PERMEABLE REACTIVE BARRIER – INNOVATIVE TECHNOLOGY FOR GROUND-WATER REMEDIATION

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ABSTRACT

Significant advances in the application of permeable reactive barriers (PRBs) for ground-water remediation have been witnessed in the last 5 years. From only a few full-scale systems and pilot-scale demonstrations, there are currently at least 38 full-scale PRBs using zero-valent iron (ZVI) as a reactive material. Of those, 26 are continuous reactive walls, 9 are funnel-and-gate systems and 3 are *in situ* reactive vessels. Most of the PRB systems have used granular iron media and have been applied to address the control of contamination caused by chlorinated volatile organic compounds or heavy metals. Many regulatory agencies have expressed interest in PRB systems and are becoming more comfortable in issuing permits. The main advantage of PRB systems is that the installation costs are comparable with those of other ground-water remediation technologies, while the O&M costs are significantly lower and are mostly due to monitoring requirements, which are required for all remediation approaches. In addition, the land use can resume after the installation of the PRB systems, since there are few visible signs of the installation above grounds except for the monitoring wells. It is difficult to make any definite conclusions about the long-term performance of PRB systems because there is no more than 5 years of the record of performance that can be used for such analysis. The two main challenges still facing this technology are: (1) evaluating the longevity (geochemistry) of a PRB; and (2) ensuring/verifying hydraulic performance. A number of public/private partnerships have been established in recent years that are working together to resolve some of these problems. This organized approach by combining the efforts of several government agencies and private companies will likely result in better understanding and, hopefully, better acceptance of this technology in the future.

Key words: ground-water, contamination, remediation technology, permeable reactive barriers

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.

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.

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.

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.

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.

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. The most common polymer for liquid shoring is guar gum (naturally occurring carbohydrate polymer derived from guar beans) and the main challenge when using biopolymer slurry is to keep the slurry active long enough to complete the required construction. Without additives (sometimes up to seven additives may be needed), the slurry will only remain active for a few hours while the additives (biocides and/or pH control) can extend its active life to about one week.

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. However, the presence of boulders severely limits the utility of this technique and may require additional excavation approaches to complete 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. Drilling methods usually involve driving a large circular casing into the ground and augering out the native material. The hole is then backfilled with reactive media and the casing is removed. Truck-mounted caisson drills can be used to create columns with diameter in the range from 0.5 to 2.5 m. Overlapping or tangential columns can be used to create longer or larger treatment zones. Deep soil mixing is a modified caisson method, which mixes the soil with a slurry *in situ* and without excavation. The reactive material is injected through the hollow kelly bar as the mixing tool penetrates the soil. Pressurized air or steam may be used to aid penetration and mixing. 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.

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 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. Vertical hydrofracturing uses a specialized tool to orient the vertical fracture and initiate the fracturing process. The tool is placed into the boreholes spaced at about 5-m intervals to the desired depth and the interval for fracturing is isolated by packers. A slurry comprised of the reactive media and biopolymer is then pumped under low pressure into the formation. Major concerns with this installation method are continuity and width of installation and those must be independently verified.

The funnel-and-gate system for *in situ* treatment of contaminated plumes consists of low hydraulic conductivity (e.g., $1x10^{-6}$ 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.

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).

Technology Applicability and Cost

Applicability

A vast majority of PRB systems in operation nowadays are using ZVI as the reactive media to treat chlorinated hydrocarbons in ground-water. The first pilot-scale PRB system was installed in 1991 in Borden, Ontario as a continuous reactive barrier (CRB). This system used iron grindings collected from a local machine shop mixed with sand to treat PCE and TCE and offers a five-year-long record of performance. The first full-scale system was installed in 1995 in Sunnyvale, CA as a funnel-and-gate (F&G) system. This system uses 100% ZVI to treat TCE, DCE, VC and CFC-113.

Besides chlorinated hydrocarbons, ZVI iron is used for the treatment of nitrate (DOE Bear Creek Valley, Y-12 Plant, TN; ETPT System at DOE Rocky Flats Environmental Technology Site, CO), uranium (DOE Bear Creek Valley, Y-12 Plant, TN; ETPT System at DOE Rocky Flats Environmental Technology Site, CO; Fry Canyon, UT; DOE Monticello Site, UT), technetium (DOE Bear Creek Valley, Y-12 Plant, TN), and hexavalent chromium (U.S. Coast Guard Air Station, Elizabeth City, NC).

Other types of PRB systems use cellulose solids as a carbon source for treatment of nitrate and sulfate (Killarney, Long Point and North Campus, Canada; Industrial Site, Sudbury, Ontario), activated carbon for the adsorption of pesticides and BTEX (Marzone Superfund Site, Tifton, GA), clinoptilolite for the adsorption of radioactive elements (Chalk River, Ontario; West Valley Demonstration Project, West Valley, NY), and simple oxygenation for enhanced biodegradation of BTEX (East Garrington, Alberta; U.S. Naval Air Station, Alameda, CA).

Cost

The potential long-term economic benefit of PRBs has been an important driving force behind the interest in this technology. At sites where ground-water contamination could persist for several years or decades, a passive technology like PRB that has no or minimal recurring operating labor or energy requirement beyond quarterly monitoring has potential long-term cost advantage over other remediation approaches like pump and treat, air sparging, bioremediation, and bioventing.

The two main categories of costs for any technology can be divided in capital investment and O&M costs. Capital costs include the two main items: preconstruction activities and construction activities. Preconstruction costs are those incurred for the activities leading to the actual construction of a PRB system. This category includes items such as preliminary site assessment (historical site data evaluation), site characterization, laboratory testing for media selection, PRB modeling and design, technology licensing costs, procurement of materials and construction contractors, and regulatory overview. These costs can constitute up to 50% of the total capital investment in the PRB. Construction activities include items like site preparation, reactive media procurement ($300-350/ton), PRB construction, and construction of the monitoring system. Table 1 lists typical reactive barrier installation costs that do not include reactive materials, mobilization and site preparation. Most of the current cost estimates have not considered the possible requirement to remove the PRB after the treatment objectives have been fully satisfied, which may substantial increase the construction costs for this technology.

O&M costs include annual costs associate with ground-water flow monitoring, ground-water sampling, and analyses of water quality parameters. Periodic maintenance costs may include replacement or rejuvenation of the reactive media. Current experience at existing sites suggests that the incorporation of proper safety factors may make it possible to keep the frequency of such maintenance as low as once in several years, if at all.

Table 2 summarizes design and cost parameters for the PRB systems described in previous sections of this document. Unfortunately, most of the literature references used in the preparation of this report have not provided adequate separation of cost categories listed above. The data shown in the last column of Table 2 should be used with caution since it is possible that some of the preconstruction activities were not included in the reported cost information.

Regulatory/Policy Requirements and Issues

Implementation of a PRB system at a hazardous waste site, as with any remedial measure, requires the approval of appropriate state and/or federal regulatory agencies. Many regulatory agencies have expressed interest in PRB systems and are becoming more comfortable in issuing permits. Individual states have formed the Interstate Technology Regulatory Cooperation (ITRC) group to build a consensus among the states on regulatory issues surrounding innovative remediation technologies. The ITRC has formed a PRB group that has developed consensus documents for the states to enhance the regulatory acceptance of the PRB technology and provide guidance on compliance monitoring requirements.

Regulatory requirements for design, construction, and monitoring are determined on a case-by-case basis. Regulatory agencies require that sufficient proof be offered that there is a compelling reason why PRB is the best choice for a given site and that expectations for the performance of a PRB are supported by credible evidence. Even when such proof can be offered, it is sometimes difficult to proceed with PRB design and installation if there is already a ROD signed for a given site because obtaining a consensus to modify the ROD is usually a formidable task. In addition, regulatory agencies may require a contingency for the installation of a PRB, which means that an alternative treatment method must be proposed along with the reactive barrier.

Potential considerations to be addressed as part of the regulatory 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 vertical and horizontal extent of the ground-water plume;
- Monitoring to measure concentrations of by-products in ground-water potentially produced 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.

At many sites, the target cleanup levels have been set to federal drinking water standards (MCLs) for the key contaminants. At some sites, state/local regulations have required even more stringent cleanup levels for some contaminants, such as VC.

Implementation of PRB technology does not involve removal of ground-water 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 ground-water or air to the environment. Major issues that may arise during installation of a PRB system are the National Pollution Discharge Elimination System (NPDES) permits, Underground Injection

Table I. Typical Reactive Barrier Installation Costs

Installation Method	Mobilization Costs	Minimal Thickness (m)	Maximum Depth (m)	Range in Costs ($/m^2)
Sheet and shore	Medium	1.3	12	150-400
Trench box	Low	1.3	6	50-125
Continuous trencher	High	0.3	7.5	50-300
Jet grouting	Low	0.6	30	200-1000
Deep soil mixing	Very high	0.75	30	90-200
Biopolymer trench	Medium	0.5	25	40-125

Table II. Design and Cost Parameters

Location	PRB Type	Cell Size (m)		Depth to Aquitard (m)	Construction Method		Cost ($)
		Thick.	Length		Cell	Funnel (m)	
Lowry AFB, CO	F&G	1.5	3	6	Cofferdam	Sealable sheet piling (2x4.6)	530,000
Dover AFB, DE	F&G (2 gates)	1.2	2x1.2	12-13.7	Caissons	Sealable sheet piling (2x9.2)	22,000 iron 25,000 pyrite 327,000 install.
F.E. Warren AFB, WY	CRB	0.3-1.2	172	10.7	Trenching box		2,350,000
Cape Canaveral, FL	CRB	1.2	15.2	15.2	Soil mixing		
Pease AFB, NH	CRB	0.8	45.7	10	Bioslurry trench		300,000
U.S. Naval Air Station, Alameda, CA	F&G	1.5	4.6	7.3	Excavation		400,000
Aircraft Maintenance Facility, OR	F&G (2 gates)	0.46 and 1	15.2 and 18	7.3-10.3	Continuous trenching	Soil-bentonite slurry	600,000
DOE Y-12 Plant, TN	CRB	0.6	7.9	6.7-9.1	Continuous trenching, guar gum for shoring	PE-lined trench (68.5)	1,000,000
Somersworth landfill, NH	CRB	0.9	7.6	12.2	Bioslurry trench		175,000
Watervliet arsenal, NY	2 CRBs	0.9	58+24.3	2.4-3.6	Sheet piles for shoring		113,000 design 278,000 install.
DOE Plant, MO	CRB	0.6-1.8	40	6	Trench box		1,300,000
Caldwell Trucking, NJ	2 CRBs	0.07	45 + 27	15.2	Hydraulic fracturing		670,000 + 450,000
Industrial site, NY	2 CRBs	0.3	394 + 113	5.5	Continuous trenching		797,000

Location	PRB Type	Cell Size (m)		Depth to Aquitard (m)	Construction Method		Cost ($)
		Thick.	Length		Cell	Funnel (m)	
Industrial site, Sidney, Australia	CRB	1.5	5	3	Trenching box		
Industrial site, Belfast	F&G	1.2	1.2	11	In-situ reaction vessel	Bentonite and cement slurry (24.4-30)	370,000
Former Drycleaning Site, Germany	CRB	0.6-1	22.5	10	Overlapping boreholes		123,000
Industrial Site, NJ	CRB	1.5	39	7	Sheet pile excavation		150,000 design 725.000 install.
Industrial Site, SC	CRB	0.3	99	8.8	Continuous trenching		400,000
Tacony Warehouse, PA	Cell	Circular cell D=1.2m H=11 m		11	Caisson auger		607,336
Federal facility, CO	F&G (4 gates)	0.9-1.2	4 x 12	7.6	Cofferdam	Sealable sheet piling (317)	1,000,000
Coffeyville, KS	F&G	1.2	6	9	Excavation	Soil-bentonite slurry	400,000
Fry Canyon – 1, UT	F&G	0.9	2.1	1.2	Backhoe excavation		30,000 design 140,000 installation
U.S. Coast Guard Station - 1, NC	CRB	0.6	46.3	7.3	Continuous trenching		500,000
Military Reservation, MA	Two CRBs	0.084	14.6	36	Vertical hydrofracturing		160,000
X-625 Facility, Piketon, OH	Above-ground			10	150-m horizontal well	4,000,000	
Moffet Airfield, CA	F&G	1.8	3	7	Backhoe, sheet pile box	Sealable joint piling (2x20)	802,375
Sunnyvale, CA	F&G	1.2	11	5.5	Cofferdam	Cement-bent. slurry (2x250)	170,000 iron 720,000 installation
Borden, Ontario	CRB	1.4	5.5	9.1	Clamshell, sheet pile box		30,000
East Garrington, Canada	F&G (3 zones)	1.8	1.8	5.5	Vertical culverts	Trench sealed with liner (2x150)	67,200
Marzone Site, GA	F&G	Removable box				Vibrating beam (400)	520,000

Control (UIC) requirements, and Air Quality Permitting considerations. NPDES permit may be required to dispose of excess water generated during installation. Also, contaminated soils generated during installation would have to be classified in accordance with state and federal Hazardous Waste regulations, which then dictates the disposal method. A UIC permit should not be required for the majority of PRB installation techniques except perhaps jet grouting and hydraulic fracturing methods. However, monitoring for leachability of the reactive media (e.g., Fe) in the downgradient aquifer should be included in the monitoring plan. Air permits would typically not be required because these installations are located downgradient of the contamination source where the release of contaminants in the air is typically below levels that would require permitting.

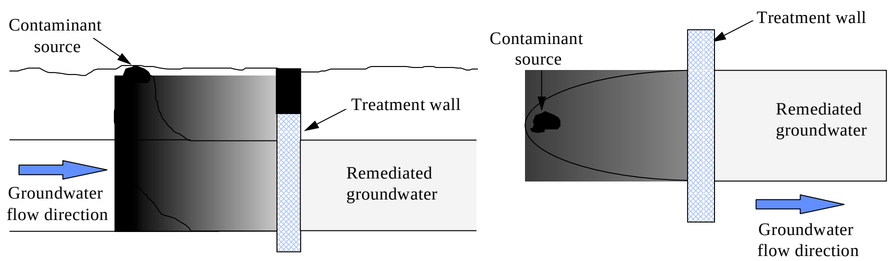

Figure 1. Schematic of a Simple Treatment Wall System

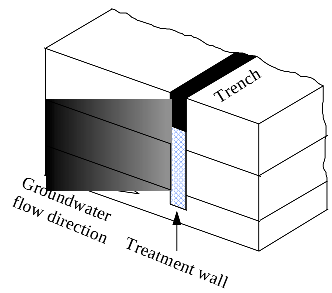

Figure 2. Treatment Wall in a Trench

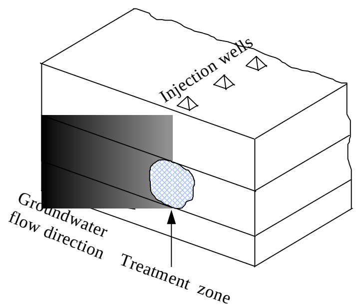

Figure 3. Injected Treatment Zone

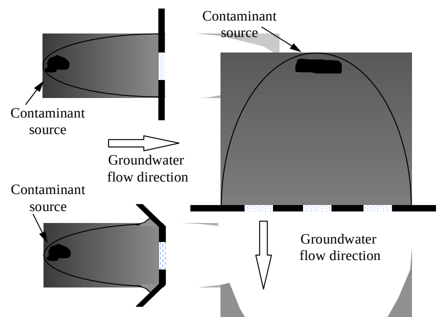

Figure 4. Funnel-and-Gate Systems