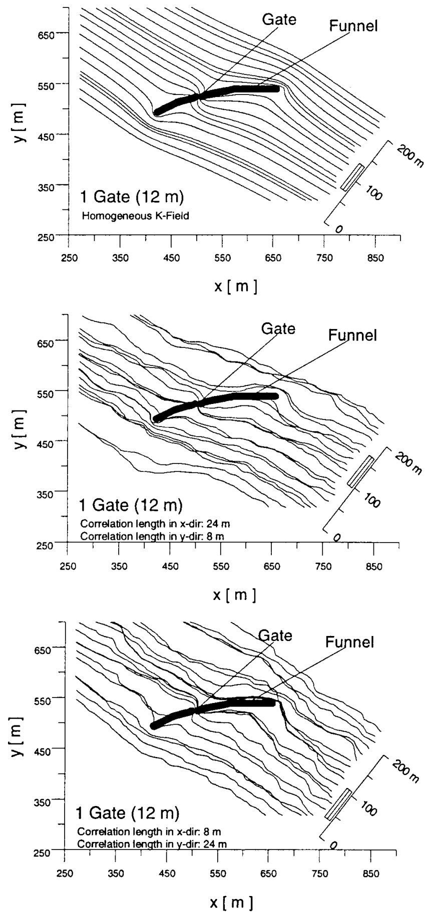

Fig. 4: Stochastic modeling of streamlines for a funnel and gate system planned at an former manufactured gas plant site in Southern Germany

With the upper two figures ("1" and "2") in Figure 6, two conceptually different possibilities of how contaminated water may flow through the gates are demonstrated: (1) horizontal flow and (2) vertical flow. Vertical flow would be favorable from sorption considerations. It can be expected that the PAH-concentrations will be different at different depths. Mixing due to vertical flow within the gravel pack will level out the concentration profile before the groundwater enters the gate. Horizontal flow would be favorable from hydraulic considerations. Owing to the aquifer geometry, the cross-sectional flow area is much larger in the case of horizontal flow, leading to a smaller hydraulic pressure build-up upstream of the gates.

The lower two figures in Figure 6 give some details about how the funnel (*e.g.*, slurry wall) may be connected to the gates.

Conclusions and Further Plans

Granular activated carbon appears to be applicable for *in situ* removal of PAHs occurring in the groundwater at the former manufactured gas plant site in Karlsruhe. For the preliminary design of a funnel-and-gate system at the site with two gates and about 400 m^3 total gate volume the sorption capacity of the activated carbon fill can be expected in the order of 8 to 12 years.

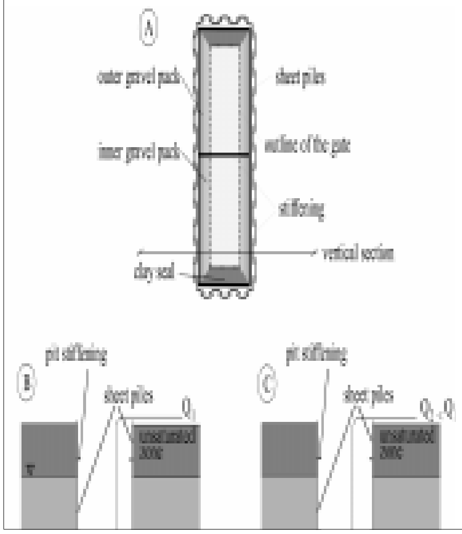

Figure 5. Conceptual horizontal and vertical sections of the gate construction pit

Numerical flow modeling showed that the PAH-plume can be captured by a two-gate system with a total gate length of 24 m. From the modeling results it also obvious that multi-gate systems are advantageous over single or two-gate systems.

Heterogeneity structures with regard to hydraulic conductivity may have a major influence on the position of the capture zone relative to the location of the funnel-and-gate system.

In order to work out the final design of the funnel-and-gate system, additional experimental and numerical work will be necessary, including the performance of sorption column experiments at the site simulating the conditions of *in situ* activated carbon filtration, laboratory experiments to optimize the choice of the type of activated carbon to be used with regard to sorptive and hydraulic considerations, numerical stochastic modeling in order to determine the length and location of the funnel and also to determine the number and geometry of the gates.

These investigations will be carried out during the first half of 1998 and will provide the knowledge required for the design and engineering of the funnel-and-gate system. The construction of the funnel-and-gate system is expected to be carried out in 1999.

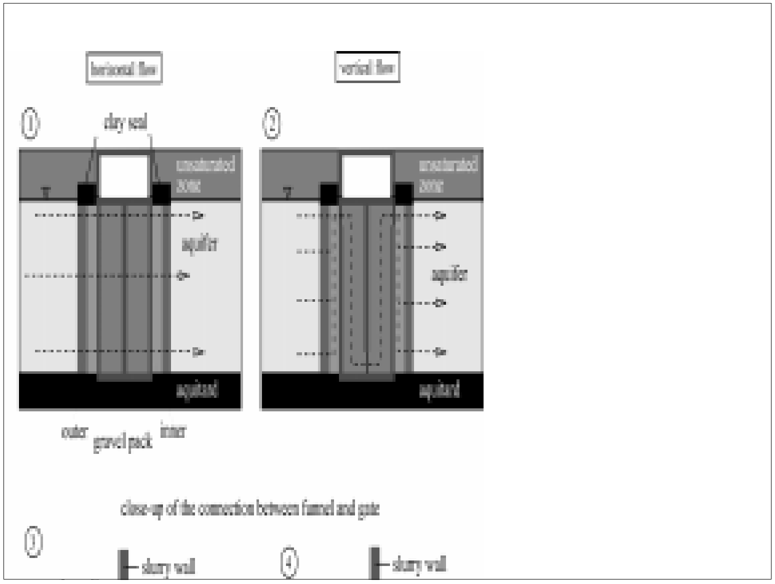

Figure 6. Design possibilities for the gates (1, 2) and for the connection between funnel and gates (3,4)

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Discussion

Noting that carbon is an excellent medium for bacterial growth, Shad was asked how to prevent bacterial slime from clogging the system. He said that the system is anaerobic and must be maintained under anaerobic conditions. He has performed laboratory column tests at 20-25°C and did not observe bacterial growth. He also plans to perform sorption column tests under *in situ* conditions, using the same water, to further examine the potential for bioclogging.

Wolfgang Wüst asked about the sum of the dissolved organic carbon in the system. Schad was not sure, but said that there is highly organic material (including humic acids) present. Dissolved organic carbon will be the main parameter examined during upcoming column tests. Schad will be assessing co-sorption of contaminants and variations in sorption rates.

Reactive Treatment Zones: Concepts and a Case History

Stephan A. Jefferis[1] and Graham H. Norris[2]

ABSTRACT

The concept of the reactive treatment zone whereby pollutants are attenuated as they move along a pathway in the ground has enabled a re-thinking of many of the concepts of containment. In particular it allows the control of the flux from a contaminated area by controlling the contaminant concentration in the pathway(s) as well as or instead of using a low permeability barrier. This paper outlines the basic concepts of the reactive treatment zone and the use of permeable and low permeability reactive systems. It then gives a case history of the design, installation and operation of a reactive treatment zone using an *in situ* reaction chamber.

1. INTRODUCTION

The use of containment systems is now widely accepted for municipal and toxic waste landfill sites but up to now it has been more reluctantly accepted for the remediation of contaminated land. This reluctance perhaps stems from a desire to use process orientated treatment technologies as a permanent means of dealing with contaminated land problems. However, as the effectiveness of some *in situ* treatment technologies remains in doubt and the costs of treatment in general remain relatively high, interest in containment continues to develop and particularly in combining treatment with containment and the prospects for using intrinsic processes as low cost longer term remedial options (Bardos and van Veen 1996).

1.1 Terminology

In the UK, it is common practice to refer to barrier systems that impede groundwater flow as passive containment systems, and the term “active containment” has been coined for those that reduce pollutant flux by treating the contaminant(s) in a flow path between a source and a receptor. However, these terms are not universally accepted. For example, in Canada and the USA, “active containment” is often used to describe processes where there is an energy input, such as pump-and-treat systems, and the term “permeable barrier” is used for the UK’s “active containment.” In this paper the more general term “reactive treatment zone” will be used for in-ground systems involving reactions that tend to reduce contaminant concentrations in a pathway, and “passive containment” for barriers designed to impede flow.

2. REACTIVE TREATMENT ZONES

The essential feature of a reactive treatment zone is that contaminants can be controlled in a pathway without necessarily preventing the flow of the carrier fluid (almost always water but gases are also amenable to such treatment).

Reactive treatment zones can be distinguished from passive (low permeability) containments by considering the controls on the flux, which for any contaminant may be written as:

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Flux = Concentration x Permeability x Hydraulic gradient x Flow area

For a traditional passive barrier, the flux is controlled by ensuring that the permeability of the system is low and hence that the flow through the barrier is low. However, as a result the flow area will be high as the barrier must surround the source and the concentration(s) of the contaminant species and the hydraulic gradient (unless modified by pumping) also may be high.

An alternative way to control the flux is to reduce the concentration of the contaminant(s). If a sufficient reduction in concentration can be achieved then permeability ceases to be the controlling parameter and it may be high or low as appropriate to the application. With a high permeability system the hydraulic gradient will be low as the carrier fluid is allowed to escape and the area for flow may be less than that of a containment as it may be deliberately focused with an engineered system or naturally higher permeability regions may be exploited—if they can be sufficiently well defined. This may simplify monitoring, and where necessary, *in situ* control. If space is available the input concentration may be varied by selecting the position of the reactive zone in relation to the contaminant source or in-ground intrinsic remediation may be exploited upstream or downstream of the reactive treatment zone. It should be noted that reactive treatment zones often will be used as pathway control mechanisms to prevent contaminants from a source reaching a receptor rather than as source clean-up technologies (at least in the short term).

2.1 Reactive Zone Configurations

In principle a reactive treatment zone or zones should completely enclose identified pathways from the pollutant sources to the receptors. In practice this may require that the zone(s) cover a substantial area. Furthermore the flow through any element of a zone may be uncertain as a result of factors including seasonal variations in groundwater level and flow. It follows that large volumes of reactive material may be necessary to ensure sufficient residence time throughout the zone under all operating conditions. Optimization of the deployment of the reactant is therefore an important consideration. Possible configurations include:

- The use of injection wells to introduce chemicals into the natural groundwater flow.
- The use of passive wells containing, for example, replaceable canisters of treatment materials that dissolve into the natural groundwater flow.
- Treatment zones in the region of the source that reduce pollutant concentrations to levels at which natural intrinsic remediation can operate in zones down gradient of the source.
- Systems that focus the flow either in plan or elevation or both.

It should also be possible to monitor and, if appropriate, control the processes within the treatment zone. The requirements for monitoring and control can present problems for *in situ* treatments or intrinsic remediation in an undefined area, given the heterogeneity typically associated with ground conditions and the large volumes of soil that may require treatment. Martin and Bardos (1996) describe examples of *in situ* treatment zones where treatment remains in the ground but under conditions of better definition. The gate of a Funnel and Gate^{TM} system is an example of such a system where monitoring can be particularly straightforward and control systems can be incorporated in the works if appropriate.

2.2 The Permeability of Reactive Treatment Zones

Reactions in a treatment zone may influence its permeability to the carrier fluid just as they may influence the permeability of a passive containment. It follows that chemical, biochemical and physical phenomena within contaminant control systems must be recognized as interrelated. Contaminant control systems should be considered as a continuum bounded by the two extreme situations:

- Permeable reactive treatment zones. The best known example is the use of zero valent iron to dechlorinate solvents in groundwater (Gillham and O'Hannesin, 1992).

- Low permeability active containments, achieved, for example, by exploiting the chemistry of, or adding species to, low permeability barriers such as a soil-bentonite (Evans, 1991) or cement-bentonite (Jefferis, 1996).

A reactive treatment zone must include some process that removes, destroys precipitates or otherwise attenuates the contaminants migrating from the source(s) towards the receptor(s). Processes that may be employed alone or in combination include: chemical reaction, physical separation, biological degradation, and sorption.

Many of these processes will rely on an interaction between the flowing groundwater and a solid phase in the treatment zone and although the permeability of the zone is not the controlling parameter it may be necessary to consider it. For example, a moderate to high permeability may be necessary if problems such as ponding within a containment are to be avoided. Designing and maintaining such a permeability may pose some problems as the reaction rate in the zone may be dependent on the surface area of a solid phase within it. As a result it may be necessary to use finely divided (and hence low permeability) materials to limit the required residence time of the contaminants in the zone. Also precipitates or biological slimes may form within the zone. Thus careful consideration must be given to the initial permeability of the treatment zone and to processes that may lead to any change over time (an increase as well as a decrease in permeability can be damaging if the water level or residence time in the reactive zone is sensitive to its permeability). It is perhaps ironic that a low permeability barrier may be compromised by an increase in its permeability whereas a reactive treatment zone may be compromised by a decrease. The problems are reciprocal and if one type of containment could be perfectly achieved there would be no need for the other.

2.3 Low Permeability Reactive Zones

Reactive treatment zones may be designed to be of low permeability, and the physical effect of the barrier may be enhanced by processes such as chemical reaction in the region of the barrier. For example, heavy metals may be precipitated by the high pH of cement-bentonite walls though credit is seldom given for this in the design of such containments (except for the containment of radionuclides in purpose-designed repositories).

A significant amount of work has been reported on the effect of contained chemicals on the physical properties of barrier materials such as clay liners and cement or soil-bentonite walls. The prime focus of much of this work has been the assessment of physical damage to the cut-off material, for example, its permeability that may be caused by contained chemicals. Much less work has been reported on the beneficial effects of chemicals, though an examination of the literature shows that some work focused on the damage has actually demonstrated beneficial effects.

Interactions in low permeability systems are potentially much more complex than in high permeability systems as it is necessary explicitly to consider the effects of chemical, biochemical and mineralogical changes on the permeability and not just design to minimize their impacts. At the laboratory scale it has been demonstrated that the chemical history of a containment material and its permeability can be strongly interlinked. For example, leaching a cement-bentonite material by sustained permeation with water, so reducing its pH, will usefully reduce its permeability and also inhibit expansive cracking and damage if it is subsequently exposed to sulfates. High pH, if required, can be re-established by permeation with lime and this can further reduce the permeability but it will re-establish sensitivity to sulfates (Jefferis 1996).

That such interaction can occur is not surprising but it does raise questions about the interpretation of laboratory investigations of chemical damage to barriers using samples that have not been exposed to the chemical history that occurs *in situ* (including, and very importantly, periods of leaching by water). Also it has been demonstrated that some chemical damage can be reversed by re-introduction of appropriate chemical species. It follows that there is considerable potential to modify the behavior of barriers once in the ground. This could be to repair them, extend their life, protect them from damaging species or modify or re-charge their chemical activity. It is therefore quite simplistic to consider cement-bentonites and indeed most passive barrier systems as having a unique permeability. They can be physically, chemically or biochemically active and if we can learn to exploit this activity new barriers concepts will be forthcoming.

3. CASE HISTORY OF THE APPLICATION OF A PERMEABLE REACTIVE ZONE

In addition to the problems of design of reactive treatment zones with appropriate chemical reactions there can be significant practical problems (and also opportunities) in fitting such systems to the circumstances of a site and this is illustrated by the following case history.

At an industrial site in Belfast, Northern Ireland, currently being used for the manufacture of electronic components, historic spillages of chlorinated solvents had led to an intense though localized contaminant source and plume. A site investigation identified the following contamination in the groundwater:

- Trichloroethene (TCE) at concentrations up to 390 mg/l
- Trichloroethane (TCA) at concentrations between 100 and 600 μg/l
- Tetrachloroethene (PCE) at concentrations of the order of 100 μg/l

A particular problem with chlorinated solvents is that they tend to be of low solubility (typically less than about 1,000 mg/l) and thus can remain as a free phase product in the ground for substantial times but the regulatory control levels are typically of the order of tens of mg/l—*i.e.*, of the order of one hundred thousand times less than their solubility. Also they are generally recalcitrant and not easily biodegraded. Thus even quite a modest chlorinated solvent spill may persist in the groundwater and continue to pollute it for a substantial time.

The soil profile at the site was complex, with glacial till interbedded with lenses of silts, sands and gravel. *in situ* pumping tests showed that the till acted as an effective barrier to the vertical and lateral migration of the contaminants but the silt, sand and gravel lenses were sufficiently permeable to allow off-site migration of dissolved solvents from the source that included free phase solvents present as a dense non-aqueous phase liquid (DNAPL). There were also smaller discrete lenses of clay or clayey silt that complicated the flow regime.

In situ permeability tests and pumping tests conducted to evaluate potential remedial strategies showed that conventional pump and treat remediation would require numerous extraction wells to address the thin saturated zone and this, together with the presence of a free product DNAPL source, meant that such a system would have to be maintained for many years. Similarly there would be major problems with a soil vapor extraction system.

3.1 Reductive Dechlorination

One of the best known and researched reactive treatments is the use of iron filings to reductively dechlorinate chlorinated solvents (Gillham and O’Hannesin, 1994). The process essentially leads to the development of an extremely reducing environment, allowing reactions occurring on the surface of the iron to strip halogens from the dissolved organic compounds as they flow through the zone. The reaction is abiotic and chlorinated solvents are converted to chloride ions and various hydrocarbons.

The process does not degrade the resulting hydrocarbons but as non-chlorinated species they have much higher permissible regulatory control concentrations. Also they are much more readily bio-degraded by intrinsic remediation processes occurring in the ground. The iron filings reactive containment is thus a conversion process that reduces toxicity. This demonstrates a general principle that a reactive treatment zone need not degrade organic contaminants to basic species such as carbon dioxide and water, but need only convert them to species that are acceptable toxicologically and environmentally in the local setting.

The iron filings technology seemed to have potential for the Belfast site and samples of the site groundwater obtained from sampling wells were shipped to EnviroMetal Technologies, Inc., Guelph, Ontario, for treatability studies. The results of these studies are reported in Thomas *et al.* (1995). Briefly, a series of laboratory column studies were undertaken to determine the degradation kinetics of the species of interest and to identify whether there were any constraints imposed by the natural geochemistry of the site groundwater. The results showed that TCE, PCE and TCA were completely degraded from initial concentrations in the test groundwater samples of 300,000, 170 and 200 µg/l respectively. The half life of TCE in the site water was estimated to be 1.2 hours in the presence of iron filings.

In contrast small concentrations of cis-dichloroethene (DCE) and vinyl chloride (VC) built up in the water as a result of the dechlorination of the TCE, *etc.*, with VC reaching a peak at the end of the column of 700 µg/l in the initial studies. The reason for this is that although the dechlorination does not appear to be a stepwise process (*i.e.*, tetrachloroethene to tri- and then dichloroethene, vinyl chloride, and ultimately to chlorine-free hydrocarbons), and it seems that the majority of the solvent is dechlorinated in a single step. A small amount may be released from the surface of the iron prior to full degradation. This leads to a temporary increase in species, such as DCE and VC, as these species are more slowly dechlorinated by iron filings. Considerable care was necessary in the design to ensure that the DCE and VC would be satisfactorily degraded. Otherwise, the net effect of the treatment zone could be to increase the concentrations of these species, which would be most unsatisfactory, particularly as vinyl chloride has markedly lower regulatory control limits than many other chlorinated solvents.

Further column studies were then undertaken at lower flow rates, the increased residence time resulting in much earlier degradation of the parent compounds thus enabling estimation of the degradation rate of vinyl chloride. From these laboratory trials, it was concluded that a residence time in contact with the iron filings of about 12 hours was required for the site water to achieve removal of all chlorinated species to below regulatory limits. This result, together with the results of a groundwater modeling exercise, enabled the calculation of the required reactive zone path length from the estimated groundwater flow rate and the required residence time of the contaminated groundwater in contact with the iron filings.

3.2 Design of the Reactive System

A preliminary review of the site situation concluded that the optimum strategy for deployment of the iron filings was in the gate of a Funnel and Gate™ system. However, the site geology and site circumstances placed a number of constraints on the design:

- The contaminant source extended to within a few meters of the site boundary, outside which there was a public road. The reactive treatment zone therefore needed to be very compact.

- The solvent source was underlain by a thin layer of clay, which had inhibited its migration to greater depths. If this layer were penetrated by the gate the free product solvents would sink and pollute a lower aquifer stratum.

- The groundwater perched on the thin clay layer was shallow and showed seasonal variations in depth. It would be difficult to maintain any significant depth of horizontal flow in a gate seated on this layer.

- A perched water table also existed in the fill covering the surface of the site. In wet seasons this water, if allowed to enter the gate, could dominate flow through it and unacceptably reduce the residence time. It therefore had to be excluded.

- Because of the proximity of buildings and the risk of damage by vibration and also the cost, sheet piles could not be used to form either the funnel or the gate of the system.

- If a slurry trench procedure were used to form the system then it was imperative that the iron filings were not inundated and thus blocked by slurry from the wall construction. It would therefore be necessary to contain the iron or to construct the slurry wall before placing the iron filings. Prior formation of the cut-off wall could allow it to slump during excavation for the iron gate and thus a poor seal between the wall and the iron filings.

- The residence time of groundwater within the reactive treatment zone is critical. A zone that is too thin may lead to the escape of lower chlorinated species, such as vinyl chloride, which can pose a greater toxicological or environmental threat. Extensive groundwater modeling studies were undertaken to ensure that the design residence time could be achieved.

- The clean-up was being undertaken voluntarily by the owner of the site.

After consideration and rejection of many reactive treatment zone designs, the *in situ* reactor configuration shown in Figure 1 was developed as best fitting the constraints imposed by the site. In place of previously used horizontal flow reactive treatment zones the flow was arranged to be vertical in a 12 m tall by 1.2 m diameter steel reactor shell which was filled with iron filings as shown in the figure. This design enabled the reactor to be placed between the contamination and the site boundary. This could not have been achieved with a horizontal flow regime as the design calculations had shown that the flow path length needed to be at least 5 m plus entry and exist zones to collect and disperse the flow. The vertical flow direction within the reactor also ensures that the full depth of the iron filings will be saturated whatever the seasonal variation in groundwater level.

The reactor was placed in an enlargement in a cement-bentonite cut-off wall (Figure 1), which was used to funnel the flow to the reactor. This wall was toed into an aquiclude layer at 10 m and the enlargement was taken to a depth of slightly over 12 m to accommodate the reactor shell. The cut-off and enlargement penetrated through the clay layer on which the chlorinated solvents were retained. However, as the cut-off material was designed to have a permeability of $<10^{-9}$ m/s minimal downward migration of solvents will occur.

Because of the relatively low permeability and heterogeneity of the adjacent soil, it was decided that the flow to the reactor should be collected via an upstream high permeability collector and that downstream of the reactor there should be a similar

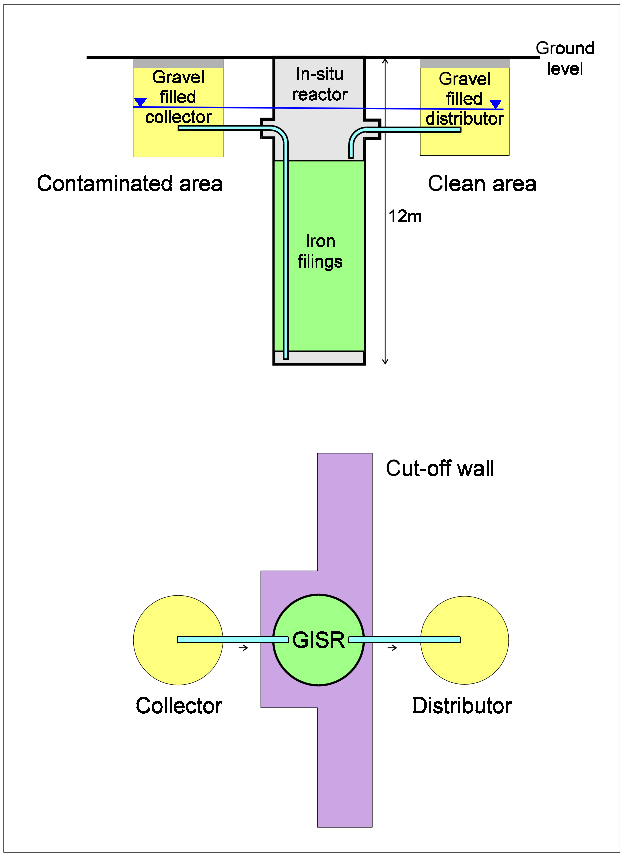

Figure 1. Reactor configuration, elevation, and plan view

distributor. The collector and distributor were formed from gravel filled piles taken down to the top surface of the thin clay layer. A gravel backfilled trench, excavated under a degradable polymer slurry, could have been used to form the collector and distributor but there were concerns about the effect, on the iron filings, of any polymer remaining in the trench and so augured pile holes were used.

Finally, the internal geometry of the reactor was arranged so that the pipe connections to the gravel filled collector and distributor piles could be made from within the clean environment of the reactor shell without the need for any hand excavation or for anyone to enter the excavations all of which were undertaken either with a backhoe under cement-bentonite slurry or with a piling auger. During the works airborne solvent concentrations were monitored and found to be undetectable.

3.3 Performance of the Reactor

The performance of the reactor has been and continues to be very satisfactory though there are two marginal complicating factors:

- The flow rate through the reactor was very low during the first months of operation and is likely to remain quite modest (this is as expected from the hydrological investigation). It follows that the internal pore water chemistry is rather sensitive to any disturbance of the flow regime
- Sampling from within the relatively modest volume of the reactor has proved to be a problem if traditional procedures are used. Only small volumes of water can be withdrawn if the local chemistry within the reactor is not to be disturbed. Particular techniques are being developed to obtain small but representative samples from the reactor whilst avoiding the need to purge the sampling tubes.

The results of five campaigns of sampling within the reactor and in the upstream collector and downstream distributor are shown in Figures 2, 3, and 4. The results relate to a period of 19 months from installation of the reactor.

Figure 2 shows the data for TCE as a three dimensional plot of concentration as a function of position in the reactor system and time. There are five sampling points within the reactor shell. Sampling point R5 is at the entry point to the iron filings bed from the collector and R1 at the discharge point to the distributor. The other three sampling points, R2 through R4, are distributed at 1.5 m intervals through the 6 m deep bed.

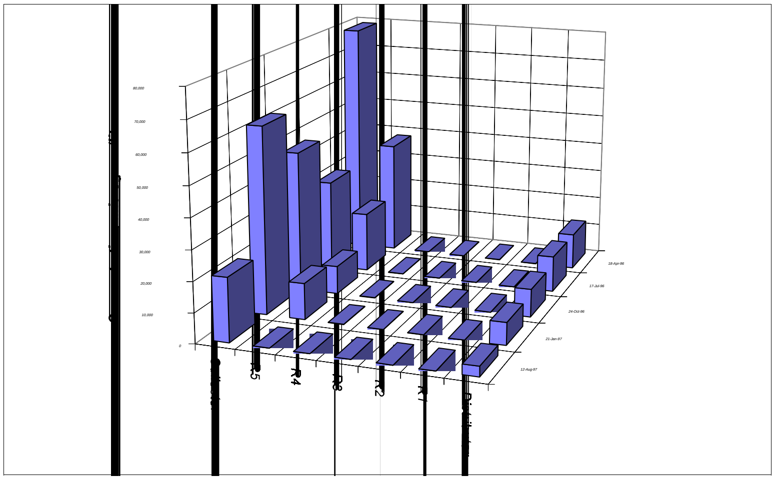

Figure 2. TCE concentrations in the reactor zone

It can be seen that the of TCE within the reactor drops very rapidly and is at very low levels by the time it has reached the first sampling point (R4) at 1.5m into the reactor bed. In August 1997 the average TCE concentration within the reactor bed was less than 4 micrograms/liter. Figure 2 also shows that there is still a significant, though reducing, TCE concentration in the downstream distributor and the reactor discharge point (R1). This is as a result of the TCE originally present in the downstream area some of which may have diffused back into the reactor exit zone or have been drawn back into the reactor by the sampling process. However, it seems most likely that the actual reason for its presence is the advection of TCE contaminated groundwater through the distributor zone as a result of groundwater flow in the downstream area. It should not be forgotten that there may be a downstream flow vector parallel to as well through a gate.

Figure 3 shows the chlorine balance in the reactor zone. For this it is necessary to consider both the chlorine in the inorganic chloride ion and in the TCE. The TCE chlorine drops rapidly with distance into the reactor and only increases again in the distributor area. The total chlorine shown in the figure is the sum of the TCE and chloride chlorine and it can be seen that it is relatively consistent throughout the reactor (the high total chlorine on 21 August 1997 was as a result of a high chloride ion concentration, the reason for it is not known but could be as a result of some slight seepage of de-icing salts used in winter time.

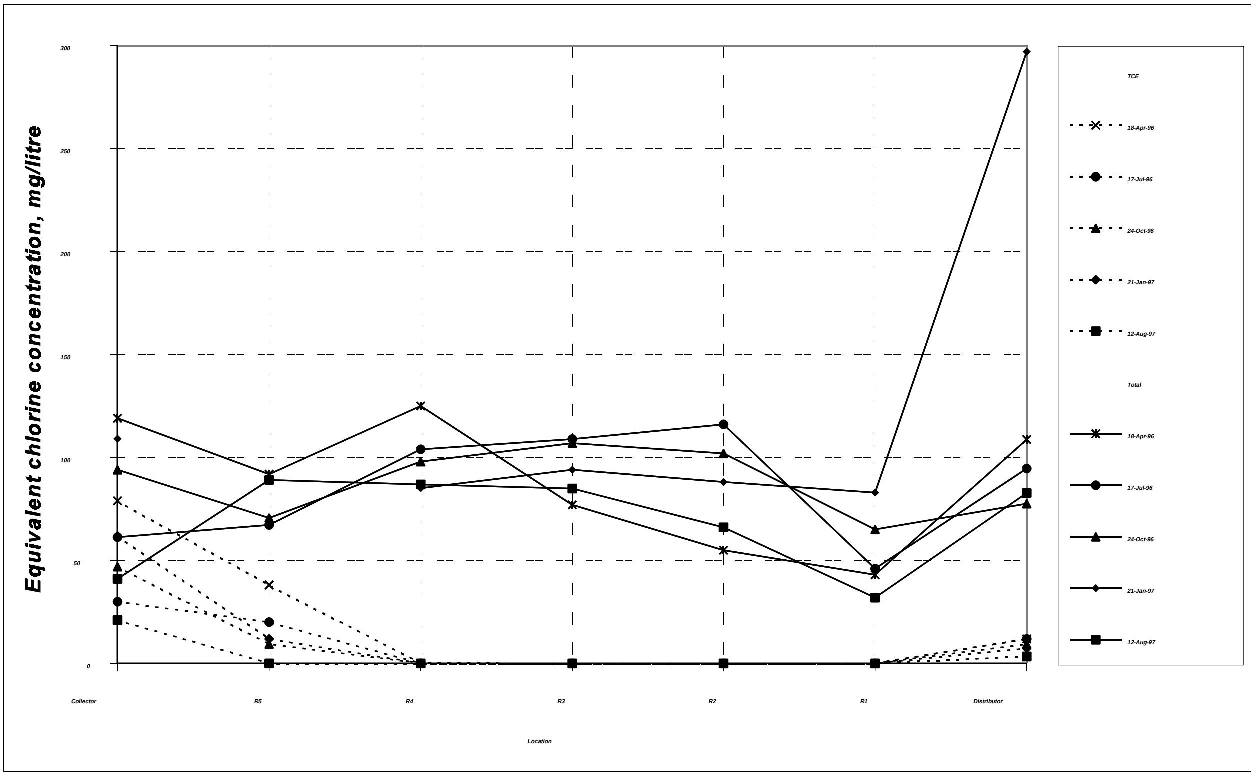

Figure 3. Chlorine balance in the reactor zone

On each sampling occasion TCA was at undetectable levels. Vinyl chloride was found at a single sampling point within the reactor at 4 months (at a level of 0.4 mg/l) but not in the collector or distributor and has not been detected on any subsequent occasion.

With regard to the remaining downstream contamination it is interesting to note, that at times of low seasonal flow, there is potential for the recycling groundwater from wells downstream of the reactor to the upstream collector (by pumping) to treat the downstream area should treatment of this contamination be required. Also the reactor will work with the flow in either direction. Thus, if, for some reason, the flow should be reversed naturally then the site would be protected from the inflow of any contaminants spilled or remaining outside the reactor system.

4. CONCLUSIONS

The reactive treatment zone concept offers not only a new tool for the control of contamination but also forces a re-thinking of low permeability barrier systems. Prior to the development of the concept, contaminant/barrier interaction had generally been considered only as a possibly damaging process that could increase the permeability of a barrier. Now barrier interactions should be seen differently. They may be deliberately engineered to be beneficial.

Reactive treatment zones may be most economically employed as pathway control procedures but will contribute to the slow clean-up of a source. The pathway control they offer is their essential feature and it may be argued that they should not be designed to achieve more than slow source clean-up as this minimizes the rate at which any treatment chemicals, energy or other process inputs are required i.e. it minimizes the process demands and operating costs whilst maximizing the opportunity for natural, intrinsic, remediation.

At the present time a significant limitation to the use of reactive treatment zones is the rather narrow range of contaminants that can be treated and the complications introduced by mixed contaminants etc. However, work is in progress and the technology has strong parallels with intrinsic remediation (*e.g.*, intrinsic bioremediation), and it is likely that the reactive treatment zone concept will find much application in stimulating intrinsic degradation or attenuation.

The Funnel and Gate^{TM} concept is a powerful adjunct to the technology as it can allow the treatment zone to be at some distance from the source, if this is required by surface or buried structures, geological conditions or for process optimization (*e.g.*, exploiting natural dilution or attenuation in the soil), *etc.* Sites need not be capped to prevent rainwater ingress, indeed it can be an advantage in driving groundwater flow to a treatment zone.

The concept of an *in situ* reactor adds further flexibility to the design of reactive treatment zones, allowing more precise control of the reactive zone and also recharging or recovery and replacement of the active material should this be required. Furthermore several reactors may be linked in series to treat mixed contaminants.

Although most reactive treatment systems that have been advanced to date have been for the control of groundwater pollution there is no reason why other systems such as reactive caps should not be developed to control, for example, the escape of semi-volatile or volatile organics from petroleum impacted sites or gas or odor from landfills. Peat or humic based materials could be particularly cost effective in this respect (and of course for the removal of organics from impacted water). Bio-oxidation zones to control methane migration through unsaturated soils offer some exciting prospects but there could be difficulties with excessive local heating.

Low-permeability reactive treatment zones are a more specialist application and may require site capping or groundwater pumping (and treatment) to avoid ponding. Reactive treatment zone concepts will be useful where long term secure containment is necessary as chemical interactions can provide additional security and lifetime to a physical containment. Furthermore the concepts may be useful in developing *in situ* repair strategies for barriers that have suffered damage and in analyzing the effects of reaction on the permeability of these systems (Jefferis, 1996).

5. ACKNOWLEDGMENTS

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Discussion

There was some discussion concerning the placement of the reactor vessel relative to the collector and distributor, and whether there would be any cost savings in installing the reactor at the same time as the cut-off wall, collector, and distributor. Jefferis replied that there are circumstances where there would be no cost savings for simultaneous construction. He said that sometimes it would be cheaper to build a pipe through the cut-off wall rather than place the reactor within it.

The reactor was designed to have a retention time of approximately 1 day. It is difficult to determine the exact flow through of the reactor because it was operated in the summer when the through-flow was too low to measure. The highest flow occurs in the winter, and the reactor was designed for a maximum flow through of 5 m^3/day. Other chemical parameters measured at the site were pH, PCE, DCE, vinyl chloride, and some inorganics.

Harald Burmeier questioned whether the groundwater was pumped through the reactor. Jefferis indicated that it is a gravity-flow reactor, but if necessary, groundwater could be pumped through to treat water, or to pump down in the winter during peak flow to augment the low flow during the summer.

Wüst commented that the system seemed to work well, but wondered whether the hydraulic design was adequate to clean up other contaminants besides TCE. Jefferis noted that no other contaminants were present, other than *cis*-DCE, which was found only in the distributor (not in the flow through). He added that the higher concentrations shown in Figure 2 were found in the distributor located downstream of the reactor. He said that the reactor has unused capacity, and he would like to pump back the flow through; he acknowledged his disappointment in how slowly the concentration was dropping. Geologically, it is a very heterogeneous, complex site. There may be some cross-flow bringing in contamination directly from the plume.

Horizontal Treatment Barriers of Fracture-Emplaced Iron and Permanganate Particles

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Traci L. Case[1], Douglas A. Pickering[2], and Thomas C. Houk[4]

1.0 Abstract

In many contaminated sites, vertical leaching and/or volatilization of organic compounds can lead to high exposures and unacceptable human health or environmental risk. One remediation alternative for these sites is to emplace horizontal treatment barriers to reduce the source concentration and mass as well as intercept and treat any mobile organics in the subsurface. Development and demonstration activities have been conducted to evaluate the feasibility of creating horizontal treatment barriers by employing hydraulic fracturing for emplacement of chemically reactive solids. In this work, iron metal particles and a new permanganate solid media were both tested in horizontal barriers to achieve interception and degradation of chlorocarbons like trichloroethene (TCE). Laboratory experiments were completed to develop suitable delivery fluids and to determine reaction rates and efficiencies. The iron metal particles could be suspended and delivered using a typical guar gum gel while the permanganate solids required a new mineral-based carrier fluid. Degradation of TCE at ~10 to 80% aqueous solubility with iron metal particles exhibited a half-life in the range of 1 to 2 hr while that of the permanganate solid was much faster with a half-life of only several min or less. A full-scale field test was subsequently conducted at an old land treatment site in the midwestern USA. Two test cells were installed with horizontal barriers comprised of reactive fractures emplaced at ~1.2, 2.4, and 3.6-m depth in silty clay soils using hydraulic fracturing methods. After 3, 10 and 15 mon of emplacement, continuous cores were collected across the emplaced fracture zones and morphology was observed, geochemical properties were measured, and degradation tests were completed with TCE contaminated groundwater (TCE concentrations at ~5-50% solubility). These analyses revealed strong short-range trends in redox potential and pH consistent with the anticipated behavior of the two different reactive media emplaced. Highly oxidizing zones were present in and around the permanganate barriers. TCE degradation efficiencies during 2 hr of contact of >99% in 10-cm thick soil zones after ~3 mon of emplacement with even broader effects at ~10 and 15 mon. The treatment barrier comprised of 200 µm iron-metal particles exhibited highly reducing conditions within the iron-metal fracture but no marked effects in the soil zone surrounding it. Degradation of ~35% was achieved after 24-48 hr of contact but only in the iron-metal itself. The iron exhibited some corrosion, but this did not appear to affect its reactivity. The results of the work to date are very positive regarding the performance for both types of horizontal barriers and the estimated costs for a typical application are comparably low at only \$30/m^3. Further work is ongoing to enable design and deployment of this technology.

2.0 Introduction

Petrochemicals (*e.g.*, benzene) and chlorocarbons (*e.g.*, TCE) are common and problematic contaminants of concern (COCs) at federal facilities and industrial sites across the U.S. and abroad (USEPA, 1992; API, 1995; DOE, 1996). These contaminants can be released to the environment through leaks in storage tanks and transfer lines, spills during transportation, and the land treatment of wastes. They are often present in source areas and in soil and groundwater plumes as dissolved or sorbed phase constituents as well as nonaqueous phase liquids (NAPLs). When these COCs are present in silt and clay media either as massive

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surface deposits or as interbedded lenses in otherwise permeable formations, there are major challenges with assessment of their behavior and implementation of effective in situ remediation technologies. Despite a low bulk permeability of silts and clays (*e.g.*, $K_{sat} < 10^{-7}$ cm/s), organic compounds can contaminate fine-grained deposits by preferentially moving into and through naturally occurring pore and fracture networks and partitioning between the nonaqueous, gas, aqueous, and sorbed phases. In the unsaturated zone, organics can continually volatilize into the soil air or leach into percolating water while in the saturated zone they can slowly dissolve into advecting groundwater. Exposures and unacceptable risk can result from ingestion of contaminated drinking water or surface soil media, or inhalation of vapors in ambient air or emitted during showering events. In recognition of the severity of the problem and the need for effective in situ treatment methods, organic compounds in fine-grained deposits was recently ranked as one of the top environmental restoration needs across the DOE Complex (DOE, 1996). Similarly, within the petroleum industry, nearly 40% of the underground storage tanks in the world are located on clay soils and leaking underground tanks and remediation of organic contamination in these settings remains a major challenge (API, 1995).

In situ remediation by conventional methods such as mass recovery by soil vapor extraction (SVE) or *in situ* destruction by biodegradation or chemical oxidation are often ineffective for NAPL compounds at sites with silt and clay media. Poor accessibility to the contaminants and difficulty in delivery of treatment reagents throughout these deposits have made rapid and extensive *in situ* remediation difficult. Some aggressive techniques have been developed involving subsurface disruption by soil mixing or alternative driving forces based on electrokinetics (*e.g.*, Siegrist *et al*., 1995). In seeking less intensive methods that could be used over larger areas, soil fracturing techniques have been developed whereby hydraulic or pneumatic fluids can be injected to create permeable horizontal layers. This can increase the overall permeability of the subsurface and improve contaminant recovery as existing channels or pathways can be expanded or new channels or pathways can be created (U.S. EPA, 1993; Murdoch *et al.*, 1997). Hydraulic methods normally employ an agent or proppant (*e.g.*, sand) to fill and support the fracture opening that was created and thereby prevent fracture closure during natural healing processes in unconsolidated deposits. If the fractures can be spaced throughout the deposit, they potentially could be used to (1) enhance the recovery of organic compounds, (2) deliver and distribute treatment fluids into the deposit and accomplish destruction in place, or (3) place reactive solids as an integral part of the emplaced fracture that could serve as a horizontal treatment barrier.

Two reactive media that appeared appropriate for use in horizontal treatment barriers included: (1) iron metal particles and (2) permanganate crystals. The use of zero valent iron metal as a reactive barrier media has been developed and deployed in vertical orientations for several years (*e.g.*, O'Hannesin and Gillham, 1998). The reductive dechlorination reaction for TCE is shown in equation 1. The reaction involves single and multiple electron transfers following pseudo-first order kinetics (at least at lower TCE concentrations) with half-lives on the order of 30-60 min as normalized to solution to solid surface area. The pH of the reacting system tends to rise, but appears to stabilize in the pH 9-10 range due to iron hydroxide precipitation.

$$2Fe^{o} + C_2HCl_3 + 3H_2O \rightarrow C_2H_2Cl_2 + H_2 + Cl^{-} + 3OH^{-} + 2Fe^{++} \quad [1]$$

The use of potassium permanganate for oxidative degradation of organic pollutants in contaminated land has evolved over the past few years (*e.g.*, Gates *et al*., 1995). The oxidative destruction of TCE is given in equation 2. The reaction can include destruction by direct electron transfer or free radical advanced oxidation. The reaction follows pseudo-first order kinetics and is very rapid with half-lives on the order of sec to min. The pH of the reacting system can decline to very low values depending on the buffering capacity of the system.

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2KCl + HCl \quad [2]$$

3.0 Horizontal Treatment Barriers

3.1 Development and Demonstration Activities.

While there has been extensive research and development followed by increasing application of vertical treatment walls, research and development of horizontal treatment barriers has only recently been accomplished (*e.g.*, Murdoch et al. 1997, Siegrist et al. 1997). During the past three years, these authors have been studying horizontal barriers comprised of either iron metal or permanganate solids delivered via hydraulic fracturing methods. This work has included laboratory and field testing to evaluate their feasibility and performance for in situ degradation of TCE in fine-grained media deposits (Figure 1). The results and implications of this work are highlighted in this paper while details regarding the methods and results can be found elsewhere (*e.g.*, Murdoch *et al.*, 1997; Siegrist *et al*., 1997; Case and Siegrist 1997).

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The laboratory and field research conducted by these authors has demonstrated that conventional hydraulic fracturing equipment and methods could be employed to emplace reactive solids in silty clay soils at depths of 1.2-5 m with diameters of 6-9 m. Fractures containing 200 µm iron particles as the proppant were successfully emplaced at depths of ~1.8, 2.4, and 3.6 m**.** Based on morphology and geochemical measurements along profiles transecting the fractures, the iron proppant remained reactive even after 10-15 months of emplacement, but there was little effect on the enveloping soil matrix (Figure 2). Based on batch degradation tests with samples of the iron from the fracture or soil media surrounding it and initial TCE groundwater concentrations ranging from ~50-500 mg/l (equivalent to ~400-4000 mg/kg), the degradation achieved was equal to only ~35% during reaction periods of 24- or 48-hr. While the iron metal in the fracture did show signs of surface corrosion, its degradation efficiency was comparable to that of unused iron even after nearly a year of emplacement in the moist silty clay subsurface.

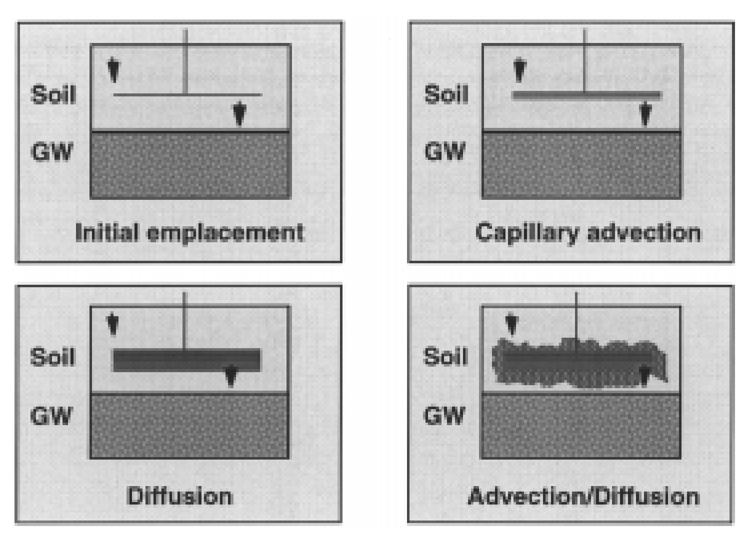


Figure 1. Illustration of a horizontal treatment barrier concept with hydraulic fracturing for reactive media emplacement (Note: the barriers shown contain reactive media that has the ability to dissolve and effect soil-solution biogeochemistry changes).

Fractures containing a new permanganate solid mixture as the fracturing fluid and proppant were successfully emplaced at depths of ~2.1, 2.7, and 3.4 m. Morphology and geochemical measurements along representative profiles indicated that this process created highly reactive fractures enveloped by zones of reactive soil 30-60 cm thick (Figure 3). Dissolved TCE with initial concentrations of from ~50-500 mg/l (equivalent to ~400-4,000 mg/kg) was completely degraded (100% efficiency) in batch tests using either material from the fractures or the reactive soil from above and below the fractures. Complete degradation was observed in as little as 2 hr. The degradation potential as a function of time and space, was controlled by the mass of permanganate ion that was present in the fracture or the fraction of it that had migrated into the soil matrix and had not been previously consumed.

3.2 Discussion and Implications.

The viability of reactive fractures emplaced by hydraulic fracturing methods as horizontal barrier systems requires consideration of the horizontal continuity, degradation capacity, and longevity. The results obtained by these authors enable a very interesting contrast between reactive fractures created with surface reactive particles (*i.e.*, iron metal particles) *versus* those created with a reactive grout that dissolves and yields a wider reactive zone (*i.e.*, permanganate grout). Both types of reactive media were successfully handled and emplaced by conventional hydraulic fracturing equipment and methods. The geometry of the fractures was similar to that of conventional sand-filled fractures emplaced at the same site. Thus, there was no unusual behavior associated with the different fracturing proppants (*i.e.*, iron particles in guar gum *versus* permanganate particles in mineral carrier *versus* sand in guar gum).

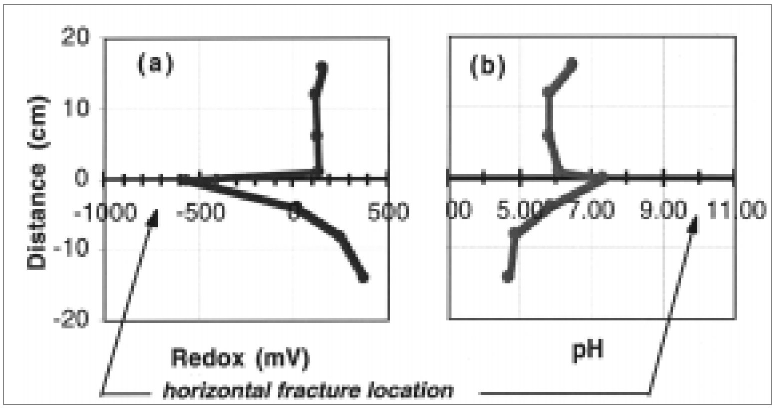
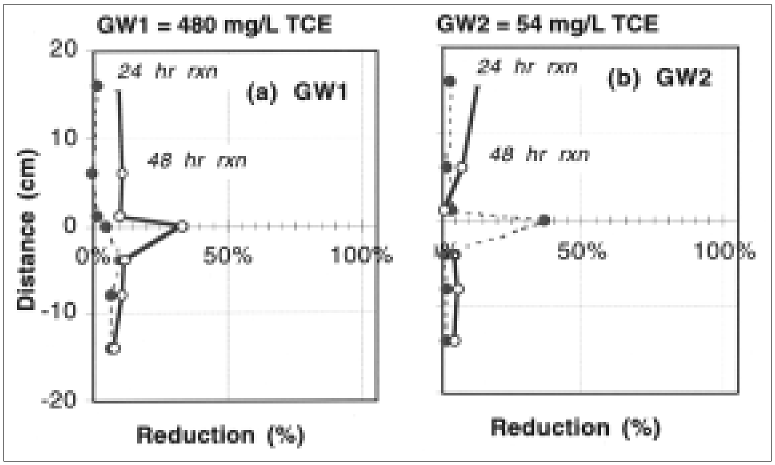
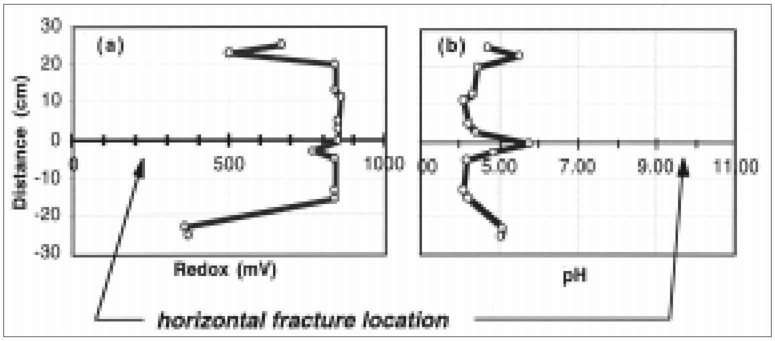


Figure 2. Features of iron metal horizontal barriers 10 months after initial emplacement in a silty clay soil (after Siegrist *et al.*, 1997). (a) Media redox potential and pH above and below the horizontal treatment fracture. (b) TCE degradation potential above and below the horizontal treatment fracture as measured in batch tests using 3-5 g of media in 40 ml of groundwater.



Since the iron metal fractures are discrete reactive sheets, it is not likely that these fractures would be self-healing within or between fractures or effective beyond the boundary of initial emplacement. This challenges the fracture emplacement to be continuous and uniform horizontally with no breaches through it. Also, degradation of the TCE or related compounds within the deposit must rely on their being mobilized to the fracture where they can contact the metal surface. Since the TCE reaction rates with iron metal are comparatively slow, any mobile contaminants must remain in contact with the iron metal for a reasonably long period of time (*e.g.*, on the order of 18-24 hr). If flow through the fracture is controlled by unsaturated conductivity in the surrounding soil media and assuming the conductivity is about 10^{-6} cm/s, then the retention time in a fracture of 5 mm thickness could be on the order of a day or more depending on the effective porosity in the iron. Thus, adequate retention time can be reasonably expected. As a treatment barrier, the reactivity of the iron surface would need to exist for an extended period (*e.g.*, 2-5 years or more). Analysis of the micromorphology of the surface of the unused and used iron metal revealed some corrosion of the iron surface after emplacement for ~10 months. The effect was limited however to only a fraction of the available iron surface and this corrosion had no apparent effect on TCE degradation. Whether this would hold true for longer emplacement periods is currently unknown.

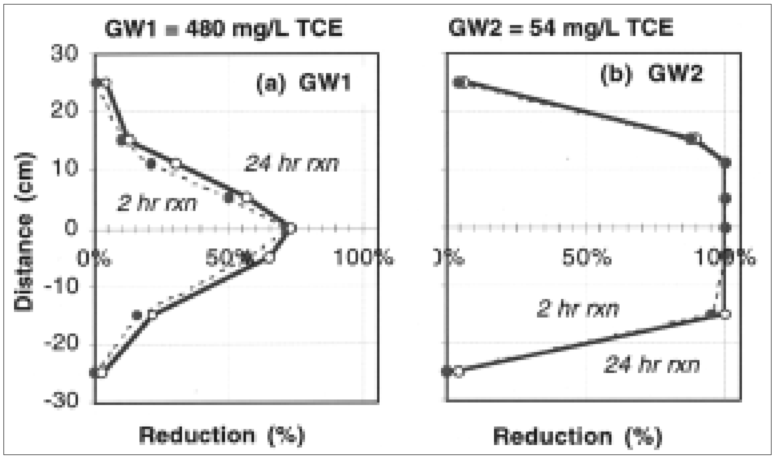
With permanganate fractures, the dissolution of the solid permanganate particles will yield MnO_4^- ions that will enter the soil solution and migrate away from the original location of emplacement by advection and/or diffusion. This will yield an oxidizing zone that can treat TCE within the affected zone enveloping the fracture as well as intercept and degrade mobile contaminants that enter the oxidation zone. This behavior suggests that the permanganate fractures will be somewhat self-healing internally and between horizontally proximal fracture emplacements. With regard to longevity, the permanganate solids present in a 5 mm thick fracture contains about 0.4 g $KMnO_4$ per cm^2 or fracture horizontal area Based on complete oxidation and a stoichiometric dose of ~2.5 wt./wt., each cm^2 of fracture can treat ~0.16 g of TCE, which is equivalent to roughly 16 l of percolate with a concentration of 10 mg/l of TCE. At a deep percolation flux of 1 cm/day, this potential is equivalent to about 50 years of life. Realistically though, it is anticipated that advective loss of oxidant out of the treatment region or the oxidant demand of natural organic matter will markedly diminish this life. Based on direct observation in this study, the oxidation capacity within and around the permanganate fracture was very high even after 10-15 months of emplacement. If alkenes, such as TCE, were migrating downward in percolating groundwater at reasonably high levels (*e.g.*, 10-100 mg/l), the capacity of the fractures seemingly would be high enough to intercept and treat this mobile TCE.



(a) Media redox potential and pH above and below the horizontal treatment fracture.

Figure 3. Features of permanganate horizontal barriers as observed 10 months after initial emplacement (after Siegrist et al., 1997).

(b) TCE degradation potential above and below the horizontal treatment fracture as measured in batch tests using 3-5 g of media in 40 ml of groundwater.



The cost of a horizontal treatment barrier comprised of reactive fractures such as tested in this study were estimated. When compared to standard hydraulic fracturing and SVE, the major cost differences would be added costs for the reactive media (~\$1.6/lb for permanganate and ~\$0.38/lb for iron metal) as compared to standard fracturing sand (~\$0.10/lb) but lower operational costs. The costs for media per fracture amounts to roughly \$100 for sand, \$1,000 for iron, and \$1,500 for permanganate. This increases the installation cost for the iron and the permanganate fractures. However with lower resource consumption (*e.g.*, power), less sampling and analysis (*e.g.*, no off-gas), reduced labor requirements, and no off-gas treatment costs, the operational costs would be substantially lower for the horizontal barriers as compared to fracture-enhanced vapor extraction. For a 2.2 ha site and a 5-m deep zone of contamination, the costs for emplacement of horizontal treatment barriers was estimated to be in the range of \$30/m^3.

In summary, horizontal treatment barrier systems appear viable for TCE contaminated sites with silt and clay deposits. Further work is necessary and appropriate, however, to fully develop this horizontal treatment barrier approach and provide needed design and performance data for a range of full-scale applications. For example, information is still needed on the depth and interval of emplacement as well as reactivity and degradation capacity over time. The behavior of horizontal barrier systems under conditions of forced advection also needs to be evaluated to understand the benefits/costs of recirculation approaches to *in situ* treatment and source area mass reduction as opposed to more passive barriers for simple interception and treatment.

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Discussion

Noting the rapid release rate for permanganate, Resat Apak asked whether permanganate sheets can be used only in low-permeability aquifers. Siegrist acknowledged that his work involves the use of permanganate grout in low-permeability zones; however, there is work being done with controlled releases of permanganate. With a slower release rate, perhaps the technology can be tailored to higher permeability zones.

Apak also whether Siegrist has observed clogging due to the formation of manganese hydroxide. Siegrist noted that the product of the reaction between manganese and TCE is manganese oxide precipitate, which ranges in size from 1-2 µm. The formation of the solids is somewhat related to the concentration of reactants. Siegrist has observed limited formation of solids at the test site, but has not seen an accumulation at the interface. Clogging has not been a problem with low-permeability zones, but may be a problem with higher permeability zones.

Paul Bardos questioned whether the capacity of the permanganate is reduced due to oxidation of organic matter in the soil. Siegrist agreed that permanganate is an oxidant that reacts with TCE and natural organic matter in the soil. However, permanganate does not seem to be consumed as much by the organic matter. Siegrist noted that residual permanganate remains in zones with organic material after 15 months; however, the soil matrix should be assessed for the potential to consume the permanganate.

The cost difference between using permanganate and iron is not significant. The cost per fracture of using sand alone is approximately US$100. The cost per fracture is US$1,000 for iron and US$1,500 for permanganate. The retention time in the iron-filled fracture is 1-5 days, during which there is 30-40 percent degradation. Siegrist noted that the cost estimate of US$30/$m^3$ that he cited during his presentation applies to both iron and permanganate. Both materials appear to be viable, although they have different characteristics.

In Situ Remediation Research in a Complexly Contaminated Aquifer: The SAFIRA Test Site at Bitterfeld, Germany

H. Weiss[1], F.-D. Kopinke, P. Popp, and L. Wünsche

The experience of the last 20 years has shown that hydraulic soil and groundwater remediation schemes are often very ineffective. This is especially true of large-scale pollution, where the source of contamination either cannot be precisely located or is problematical to remove. Owing to the frequently low solubility of hydrophobic organic substances (for example), the existence of a separate residual phase, the usually uneven subterranean flow, and the sometimes slow return diffusion of pollutants that have penetrated the rock over a period of years or even decades, solely hydraulic remediation can only achieve limited clean-up. The consequences are very prolonged (and thus expensive) pump-and treat remedies, whose completion is usually impossible to predict.

Against the background of the now generally acknowledged problems of pump-and-treat activities, intensive work has been carried out in recent years on developing low-price *in situ* remediation measures. The currently most advanced remediation technology working in the flow is that of "*in situ* reaction/adsorption walls" [1], which have already been tried out for simple pollutant mixtures (*e.g.*, LCKW, BTEX, and PAK) at a number of model sites. Nevertheless, there is still a great deal of development work to be done with respect to the complex pollutant mixtures commonly encountered above all in the vicinity of abandoned chemical plants.

As this problem is extraordinarily important in connection with the large-scale ecological remediation schemes in eastern Germany, the SAFIRA[2] project has been set up to examine and further develop the usage of *in situ* reaction walls at a contaminated model field location.

In order to create the necessary basis for this model project, a preliminary study was carried out by UFZ in cooperation with the Universities of Dresden, Halle, Leipzig, Stuttgart, and Tübingen. During the course of this preliminary study, the hydrogeological and hydrogeochemical conditions at the planned field location were investigated and various technologies for the design of the *in situ* pilot plant were examined and tested.

Choosing the Model Location

The Bitterfeld region was selected as the model location for investigations into developing powerful *in situ* technologies for the remediation of complexly contaminated groundwater.

The soil and water environmental compartments in the Bitterfeld/Wolfen district have suffered sustained damage as a result of over a century of lignite-mining and chemical industry. Whereas relevant soil pollution is mainly confined to industrial locations (plant sites) and landfills, the persistent penetration of the groundwater by pollutants has resulted in contamination attaining a regional scale. Consequently, an area of about. 25 km^2 with an estimated volume of some 200 million m^3 is now partly highly polluted and must

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[2] "***Sa***nierungs-***F***orschung ***I***n ***R***egional kontaminierten ***A***quiferen" – Remediation Research in Regionally Contaminated Aquifers

be regarded as an independent source of contamination [2]. This pollution is characterized by the extensive distribution of halogenized hydrocarbons, especially chlorinated aliphatics and chlorinated aromatics.

The development of the hydraulic conditions and thus regional pollutant transport is determined by the draining techniques used for lignite-mining and its subsequent abandonment, as well as the imminent flooding of Goitsche opencast mine. Since 1990, the hydraulic and conditions have been described and evaluated in several studies (*e.g.*, [2, 3, 4]; for further reading see [5]), so that there is an extraordinarily high level of knowledge concerning the area in question. The containment and remediation concepts drafted since 1994 [2-4] feature both "active" and "passive" hydraulic containment measures to minimize groundwater mobility. Successive measures to contain landfills (*e.g.*, encapsulation) are also being discussed. "Active" measures for groundwater remediation on a regional scale are not under consideration owing to the volumes involved and the *ad infinitum* emission of pollutants from the landfills.

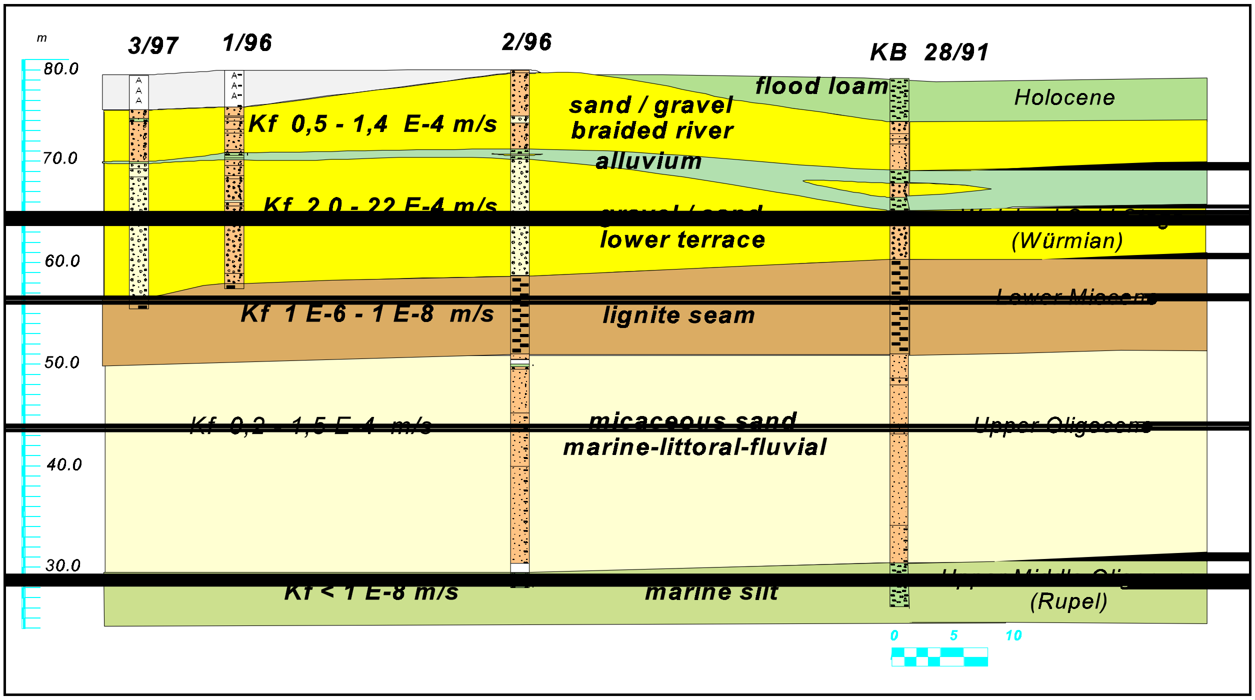


Figure 1. Geological section (E–W) at the experimental site in the Bitterfeld area

Given this background, Bitterfeld appears especially appropriate as the SAFIRA model location for developing methods and technologies for minimally invasive "passive" decontamination techniques for complexly polluted groundwater within a genuine scenario, as well as demonstrating their suitability in the field. The results of the feasibility study for the experimental site are compiled in [6]. Figure 1 contains a geological section of the area under investigation.

Pollution

Groundwater

Contamination of the groundwater with inorganic pollutants (*e.g.*, heavy metals, arsenic, *etc.*) has proved minor. The only noteworthy feature is the high levels of sulphate (up to 1,000 mg/l) and chloride (1,300 mg/l).

In order to characterize the organic pollution of the groundwater at the various water levels, several samples were examined from different levels. The "main components" of organic contamination were found to be chlorobenzene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, benzene, trichloroethene, cis-1,2-dichloroethene and trans-1,2-dichloroethene. Mass-spectrometry screening also detected other substances, albeit in very low concentrations.

Although high organic pollution with halogenated hydrocarbons was confirmed in both the upper and lower aquifers, contamination considerably varied between the two in terms of both quality and quantity. The lower aquifer is dominated by aliphatic chlorinated hydrocarbons (trans-1,2-DCE, cis-1,2-DCE and TCE), while the main component of the upper aquifer is chlorobenzene. During depth-oriented sampling, contamination was found to display significant stratification: whereas the sample from a depth of 7-8 m only contains very low amounts of pollutants, samples from depths between 16 and 20 m were above all found to contain high levels of chlorobenzene (8-51 mg/l), as well as substantial concentrations of dichlorobenzenes (up to 1 mg/l).

Solid samples from the cores

In addition to the water samples, core material was also examined. The core samples from bore Saf Bit 2/96 were subjected to headspace-screening over the entire profile between 0 and 48.5 m. The relative sensitivities, which are proportional to the concentration of the substances in the sample, are summarized in Figure 2, showing clearly the influence of the lignite seam on the contaminant distribution.

One striking aspect is that the aliphatic halogen hydrocarbons and benzene chiefly occur in the strata between 19.5 m and 24.5 m, while chlorobenzene and the dichlorobenzenes are found in higher concentrations in the strata between 12 m and 22.65 m. The main components are trans-1,2-dichloroethene, cis-1,2-dichloroethene, chlorobenzene, trichloroethene, and benzene. Bromobenzenes and perchloroethene were also identified by mass spectrometry.

Investigations into the adsorption and desorption of the pollutants in coal samples revealed that the sorption capacity of the coal has not yet been exhausted. Hence the coal can act as both a pollutant sink (high concentrations in the groundwater) and a pollutant source (lower concentrations of the pollutants in the groundwater).

Laboratory Experiments on Pollutant Decomposition

Bioremediation

The basic requirements for deciding whether microbiological *in situ* remediation techniques can in principle be used, selecting the most suitable technique and assessing the prospects of success are as follows:

- Determining the microbial density.
- Determining the pollutant breakdown capacity of the autochthonous microbial biocenoses under *in situ* conditions.
- Examining ways of boosting the breakdown capacities of autochthonous microbial biocenoses *in situ* using technically and financially feasible measures.
- Determining the microbial density.
- Determining the pollutant breakdown capacity of the autochthonous microbial biocenoses under *in situ* conditions.

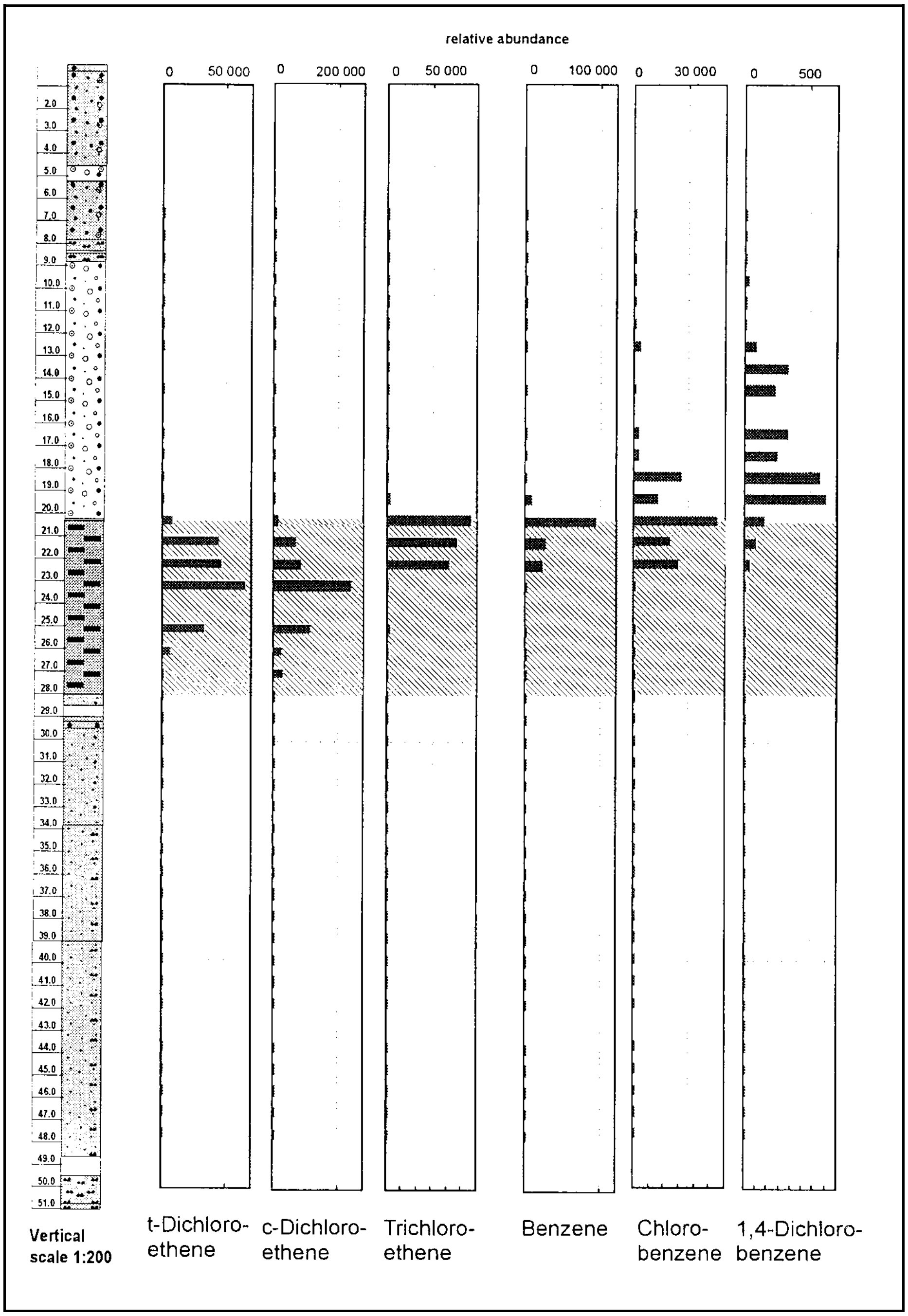


Figure 2. Contaminant profile, core 2/96

- Examining ways of boosting the breakdown capacities of autochthonous microbial biocenoses *in situ* using technically and financially feasible measures.

In addition to the pollutant level, the aquifers at the location are characterized as microbial habitats by certain combinations of microbe-ecologically relevant abiotic milieu factors. The quaternary aquifer has a lack of oxygen. Sulphate and nitrate are present as potential electron acceptors for anaerobic processes. The pH levels are around 7 and the temperatures about 13°C, only varying slightly along the depth profile.

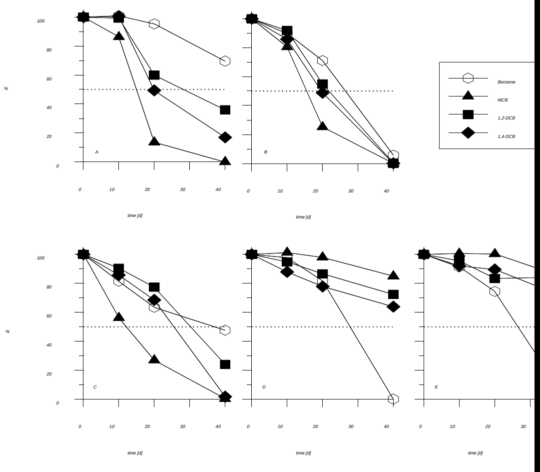
The groundwater and aquifers are inhabited by bacteria down to the maximum drilling depth (50.5 m below the surface). Nitrate, iron, and manganese reducing bacteria predominate in the autochthonous biocenoses.

As expected, a lack of yeasts and mycelium-forming fungi was found in most habitats; a tiny abundance ($<5\times10^2$ g^{-1}) was only detected in the coal-bearing strata, individual horizons of the quaternary aquifers (6, 16–17 and 19–21 m) and the tertiary aquifer at 48 m.

The pollutants found to be the main contaminants in the quaternary aquifer were selected for investigations into microbiological breakdown. These were monochloro-benzene (MCB, 30 mg/l), 1,2-dichlorobenzene (1,2-DCB, 10 mg/l) and 1,4-dichlorobenzene (1,4-DCB, 10 mg/l). Benzene (100 mg/l) was also included in the investigation as the expected product of the chemically catalyzed dehalogenation of chlorobenzenes.

The three primary pollutants MCB, 1,2- and 1,4-DCB (as well as benzene) were removed from the autochthonous bacteriocenoses under simulated *in situ* conditions within technologically relevant periods of times. However, the extent and speed of removal significantly differed depending on the pollutants' chemical structure, the metabolism type of the ecophysiological groups involved, and the availability of electron acceptors and additional carbon substrates (Figure 3).

Of the three chloroaromatics, 1,2-DCB easily proved to be the hardest compound to break down; in fact under anaerobic conditions no decomposition whatsoever was established without the availability of additional carbon substrates. After adding non-resident carbon substrates (a mixture of acetate and lactate), the 1,2-DCB was however almost completely removed after just 20 days under nitrate, sulphate and iron reducing conditions. When using these approaches, the other pollutants were no longer detectable either by this time.



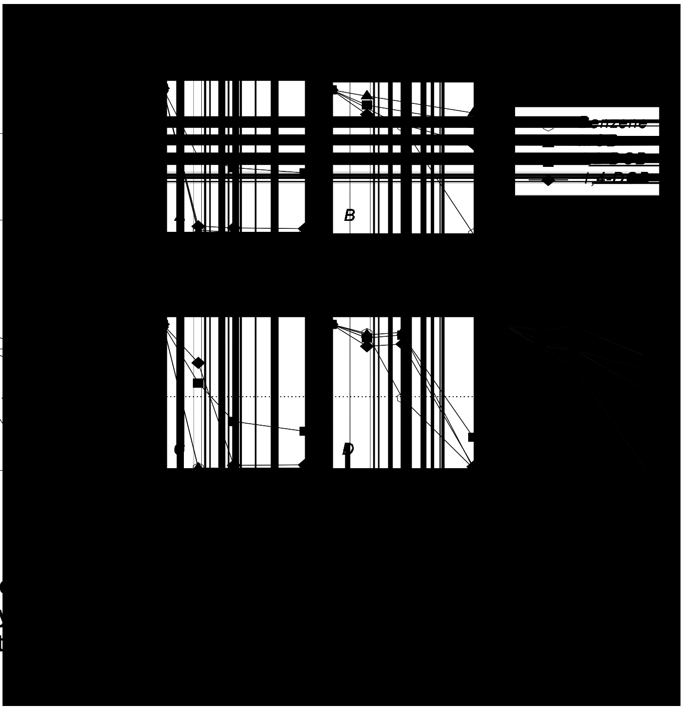


Figure 3. Decomposition of chlorobenzenes and b
by autochthonous bacteria groups in the boundary
of the quaternary aquifer and coal (19-23 m beneat
surface)

Figure 3. a) Without the addition of substrates (A aerobic; B-E anaerobic; B without additional electron acceptors; C nitrate; D sulfate; E hydrated iron oxide)

b) With the addition of substrates (lactate, acetate, yeast extract, ammonium, and phosphate); A-E

Under aerobic conditions, 1,2-DCB was in all experiments only broken down very slowly (if at all). The residual concentrations found after an incubation time of 40 days were usually 40 – 50 %, and in just one case about 30% of the initial concentration - thus on the whole they were only slightly below the residual concentration of 50 % defined as the evaluation limit for biological removal.

Assuming sufficient quantities of terminal electron acceptors and carbon substrates were available, the pollutants were, somewhat surprisingly, broken down relatively quickly in the anaerobic environment under nitrate-, sulphate-, and iron-reducing conditions.

The findings of the screening programme indicate that in principle the microbiological *in situ* remediation of the contaminated aquifers under the anaerobic conditions prevailing at the location is possible. Furthermore, the *in situ* removal capacities can be increased by stimulating autochthonous anaerobic groups via the addition of electron acceptors and usable carbon substrates.

Abiotic pollutant removal

Physical and chemical methods for pollutant reduction in the groundwater are grouped together within the SAFIRA Project under the term abiotic techniques. Starting from the familiar process of dehalogenating aliphatic chlorinated hydrocarbons with Fe° walls, new methods were sought that above all enable the removal of chloroaromatics and are suitable as *in situ* techniques. Initial approaches are seen in electrochemical techniques, sonochemical methods and bimetal systems. In addition, the usage of activated carbon adsorption was tested, which could in particular be interesting as an *in situ* method if the residence times were extended by microbial inhabitation. The goal of the preliminary study was to assess the possibilities of such methods and to find new approaches. In the following, the findings of electrochemical removal are presented by way of example; it should be pointed out that other approaches also yielded very promising results.

A distinction was made between two different techniques for electrochemical dechlorination: systems using palladium as a catalyst for hydrogen activation and those without palladium. The former represent the current state of research, whereas the latter have not previously been described for chlorobenzene degradation.

Pd was either precipitated electrochemically on the carbon cathode or mixed with the cathode material as a carrier catalyst (*e.g.*, 5% Pd on activated carbon). The main difference between the two methods is that in the first case the Pd is on the electrode potential, whereas in the second it is not conductively linked to the electrode.

In both methods, water electrolysis produces molecular hydrogen, which is activated at the surface of the Pd. The concentration of chlorobenzene in the electrolytes (Bitterfeld groundwater) in these experiments was 50–150 ppm. In many cases, chlorobenzene was completely removed. Figure 4 shows a typical course of concentration over time for a mixture of mono-, di-, and trichlorobenzenes. The constancy of the chlorobenzene concentrations was measured up to 450 hours in order to record sorption and other losses. After starting water electrolysis, the chlorobenzenes were mostly removed within about 50 hours. The regular arrows indicate the renewed addition of the chlorobenzene mixture; the jagged arrows mark the beginning of electrolysis. This sequence can be repeated several times without a drop in activity. The only reaction products found were benzene and chloride (>90% of the converted chlorobenzenes). Similar results were obtained when Pd on different carriers (activated carbon, soot) was freely suspended as a powder in the groundwater.

Scaling Up

By now, the main site-specific investigations have been completed. The location has been found to be suitable and the fundamental mechanisms for removing the “pollutant cocktail” are known. The investigations still underway are mainly designed to refine the data basis for hydraulic and matter transport modeling, and to test and optimize additional removal techniques. Moreover, the technical principles for structural planning are being worked out.

The next stage is to scale up the experiments carried out so far in the laboratory. For this purpose a mobile decontamination unit has been designed as a “window in the aquifer”. Groundwater from a depth of about 20 m is pumped into a storage tank without coming into contact with oxygen from the air. This polluted water will then be used to charge five possible test columns with the physico-chemical conditions of the aquifer being preserved (T = 13°C, pH = 7, eH = -250 mV, χ = 2.5 mS/cm, AOX ≅ 100 mg/l).

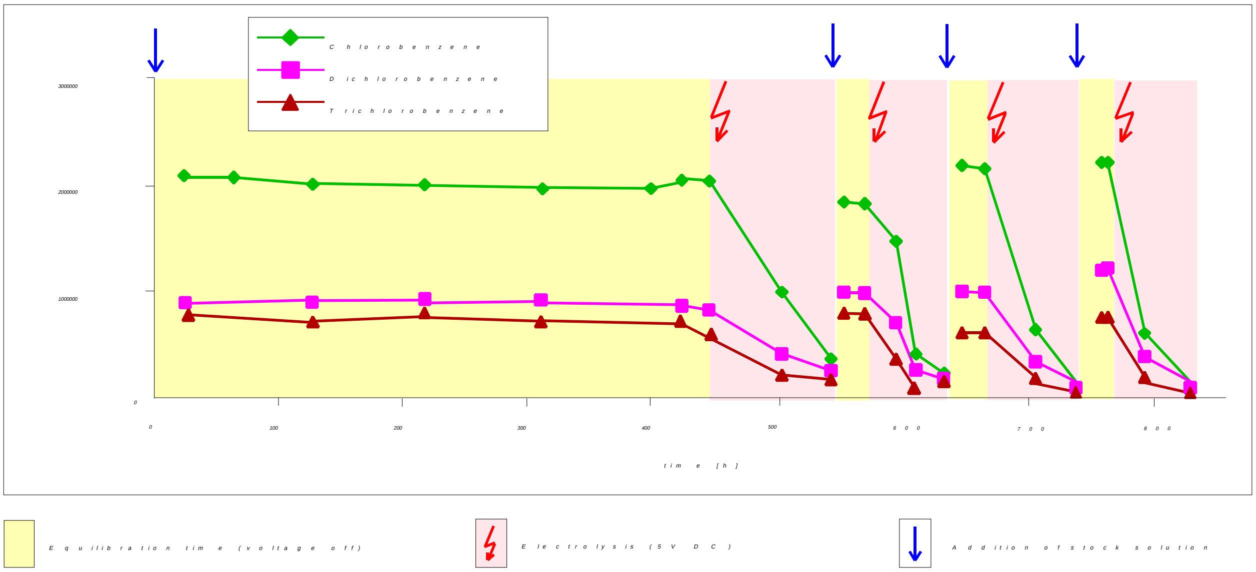


Figure 4. Reductive dechlorination of mono-, di- and trichlorobenzenes (c_0 = 100 ppm MCB, 30 ppm DCB and 10 ppm TCB) on Pd (5 wt-% on 15 mg activated carbon) with hydrogen produced by electrolysis (cathode: 150 mg electrographite, U = 5 V, I = 2 mA, electrolyte: 150 ml groundwater).

The methods tested successfully in the laboratory and in the mobile decontamination unit have to prove their chemical and hydrological long term stability and will be optimized in a pilot plant. Several vertical, experimental columns (up to 3 m in diameter) will be installed to a depth of 20 m directly into the aquifer. Numerous sampling and process controlling facilities and a variable design of the reaction columns will enable the analyses of relevant chemical and hydraulic processes during operation and a competitive technology development under real-world conditions. Operation of the pilot plant will start by the end of this year. Subsequently an extension of the pilot plant for a horizontal groundwater flow is intended.

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Discussion

Kahraman Ünlü asked whether the removal of iron chloride is a concern. Weiss noted that lowering chloride concentrations is not feasible due to the presence of underground brine.

Weiss was asked if he considered using iron to produce hydrogen because it is cheaper than producing it electrolytically. Weiss indicated the oxygen that is produced in the electrolytical reaction can be used for aerobic reactions.

One of Weiss's photographs showed gas bubbles being produced at the water surface during the reaction, which were identified as methane and nitrogen.

Summary and Conclusions

Harald Burmeier

Construction of Treatment Walls

The costs of pilot studies and field studies should be considered when computing the costs of implementing a technology. The costs presented for the funnel-and-gate technology only reflect the materials (iron) and construction. Field demonstrations are not conducted very frequently anymore; in most cases, laboratory studies suffice. At approximately 90 percent of the North American sites for which treatment walls, TCE or PCB is the primary contaminant; with few exceptions, the half-lives fall within a narrow range (30 minutes to 1 hour). Therefore, it becomes difficult to justify field tests as cost-effective.

Eberhard Beitinger recently performed field tests with two columns of activated carbon at a site with several types of contaminants. The columns were installed on site to model actual conditions. The results of the column tests were very encouraging; the performance time of the wall would be higher than had been expected. The minimum time designed for the wall was 30 years for the first removal of reactive materials. A 50-m continuous wall will be installed with impermeable "wings."

Although residence times to degrade chlorinated solvents are generally known, geological and hydrogeological characterization is needed for any treatment approach. Furthermore, information on the plume's location and where it is moving is also necessary. If this information is well understood, design costs can be lowered.

Harry Whittaker doubted that chromium can be removed permanently with an iron treatment wall because iron becomes very finely divided ferric oxide in the environment, especially in wet soils. He suggested that there is a continuous long-term cycle of Fe^{2+}, Fe^{3+}, Fe°, and Cr^{3+} and Cr^{6+}. Once all of the iron is converted to Fe^{3+}, the chromium that was retained by the treatment wall will be released. Wolfgang Wüst added that he has seen this occur in column tests.

Bob Puls said that the state environmental agency in North Carolina had to be convinced that chromate would not be released eventually from the permeable reactive barrier (PRB) at Elizabeth City. Originally, natural attenuation of the chromate was examined. There was a natural reduction of chromate observed (primarily due to the high organic carbon content of the surface soils), and the chromate was immobilized in a chromium and iron hydroxide phase. Researchers had to prove to the regulatory authority that the iron would not reoxidize the Cr^{3+} to Cr^{6+}. The only oxidant in natural soil strong enough to oxidize chromium is manganese oxide. As a result, they analyzed the manganese oxide content of the soil and groundwater to prove that whatever immobilization method was occurring would not reverse itself. The PRB was not considered a permanent remedy for the chromate plume, and they are looking into eliminating the chromate source.

Harald Burmeier said that long-term aspects of installing treatment walls must be considered during the feasibility study. For example, the construction of the wall should be approached so that the reactive media can be removed and replaced as necessary. Although it may be relatively inexpensive to construct a treatment wall, the need to remove it 30 years in the future must be considered in cost estimates.

Paul Bardos asked if there is any true distinction between permeable reactive barriers and treatment walls. Burmeier explained that permeable reactive barriers are a type of treatment wall that uses a material that is permeable and reactive to treat the groundwater. Treatment walls can also be partially permeable and treat groundwater using adsorptive, biological, or electrochemical processes. In addition to treatment wall construction, treatment barriers can be constructed as piles, drainage trenches, and funnel and gate systems.

There was additional discussion on the issue of patents for treatment walls. To the extent that EnviroMetal Technologies has a worldwide patent on the emplacement of iron in the ground for remediation of chlorinated organic solvents, there may be cases where researchers are not adhering to the patent restrictions. Hermann Schad indicated that the funnel-and-gate patent applies to situations where groundwater flow is diverted toward the treatment wall. This design is protected in Germany and several other countries in the European Union. Schad noted that funnel-and-gate systems are advantageous when intending to use a material to react with or absorb a contaminant. The continuous walls, however, have hydraulic advantages.

In response to a question regarding treatment walls that do not work as designed, Burmeier acknowledged that the examples presented in the session emphasized successes rather than failures. However, he emphasized that reactive materials must be tested prior to emplacement. He added that when building a wall over 10 to 20 m deep, technologies must be matched to the permeability of the subsurface as well. Gillham was aware of at least three cases in the United States where regulators required a contingency for the installation of a reactive barrier. He added that in any case, an alternative treatment method is almost always proposed along with the reactive barrier.

Walt Kovalick emphasized that the cost savings of using PRBs instead of pump-and-treat systems is significant. He suggested that 10 to 20 percent of the pump-and-treat systems currently active in the United States could benefit from the installation of PRBs. The issue of contingencies was insignificant from a cost standpoint because the cost of a typical wall (US$400 thousand) is significantly less than a pump-and-treat system (US$12-14 million). Therefore, the cost of research and development is also justified.

Reactive Materials, Full-Scale Projects, and General Conclusions

Harald Burmeier summarized the topics discussed and the questions on treatment walls that still remain to be answered. He pointed out that the Special Session presentations have examined the reaction, absorption, and degradation processes of treatment walls, but noted that combinations of processes are also being considered.

Several issues need closer examination, such as how to estimate and influence the long-term performance of treatment wall; determination of by-products of organic contaminant degradation; the cost of materials (*e.g.*, the range in costs and corresponding effectiveness of zero-valent irons); calculation of mass balances; the determination of what reactive substances can be placed in the groundwater without risk; and how to influence biological processes in combination with treatment walls.

The presentations showed that zero-valent iron can be used to degrade chlorinated solvents and adsorb uranium, but the nature and toxicity of the adsorbed uranium still must be determined. Clearer explanations are needed from scientists on how to evaluate degradation and sorption processes. Optimization of reactive materials using bench-scale tests have frequently been replaced by laboratory tests followed by trial-and-error field testing. Further research on bioscreens is needed to determine long-term effects on remediation as well as possible limiting factors such as bioclogging, redox limitations, and concentrations or combinations of contaminants. There are questions beyond technological solution, that cross into regulatory, legal, and public policy, such as what concentration of a contaminant is harmless? Can reactive materials be emplaced in the groundwater, and at what concentrations? What is the long-term implication of *in situ* chemical engineering, including any production of toxic by-products?

From the standpoint of constructing treatment walls, good definitions of terms such as “permeable reactive barriers” and “treatment walls” must be developed. Although it is now possible to excavate and install deep walls, the cost effectiveness of such constructions should be evaluated in order to access the market.

In conclusion, treatment wall technology has been proven to work; however, there are some limitations to its use. Several questions still must be answered before their use can become widespread.

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Robert Gillham has been a professor in the Department of Earth Sciences at the University of Waterloo since the early 1970s. He was Director of the Waterloo Centre for Groundwater Research from 1987 to 1992, was Chair of the Earth Sciences Department from 1993 to 1997, and currently holds the NSERC/Motorola/ETI Industrial Research Chair in Groundwater Remediation. In 1997 Dr. Gillham was elected a Fellow of the Royal Society of Canada. Dr. Gillham's primary research areas concern contaminant transport in groundwater systems and groundwater remediation.

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Stephan Jefferis (M.A., M.Eng., M.Sc., Ph.D., C.Eng., M.I.C.E., C.Geo.l, F.G.S.) has qualifications in natural sciences, chemical engineering, civil engineering, and law. He spent 20 years, with the University of London (UK) where his research group developed a class of cement-bentonite cut-off materials that has been used at many contaminated sites in Europe. Dr. Jefferis is presently an associate of Golder Associates, where his role is world-wide and typically involves the investigation and resolution of unusual geotechnical, geoenvironmental and materials problems often associated with aggressive chemical and microbiological processes in the ground. He is also a visiting professor in the Department of Civil Engineering, Imperial College, London.

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