Permeable reactive barrier (PRB) for groundwater

2010. 10. 15.

Hanyang University

1. Introduction

- Groundwater is a limited ecological resource representing a small percentage of the total water distribution. The contribution from groundwater is vital; perhaps as many as two billion people depend directly upon aquifers for drinking water, and 40% of the world's food is produced by irrigated agriculture that relies largely on groundwater.

1. Introduction

- There are many reports of serious incidents of groundwater contamination due to accidental spills, or unsatisfactory disposal of industrial chemicals, agricultural practices, mining activities, etc.

- Attempts at large-scale groundwater cleanup began in earnest in the 1980s and the results of early remediation efforts seldom produced the expected reduction in contamination levels.

1. Introduction

- Studies by the U.S. Environmental Protection Agency (EPA) found that the commonly used pump-and-treat (P&T) technologies (pump the water and treat it at the surface) rarely restored sites that had contaminated groundwater to background conditions.

- This was confirmed in a much more extensive 1994 National Research Council (NRC) study that explicitly reviewed 77 sites across the United States where full scale pump-and-treat was being used.

1. Introduction

- One of the most promising remediation technologies is the use of permeable reactive barriers (PRBs) filled with reactive material(s) to intercept and decontaminate plumes in the subsurface.

- In the last decade, there has been an explosion of activities directed at the development and implementation of PRBs.

2. Sources and types of groundwater contamination

- Broadly, groundwater contaminants come from two categories of sources:

  (a) Point Sources and

  (b) Distributed, or Non-Point Sources.

- Localized sources are known as point sources of contamination.

- The contaminant interacts with the moving groundwater and the soil and spreads out to form a plume moving in the same direction as the groundwater.

2. Sources and types of groundwater contamination

- The resulting groundwater contamination plume may extend several hundred meters or even further away from the source of pollution.
- Groundwater can also be contaminated by diffuse sources over a wide area, for instance widespread use of fertilizers on gardens and fields.
- Diffuse contamination may have greater environmental impacts than contamination from point sources because a much larger volume of water is affected.

2. Sources and types of groundwater contamination

- Pollutants from point sources are generally related to urban development, while diffuse sources are generally rural in nature. Some of the examples of point and diffuse pollutions are given in Table 1.

Table 1
Examples of point and diffuse pollutions

Point source	Non-point or diffuse pollution
Municipal landfills, industrial waste disposal sites, leaking gasoline storage tanks, leaking septic tanks, and accidental spills and leaks of petroleum products and of dense industrial organics	Atmospheric deposition, contaminated sediments, and many land activities that generate polluted runoff, such as agriculture (pesticides and fertilisers), logging, and onsite sewage disposal

3. Permeable reactive barrier

- This technology termed as Permeable Reactive Barriers is defined as:

'An emplacement of reactive media in the subsurface designed to intercept a contaminated plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals down-gradient of the barrier'

3. Permeable reactive barrier

- The concept of PRBs is relatively simple.

- A permeable reactive barrier material consisting of permanent, semi permanent or replaceable reactive media is placed in the subsurface across the flow of path of a plume of contaminated groundwater, which must move through it as it flows, typically under its natural gradient, thereby creating a passive treatment system.

3. Permeable reactive barrier

- As the contaminant moves through the material, reaction occur that transform the contaminants into less harmful (non-toxic) or immobile species.

- The PRB is not a barrier to the groundwater, but it is a barrier to the contaminants.

3. Permeable reactive barrier

- PRBs potentially have several advantages over conventional pump-and-treat methods for groundwater remediation.

(1) PRBs can degrade or immobilize contaminants in situ without any need to bring them up to the surface. Hence no need for expensive above ground facilities for storage, treatment, transport, or disposal other than monitoring wells. After the installation the above ground can be re-used for other purposes. Also, as the contaminants are not brought to the surface; there is no potential cross media contamination.

3. Permeable reactive barrier

(2)They also do not require continuous input of energy, because a natural gradient of groundwater flow is used to carry contaminants through the reactive zone. Only periodic replacement or rejuvenation of the reaction medium might be required after its reactive capacity is exhausted or it is clogged by precipitants and/or microorganisms. However, the drastically reduced operating costs offsets the higher construction cost that are typical for PRBs, which results in an overall reduction in the life cycle cost of this technology.

3. Permeable reactive barrier

(3)Degradation of most of the contaminants is achieved rather than mere change of phase of contaminants. The barrier provides effective contaminant remediation, much more than simple migration control of the pollutants.

(4)Technical and regulatory problems related to ultimate discharge requirements of effluent from pump-and-treat systems are avoided with the PRB technology.

4. Configuration of PRBs

4.1. Conventional systems

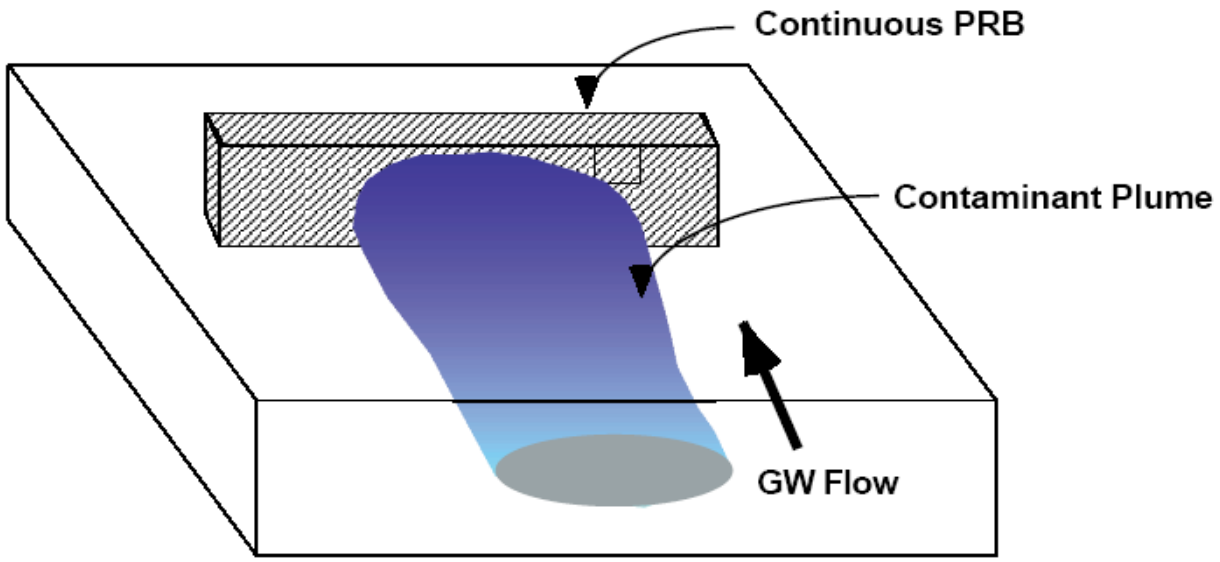
- Two installation schemes are more frequently used in field applications; Continuous and Funnel-and-Gate PRB.

- The continuous PRB configuration consists of a single reactive zone installed across the contaminant plume, while the funnel-and-gate system consist of a permeable gate (reactive zone) placed between two impermeable walls that direct the contaminated plume towards the reactive zone.

4. Configuration of PRBs

4.1. Conventional systems

- A continuous PRB trench system

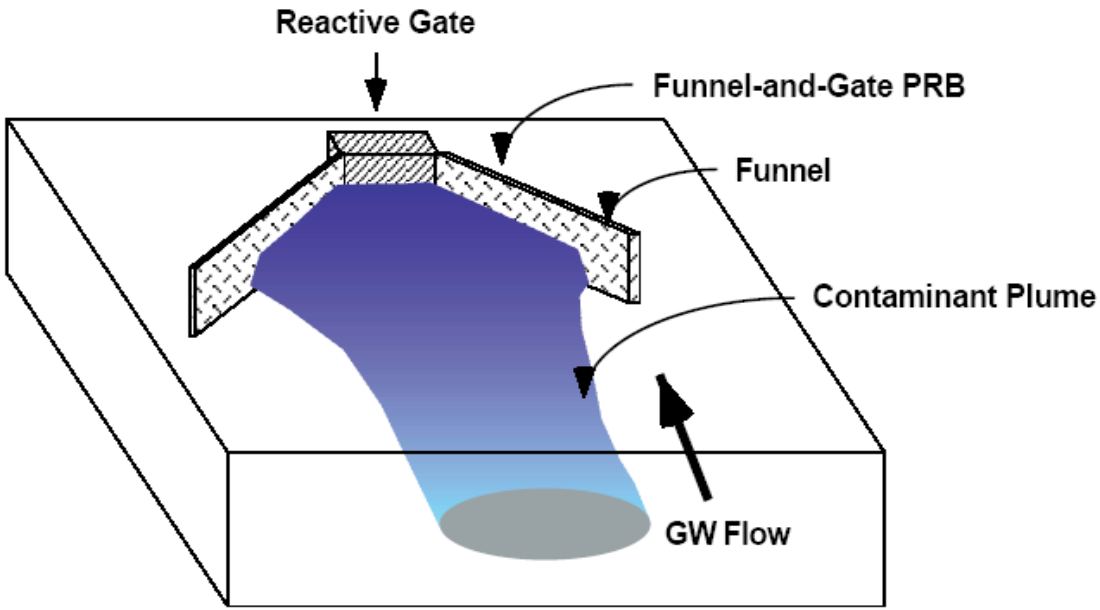


✓This system consists of a trench or series of trenches that are excavated across the entire path of the plume and backfilled with reactive media.

4. Configuration of PRBs

4.1. Conventional systems

- A funnel-and-gate systems



✓Funnel-and-gate systems have solid walls that direct the flow of contaminated groundwater plume through a gate containing the reactive media.

4. Configuration of PRBs

4.1. Conventional systems

- The choice between the two configurations depends on both the hydrogeological characteristics of the site and the reactive material cost.

- When a high cost reactive material is used, funnel-and gate configuration is preferred since the reactive zone requires less material.

- However, construction cost of continuous type barrier is much cheaper than funnel and-gate system.

4. Configuration of PRBs

4.1. Conventional systems

- Hence a balance must be struck between the cost of reactive material and the construction cost of the barrier, in accordance with the target pollutant and level of removal to be achieved.

- Multiple reactive medium in succession or in series can be installed in the funnel-and gate setup.

- Alternatively, a relatively less expensive method using multiple caisson gates can also be installed.

4. Configuration of PRBs

4.1. Conventional systems

- Usually, the conventional PRB installation techniques require some degree of excavation, which limits the PRB to fairly shallow depths of 20 m .

- However, use of new construction techniques, such as slurry injection and hydrofracturing are able to overcome this depth limitation.

4. Configuration of PRBs

4.2. Advanced methods

(1) Injection system:

- Injection system involves creating a treatment zone within the contaminant boundary by drilling series of bore holes or injection wells and injecting the reactive material (chemical/particulate mixture) into the treatment zone.

- Potential advantages of this approach are that there is no need to construct a trench and possible aquifer access at greater depths.

4. Configuration of PRBs

4.2. Advanced methods

- Usually, two or three rows of overlapping, interlocking columns can offer effective barrier.

- Nevertheless, it has to be made sure that the contaminant plume is efficiently taken care of and no by-passing or fingering occurs, which may impair the remediation effect.

4. Configuration of PRBs

4.2. Advanced methods

(2) Hydraulic/pneumatic fracturing :

- Hydraulic/pneumatic fracturing is intentional fracturing (cracking) of a subsurface using pumped water and/or air under high pressure.

- As the confining pressures are exerted in the borehole, fractures will open and propagate out laterally from an initiation point.

- A fracture fill slurry composed of the reactive medium, can then be injected into the fracture to form a reactive treatment zone.

4. Configuration of PRBs

4.2. Advanced methods

(2) Hydraulic/pneumatic fracturing :

- More than one fracture may be required within the treatment zones. Fractures have a preferred direction of propagation, they are therefore asymmetric with respect to the borehole and they climb in the preferred direction of propagation. Fractures can be controlled to happen either horizontally or vertically. Some advantage to this technique includes the ability to emplace a barrier to a depth greater than 80 ft.

4. Configuration of PRBs

4.2. Advanced methods

(2) Hydraulic/pneumatic fracturing :

- Also, fracturing causes minimal disturbance, does not generate contaminated soils, and is inexpensive.

- Fractured zones may also be applied to direct groundwater flow towards the gates in funnel-and-gate system. Some drawbacks of emplacement by hydraulic fracturing include difficulty in controlling the fracture direction and the limited soil conditions in which it can be used effectively.

4. Configuration of PRBs

4.2. Advanced methods

(3) Passive groundwater capture and treatment by reactor cells:

- This technique involves emplacement of reactor cell(s) in the subsurface consisting of reactive medium and capturing the contaminated plume into the reactor for treatment.

- This system does not involve any pumping equipment and the plume is directed into the reactor by siphoning or by natural gradient. Because of the passivemode of operation, the operating and maintenance requirements are relatively minor.

Construction

Conventional Excavation

- Basic construction practice
  - Using backhoes, excavators, cranes
  - Depths of about 35 ft
- Modified construction practice
  - Using clamshell : Attaining greater depths (150 ft)
- Deep trenches may need to be supported prior to being backfilled.
  - Trench box & slurries

Construction

Conventional Excavation

- Trench box
  - It is most widely used because of convenience
- Slurries
  - Significant cost savings
  - It is hard to construct permeable zones

  → biodegradable polymer solution

Construction

Conventional Excavation

- Trench box
  - It is most widely used because of convenience
- Slurries
  - Significant cost savings
  - It is hard to construct permeable zones

  → biodegradable polymer solution

Construction

Conventional Excavation



Backhoe



Clamshell

Construction

Conventional Excavation



Trench Box



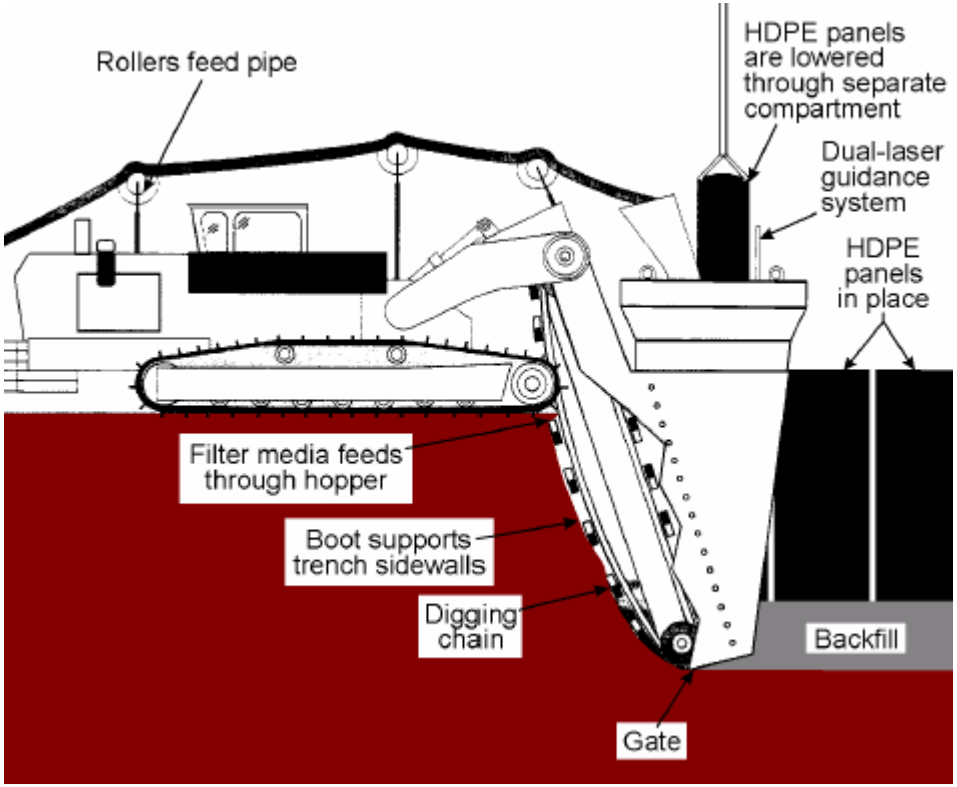
Construction

Biopolymer Trenching



Construction

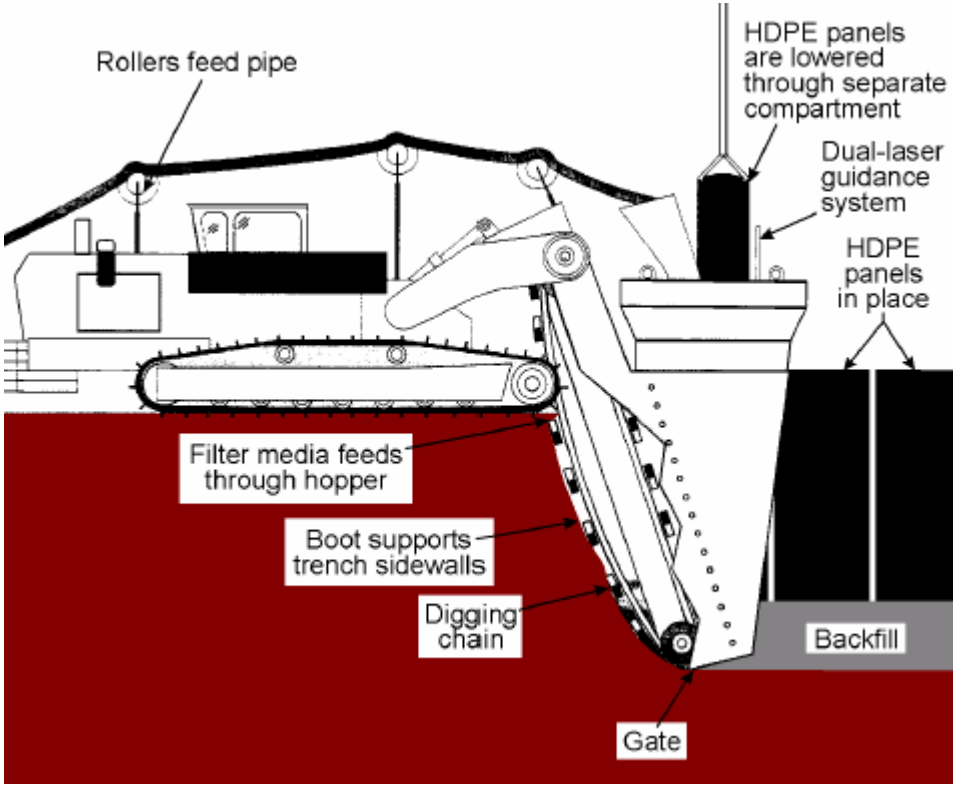
Continuous Trenching





Construction

Continuous Trenching

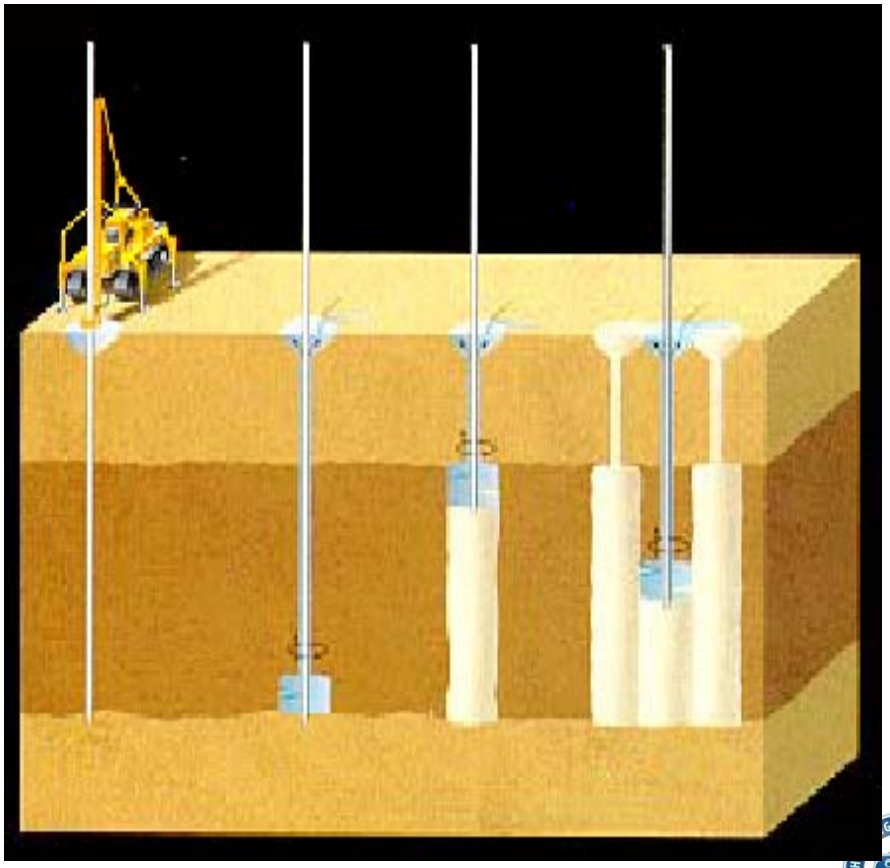




Construction

Jetting





Construction

Jetting

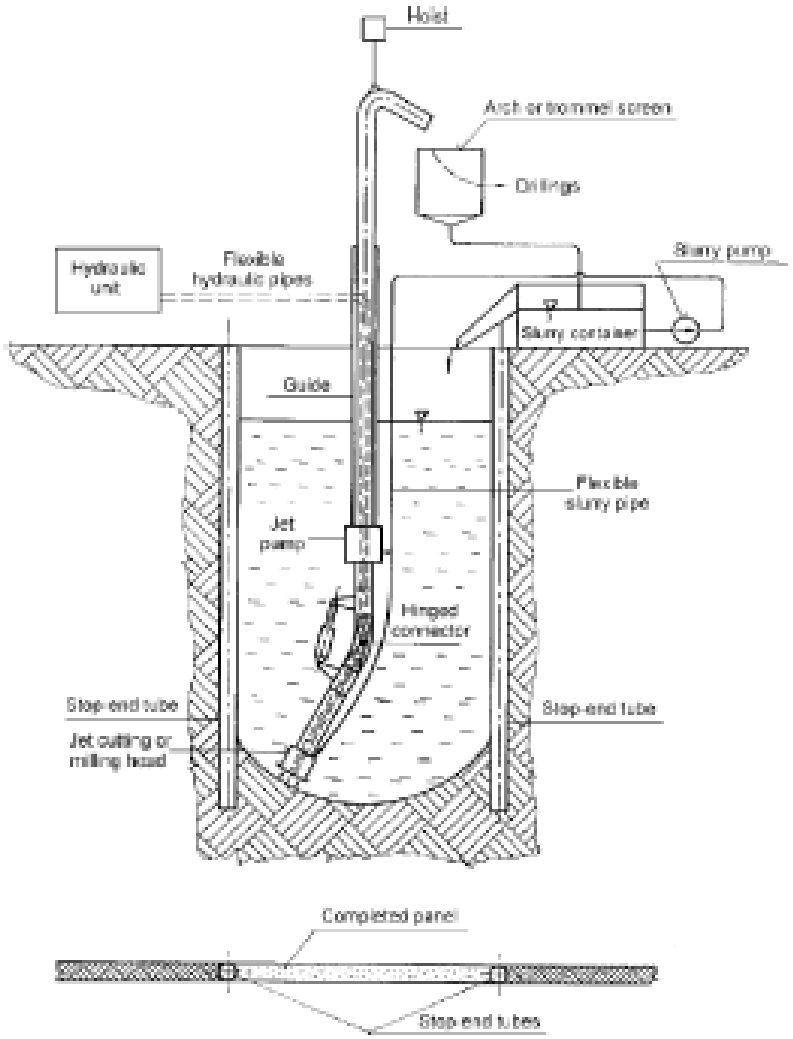
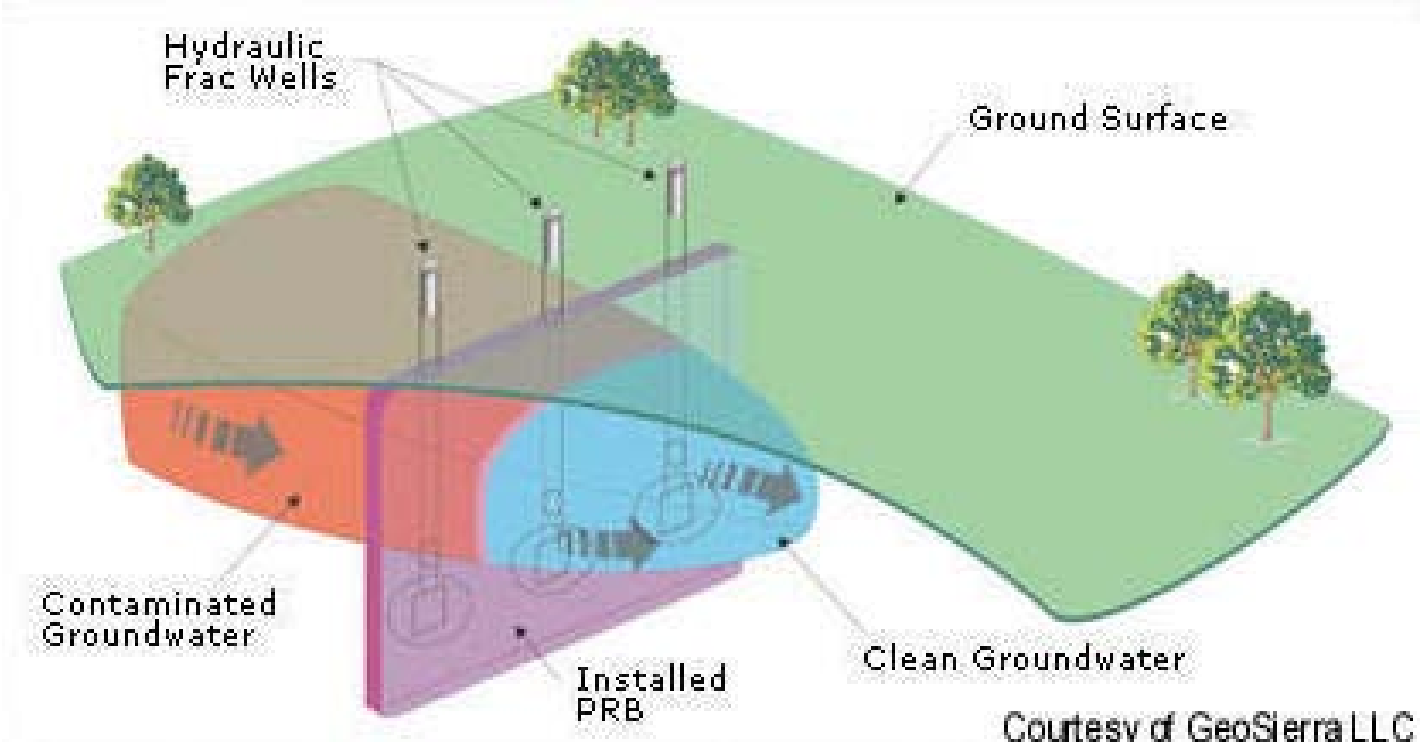


Figure 2. Swinging-pipe jet equipment for cut-off wall or reactive barrier construction

Construction

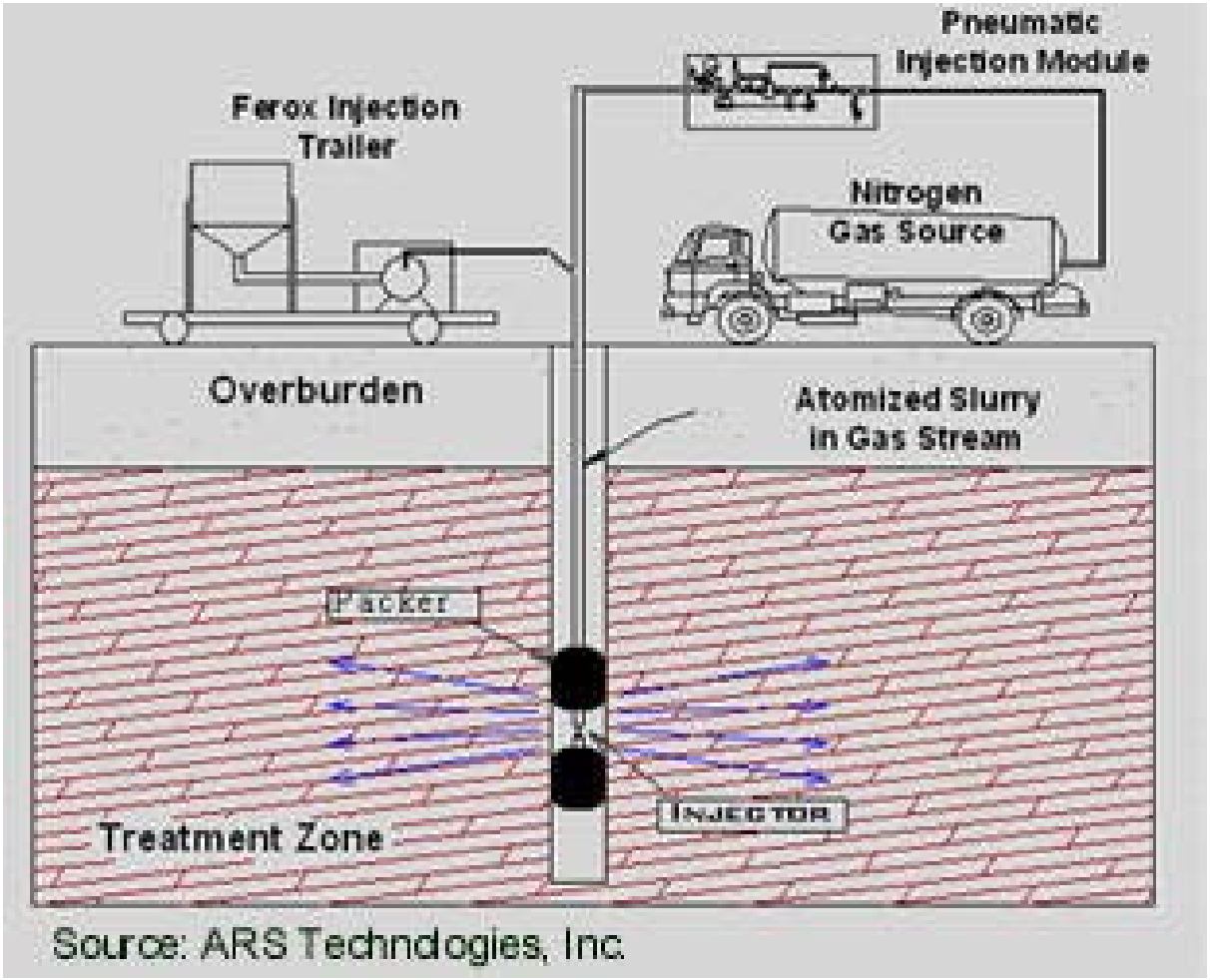
Vertical Hydrofracturing (VHF)



- VHF construction methods (300 ft deep)

Construction

Pneumatic fracturing and injection



Construction

Soil Mixing



- It use one or more large diameter augers to inject iron media.
  1) The iron is initially mixed with biopolymer and pumped to the mixing augers
  2) Over time the biopolymer breaks down allowing the groundwater to flow through the treatment zone.

4. Configuration of PRBs

4.2. Advanced methods

- This system does not involve any pumping equipment and the plume is directed into the reactor by siphoning or by natural gradient. Because of the passivemode of operation, the operating and maintenance requirements are relatively minor.

- The selection of the construction technique to be used depends upon the site characteristics such as depth of PRB, geotechnical consideration, soil excavation.

4. Configuration of PRBs

4.2. Advanced methods

- Common contaminants being treated using PRB technologies are given in Table 2.

Table 2
Some of the common contaminants in groundwater for remediation

Groups	Pollutants
Organic compounds	
Methane	Tetrachloromethane, trichloromethane, dichloromethane
Ethanes	Hexachloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane 1,1-dichloroethane
Ethenes	Tetrachloroethene, trichloroethene, *cis*-1,2-dichloroethene
Propanes	1,2,3-Trichloropropane, 1,2-dichloropropane
Aromatics	Benzene, toluene, ethylbenzene
Others	Hexaxhlorobutadiene, 1,2-dibromoethane, Freon 113, *N*-nitrosodimethylamine
Inorganic compounds	
Trace metals/heavy metals	Chromium, nickel, lead, uranium, iron, manganese, technetium, selenium, copper, cobalt, cadmium, zinc
Anion contaminants	Sulphate, nitrate, phosphate, arsenic

5. Mechanism of interaction

- Proper understanding of the underlying process by which the reactive material interact with the pollutants and the mechanism of removal is very important.

- In general, the contaminant removal mechanisms can be classified broadly into three categories:

(1) Degradation: Through chemical or biological reactions that lead to decomposition or degradation of contaminants into harmless compounds.

5. Mechanism of interaction

(2) Precipitation: Immobilization of contaminants within the reaction zone by formation of insoluble compounds. Here, the chemical state of the contaminant is not altered.

(3) Sorption: Immobilization of contaminants within the reaction zone by adsorption or complex formation. Here, the chemical state of the contaminant is not altered.

5. Mechanism of interaction

- More specifically, the principal processes are:

✓ Reductive degradation of organic pollutants.

✓ Oxidative degradation of organic pollutants.

✓ Retardation and biodegradation of organic pollutants.

✓ Sorption of organic or inorganic pollutants.

✓ Reduction and/or precipitation of heavy metal compounds.

5. Mechanism of interaction

- In general, the types of reactive materials used for the construction of permeable reactive barriers, are :

✓ Those changing pH or redox potential,

✓ Those causing precipitation,

✓ Materials with high sorption capacity, and

✓ Those releasing nutrients/oxygen to enhance biological degradation.

5. Mechanism of interaction

- In general, the types of reactive materials used for the construction of permeable reactive barriers, are :

✓ Those changing pH or redox potential,

✓ Those causing precipitation,

✓ Materials with high sorption capacity, and

✓ Those releasing nutrients/oxygen to enhance biological degradation.

5. Mechanism of interaction

- A study by USEPA, classified the reactive barrier materials according to the target pollutant and the mechanism of removal (Table 3).

Table 3
Reactive materials classified based on the target pollutant and the mechanism of removal

Target and mechanism of removal	Reactive materials
Inorganics-sorption or substitution barriers	Activated carbon, activated alumina, bauxite, exchange resin, ferric oxides and oxyhydroxides, magnetite, peat, humate, lignite, coal, phosphates, titanium dioxide, zeolite
Inorganics-precipitation barriers	Biota, dithionite, ferrous hydroxides, ferrous carbonates, ferrous sulfide, hydrogen sulfide gas, lime, flyash, limestone, miscellaneous ($Mg(OH)_2$, $MgCO_3$, $CaCl_2$, $CaSO_4$, $BaCl_2$, zero-valent metals
Inorganics-degradation barriers	Biota, zero-valent metals
Organics-degradation barriers	Ferrous minerals, oxygen release, ultramicrobacteria, zero-valent metals
Organics-sorption barriers	Zeolite, activated carbon, clays

5. Mechanism of interaction

- Zero-valent iron (Fe^0) is the most common reactive material in the current field of application.

- Apart from iron based materials, other types of materials such as organic based (activated carbon, leaf, peat, sewage sludge, sawdust, etc.), alkaline-complexing agents (hydrated lime, ferrous sulphate), phosphate minerals like hydroxyapatite and biogenic apatite (e.g. fishbone), zeolites, clay, metal oxides, microorganisms, polymers, innovative polymer membrane (as liner) containing iron are also being evaluated.

5. Mechanism of interaction

- Finer iron particles can also be mixed with sand in order to increase the hydraulic conductivity.
- Iron with several amendments has been tested to improve the performance.

5. Mechanism of interaction

(1) During the reaction, oxidation of Fe^0 to Fe^{2+} results in an increase in pH, which eventually leads to the formation of precipitation of number of minerals. In order to overcome this, pyrite or iron sulfide are added (oxidation of pyrite produces acid) which lowers the pH and increases the organic removal efficiency. One negative effect of addint pH controlling amendments could be the increased possibility of higher levels of dissolved iron in water downstream after there active cell.

5. Mechanism of interaction

(2) Instead of using granular sized iron medium, use of colloidalsize iron (1–3 mm) or of nanosize (1–100 nm = 0.001–0.1 mm) would significantly increase the surface area and a lower total iron mass may be required in the treatment zone. Nanosized or as emulsion state have also been studied. Colloidal or nono-state iron allows the formulation of slurries that can be injected in PRB by boreholes or fractured media.

5. Mechanism of interaction

(3) Bimetallic systems where several metals are plated onto zerovalent iron (ZVI) (e.g. Fe–Cu, Fe–Pd, Fe–NI) have shown to produce greater performance compared to having ZVI alone. Some bimetals enhance the degradation by acting as catalysts and as galvanic couples (increase electron activity).However it has been cited that reactivity of bimetallic system may be high initially but may decline gradually.

5. Mechanism of interaction

(4) Acid pre-treatment of ZVI was also found to increase the degradation efficiency; probably due to removal of oxide coating layer on the iron surface or due to increase in surface area by etching or pitting corrosion.

6. Treatment of inorganic and organic pollutants

- Fundamental difference exists between organic and inorganic contaminant remediation.

- Organic contaminants can be broken down into innocuous elements and compounds, such as carbon dioxide and water because they are molecules consisting of carbon, hydrogen, halogens, oxygen, and sometimes sulphur, phosphorous, and nitrogen.

- Conversely, most inorganic contaminants are themselves elements. They cannot be destroyed but can only change speciation.

6. Treatment of inorganic and organic pollutants

- Therefore, remediation strategies must focus on transforming inorganics into forms that are non-toxic, not bioavailable, immobile, or capable of being removed from the subsurface. The characteristics of these elements have in common is that they can undergo redox reactions and can form solid precipitates with carbonates, sulphide and hydroxide.

7. Zero-valent iron

- ZVI tend to be oxidized, passing its electron to contaminants (organic-halogenated hydrocarbons, inorganic-some metal; U(VI), Cr(VI), etc., which undergo reductive mechanism resulting in precipitation or degradation.

- In the case of reductive precipitation, there is also a potential risk of remobilization due to dissociation.

- Interferences with reactions can occur while treating groundwater with ZVI.

8. Activated carbon

- Activated carbons are chemically stable materials and are widely considered as suitable adsorbent for on-site or off-site treatment of polluted groundwater.

- This material presents a high adsorption capacity for many organic and inorganic contaminants largely due to its high surface area (about 1000 m^2/g) and the presence of different types of surface functional groups (hydroxyl, carbonyl, lactone, carboxylic acid, etc.).

8. Activated carbon

- In granular form, activated carbon appears to be highly suitable for use in permeable barriers.
- Significant removal of hexavalent chromium from contaminated groundwater using granular activated carbon (GAC) was achieved.
- Regeneration of carbon by phosphate extraction and acid washing also appeared to be successful, allowing the possibility for repeated use of the material.

9. Zeolites

- Zeolites are tectosilicates with three-dimensional aluminosilicates structure containing water molecules, alkali and alkaline earth metals in their structural framework.

- These minerals have very high ion-exchange, adsorbing, catalytic, molecular sieving capacities and make them potentially useful as treatment mineral for use in the PRBs.

- As the mineral is anionic (negatively charged), it can be used to remove cations from aqueous solutions.

10. Alkaline materials-complexing agents

- Hydrated lime ($Ca(OH)_2$) is a cheap reagent which can be used in PRBs for groundwater remediation. Previously, it has been used for remediation of acid mine drainage.

- Lime barriers cause pH to increase to 12–12.5 in order to facilitate the formation of metal hydroxides, which reduce the solubility of certain metals.

- They have proved to be successful in remediation of anionic and cationic pollutant species.

11. Bioremediation

- Remediation of pollutants using microorganisms (bioremediation) is one of the promising and viable technologies, which utilizes naturally occurring microorganisms and biological reactions for the degradation of toxic contaminants (mostly organic and in some instances inorganic compounds) in the subsurface groundwater. In situ bioremediation creates subsurface environmental conditions (without withdrawing the contaminated water from under the ground), typically through the principle of oxidation–reduction manipulation, which induce the degradation of chemicals via microbial catalyzed biochemical reactions.

11. Bioremediation

- Many environmental pollutants such as petroleum hydrocarbons are highly reduced, which allows oxidation of these pollutants to innocuous final compounds like carbon dioxide and water.

- On the other hand some pollutants like chlorinated solvents and nitrates are highly oxidized and are prone to undergo reduction. Microorganisms mediate such redox reactions (anaerobically or aerobically) and thrive on the contaminant degradation process to obtain it energy and food for its growth.

Table 4
Advantages and limitations of various reactive barriers used in PRB technology

Material	Advantages	Limitations
Zero valent iron (ZVI)	Most commonly used reactive barrier material. Vast amount of background data available	Not effective on all types of organic compounds especially certain dense non-aqueous phase liquid compounds like 1,2-dichloroethane and dichloromethane [54]
	Ability to be used in different states: as a pile [24,90], powder/granular [62], filing [91], colloidal [58,59], nanosized [61,62], emulsion that can be injected [63]	Lifetime of the material could be reduced due to the formation of surface coating due to geological condition of the site [93]
	High reactivity with organic and inorganic contaminants [92]	Increase in pH during reaction induces corrosion and subsequent precipitation of minerals would lead to decreased permeability of reactive material [94]
	Ability to combine with other treatment methods, e.g. bioremediation	H_2 gas produced and the microorganism (biofouling) could reduce the porosity of reactive material
	Less or no major problems associated with occupational health and safety (OHS) in handling this material	Limited information available on long term performance of the system especially on the build-up of surface precipitates and biofouling.
		Compounds like silica or natural organic matter (NOM) have passivating effect; reducing the iron reactivity [18,93]
		Competitive reaction inhibits the reactivity in the presence of certain compounds. In the presence of nitrate the dehalogenation of chlorinated compounds is decreased [95,96]

Activated carbon	Different types (with different reactivities) of activated carbon can be obtained from low cost natural products, e.g. coconut shell based Effective in the treatment of organic and heavy metal contaminants [97] Excellent material to combine with biotreatment Chemically stable material	Vast data on ex situ water and wastewater treatment. But very limited data on in situ treatment under field conditions Rapid breakthrough and thus frequent carbon change-outs or regeneration. Requires optimization studies Performance highly dependent on temperature and other extrinsic parameters Surface coatings may decrease sorption capacity Competitive adsorption
Lime (calcium carbonate or hydroxide)	Low cost reactive PRB material Effective in neutralization; reducing the solubility of certain metals or conditioning hydrochemical system to assist with other treatment processes, e.g. bioremediation Used extensively for acid mine drainage remediation or acidic agricultural soils	Slow reaction time Loss in efficiency of the system because of coating of the limestone particles with iron precipitates Difficulty in treating acid mine drainage with a high ferrous–ferric ratio, and ineffectiveness in removing manganese Limestone treatment is generally not effective for acidities exceeding 50 mg/L Voluminous sludge is produced with hydrated lime (calcium hydroxide)
Microbial bioremediation	Less expensive and easy to install Natural processes to treat contaminants Capability to degrade organic contaminants into relatively less toxic end products Reduced risk of human exposure to contaminated media Remediation is not restricted to the treatment zone alone Works well for dissolved contaminants and contamination adsorbed onto higher permeability sediments (sands and gravels)	A perceived lack of knowledge about biodegradation mechanism Specific contaminants may not be amenable to biodegradation [98] In the case of mixed wastes, some are amenable only under aerobic condition and some only under aerobic condition Site characterization and optimization studies are required for each contaminated site. Chemical characteristics of the contaminants dictate the extent of biodegradability

12. Two sequential reactive media

- Two of the most common classes of organic contaminants in groundwater are chlorinated solvents and petroleum derived aromatics.

- These chemicals are known to contaminate vast quantities of water and are difficult to remediate.

- Chlorinated solvents including chlorinated ethenes and chloromethanes have densities grater than water, allowing them to penetrate far below the water table. In addition, they have very low solubilities in water and are resistant to degradation.

12. Two sequential reactive media

- Even if they do degrade, it is often along pathways that can lead to products of greater concern than the original contaminants.

- These characteristics have led to the phrase "dense nonaqueous phase liquids" (DNAPL) to describe such chemicals.

Table 5
Examples of sequential PRBs

• Granular zero-valent iron to treat chlorinated hydrocarbons followed by aerobic bioremediation (using oxygen release compounds) to treat aromatic hydrocarbons
• Granular zero-valent iron to treat chlorinated hydrocarbons followed by nutrient addition or solid carbon source addition to promote anaerobic biodegradation of volatile organic carbons (VOCs) that cannot be degraded by granular iron
• Sequential anaerobic biodegradation of chlorinated solvents followed by aerobic biodegradation for toluene degradation
• Solid carbon sources to treat nitrate followed by granular iron to treat VOCs
• A four component PRB consisting of four reactive media in series for treating (immobilizing or destroying) multiple contaminants

13. In situ chemical oxidation (ISCO)

- ISCO can be applied to a variety of soil types and sizes and can treat volatile organic chemicals (VOCs) including dichloroethene (DCE), trichloroethene (TCE), tetrachloroethene (PCE), and benzene, toluene, ethylbenzene, and xylene (BTEX) as well as semi-volatile organic chemicals (SVOCs) including pesticides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs).

- The oxidants such as hydrogen peroxide (H_2O_2), potassium permanganete ($KMnO_4$), ozone (O_3) are applied.

13. In situ chemical oxidation (ISCO)

- The mechanism of degradation is the production of hydroxyl radicals, which are capable of oxidizing complex organic compounds. For most in situ reactive zone targets, hydroxyl radical oxidation is a much faster treatment method. Some of the advantages and limitations in adopting ISCO is given in Table 6.

Table 6
Advantages and limitations in using ISCO method in PRB technology

Advantages	Limitations
Rapid treatment Capability of contaminants to be degraded into final innocuous compounds like carbon dioxide, water and chloride Oxidants can be injected and can be applied to greater depths compared to method which require excavation Also suitable for complex organics (recalcitrant compounds) and mixed waste streams	Limited information is available on the operational history Proper oxidant selection must be made depending on site characteristics and nature of contaminants Problems such as gas evolution (also explosive vapors), toxic by-products, resolubilization of metals and reduction of biomass Precise control of pH, temperature, and contact time is important Certain materials like natural organic matter (NOM), reduced inorganics such as iron and manganese can exert a demand for oxidant Occupational health and safety concerns

13. In situ chemical oxidation (ISCO)

13.1. Use of oxidants

1 Potassium or sodium permanganate ($KMnO_4$/$NaMnO_4$):

- Permanaganate is an oxidizing agent and has an affinity towards organic compounds containing carbon-carbon bonds, aldehyde groups, or hydroxyl groups.

- As the permanganate dose increases, organic degradation also increases and the permanganate consumption also increases.

13. In situ chemical oxidation (ISCO)

13.1. Use of oxidants

1

- In some instances where permanganate is used for the degradation of DNAPL, production of MnO_2 (s) may significantly lower the permeability of the soil matrix and form a coating on DNAPL.

- Permanganate reaction rate is much slower than those of hydroxyl radical reactions, which gives it s significant advantage in achieving greater contact with contaminants, especially with DNAPL compounds.

13. In situ chemical oxidation (ISCO)

13.1. Use of oxidants

2 Hydrogen peroxide (H_2O_2)/Fenton (H_2O_2–Fe) oxidation:

- Concentration of peroxide injection generally varies between 3% and 35% (w/w) at a pH range of 3.5–6, with or without a metal catalyst (usually iron).

- The process involves the production of hydroxyl radicals (OH.), which act as a powerful oxidizing agent for the degradation of organic contaminants.

13. In situ chemical oxidation (ISCO)

13.1. Use of oxidants

2

- The initial amount of H_2O_2 and Fe catalyst also depends on the contaminant level in the soil, and the volume of groundwater remediated.

- Hydrogen peroxide and Fenton oxidation has been applied for the remediation of several contaminants including petroleum hydrocarbons, hexadecane, atrazine, aromatic compounds, dioxins and chlorinated solvents.

13. In situ chemical oxidation (ISCO)

13.1. Use of oxidants

2 ●The usefulness of Fenton oxidation may be limited by low soil permeability, subsurface heterogeneities, and highly alkaline soil (where carbonate ions are free radical scavengers.

13. In situ chemical oxidation (ISCO)

13.1. Use of oxidants

3 Persulfate:

- Sodium persulfate ($Na_2S_2O_8$) is recently being used in ISCO.
- The conversion of the persulfate results in the production of sulfate radicals or a single electron radical.
- Free radicals act as strong oxidizing agents and are known to oxidize many VOCs.

13. In situ chemical oxidation (ISCO)

13.1. Use of oxidants

3

- Many sites have sufficient background conditions which allow the persulfate to oxidize the targeted VOCs present in the soils and groundwater without the addition of a catalyst.

- In some instances, chelated iron compounds have been used as activators.

13. In situ chemical oxidation (ISCO)

13.1. Use of oxidants

4 Ozone (O_3):

- Ozone is a very powerful oxidant and is commonly used for the remediation of hydrocarbon and chlorinated solvent contaminants.

- Ozone solubility and the concentration of ozone in the injected gas stream are the key variables affecting the rate of treatment.

- Ozone degrades to oxygen and promotes biodegradation in combination to ozone oxidation process.

13. In situ chemical oxidation (ISCO)

13.1. Use of oxidants

- The characteristics of various oxidants used in the ISCO technology are given in Table 7.

Table 7
Characteristics of common oxidants

Technology features	Fenton's reagent	Permanganate	Persulfate	Ozone
Physical state as injected	Liquid	Liquid	Liquid	Gas
Key oxidant	OH^-	MnO_4^-	SO_4^{2-}	O_3 and OH^-
Oxidation potential	2.8 V	1.7 V	2.5 V	2.07 V/2.8 V
By-products	Fe(III), O_2, H_2O	Mn(VI)	Sulfate	Oxygen
Reagent costs	Moderate	Moderate for $KMnO_4$; high for $NaMnO_4$	Moderate	Moderate
Subsurface fouling	Possible	Yes, due to MnO_2 formation	No	No

Thank you !!!