Treatment Walls

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FOREWORD

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ACKNOWLEDGMENTS

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ABBREVIATIONS

AFB	Air Force Base
ASF	Anderson-Schultz-Flory
CFC	chloro fluoro carbon
DBCP	1,2-dibromo-3-chloropropane
DCA	1,1-dichloroethane
1,2-DCB	1,2-dichlorobenzene
1,2-DCE	1,2-dichloroethylene
DO	dissolved oxygen
EPA	Environmental Protection Agency
HDPE	High Density Polyethylene
HDTMA	hexadecyltrimethylammonium
MEK	methyl ethyl ketone
O&M	operation and maintenance
PCBs	polychlorinated biphenyls
PCE	tetrachloroethylene
PCP	pentachlorophenol
TCA	1,1,1-trichloroethane
TCE	trichloroethylene
TCP	1,2,3-trichloropropane
THM	trihalomethane
UMTRA	Uranium Mill Tailing Remedial Action
VC	vinyl chloride
VOCs	volatile organic compounds

1.0 SUMMARY

Development of treatment wall technology for the clean up of contaminated ground-water resources has expanded in the past few years. The main perceived advantage of this technology over *ex situ* and other *in situ* ground-water remediation approaches is reduced operation and maintenance costs. Since the first commercial application of zero-valent iron using a funnel-and-gate system for the removal of chlorinated hydrocarbons in February, 1995, several field- and pilot-scale studies are evaluating the feasibility of this technology for treatment of both organic and inorganic contaminants as indicated in the following summary.

1996 Status of Treatment Wall Technology

CONTAMINANT	BARRIER TYPE	REACTIVE MEDIA	STATUS
Organics - DCE, TCE, PCE - BTEX - nitrobenzene - DCA, TCA - PCBs, PAHs	Degradation	zero-valent iron iron(II) porphyrins resting-state microorganisms oxygen-releasing compound dithionite	commercial laboratory field field field
	Sorption	zeolite surfactant modified silicates organobentonites activated carbon	laboratory laboratory laboratory laboratory

Inorganics
- heavy metals
  (Ni, Pb, Cd, Cr, V, Hg)
- radioactive
  (U, Ra, Sr, Cs, Tc)
- nitrate
	Sorption	peat
		ferric oxyhydroxide
		bentonite
		zeolites and modified zeolites
		chitosan beads
			laboratory
			field
			laboratory
			laboratory
			laboratory

	Precipitation	hydroxyapatite zero-valent iron dithionite lime or limestone	laboratory commercial field commercial
	Degradation	saw dust	field

Although, considerable design details have already been developed through field- and pilot-scale applications of this technology, some critical issues (e.g., establishing tested and proven design procedures, improving construction technologies, documenting long-term performance, and evaluating synergy with other ground-water remediation technologies) still remain to be resolved. Currently planned field-scale tests and many ongoing laboratory studies are designed to address these issues and facilitate wider implementation of this technology.

2. 0 TECHNOLOGY DESCRIPTION

Treatment walls involve construction of permanent, semi-permanent, or replaceable units across the flow path of a contaminant plume. As the contaminated groundwater moves passively through the treatment wall, the contaminants are removed by physical, chemical and/or biological processes, including precipitation, sorption, oxidation/reduction, fixation, or degradation. These mechanically simple barriers may contain metal-based catalysts, chelating agents, nutrients and oxygen, or other agents that are placed either in the path of the plumes to prevent further migration or immediately downgradient of the contaminant source to prevent plume formation (Figure 1). The reactions that take place in such systems depend on a number of parameters such as pH, oxidation/reduction potential, concentrations, and kinetics. Therefore, successful application of this technology requires a sufficient characterization of contaminants, ground-water flow regime and subsurface geology.
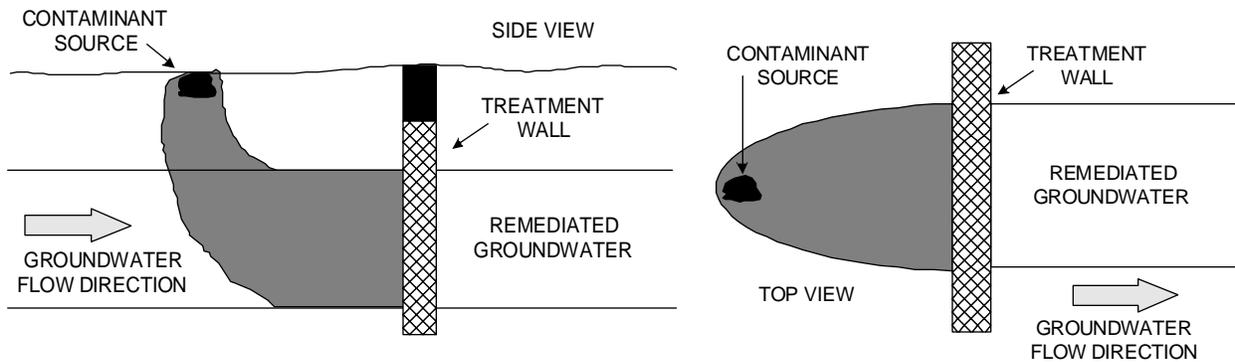
Figure 1. Schematic of a Simple Treatment Wall System

Permeable reactive walls potentially have several advantages over conventional pump-and-treat methods for ground-water remediation. Reactive walls can degrade or immobilize contaminants *in situ* without any need to bring them up to the surface. They also do not require continuous input of energy, because a natural gradient of ground-water flow is used to carry contaminants through the reaction zone. Only periodic replacement or rejuvenation of the reaction medium might be required after its capacity is exhausted or it is clogged by precipitants and/or microorganisms. Furthermore, technical and regulatory problems related to ultimate discharge requirements of effluents from pump-and-treat systems are avoided with this technology.

The key issues associated with the application of treatment walls are discussed below.

2.1   SITE CHARACTERIZATION

Site characterization is the first step in assessing the potential applicability of treatment wall technology for ground-water remediation, and involves hydrological, geological, and geochemical description of the site and contaminant properties and distribution.

Hydrogeologic modeling and monitoring of the site define the basic dimensions of the contaminant plume, direction of the plume movement, and most appropriate location for the treatment wall. Site geologic characterization includes lithology, stratigraphy, grain size distribution and structural relationships, and should be documented in a set of geologic cross sections for the wall location. Hydrologic characterization of the site should include aquifer/aquitard boundaries, hydraulic conductivity, and ground-water gradient and flow direction.

Spatial distribution of the contaminant as well as its properties (solubility, vapor pressure, specific density, partitioning, etc.) and chemical relationship to site geology should be determined using literature information and analytical testing of soil and ground-water samples collected during site investigations.

Many of the above-mentioned parameters are difficult to determine with certainty which results in considerable variation in the level of contaminant mass flux. Therefore, treatment wall design must account for this inherent variability by incorporating features or safety factors capable of compensating for uncertainty.

2.2   TREATMENT WALL DESIGN

Major issues associate with the design of a treatment wall include the selection of the reactive media (chemical makeup, particle size distribution, proportion and composition of admixtures, etc.), residence time in the reaction zone, and the reaction zone size for appropriate life span, as well as addressing issues like the effect of the reaction zone medium on ground-water quality and the ultimate fate or disposition of a treatment wall.

Selection of the reactive media is based on the type (i.e., organic vs. inorganic) and concentration of ground-water contaminants to be treated, ground-water flow velocity and water quality parameters, and the available reaction mechanisms for the removal of contaminants (i.e., sorption, precipitation, and degradation). Tables 1 and 2 in Section 4 provide useful information for the initial selection and effectiveness of various reactive media for different contaminants.

Typically, treatment wall system design is based on the results of treatability studies that can incorporate both batch reaction tests and laboratory- or field-scale column experiments. Batch tests are intended to obtain initial measures of media reactivity (i.e., degradation half life, sorption kinetics and capacity, etc.) that form the basis of the reactor design. Alternatively, literature information can be utilized to asses the initial information about media reactivity (e.g., Johnson, *et al*., 1996 provide a comprehensive review of the kinetic data obtained for zero-valent iron degradation of halogenated hydrocarbons). Column tests are typically conducted by packing a column with the reactive medium and passing the contaminated groundwater through the column until steady-state performance of the reactor is obtained. Flow velocities are adjusted to simulate ground-water velocity and reactor residence time. In addition, information about geochemical reactions between the contaminated groundwater and the reactive medium as well as the impact of the treatment wall on ground-water quality can be assessed from these studies. Information about several batch and column studies can be found in Sections 3.1.2 and 3.2.2.

Life span of sorption and precipitation barriers is limited by the ultimate capacity of the medium to facilitate appropriate removal reactions. Once the ultimate capacity of the medium is exhausted, contaminant breakthrough will occur. In addition, contaminant release or resolubilization may occur

after the plume or reactive medium is expanded. In the case of sorption and precipitation barriers for treatment of radioactive contaminants (i.e., Sr, U), an important issue is the possibility of exceeding the limits for Class A low-level nuclear waste as a result of excessive accumulation of these materials on the surface of the reactive medium. This might mean that the wall would have to be replaced at that time, regardless of the fact that the ultimate capacity of the medium might not be exhausted, because low-level nuclear waste above Class A must be solidified/stabilized. Alternatively, it might be possible to rejuvenate the media by *in situ* leaching methods. These issues are generally not of concern for the treatment walls designed for contaminant degradation.

2.3   INSTALLATION AND CONSTRUCTION

Several methods have been conceived for the installation of permeable treatment walls (MSE, 1996). Most experience with installation of these walls pertains to relatively shallow emplacements (less than 10 m) using standard geotechnical design and construction approaches, although a few technologies for deeper installations have been identified.

In the simplest case, a trench of the appropriate width can be excavated to intercept the contaminated strata and backfilled with reactive material (Figure 2). This method would normally be limited to shallow depths in stable geologic materials. More often, steps like shoring of the trench and use of an appropriate slurry or steel sheet piling are required for excavation to greater depths. Unlike conventional construction approaches for ground-water cutoff walls that utilize a soil-bentonite slurry (or cement or cement-bentonite slurry), installation of permeable treatment walls requires use of biodegradable polymers instead of bentonite or cement to avoid the problems of plugging the wall with residual slurry material.
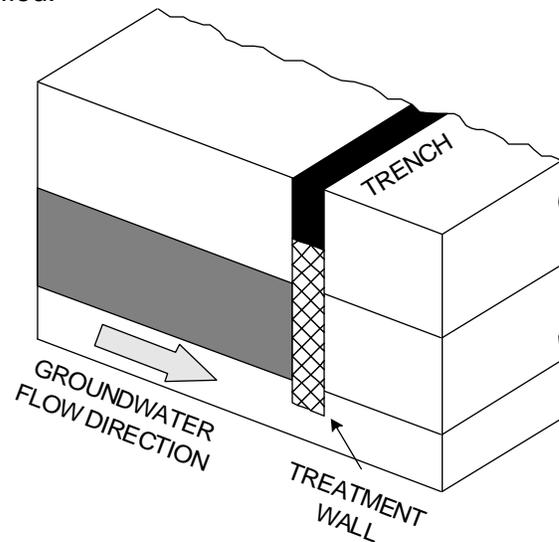
Figure 2. Treatment Wall in a Trench

Frequent criticism that the life expectancy of the reactive media in a treatment wall may degrade with time has been addressed by developing a construction approach whereby the reactive media is placed in the subsurface in removable cassettes (MSE, 1996). A temporary sheet pile box or a large diameter caisson is installed into the subsurface and the screen panels are placed on the up- and downgradient side, while impermeable panels are placed on the lateral sides. Steel rail guides for the cassettes are installed within this interior compartment and the temporary sheet piles or caisson are removed. The cassette is a steel frame box (2.5-m long, 1.5-m wide and 0.5-m thick) with two opposing screened sides and two impermeable sides which is filled with the reactive media and lowered into the cavity. By allowing replacement of cassettes with depleted reactive media, the full-scale remediation system operation life can be extended nearly indefinitely.

Specialized trenching methods require the use of trenching machines that have been developed for installing underground utilities and constructing french drains and interceptor trenches. The most widely available utility trenching machines have depth capability of less than 7 m, while some specialized machines used for interceptor well construction can excavate up to 8-10 m.

These machines incorporate a mechanism to temporarily shore the trench behind the cutter in a more or less continuous operation until the drain pipe and backfill are placed. Excavation rates on the order of 0.3 m of trench per minute to a depth of 7 m achieved with these specialized machines may lower the cost of treatment wall installation.

Soil mixing processes that are commercially used in solidification and stabilization of soils and sludges rely on soil augers to drill into the soil and inject and mix reagents. Commercially available equipment can penetrate soils up to 12 m with 2.5 to 3.5-m diameter augers, or up to 45 m in soils with a 1-m diameter auger, and has been used to form soil-cement ground-water cutoff walls by augering in an overlapping, offset pattern. The particular advantage of this method compared to traditional excavation approaches is that there is no need for handling of the excavated material as possible hazardous waste. Other specialized technologies like jet grouting, mandrel-based emplacement, and vibrating beam technology also have the potential to be adopted for continuous treatment wall installation.

Creation of treatment zones in place of treatment walls, that are confined within strict boundaries, can be accomplished with injection wells (Figure 3) or by hydraulic fracturing. Well systems typically involve injection of fluids or fluid/particulate mixtures for distribution into a treatment zone within the target area of the aquifer. Potential advantages of this approach are that there is no need to construct a trench and possible aquifer access at greater depths. However, there is a question of reliability of injection for creating homogeneous treatment zones. Horizontal hydraulic fracturing is capable of creating propped fractures generally less than 2.5-cm thick and 7 to 12 m in diameter that can be filled with reactive material. However, this technology is

Figure 3. Injected Treatment Zone

typically used at shallower depths (3 to 12 m), and there is no current record of a field application to treatment zones. On the other hand, depending on the soil type, vertical hydrofracturing (MSE, 1996) can create fractures up to 20-cm wide, which may be suitable for treatment wall applications.

The funnel-and-gate system for *in situ* treatment of contaminated plumes consists of low hydraulic conductivity (e.g., 1×10^{-6} cm/s) cutoff walls with gaps that contain *in situ* reaction zones (Figure 4). Cutoff walls (the funnel) modify flow patterns so that groundwater primarily flows through high conductivity gaps (the gates). The type of cutoff walls most likely to be used in the current practice are slurry walls, sheet piles, or soil admixtures applied by soil mixing or jet grouting. Starr and Cherry (1994) provide a comprehensive modeling study of various alternative funnel-and-gate systems and guidance for optimizing the design of such systems.
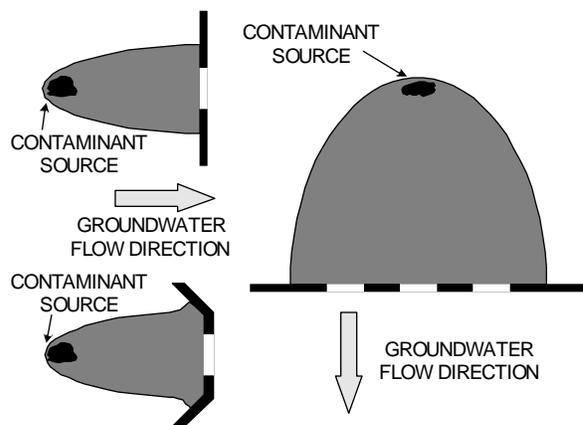
Figure 4. Funnel-and-Gate Systems

2.4   MONITORING REQUIREMENTS

Although it is desirable to preserve the utility of the property at which a ground-water remediation project is being conducted, which is one of the main potential advantages of permeable treatment walls installed below ground level, careful performance monitoring is required during the operation of both pilot- and full-scale systems. Parameters requiring monitoring to assess performance include:

- contaminant concentration and distribution;
- presence of possible by-products and reaction intermediates;
- ground-water velocity and pressure levels;
- permeability assessment of the reactive barrier;
- ground-water quality parameters (e.g., pH, redox potential, alkalinity); and
- dissolved gas (e.g., oxygen, hydrogen, carbon dioxide) concentrations.

Monitoring wells would have to be installed on both sides (upgradient and downgradient) of the treatment zone in order to obtain information about the long-term performance of the technology. In addition, several monitoring methods (i.e., tracer, nuclear, and electromagnetic) are being developed to evaluate the existence, size, and location of breaches in a subsurface barrier as well as to monitor the barrier longevity (MSE, 1995).

3.0 PERFORMANCE

3.1   TREATMENT WALLS FOR ORGANIC COMPOUNDS

3.1.1   Commercial Applications and Field-Scale Studies

1.   Sunnyvale, CA

Participants: Geomatrix Consultants, Inc.; EnviroMetal Technologies, Inc.; Intersil, Inc.

Demonstration date: Wall constructed in February, 1995

Compounds treated: TCE, *cis*-1,2-DCE, VC, CFC-113

Treatment summary: The main contaminants resulting from the semiconductor manufacturing process are trichloroethylene (TCE) (0.05 - 0.2 mg/L), cis-1,2-dichloroethylene (*cis*-1,2-DCE) (0.45 - 1.0 mg/L), vinyl chloride (VC) (0.1 - 0.5 mg/L), and CFC-113 (0.02 - 0.06 mg/L). The treatment wall system consists of a 75-m slurry wall on either side of 12-m long, 1.2-m wide, and 6-m deep permeable wall that is charged with 100% granular iron (i.e., no sand mixture) to a total depth of about 3.5 m. Total construction and reactive media costs were $720,000. Ground-water velocity through the wall is approximately 30 cm/day, which provides a residence time of 4 days. Ground-water samples collected from performance monitoring wells within the wall showed no volatile organic compounds (VOCs) above the detection limit of 0.5 µg/L.

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References:

Yamane, C.L., Warner, S.D., Gallinati, J.D., Szerdy, F.S., Delfino, T.A., Hankins, D.A., Vogan, J.L. (1995) "Installation of a Subsurface Groundwater Treatment Wall Composed of Granular Zero-Valent Iron." Proceedings of 209th ACS National Meeting, Anaheim, CA, April 2-7, 792-795.

Shoemaker, S.H., Greiner, J.F., and Gillham, R.W. (1996), in Assessment of Barrier Containment Technologies: A Comprehensive Treatment for Environmental Remediation Applications, R.R. Rumer and J.K. Mitchell, Eds., Chapter 11: Permeable Reactive Barriers, report prepared for US DOE, US EPA, and DuPont Company.

2. Moffet Federal Airfield, CA

Participants: Department of the Navy; PRC Environmental Management, Inc.

Demonstration date: Wall installed in March, 1996

Compounds treated: TCE, PCE

Treatment summary: The wall consists of two wing walls, 6.5 m long, constructed of interlocking sheet piles which channel the groundwater into a 3.2-m wide, 3.2-m thick, and 8.2-m deep reaction cell. There is 0.6 m of concrete beneath the wall to prevent ground-water infiltration from below. Groundwater flowing into the wall encounters 0.6 m of pea gravel, 2 m of 100% granular iron and another 0.6 m of pea gravel. Pea gravel was used to ensure adequate distribution of groundwater, because there are sand channels in the area. Preliminary estimates place the cost of the wall at approximately $300,000. Ground-water quality sampling was performed in June, 1996 and indicated that the influent TCE concentration of 850 - 1180 μg/L was degraded to 3 - 320 μg/L within 0.3 m into the iron wall, and to 11 - 36 μg/L within 1.3 m into the wall. Samples taken from the downgradient pea gravel section of the wall indicated TCE concentrations of 16 - 45 μg/L, which were assumed to be residual TCE contamination within the pea gravel remaining from the wall installation. Although there was no VC in the influent groundwater, 3 μg/L was detected 0.3 m into the iron wall, while no VC was detected within 0.6 m of the iron wall.

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3. Coffeyville, KS

Participants: SECOR International, Inc.

Demonstration date: Wall constructed in January, 1996

Compounds treated: PCE, TCE, TCA, 1,2-DCE

Treatment summary: Site investigation and remediation are being driven by the RCRA Corrective Action process under the authority of EPA Region VII. Prior releases at this site have generated a dissolved plume approximately 800 m long containing TCE, PCE, TCA, and 1,2-DCE. Contaminant transport has occurred to the greatest lateral extent in a basal sand and gravel unit just above shale bedrock, which lies 9 m beneath the site. Because of nearby

public use of the shallow groundwater, EPA required implementation of interim corrective measures to prevent additional off-site migration of the dissolved plume. Installation of the funnel-and-gate was completed in January 1996, and consisted of a 150-m slurry wall on either side of 6-m long and 9-m deep gate (3.8-m vertical and 1-m flowthrough thickness of iron) containing 73 tons of zero-valent iron. Laboratory column studies, geotechnical testing, and ground-water modeling were conducted to support design and construction.

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4.   U.S. Coast Guard Air Station, Elizabeth City, NC

Participants: U.S. Coast Guard; Parsons Engineering Science; Industrial Marine Services; Horizontal Technologies

Demonstration date: Wall installation completed on June 22, 1996

Compounds treated: TCE (also, hexavalent chromium)

Treatment summary: A full-scale reactive iron wall (45-m long, 5.5-m deep, and 0.6-m wide) was installed in a matter of hours using a novel installation approach developed by Horizontal Technologies. Thickness of the wall was dictated by the presence of TCE in groundwater. The only problem during installation resulted from running sands undermining the concrete used in the wall. Preliminary estimates place the entire cost of the treatment wall (installation, iron fillings, contractor costs) at approximately $420,000. No results are available.

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5.   Borden, Ontario, Canada

Participants: University of Waterloo; EnviroMetal Technologies, Inc.

Demonstration date: Wall constructed in 1991

Compounds treated: TCE, PCE

Treatment summary: A treatment wall consisting of an iron-sand mixture was installed at Canadian Forces Base, Borden, Ontario approximately 5 m downgradient from the source of contaminant plume. The plume was about 2 m wide and 1 m thick, with maximum concentrations along the axis of about 250 mg/L of TCE and 43 mg/L of PCE. The wall was constructed using sealable joint sheet piling to a depth of about 10 m, with a total width of 1.5 m and length of 5.5 m (transverse to the flow). The reactive media backfill consisted of 22% by weight iron grindings collected from a local machine shop, and 78% concrete sand to ensure sufficient porosity of the wall. Ground-water flow velocity was about 10 cm/day, which provided a residence time in the wall of approximately 15 days. During the four-year monitoring period, the wall consistently removed 90% of TCE and 86% of PCE in the incoming water. The principal product detected at a monitoring point located downgradient of the wall was 1,2-DCE, with a maximum concentration of 0.2 mg/L. No vinyl chloride was detected in the treated groundwater. No visible precipitate formed on the surface of iron grindings, although losses of 185 mg/L and 82 mg/L of calcium and bicarbonate, respectively, were measured across the wall. Subsequent laboratory studies aimed at simulating the performance of the treatment wall revealed that a higher percentage of iron grindings in the wall might have resulted in complete removal of TCE and PCE across the wall.

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References:

Environmental Protection Agency (1995) In Situ Remediation Technology Status Report: Treatment Walls, United States Environmental Protection Agency, EPA542-K-94-004, Washington, DC.

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6.   U.S. Coast Guard Air Station, Elizabeth City, NC

Participants: U.S. EPA; ManTech Environmental Research Services

Demonstration date: Initiated in September, 1994

Compounds treated: TCE, 1,2-DCE (also, hexavalent chromium)

Treatment summary: Zero-valent iron has been evaluated for the removal of chromate through a treatment wall constructed from a series of large-diameter augered holes in a staggered 3-row array. Twenty one 20-cm columns were installed to a depth of 6.7 m throughout a 5.5 m^2 area. The mixed waste contaminant plume was between 4.2 and 6 m below the surface, and the water table ranged from 1.5 to 2 m below the surface. Columns were charged with a mixture of 50% iron filings (two types), 25% clean coarse sand and 25% aquifer material, to a depth between 3 and 8 m below the surface. Untreated groundwater contained a total concentration of TCE and DCE of about 6.5 mg/L that was reduced to about 1.5 mg/L in the treated water. Most of the reduction was due to a decrease in TCE concentration of about 75%, while 1,2-DCE showed almost no change. Dissolved iron in the groundwater increased from 0.05 mg/L to 1 - 20 mg/L, while dissolved oxygen decreased from 0.6 mg/L to 0.1 mg/L with a slight increase in alkalinity.

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References:

Powell, R.M., Puls, R.W., Hightower, S.H., and Sabatini, D.A. (1995) "Coupled Iron Corrosion and Chromate Reduction: Mechanisms for Subsurface Remediation." *Environ. Sci. Technol*., 29:8, 1913-1922.

Puls, R.W., Powell, R.M., and Paul, C.J. (1995) "In Situ Remediation of Ground Water Contaminated with Chromate and Chlorinated Solvents Using Zero-Valent Iron: A Field Study." Proceedings of the 209th ACS National Meeting, Anaheim, CA, April 2-7, 788-791.

7. Lowry Air Force Base, CO

Participants: Booz-Allen & Hamilton, Inc.; Versar, Inc.; Air Force Center for Environmental Excellence; Air Force Base Conversion Agency; Dames & Moore, Inc.

Demonstration date: Wall constructed in December, 1995

Compounds treated: TCE, *trans*- and *cis*-1,2-DCE, VC, 1,1-DCE, TCA, DCA, PCE

Treatment summary: A funnel-and-gate system consists of a 3.5-m wide and 1.6-m thick gate with 5-m long cutoff walls, oriented at a 45° upgradient angle, that were installed on each side of the reaction zone. Ground-water level is approximately 2.6 m below the surface, and the top of the weathered claystone bedrock confining layer is approximately 5.7 m below the

surface. The predominant contaminant in the incoming groundwater was TCE (source located 100 m upgradient from the wall location) at a concentration of 850 μg/L, while the average total concentration of all other chlorinated hydrocarbons (VC, 1,1-DCE, *trans-* and *cis*-1,2-DCE, 1,1,1-trichloroethane (TCA), 1,1-dichloroethane (DCA), 1,2-DCA, and PCE) was about 300 μg/L. Results during a six-month monitoring period indicate complete degradation of the chlorinated hydrocarbons within the first 0.3-m of the wall (9 hours residence time). Only *cis*-1,2-DCE was present at significant concentrations (10 μg/L) after 9 hours of residence time inside the wall, having the highest calculated half-life among all contaminants of 2.2. hours. By approximately 18 hours of residence time (0.6 m into the wall) all analytes had degraded to their respective analytical quantitation limits. Redox potential in groundwater dropped to about 500 mV while pH increased from 6.5 to 10.0 across the wall. Total alkalinity decreased rapidly with cross-sectional distance into the wall from about 550 mg/L to below 50 mg/L, while Fe^{+2} and Fe^{+3} were not detected at concentrations above 1 mg/L due to precipitation of iron salts. Cost analysis estimated a decrease in treatment costs from $440,000 per kilogram of contaminants removed from groundwater during the first year of operation down to $50,000 per kilogram of contaminants removed for a 10 year treatment period.

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References:

Duster, D., Edwards, R., Faile, M., Gallant, W., Gibeau, E., Myller, B., Nevling, K., and O'Grady, B. (1996) "Preliminary Performance Results from a Zero Valence Metal Reactive Wall for the Passive Treatment of Chlorinated Organic Compounds in Groundwater." Presented at Tri-Service Environmental Technology Workshop, May 20-22, Hershey, PA.

8.   Borden, Ontario, Canada

Participants: University of Waterloo

Demonstration date: Completed in 1994

Compounds treated: Benzene, toluene

Treatment summary: This study evaluated the ability of a proprietary solid peroxide formulation (referred to as an oxygen-releasing compound or ORC) to provide sufficient dissolved oxygen and enhance biodegradation of benzene and toluene. Benzene (3947 ± 284 μg/L) and toluene (3819 ± 264 μg/L) were

injected through 16 1.5-m sections of 25-cm O.D. PVC well screen jetted to approximately 1.5 m below ground surface. Background samples were collected from a location approximately 4 m upgradient from the source, while the downgradient concentrations were monitored along the lines of four monitoring points (0.6-cm stainless steel sampling points with a 2.5-cm screen) located every 0.5 m from the source. ORC in briquette form raised the concentration of DO in the groundwater to as much as 15 mg/L, while benzene and toluene concentrations decreased below detection limits. After the injection of benzene and toluene ceased, the DO levels rose to 45.6 mg/L and the oxygen production continued for at least 10 weeks. ORC in the pencil form also released oxygen into the groundwater, but the levels of DO were not as high as with ORC in the briquette form, and benzene and toluene concentrations remained above those measured when briquettes were used.

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References:

Bianchi-Mosquera, G.C., Allen-King, R.M., and Mackay, D.M. (1994) "Enhanced Degradation of Dissolved Benzene and Toluene Using a Solid Oxygen-Releasing Compound." *Groundwater Monitoring and Remediation*, 14:1, 120-128.

9.   Belen, New Mexico

Participants: Regenesis, GRAM, UST Bureau of the New Mexico Environment Department

Demonstration date: Initiated in March, 1995

Compounds treated: BTEX

Treatment summary: A total of 20 PVC wells was installed and loaded with a total of 342 oxygen releasing compound (ORC) socks to remediate a groundwater at a site where an unknown quantity of gasoline spill occurred for an unknown length of time. The aquifer is shallow, unconfined and comprised mainly of well sorted sands, with a groundwater level at 1.5 m bellow ground surface and the average groundwater gradient of 0.0015. The range of interstitial velocities at the site was estimated at 3.0 - 3.3 cm/day. The average background concentration of DO and BTEX were approximately 1 and 2 mg/L, respectively. Less than two weeks after installation, dissolved oxygen mass increased an order of magnitude

(maximum levels in excess of 18 mg/L) and remained constant for at least another month. There was a 78% decrease in the total BTEX mass in the immediate vicinity of the barrier and 58% decrease in the broad study area of 36 x 30 m. After three months of operation, approximately half of the oxygen placed in the system was exhausted and a concomitant decrease in the BTEX mass was observed. After 279 days of operation, 47% of the socks were replaced with fresh ones, since an increase in BTEX levels was observed. BTEX levels were once again noted to decrease from about 10 mg/L to below detection limits in proportion to the available oxygen.

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References:

Koenigsberg, S., Johnson, J., Odenkrantz, J., and Norris, R (1995) "Enhanced Intrinsic Bioremediation of Hydrocarbons with Oxygen Release Compound (ORC)" Sixth West Coast Conference on Contaminated Soils and Groundwater, March 11-14, Newport Beach, CA.

Johnson, J. and Methvin, R. (1996) "Enhanced Intrinsic Remediation of Dissolved Phase Hydrocarbons Using an Oxygen Releasing Compound: Field Demonstration in Belen, New Mexico." Proceedings of the Emerging Technologies in Hazardous Waste Management VIII, I&EC Div., ACS, September 9-11, Birmingham, AL, pp. 65-69.

10.   Chico Municipal Airport, CA

Participants: Lawrence Livermore National Laboratory; Brown and Caldwell

Demonstration date: Completed in 1995

Compounds treated: TCE

Treatment summary: The study demonstrated the effectiveness of resting-state (no nutrients) *in situ* microbial filters approach for remediating groundwater contaminated with TCE. The first field test of this technology, conducted at the Wilson Corners site at the Kennedy Space Center, FL, was terminated prematurely because only 1 - 2 ppm of the total contaminant load was biodegraded. This low biodegradation rate was attributed to insufficient oxygen in the groundwater. A second field trial was conducted at Chico Municipal Airport in Chico, CA where the groundwater was contaminated with 425 ± 50 μg/L of TCE and the dissolved oxygen was 7.0 mg/L. About 5.4 kg (dry weight) of a pure strain methanotrophic bacteria, *Methylosinus trichosporium* OB3b, was suspended in groundwater and

injected into the aquifer through a single well at a depth of 28 m and at a rate of 3.8 L/min. Approximately 50% of the injected bacteria attached to the soil, forming an *in situ*, fixed-bed, quasi-spherical bioreactor with an average radius of about 1.2 m. Contaminated groundwater was subsequently withdrawn through the biofilter by extracting groundwater through the injection well at 3.8 L/min for 30 hr and then at 2 L/min for the remaining 39 days of the field experiment. During the first 50 hr of ground-water withdrawal, 98% of TCE was biodegraded. TCE concentration in the extraction well then gradually increased as biofilter degradation capacity and/or longevity were exceeded in various parts of the biofilter.

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References:

Duba, A.G., Jackson, K.J., Jovanovich, M.C., Knapp, R.B., and Taylor, R.T. (1996) "TCE Remediation Using In Situ Resting-State Bioaugmentation." *Environ. Sci. Technol.,* 30:6, 1982-1989.

3.1.2   Pilot and Laboratory-Scale Studies

A pilot-scale study conducted at the SGL Printed Circuit Site, Wayne, NJ utilized commercial granular iron for the removal of 4 - 12 mg/L of PCE, 1 mg/L of TCE, and 0.15 mg/L of 1,2-DCE from contaminated groundwater (Vogan *et al.*, 1995; Shoemaker *et al.*, 1996). Design of the pilot-scale reactor was based on half-lives, determined using 100% granular iron, of 0.4 - 0.6 hr for PCE, 0.5 - 0.7 hr for TCE, 1.5 - 3.7 hr for DCE, and 1.2 - 0.9 for vinyl chloride. In order to achieve a New Jersey standard of 0.01 mg/L for 1,2-DCE, residence time in the fixed-bed reactor was set at 24 hr. The reactor was built in a 2.4-m diameter fiberglass tank filled with granular iron to a depth of 1.7 m. Concentration profiles for PCE, TCE, and *cis*-1,2-DCE after 30 and 60 days of operation showed nondetectable levels in the effluent. In fact, disappearance of all three constituents occurred about midway through the reactor. Based on laboratory testing, calcium carbonate, siderite, and possibly iron hydroxide could have precipitated in the reactor.

Three different reactive media: (1) fine grade iron filings (40-mesh) from MasterBuilder, Inc., (2) stock iron filings (-8+50-mesh) from Peerless Metal Powders & Abrasive, Inc., and (3) palladized iron filings obtained by chemically plating palladium (at 0.05% of iron) on a 40-mesh iron filings from Fisher Scientific, were tested in parallel treatment trains for the removal of TCE from a contaminated groundwater at Portsmouth Gaseous Diffusion Plant in Piketon, OH (Liang *et al*., 1996). Each treatment train consisted of three 55-gal drums packed with a total of 488 L of iron filings except in the case of palladized iron where only one drum packed with 45 L was used due to much faster TCE degradation rates on palladized iron observed in the laboratory studies. This pilot plant was constructed on February 29, 1996 and operations began on March 5, 1996. During the initial start-up phase of this study, problems with maintaining gravity flow through the system (1.1 - 1.5 L/min), encountered due to the build-up of the gas (believed to be hydrogen produced by reductive

dissociation of water by iron filings) in the drums and manifolds, were resolved by installing pressure release valves on the drums. During first week of operation, influent TCE concentrations on the order of 170 μg/L were reduced in all treatment trains to below detection limit (2 μg/L). After 51 days of operation, effluent TCE concentrations were still below detection limit in the treatment train (1), while they were 3 and 12 μg/L in the treatment trains (2) and (3), respectively. TCE half-lives increased from 1.4, 14, and 19 minutes after seven days of operation to half-lives of 4.1, 16, and 35 minutes after 51 days of operation for the treatment rains (3), (1), and (2), respectively. The more rapid deterioration of palladized iron filings may be attributed to the substantially higher number of pore volumes that have passed through this treatment train (about 3345 pore volumes compared to 331 pore volumes for the treatment trains (1) and (2)), as well as possible reactions of sulfides with palladium.

Contaminated groundwater at Hill AFB, UT was treated above ground in a 1.4-m long and 0.3-m diameter fiberglass canister filled with 100% Master Builder iron, "Blend B, GX-27" (Strongsville, OH) (Shoemaker *et al.*, 1996). The reactor was operated in an upflow mode with a flow rate of 0.38 to 3.8 L/min. Influent pH was stable at about 7.5, while dissolved oxygen varied from 4 to 6 mg/L. Effluent pH rose above 9 while dissolved oxygen (DO) decreased to 1-2 mg/L. The majority of the influent TCE, at 2 mg/L, was degraded prior to reaching the first port, located about 22 cm into the canister. Concentrations of cis 1,2-DCE and VC were observed to increase within the canister, but were below 0.001 mg/L in the effluent, while ethane and ethene in the effluent accounted for 60% of the initial TCE mass in the influent. The experiment was terminated when the pressure drop across the canister increased from an initial value of 3.45 kPa to 6.89 kPa. X-ray diffraction tests indicated that precipitation of iron and calcium carbonate compounds caused clogging of the bed.

Pilot-scale tests using a contaminated groundwater from an electronics manufacturing facility located near Belfast, Northern Ireland, were performed in a 100-cm long acrylic column charged with 100% granular iron and equipped with several sampling ports along the column length (Thomas *et al.*, 1995). The results of TCE analyses of the groundwater indicate that TCE is present at a maximum identified concentrations of up to 390 mg/L. Column tests at flow velocities of 109 and 54 cm/day were conducted until steady state contaminant profiles were established in each test. Using the flow velocity, the distance along the column was converted to time and the degradation rate constants were calculated for the organic compounds using a first-order kinetic model. Rapid declines in TCE concentration were observed for both tests and the detection limits were reached between 40 and 60 cm along the column. Calculated half-lives for TCE were 1.2 hours (flow velocity of 109 cm/day) and 3.7 hours (flow velocity of 54 cm/day). Concentrations of *cis*-1,2-DCE increased to between 10 and 22 mg/L due to dechlorination of DCE. Interpretation of *cis*-1,2-DCE profiles was difficult because of the presence of methyl ethyl ketone (MEK) in groundwater which eluted at the same time on the photo ionization detector as the target compound. Since MEK should be neither produced nor degraded in the presence of iron, the declines in the combined *cis*-1,2-DCE/MEK concentration was used to calculate *cis*-1,2-DCE half-lives of 12.5 and 23.9 hours for the flow rates of 109 and 54 cm/day, respectively. VC was produced due to TCE and *cis*-1,2-DCE degradation with a maximum concentration in the downstream portion of the column reaching 100 - 300 μg/L. No substantial increase in the pH over the influent levels was observed in these tests, most likely due to the high concentration of dissolved organics in the groundwater. Measured Eh declined from about 250 mV to about -200 mV and marked increases in iron were measured in the column effluent due to the corrosion of iron metal by water.

Four different iron millings or filings (70 - 99.9% iron in spherical particles, cylindrical pieces and polygons with densities ranging from 7.81 - 8.06 g/mL) from various iron fabrication processes were investigated for the removal of ground-water contamination at Moffet Federal Airfield, CA (PRC, 1996) using batch and column studies. The groundwater used in the batch studies contained approximately 22 mg/L of TCE, while the sample collected for column studies contained 1.2 mg/L TCE and 0.12 mg/L PCE. TCE removal efficiency in batch tests ranged from 64% to 100% for different iron types, while the column tests revealed a TCE half-life of 0.63 hr and a PCE half-life of 0.29 hr. In addition, half-lives of the reaction by-products 1,2-DCE and VC were estimated at 3.1 hr and 4.7 hr, respectively.

Agrawal and Tratnyek (1996) established that nitrobenzene can be reduced by iron under anaerobic conditions to aniline, with nitrosobenzene as an intermediate product. The rate of nitrobenzene reduction increased linearly with concentration of iron surface area, giving a specific reaction rate constant of 3.9×10^{-2} L/min×m^2. The observed decrease in the reduction rate for nitrobenzene was proportional to an increase in the concentration of dissolved carbonates, which indicated that the precipitation of siderite on the metal inhibits the reaction.

Hardy and Gillham (1996) hypothesized that the reduction of aqueous carbon dioxide (CO_2) by zero-valent iron leads to formation of various hydrocarbons up to C5 that have Anderson-Schultz-Flory (ASF) product distribution. Other possibility is that the carbide carbon from cast iron can act as a source for hydrocarbon generation. Iron acts both as a reactant, by corroding to supply electrons, and as a catalyst, by promoting hydrocarbon formation. The direct consequence of ASF product distribution is that a significant mass of hydrophobic hydrocarbons may remain sorbed onto the iron surface.

Orth and Gillham (1996) evaluated the degradation of TCE by granular iron metal using flow-through column tests. Degradation of TCE followed a pseudo-first-order rate, with a reaction rate constant being relatively insensitive to the initial TCE concentration in the range from 1.3 to 61 mg/L. The principal degradation products were ethene, followed by ethane and substantially smaller amounts of other C1 - C4 hydrocarbons. The chlorinated by-products included *cis*-1,2-DCE, *trans*-1,2-DCE, 1,1-DCE, and VC which collectively accounted for only about 3 - 3.5% of the TCE degraded. The mean half-life for degradation of TCE was 3.25 h and if normalized to 1 m^2 of iron surface area/mL of column volume, the half-life was 0.68 h.

Roberts *et al.* (1996) conducted experimental investigations of reductive elimination of chlorinated ethylenes by zero-valent iron and zinc (Fe(0) and Zn (0)). Both *trans*- and *cis*-1,2-DCE were reduced by Fe(0), with acetylene and ethylene as intermediate products. Complete degradation of these compounds did not occur after 140 hours of contact with metallic iron. On the other hand, reduction of PCE on Zn(0) yielded TCE as a principal product that accumulated in solution during 8 hours of reaction time.

Schlimm and Heitz (1996) evaluated the ability of aluminum (Al), Fe, Mg, and Zn to promote degradation of lindane (hexachlorocyclohexane), chloroform ($CHCl_3$) and TCA in weak acid or neutral medium (pH range 4 - 7). Among the metals tested, Zn proved to be the most suitable reagent, because it achieved the best space-time yield. Degradation of lindane, which was up to 99.3% efficient, yielded chloride and benzene as the main products, with small amounts of chlorobenzene. Degradation of chloroform produced methane and ethane while degradation of TCA produced ethene.

Weber (1996) suggested that the reduction of chlorinated solvents by zero-valent iron requires a contact between the organic compound and iron surface, which limits the treatment scheme with Fe(0) to water soluble chemicals, and requires a close investigation of the rate of chemical mass transport to the iron surface. In addition, treatment of many soil contaminants which have functional groups that are reducible but are strongly sorbed to sediments and soil (e.g., polychlorinated biphenyls (PCBs), dioxin, DDT, toxaphene, mirex, lindane, hexachlorobenzene) may not be feasible with this technology.

Burris *et al*. (1995) evaluated sorption and reduction kinetics of TCE and PCE with metallic (zero-valent) iron in a closed, well-mixed, anaerobic batch system. It was established that sorption of TCE and PCE to zero-valent iron, which occurs primarily at nonreactive sorption sites, is nonlinear and can be described by the generalized Langmuir isotherm. The reduction of TCE and PCE on zero-valent iron is not pseudo-first order, but is a complex reaction involving a series of interconnected processes. Accounting for sorption to nonreactive sites, the loss of TCE and PCE from aqueous solution was shown to be a first-order process.

Gillham and O'Hannesin (1994) conducted laboratory batch and column tests to examine zero-valent iron as an enhancing agent in the dehalogenation of 13 halogenated methanes, ethanes, and ethenes which all exhibited significant degradation rates (50% degradation of the initial concentrations of about 2 mg/L occurred within 0.013 to 20 hours in the presence of 1 m^2 iron/mL solution) except for dichloromethane. Based on these results, it was estimated that 1 kg of iron could completely dechlorinate tetrachloromethane in 0.5×10^6 L of water at an initial concentration of 1 mg/L. However, the issues of iron corrosion and the consumption of iron at rates much faster than dechlorination reactions, and accumulation of breakdown products, still require serious consideration.

Matheson and Tratnyek (1994) established that zero-valent iron sequentially dehalogenates carbon tetrachloride via chloroform to methylene chloride, but no significant reduction of methylene chloride was observed over a period of one month. They proposed that the pathways for reductive dehalogenation under anoxic conditions can be through direct electron transfer from iron metal at the metal surface, reduction by Fe^{2+} which results from corrosion of the metal, and catalyzed hydrogenolysis by the H_2 that is formed by the reduction of water during anaerobic corrosion.

One of the major potential disadvantages of zero-valent iron for the treatment of halogenated volatiles is the possible accumulation of by-products like *cis*-1,2-DCE (EPA, 1995) or dichloromethane (CH_2Cl_2) which is resistant to further degradation (Gillham and O'Hannesin, 1994). However, studies by Muftikian *et al*. (1995) established that the addition of a small amount of palladium to zero-valent iron yielded significant improvements in the rate of dechlorination of PCE, TCE, and *cis* and *trans* 1,2-DCE without any by-product accumulation. Chloromethanes (CCl_4, $CHCl_3$, and CH_2Cl_2) were also dechlorinated to methane on palladized iron with CH_2Cl_2 requiring the longest reaction time (4 - 5 hours). Grittini *et al*. (1995) established that palladized iron can also accomplish complete dechlorination of PCBs in an aqueous methanol solution in a few minutes. Chuang and Larson (1995) established that high temperature (300 - 600 °C) can also promote dechlorination of PCBs by zero-valent iron. Other compounds that have been successfully degraded by zero-valent iron include pentachlorophenol (PCP) (Ravary and Kochany, 1995), 1,2-dibromo-3-chloropropane (DBCP) (Siantar *et al*., 1995), and 1,2,3-trichloropropane (TCP) (Focht and Gillham, 1995), while degradation of atrazine (Pulgarin *et al*., 1995) required visible light activation.

Studies by Gantzer and Wackett (1992) investigated the ability of transition-metal coenzymes (vitamin B_{12}, coenzyme F_{430}, and hematin) to catalyze reductive dechlorination of polychlorinated ethylenes and benzenes. It was suggested that vitamin B_{12} and coenzyme F_{430} have the capacity to mediate eight-electron reduction of PCE to ethylene. On the other hand, hematin catalyzed the reductive dechlorination of PCE only to VC, while the reductive dechlorination of TCE yielded cis-1,2-DCE as the principal product. Similar relative kinetics of reductive dehalogenation and dechlorination products have been observed in anaerobic cultures, suggesting a possible role of transition metal coenzymes in natural and engineered environments.

Amonette et al. (1994) and Williams et al. (1994) investigated the possibility of injecting sodium dithionite (2-day half-life) into the subsurface where it would act as a reductant for structural iron in clay-sized layer silicate minerals. The resulting reducing conditions created in the subsurface would react with halogenated volatile compounds (tetrachloromethane (CCl_4)) present in the incoming groundwater. It was established that 90% of the initial CCl_4 concentration of 50 µL/L was destroyed by the reduced sediment within one week. Less than 10% of the removed CCl_4 was converted to $CHCl_3$, while CH_2Cl_2 levels were below detection limit.

Taylor et al. (1993) evaluated the possibility of injecting microorganisms into the subsurface ahead of migrating contaminant plumes to accomplish biodegradation of organic contaminants in the plumes. Methylosinus trichosporium OB3b, previously inoculated in the laboratory, was used to create a subsurface microbial filter containing attached resting cells. TCE was injected into the laboratory-scale test bed in two separate pulses (one week apart) and pumped through the system at 15 mm/hr (109 ppb and 85 ppb) with no TCE being detected downstream of the microbial filter. Subsequent excavations of the sand material used in the test bed revealed the existence of a TCE-bioactive zone 21 days after it was created. TCE biotransformation capacity of these resting cells was measured at 0.25 mg TCE/mg of bacteria.

Bowman et al. (1994a, b) evaluated the possibility of using low cost natural zeolites ($110/tonne) treated with cationic surfactants (hexadecyltrimethylammonium (HDTMA) or methyl-4-phenylpyridinium) for the removal of benzene, toluene, p-xylene, ethylbenzene, TCA, and PCE from aqueous solution. Unmodified zeolites had no affinity for the organic compounds, while surfactant-modified zeolites, which remained stable in aggressive aqueous solution and organic solvents, sorbed these organic compounds via a partitioning mechanism; sorption affinity was in the order of the sorbates' octanol-water partition coefficient. Cost of the modified zeolites was estimated at $330 - $550/tonne.

Burris and Antworth (1992) injected a cationic surfactant (HDTMA) into subsurface material derived from an aquifer located in Columbus AFB, MI. Injection of the surfactant created a stationary zone of HDTMA-modified aquifer material that showed excellent properties for the adsorption of PCE and naphthalene without significant modifications in the permeability of the aquifer material. PCE and naphthalene sorption isotherms onto HDTMA-modified material were linear for aqueous phase concentrations of up to 10 µg/mL and 2.5 µg/mL, respectively. The linear sorption coefficients were increased by over two orders of magnitude relative to the original material.

Smith and Jaffe (1994a,b) and Smith and Galan (1995) evaluated the ability of organic-cation-modified bentonites (organobentonites) to adsorb benzene, CCl_4, TCE, 1,2-dichlorobenzene (1,2-DCB), and naphthalene. Organobentonites were prepared by replacing inorganic ions on the surface of Wyoming bentonite with four quaternary ammonium cations. Bentonites modified by small

organic cations (e.g., quaternary ammonium cations with methyl, ethyl or benzyl functional groups) exhibited nonlinear sorption isotherms, strong solute uptake, and competitive adsorption, while bentonites modified with large organic cations (e.g., quaternary ammonium cations with dodecyl, tetradecyl, or hexadecyl functional groups) were characterized by linear isotherms, relatively weak solute uptake and noncompetitive sorption. The results of a mathematical simulation of benzene transport through a liner that incorporated small amounts of organobentonites (4%) into the compacted sand (88%) and bentonite (8%) of the liner indicated that the maximum benzene concentration on the effluent side would reach only 0.05 mg/L after 275 years (influent side contained 10 mg/L of benzene) compared to a maximum of approximately 2 mg/L appearing after 4 years for a liner (88% sand and 12 % bentonite) with no modified bentonite component.

3.2   TREATMENT WALLS FOR INORGANIC COMPOUNDS

3.2.1   Commercial Applications and Field-Scale Studies

1.   U.S. Coast Guard Air Station, Elizabeth City, NC

Participants: U.S. Coast Guard; Parsons Engineering Science; Industrial Marine Services; Horizontal Technologies

Demonstration date: Wall installation completed on June 22, 1996

Compounds treated: Hexavalent chromium (also, TCE)

Treatment summary: A full-scale reactive iron wall (45-m long, 5.5-m deep, and 0.6-m wide) was installed in a matter of hours using a novel installation approach developed by Horizontal Technologies. Thickness of the wall was dictated by the presence of TCE in groundwater. The only problem during installation resulted from running sands undermining the concrete used in the wall. Preliminary estimates place the entire cost of the treatment wall (installation, iron fillings, contractor costs) at approximately $420,000. No results are available.

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2.   U.S. Coast Guard Air Station, Elizabeth City, NC

Participants: U.S. EPA; ManTech Environmental Research Services

Demonstration date: Initiated in September, 1994

Compounds treated: Hexavalent chromium (also, TCE, 1,2-DCE)

Treatment summary: Zero-valent iron has been evaluated for the removal of chromate through a treatment wall constructed from a series of large-diameter augered holes in a staggered 3-row array. Twenty one 20-cm columns were installed to a depth of 6.7 m throughout a 5.5 m^2 area. The mixed waste contaminant plume was between 4.2 and 6 m below the surface, and the water table ranged from 1.5 to 2 m below the surface. Columns were charged with a mixture of 50% iron filings (two types), 25% clean coarse sand, and 25% aquifer material to a depth between 3 and 8 m below the surface. Untreated groundwater contained between 1 and 3 mg/L of chromate, while the treated groundwater contained below 0.01 mg/L. Dissolved iron in the groundwater increased from 0.05 mg/L to 1 - 20 mg/L, while dissolved oxygen decreased from 0.6 mg/L to 0.1 mg/L with a slight increase in alkalinity.

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References:

Powell, R.M., Puls, R.W., Hightower, S.H., and Sabatini, D.A. (1995) "Coupled Iron Corrosion and Chromate Reduction: Mechanisms for Subsurface Remediation." *Environ. Sci. Technol*., 29:8, 1913-1922.

Puls, R.W., Powell, R.M., and Paul, C.J. (1995) "In Situ Remediation of Ground Water Contaminated with Chromate and Chlorinated Solvents Using Zero-Valent Iron: A Field Study." Proceedings of the 209th ACS National Meeting, Anaheim, CA, April 2-7, 788-791.

3.   UMTRA Site, Durango, CO

Participants: Sandia National Laboratories; Applied Geotechnical Engineering and Construction, Inc.

Demonstration date: Wall in operation since April, 1996

Compounds treated: U, Mo, nitrate

Treatment summary: Four different treatment zones were installed below surface in the path of the uranium mill tailing drainage. Two were in baffle style boxes about 1.8 x 1 x 1.2 m and two were horizontal beds approximately 4.5 x 9 m with 0.3 m of steel wool. Bi-metallic, zero-valent iron steel wool, and zero-valent iron foam from Cercona are the media being tested at the site. Influent concentration have varied from May through July in the range of 2.9 - 5.9 mg/l for U, 0.9 for Mo and 27 - 32 mg/l for NO$_3^-$. The first test started in May 1996 with Cerona iron foam in the baffle design as the

first media to be tested. The earliest results showed a decrease in U concentration to 0.4 mg/L and NO_3^- to 20 mg/L. The results after 3 months of operation showed a decrease in U and nitrate to below detection limits while Mo decreased to 0.02 mg/L. Although not confirmed, it is suspected that biological reduction enhanced by the high hydrogen environment produced by the contact between iron and water has resulted in the removal of nitrate from the system.

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4. Long Point, Killarney, and Borden, Ontario, Canada

Participants: University of Waterloo

Demonstration date: Initiated in May, 1992

Compounds treated: Nitrate

Treatment summary: *In situ* nitrate attenuation by heterotrophic denitrification using an alternative septic system design that utilizes a treatment wall charged with an organic carbon source (sawdust) is currently being evaluated at three sites in Ontario, Canada. Two barrier configurations (horizontal layer positioned in the vadose zone below a conventional septic-system infiltration bed and a vertical wall intercepting a horizontally-flowing downgradient plume) were evaluated in four field trials. During one year of operation, both barrier configuration have been successful in substantial attenuation (60 to 100%) of input NO_3^- levels of up to 125 mg/L as N. Mass balance calculations and preliminary results suggest that conveniently sized barriers have the potential to last for decades without replenishment of the reactive material.

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References:

Robertson, W.D. and Cherry, J.A. (1995) "In Situ Denitrification of Septic-System Nitrate Using Reactive Porous Media Barriers: Field Trials." *Ground Water*, 33:1, 99-111.

3.2.2   Pilot and Laboratory-Scale Studies

Morrison *et al.* (1993, 1995a, b) investigated the possibility of using amorphous ferric oxyhydroxide for the adsorption of uranium(VI) from mill tailings at the former uranium millsite in Monticello, UT. The process was effective in preventing the release of uranium (VI), especially for neutral-pH mill tailings. However, no uranium(VI) retardation occurred in tailings with alkaline pore fluids. The cost of installing the barrier for a 3×10^6 yard^3 (2.3×10^6 m^3) repository was estimated not to exceed $150,000 or 1% of the estimated cost for the repository, with an effective barrier (concentrations limited to 0.05 mg/L U(VI) to within 88 ft (27 m) of the repository boundary) for a period of at least 216 years.

Morrison and Spangler (1992) evaluated a number of industrial materials for use in chemical barriers for uranium mill tailings remediation. More than 99% of dissolved uranium was extracted from a synthetic wastewater (initial concentration of 30 mg/L) by the addition of hydrated lime, fly ash, barium chloride, calcium phosphate, titanium oxide, peat and lignite. More than 96% of molybdenum (initial concentration of 8.9 mg/L) was extracted by ferrous sulfate, ferric oxyhydroxide, titanium oxide, peat, hematite, calcium chloride, and barium chloride. Some materials were effective only for a limited range of pH values. Extraction was caused by both precipitation (as calcium uranate, calcium molybdate, ferrous molybdate, or barium molybdate) and sorption (on ferric oxyhydroxide, hematite, calcium phosphate, peat, or titanium dioxide).

Fuhrmann *et al.* (1995) conducted laboratory studies to support the design of a full-scale, *in situ* sorbent barrier for intercepting a strontium (^{90}Sr) plume within a surficial water-bearing sand and gravel layer.   Initial screening of the sorbent materials included natural zeolites Na-chabazite, clinoptilolite, and mordenite and various metal oxides (alumina and iron (Fe) and manganese (Mn) oxides). Based on the results of laboratory experiments, a simulation of the performance of a 1.2-m thick treatment wall containing 20 x 50 U.S. mesh size clinoptilolite, using a dispersivity of 5% and a seepage velocity of 4.6×10^{-4} cm/s, indicated that it would take more than eight years for the effluent ^{90}Sr concentration to increase to 100 pCi/L if the influent concentration was maintained at 5000 pCi/L. Based on the laboratory measurements of the partition coefficient, cost estimates, and modeling results, fine-grained natural clinoptilolite (20 x 50) from Oregon was recommended for use in a full-scale demonstration proposed for Western New York Nuclear Service Center (WNYSC) located near West Valley, New York, which was the site of the only commercial nuclear fuel reprocessing facility ever operated in the United States.

Haggerty and Bowman (1993) and Bowman *et al.* (1994a, b) evaluated the possibility of using low cost zeolites ($110/tonne) treated with quaternary amines for the removal of arsenic (As), cadmium (Cd), chromium (Cr), and lead (Pb) from a contaminated groundwater. Unmodified zeolites sorbed Pb from solution, while surfactant-modified zeolites, which remained stable in a variety of aggressive solutions, also sorbed chromate, selenate, and sulfate. The mechanism appears to be surface precipitation of a surfactant-oxyanion complex. Removal of these anions from solution was well described by the Langmuir isotherm equation, and the highest sorption was accomplished when the zeolite was modified such that 100% of its external cation-exchange capacity was satisfied with the surfactant (hexadecyltrimethylammonium). Cost of the modified zeolites was estimated at $330 - $550/tonne.

Amonette *et al.* (1994) and Williams *et al.* (1994) investigated the possibility of injecting sodium dithionite into the subsurface (2-day half-life) to reduce structural iron in clay-sized layer silicate minerals and in sediment from the Hanford formation (Hanford, WA; 100H Area test site). The reducing conditions created in the subsurface would transform metals to less soluble forms. Using a sonic drilling technology, the reagent (120,000 - 150,000 L) can be injected into the aquifer to create 18- to 30-m diameter zone where it would be allowed to react from 5 to 30 days. After the reaction period, water containing the reaction byproducts and any remaining reagent would be pumped out (three times the injection volume) to create a permeable reaction zone in advance of a contaminant plume. Preliminary results of the ongoing laboratory investigations in support of the planned field trials indicated that a chromate concentration of 0.1 mg/L can be reduced to 0.005 mg/L, which is well below the treatment goal of 0.011 mg/L.

Dwyer *et al.* (1996) evaluated the effectiveness of zero-valent iron for the removal of uranium from a uranium mill tailings site in Durango, CO. The entire experiment was conducted inside a prefabricated, leak proof detention basin (11 x 18 m and 1.8 m deep) that was lined with a 0.6-m thick clay liner covered with two 40 mil HDPE liners filled with actual tailings effluent. The three metallic iron materials, i.e., zero-valent iron (steel wool), iron foam and a bimetallic iron/copper, were all effective in reducing the uranium concentration from 6 mg/L to less than 2 mg/L in less than 24 hours. Iron foam that had an initial saturated hydraulic conductivity of 0.53 cm/s (compared to 0.0063 cm/s for steel wool) was the most effective of the three materials, with the reduction in uranium concentration to below 2 mg/L occurring in less than 5 hours.

Ouki *et al.* (1993) investigated the ability of chabazite and clinoptilolite, both containing significant amounts of exchangeable potassium (K), calcium (Ca), and sodium (Na), to remove lead and cadmium from contaminated waters. Both Pb and Cd were effectively removed by as-received zeolites (approximately 50 mg/g at aqueous concentration of 250 mg/L), with particle size having no impact on the exchange process. At Pb and Cd concentrations above 250 mg/L, pretreatment of these zeolites with NaCl (conversion to homoionic state in the Na form) greatly enhanced their capacity for the exchange of these metals (exchange capacities exceeded 200 mg/g at optimal conditions).

Rorrer *et al.* (1993), Kawamura *et al.* (1993), and Charrier (1996) evaluated the effectiveness of porous chitosan beads to remove different metallic ions from contaminated waters. The capacity of naturally occurring chitosan was dependent on particle size, with chitosan particles of mean diameter below 250 μm adsorbing as much as 500 mg vanadium (IV)/g at pH 4 and equilibrium aqueous phase V(IV) concentration of 50 mg/L (Charrier, 1996). However, the rate of vanadium uptake was slow, and it took almost 24 hours to reach equilibrium even for the smallest particle size studied (D_p < 125 μm). Gelled chitosan beads crosslinked by glutaraldehyde possessed surface areas exceeding 150 m^2/g and were insoluble in acid media at pH 2 (Rorrer, 1993). However, the capacity of the beads varied with diameter, with 1-mm beads adsorbing as much as 518 mg Cd^{2+}/g, while 3-mm beads adsorbed 188 mg Cd^{2+}/g for an aqueous phase concentration of 1690 mg Cd^{2+}/L. On the other hand, polyaminated chitosan beads exhibited appreciable chelating properties with the selectivity at pH 7 in the order: Hg(II) > UO_2(II) > Cd(II) > Zn(II) > Cu(II) > Ni(II); while Mg(II), Ca(II), Ga(II), As(III), and Sr(II) were not adsorbed onto the resin at all (Kawamura, 1993). In all cases, the saturation capacities were close to the concentrations of amino groups fixed on the resin, and low pH (500 mmol/L H_2SO_4) was appropriate for resin regeneration.

Oscarson *et al.* (1994) established that the ability of bentonite to adsorb cesium (Cs^+) was greatly affected by the extent of bentonite compaction. Using a novel test cell, the distribution coefficient, K_d, for the compacted bentonite with a density ranging from 0.5 to 1.5 mg/m^3, was about one-half to one-third of the distribution coefficients measured for the loose bentonite.

Ho *et al.* (1995) established that the ability of sphagnum peat moss to remove nickel from contaminated water is best realized at pH 4 - 7, but is still relatively poor in comparison with other metals. Sphagnum peat moss can adsorb as much as 119 mg Cr(VI)/g at pH 1.5 and 16.5 mg Cu/g at pH 5.0, while the maximum capacity for nickel was only 9.18 mg Ni/g at pH 7.0. Equilibrium for nickel adsorption was established after 25 min for an initial Ni concentration of 50 mg/L, while it took 90 min to reach equilibrium for an initial Ni concentration of 400 mg/L.

Ma *et al.* (1993, 1994) evaluated the ability of phosphate minerals (apatites) to immobilize lead *in situ*. It was suggested that Pb immobilization required hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] dissolution with subsequent precipitation of hydroxypyromorphite [$Pb_{10}(PO_4)_6(OH)_2$]. Hydroxyapatite reduced initial Pb concentrations of 5 - 500 mg/L to 0.18 - 19.7 µg/L. Aqueous Pb in Pb-contaminated soil materials was reduced from 2273 to 36 µg/L. The immobilization process was rapid and near completion in 30 min. In addition, natural apatite was shown to be effective in removing Pb from aqueous solution. Effective lead immobilization with apatites was accomplished only when the solution pH was low enough (5 - 6) to dissolve apatite and supply P to react with Pb, yet high enough to keep the solubility of hydroxypyromorphite low. However, the presence of various other metals in solution inhibited Pb immobilization through precipitation of amorphous to poorly crystalline metal phosphates, thereby decreasing the amount of dissolved P available for precipitation with dissolved Pb ions. The order of inhibition was: Al > Cu > Fe(II) > Cd > Zn > Ni and Cu > Fe(II) > Cd > Zn > Al > Ni at high and low initial Pb concentrations, respectively.

4.0 TECHNOLOGY APPLICABILITY

4.1 TREATMENT WALLS FOR ORGANIC CONTAMINANTS

The current status of treatment wall technology applications for inorganic contaminants is indicated in Table 1. Included is the nature of the reactive medium, contaminants, level of investigation, selected references, location, and some distinguishing features.

Control of organic contaminants in groundwater with treatment walls has had considerably more field and full-scale applications than the control of inorganic contaminants. Zero-valent iron has been applied in a commercial system for the control of chlorinated hydrocarbons (Shoemaker *et al.*, 1996), while a number field and pilot-scale studies with this reactive media, which are described in Sections 3.1.1. and 3.1.2., showed very encouraging results for this technology. Among other reactive media investigated for the control of organic contaminants in groundwater, resting-state microorganisms (Duba *et al.*, 1996) have been successfully applied in the field, while palladized iron (Muftikian *et al.*, 1995; Grittini *et al.*, 1995) and organobentonites (Smith and Galan, 1995) showed a good potential in pilot- and laboratory-scale studies.

4.2 TREATMENT WALLS FOR INORGANIC CONTAMINANTS

The current status of treatment wall technology applications for inorganic contaminants is indicated in Table 2. Included is the nature of the reactive medium, contaminants, level of investigation, selected references, location, and some distinguishing features.

Reactive media that have been implemented in pilot and field-scale studies for the treatment of inorganic contaminants include ferric oxyhydroxide for the control of U and Mo (Morrison *et al.*, 1995), dithionite for the removal of Cr, V, Tc, and U (Williams *et al.*, 1994), zero-valent iron for the control of U (Dwyer *et al.*, 1996) and Cr (EPA, 1995), and sawdust as a carbon source for biological removal of nitrate (Robertson and Cherry, 1995). Among other reactive media that have been investigated in laboratory studies, zeolites and hydroxyapatite showed a good potential for field applications. Detailed descriptions of the studies and pertinent findings are given in Section 3.2.

Table 1. Status of Treatment Wall Technology for Organic Contaminants*

REACTIVE MEDIA	CONTAMINANTS	STUDY TYPE	REFERENCE	LOCATION/COMMENTS
zero-valent iron	halogenated hydrocarbons	commercial	Shoemaker et al., 1996	Sunnyvale, CA / Moffet Federal Air Field, CA / Coffeyville, KS / Elizabeth City, NC
		field	EPA, 1995 / Puls et al., 1995 / Duster et al., 1996	Borden, Ontario / Elizabeth City, NC / Lowry AFB, CO
		pilot	Shoemaker et al., 1996 / Shoemaker et al., 1996	SGL Site, NJ / Hill AFB, UT / Portsmouth, OH
	halogenated hydrocarbons, nitro aromatic compounds, atrazine, DBCP, PCP, PCBs	laboratory	Agrawal and Tratnyek, 1996 / Hardy and Gillham, 1996 / Orth and Gillham, 1996 / Roberts et al., 1996 / Schlimm and Heitz, 1996 / Weber, 1996	Chuang and Larson, 1995 / Focht and Gillham, 1995 / Pulgarin et al., 1995 / Ravary and Kochany, 1995 / Siantar et al., 1995 / Gillham and O'Hannesin, 1994
palladized iron	halogenated hydrocarbons, PCBs	laboratory	Muftikian et al., 1995 / Grittini et al., 1995	Reaction completed in minutes; no accumulation of by-products
iron(II) porphyrins	polychlorinated ethylenes, benzenes	laboratory	Gantzer and Wackett, 1992	B_{12} and coenzyme F_{430} catalyze complete reduction; hematin only to VC
dithionite	halogenated hydrocarbons	laboratory	Amonette et al., 1994 / Williams et al., 1994	90% of CCl_4 reduced in one week and less than 10% converted to THM
resting-state microorganisms	TCE / TCE	field / laboratory	Duba et al., 1996 / Taylor et al., 1993	Chico Municipal Airport, CA / Kennedy Space Center, FL
oxygen-releasing compound	benzene, toluene	field	Bianchi-Mosquers et al., 1994	Borden, Ontario, Canada
zeolite	BTEX, TCA, PCA	laboratory	Bowman et al., 1994a, b	surfactant-modified zeolites sorbed organics through partition mechanism
surfactant modified silicates	PCE, napthalene	laboratory	Burris and Antworth, 1992	no reduction in permeability; 2 orders of magnitude increase in capacity
organobentonites	benzene, CCl_4, TCE, napthalene, 1,2-dichlorobenzene	laboratory	Smith and Jaffe, 1994a, b / Smith and Galan, 1995	selection of quaternary ammonium group influences sorption mechanism; 4% addition into the liner increases retention of benzene

*More details are presented in Section 3.1

Table 2. Status of Treatment Wall Technology for Inorganic Contaminants*

REACTIVE MEDIA	CONTAMINANTS	STUDY TYPE	REFERENCE	LOCATION/COMMENTS
zero-valent iron	Cr Cr U	commercial field field	 EPA (1995) Dwyer et al., 1996	Elizabeth City, NC Elizabeth City, NC UMTRA Site, Durango, CO
sawdust	nitrate	field	Robertson and Cherry, 1995	Long Point, Killarney, and Borden, Canada
peat	Ni, Cr, Cd U, Mo	laboratory laboratory	Ho et al., 1995 Morrison and Spangler, 1992	low pH enhances capacity; equilibrium reached in less than 2 hours
bentonite	Cs	laboratory	Oscarson et al., 1994	clay composition decreases sorption capacity
ferric oxyhydroxide	U, Mo U, Mo	laboratory pilot	Morrison et al., 1993, 1995	require neutral pH; effluent below 0.05 mg U/L Monticello, UT
zeolite modified zeolites	Pb, Cd Sr As, Cr, Cd, Pb	laboratory laboratory laboratory	Ouki, 1993 Fuhrmann et al., 1995 Haggerty and Bowman, 1994 Bowman et al., 1994a, b	pretreatment of chabazite and clinopitolite with NaCl or surfactants enhances capacity
chitosan beads	V, Cd, Hg	laboratory	Rorrer et al., 1993, Kawamura et al., 1993, Charrier, 1996	slow rate of uptake; capacity = 500 mg V/g
hydroxyapatite	Pb	laboratory	Ma et al., 1993, 1994	complete removal in 30 min; pH = 5 - 6; other metals inhibit removal of Pb
diothionite	Cr, V, Tc, U	field	Amonette et al., 1994 Williams et al., 1994	18 - 30 m treatment zone to react for 5 - 30 days at Hanford 100H Area, WA
lime or limestone	acid mine drainage	commercial	Kleinmann et al., 1983	various sites

*More details are presented in Section 3.2

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5.0 COST

5.1   CAPITAL COSTS

The cost of the impermeable sections of the treatment wall system can be obtained from experiences with slurry walls or sheet pile installations. If the reactive media is zero-valent iron, the cost of the media can be estimated based on the density of about 2.83 kg/m^3 and a cost of approximately $440 - 500/tonne. A recent review by DuPont (Shoemaker *et al.*, 1996) suggested that installation costs between $2,500 and $8,000 per L/min of treatment capacity can be used as a rule-of-thumb for estimating the capital cost of these systems. Since zero-valent iron treatment walls is patented technology, a site licensing fee, which has been typically 15% of the capital costs (materials and construction costs), may also be required.

Table 3 summarizes capital costs for treatment walls (mostly zero-valent iron as a reactive media) that are already built or for which costs have been estimated (augmented table of Vogan and Kwicinski, 1996).

5.2   OPERATION AND MAINTENANCE COSTS

A principal advantage of the permeable treatment walls technology over other ground-water remediation approaches is the reduced operation and maintenance (O&M) costs. Other than ground-water monitoring, the major factor affecting operating and maintenance costs is the need for periodic removal of precipitates from the reactive media or periodic replacement or rejuvenation of the affected sections of the permeable wall. It is currently difficult to predict the magnitude of inorganic precipitate formation prior to site-specific trials. A recent review by DuPont (Shoemaker *et al.*, 1996) suggested O&M costs between $1.3 and $5.2 per 1,000 L of treated water can be used as a rule-of-thumb for estimating the O&M costs of these systems.

At the Intersil site in Sunnyvale, CA, it was estimated that the total O&M costs associated with ground-water monitoring and replacement of the entire reactive media in a 12-m long, 3.6-m deep and 1.2-m wide treatment wall every 10 years could be about $2 million over a 30-year period (Fairweather, 1996).

Table 3. Capital Cost Summary for Treatment Walls

LOCATION	DIMENSIONS	CONTAMINANTS	COST ($)		
			Construc.	Media	Total
Sunnyvale, CA (full-scale) (built)	75-m slurry wall on either side of 12-m long treatment section; 6m deep; 3.5-m vertical and 1.2-m flowthrough thickness of iron	1 - 2 mg/L VC, *cis*-1,2-DCE, and TCE	550,000	170,000	720,000
Moffet Federal Air Field, CA (full-scale) (built)	6.5-m long interlocking sheet piles on either side of a 3.2-m wide, 3.2-m thick, and 8.2-m deep reaction cell	1 mg/L TCE			300,000
Coffeyville, KS (pilot-scale) (built)	150-m slurry wall on either side of 6-m long gate; 9-m deep; 3.8-m vertical and 1-m flowthrough thickness of iron	100's μ g/L TCE	350,000	50,000	400,000
Elizabeth City, NC (full-scale) (built)	45-m long, 5.5-m deep, and 0.6-m wide zero-valent iron wall	TCE, chromium	220,000	200,000	420,000
Lowry AFB, CO (pilot-scale) (built)	3.5-m wide, 1.6-m thick, and 2.9-m deep gate with 5-m long cutoff walls on each side of the reaction zone	850 μ g/L TCE 220 μ g/L cis-1,2-DCE	105,000	32,500	137,500
New Hampshire (full-scale) (estimate)	400-m long wall with several gates; 9-m deep	100's μ g/L TCE, VC, *cis*-1,2-DCE	1,200,000	900,000	2,100,000
Michigan (full-scale) (estimate)	90-m long with 3 gates; 6-m deep	10 - 100 mg/L TCE	300,000	135,000	435,000
Canada (full-scale) (estimate)	45-m long with 2 gates; 4.5-m deep	50 - 100 μ g/L TCE	130,000	52,500	182,500

6.0 REGULATORY/POLICY REQUIREMENTS AND ISSUES

6.1   REGULATORY CONSIDERATIONS

At the time of publication, the U.S. EPA was in the process of developing regulatory guidelines for the use of passive treatment wall technology. No State's regulations specifically addressing this technology are known to exist. Implementation of a treatment wall at a hazardous waste site, as with any remedial measure, requires the approval of appropriate State and/or federal regulatory agencies. Potential considerations to be addressed as part of this approval process involve site investigation, design and monitoring issues, including those listed below:

- Sufficient characterization of site geology, hydrology, contaminant distribution, and vectors impacting human health and the environment to permit adequate design of the treatment wall;

- Ability of the proposed design to account for uncertainties inherent in subsurface investigations/treatments;

- Ability of the proposed design to capture and adequately remediate the vertical and horizontal extent of the ground-water plume;

- Monitoring to measure concentrations of by-products in groundwater potentially pro- duced through treatment wall reactions;

- Monitoring to measure potential releases of gaseous by-products; and

- Monitoring to characterize precipitate formation and wall clogging that may limit the effectiveness of the treatment method.

6.1.1   Regulatory Advantages

Implementation of passive treatment wall technology does not involve removal of groundwater or air from the subsurface. Therefore, unlike other remedial technologies such as pump-and-treat and soil vapor extraction, it does not require permits for discharges of groundwater or air to the environment.

6.2   HEALTH AND SAFETY ISSUES

6.2.1   Worker Safety

Health and safety issues involved in the use of treatment wall technology are mainly associated with installation of the wall and will vary according to the method of installation used (trenching, drilling, injection, etc.). Health and safety concerns associated with these installation methods will generally be the same as for any other application of the particular installation technique. Exposure of work- ers to hazardous substances during installation and operation of the wall may be lower than with other conventional treatment technologies due to lack of direct contact with contaminated materials.

6.2.2 Community Safety

As stated above, monitoring is required to ensure that any groundwater and air releases that may result from use of treatment wall technology do not impact offsite receptors.

6.2.3 Environmental Impacts

Impacts from treatment wall installation and maintenance may be less than with other technologies due to the placement of all treatment materials underground, with minimal disturbance to surface activities.

7.0 LESSONS LEARNED

7.1 DESIGN AND CONSTRUCTION

At present, there is a general need to establish tested and proven design procedures and protocols for treatment wall technology. Protocols for site characterization have been fairly well developed so far, but the criteria for selecting the location of a treatment wall is still quite empirical. Therefore, there is a need to develop better predictive models that can assist in determining optimal location and sizing of the wall. These models should not only include ground-water hydrology and hydraulics and contaminant transport and fate in the subsurface, but also chemical reactions occurring inside the wall. It is particularly important to account for by-product generation, precipitate formation and clogging of the wall, and loss of media reactivity.

A major potential limitation of treatment wall technology is the potential for constructing the wall at depths greater than 10 m. Wall installation at depths of 10 to 30 m presents additional difficulty and escalates construction costs to the point that they may become limiting for the implementation of this technology. Installations at depths greater than 30 m are only theoretically possible with current technologies. Moreover, the existence of surface obstructions (e.g., buildings, roads) and under-ground utilities represents additional challenges to the placement of treatment walls in the subsurface.

7.2 IMPLEMENTATION ISSUES

A particular concern with treatment wall technology is the question of long-term performance under variable conditions that are commonly associated with contaminated groundwaters (e.g., seasonal variations in ground-water flow velocity and patterns, variations in the contaminant speciation and concentration). Loss of permeability over time as a result of particle invasion, chemical precipitation, or microbial activity, and possible gradual loss of media reactivity as the reactant is either depleted or coated by reaction by-products, need to be resolved before this technology can be applied with wider confidence. Currently planned field-scale tests and many ongoing laboratory studies are designed to address some of these issues.

Investigations are needed to provide more fundamental understanding of the reactions pathways and possible by-products that might be generated by the reactions of contaminants with the reactive media. This could enable engineering manipulations to force certain, more desirable reaction pathways. In addition, development of novel reactive media and optimization of the existing ones could possibly improve competitiveness of treatment walls with other *in situ* and *ex situ* ground-water remediation technologies.

The reduction of chlorinated solvents by zero-valent iron requires contact between the organic compound and iron surface, which limits treatment with Fe(0) to water-soluble chemicals. Treatment of many soil contaminants which have functional groups that are reducible, but are strongly sorbed to sediments and soil samples (e.g., PCBs, dioxin, DDT, toxaphene, mirex, lindane, hexachlorobenzene), may not be feasible with this technology. This also applies for many other reactive media that are being investigated for use in treatment walls. Subsequently, there is a need to investigate the possibility of utilizing treatment sequences, e.g., combining *in situ* soil washing technologies with treatment walls.

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