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In Situ Chemical Treatment

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FOREWORD

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TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

AFO	amorphous iron oxide
ATF	automatic transmission fluid
BaP	^{14}C-labeled benzo(a)pyrene
BTEX	benzene, toluene, ethylbenzene and xylene
CMC	critical micelle concentration
CTET	carbon tetrachloride
DCE	dichloroethene
DNAPL	dense non-aqueous phase liquid
DPTA	diethylenetriaminepentaacetic acid
EDTA	ethylenediaminetetraacetic acid
ETRS	Envirotext Retrieval System
HDTMA	hexadecytrimethyl-ammonium
HELSTF	High Energy Laser System Test Facility
ISCOR	*in situ* chemical oxidation through recirculation
MCL	maximum contaminant level
NAPL	non-aqueous phase liquid
NOM	natural organic matter
OCDD	octachlorodibenzo-p-dioxin
PAH	polynuclear aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCE	perchloroethylene
PCP	pentachlorophenol
RCRA	Resource Conservation and Recovery Act
RTDF	Remediation Technologies Development Forum
SDS	sodium dodecyl sulfate
TBA	tert-butyl alcohol
TCA	trichloroethane
TCE	trichloroethylene
TIO	Technology Innovation Office
TNT	trinitrotoluene
TPH	total petroleum hydrocarbon
UIC	underground injection control
VOCs	volatile organic compounds

1.0 SUMMARY

In situ chemical treatments have been demonstrated to be promising alternatives to conventional pump-and-treat practice for contaminated soils and groundwater. Depending on site and contamination characteristics, *in situ* chemical treatment can be achieved by either injection of liquid, gaseous, and colloidal reactive chemicals into subsurface soils and/or aquifers, or by installation of a permeable chemical treatment wall across the ground-water flow path. Both conventional well injection techniques and innovative technologies, such as deep soil mixing and hydraulic fracturing, have been field demonstrated for injection of chemicals into the subsurface. The innovative injection technologies are especially useful in injecting chemical reagents into a low permeability area. Chemical treatment walls can be installed either as a simple reactive cell or in the funnel-and-gate configuration. Several technologies, including conventional trench excavation, caisson-based and mandrel-based techniques, and jet grouting, have been commercially used for construction of treatment walls.

In situ chemical treatment techniques are particularly useful for (1) treatment of source areas to reduce mass of contaminants, such as NAPLs, and (2) interception of plumes to remove mobile organics and metals. In many cases chemical treatment methods are chosen where biological methods won't function effectively with respect to rate or extent either due to contaminant characteristics and/or site conditions. Treatment via chemical injection can be oxidative, reductive/precipitative, or desorptive/dissolvable depending on chemicals injected. *In situ* oxidation offers the advantages of being rapid, aggressive, and insensitive to contaminant characteristics and concentrations. The most extensively tested oxidants include hydrogen peroxide (Fentonís or Fenton-like reagents), potassium permanganate, and ozone. *In situ* redox (reductive) manipulation is particularly useful for immobilization of redox-sensitive contaminants and reductive degradation of chlorinated solvents dispersed over large areas deep below the surface. Dithionite, hydrogen sulfide, and colloidal Fe^0 have been tested for this purpose. *In situ* chemical flushing (desorptive/dissoluble) is very effective in removal of strongly sorbed or very low solubility compounds, such as DNAPL, from soils. *In situ* treatment walls are ideal for treatment of shallow groundwater contaminated with inorganics and organics. The treatment wall as a passive treatment technology has the least effect on the ecosystem.

Selection of a technology for *in situ* chemical treatment of contaminants at a specific site relies on careful site characterization and screening tests. Both laboratory treatability studies and field pilot tests are typically required. The successful application of a particular *in situ* chemical treatment technique requires (1) effective chemical reaction of the introduced chemical with contaminants at a proper rate and extent, and (2) effective delivery of the reagents throughout the zone to be treated.

A primary obstacle for *in situ* chemical treatment techniques involves delivery, distribution and mass transfer of chemicals in subsurface environments. A major concern for *in situ* chemical flushing is the uncertainty of the fate and effects of washing reagents in the subsurface environment. Effort is also needed to prevent mobilized contaminants from migrating into the surrounding environment. Concerns about immobilization and reductive degradation arise from the fact that some lightly chlorinated degradation products are persistent and very toxic, and that immobilized contaminants could be re-mobilized once local environmental conditions change. In addition, caution needs to be taken in handling chemicals because these chemical treatment techniques inherently involve use of potentially hazardous chemicals, sometimes in large quantities. Details on the potential application of each *in situ* chemical treatment technology, influencing factors, and possible process-induced detrimental effects are summarized in Tables 1-4.

Despite the fact that *in situ* chemical technologies offer significant benefits over conventional pump-and-treat technology, their use is still very limited because of technical uncertainties and regulatory or procedural barriers. The U. S. EPA has taken a series of measures to encourage and promote the development and application of these technologies. In addition, the U. S. DOE and the U. S. DOD, along with private industries, are also investing *in situ* chemical treatment methods and trying to accelerate their effective development across the U. S.

Table 1. Summary of *In Situ* Chemical Treatment Technologies by Chemical Injection of Oxidants[1]

Technology	**Chemical Injection - Oxidation**		
	Hydrogen Peroxide	**Permanganate**	**Ozone**
Treatable Compounds	Chlorinated solvents, polyaromatic hydrocarbons, and petroleum products. Not effective for chlorinated alkanes and saturated aliphatic hydrocarbons.		
Suitable Matrices	Soils and groundwater		
Influencing Factors			
pH	Prefer low pH of 2 to 4, but feasible up to near neutral pH.	Prefer neutral pH of 7 to 8, but effective over a wide range.	Effective at natural soil pH.
Natural Organic Matter (NOM) and Other Reduced Species	Any reduced species in the system can exert a demand for oxidant. Of particular importance are NOM, anthropogenic organic matter and reduced inorganics.		
Permeability	Prefer high permeability, but feasible for low permeability with use of advanced oxidant delivery techniques, such as deep soil mixing and soil fracturing. Fenton's reagent and ozone rely on free radical generation and thus transport away from point of injection is constrained.		
Temperature	All oxidants are affected by temperature to varying degrees.		
Depth	With use of the advanced delivery techniques, depth is generally not a limitation.		
Oxidant Degradation	Easily degraded in contact with soil/groundwater.	The oxidant is very stable.	Ozone degradation in soils is limited.
Other factors	May need to supply iron ($FeSO_4$) to form Fentonís reagent.		
Potential Detrimental Effects	Particulates can be generated and permeability loss is possible. Potential side effects include gas evolution with peroxide and ozone and generation of fugitive emissions, potentially toxic byproducts, potential effects on/of metals and reduction of biomass.		
References	Siegrist (1998); and U. S. EPA (1998a)	Siegrist (1998); and U. S. EPA (1998a)	U. S. EPA (1998a); and Masten and Davies (1997)

[1] This table provides some features for application of oxidation for *in situ* treatment. Site-specific information is needed for field application.

Table 2. Summary of *In Situ* Chemical Treatment Technologies by Chemical Injection of Reductants

Technology	**Chemical Injection - Reduction**		
	Dithionite	**Gaseous Hydrogen Sulfide**	**Colloidal Zero Valent Iron**
Treatable Compounds	Redox sensitive elements (Cr, U, Th) and chlorinated solvents dispersed over a large area.	Redox sensitive metals, such as Cr.	Redox sensitive elements (Cr, U, Th) and chlorinated solvents.
Suitable Matrices	Generally groundwater system		
Influencing Factors			
pH	Prefer alkaline condition.	No pH adjustment is required.	High pH prohibits reactions due to formation of surface coating on iron.
Natural Organic Matter (NOM)	Unknown		Potential coating on iron surface.
Permeability	High permeability.	High and low permeability.	Depends on colloidal iron delivery technique.
Depth		No field trial available	
Other factors	Effective in water saturated zone.	N_2 gas carrier is desired.	Require high soil water content and low oxygen content.
Potential Detrimental Effects	Handling difficulties and potential generation of toxic gases.		Possible generation of toxic intermediates.
References	Fruchter et al. (1997)	Thornton and Jackson (1994)	Kaplan et al. (1994) Cantrell and Kaplan (1997); and Siegrist et al. (1999)

Table 3. Summary of *In Situ* Chemical Treatment Technologies by Chemical Flushing

Technology	**Chemical Injection - *In situ* Chemical Flushing**		
	Surfactants and Cosolvents	**Surfactants and Cosolvent Foams**	**Acidic and Chelating Solution**
Treatable Compounds	Effective for treating many compounds, particularly dense non-aqueous phase liquids (DNAPLs).		Metal contaminants.
Suitable Matrices	Soils		
Influencing Factors			
pH	Effective over a wide pH range, but a high pH can enhance surfactant solubility and increase extraction for contaminants.		pH around 3 is good for acid solutions; a wide pH range is good for chelating solutions.
Natural Organic Matter (NOM)	NOM tends to tightly bind contaminants and decrease extraction efficiency.		
Permeability	High permeability.	High and low permeability.	High permeability.
Potential Detrimental Effects	The mobilized contaminants may escape into the surrounding environment.		
References	Jafvert (1996); and Roote (1998)	Peters et al. (1994)	Evanko and Dzombak (1997); and Smith et al. (1995)

Table 4. Summary of *In Situ* Chemical Treatment Technologies by Permeable Chemical Treatment Walls[1]

Technology	**Permeable Chemical Treatment Wall**		
	Sorption	**Precipitation**	**Degradation**
Treatable Compounds	A wide variety of inorganic and organic contaminants.	Heavy metals and radioactives.	Metal anions and organic contaminants.
Suitable Matrices	Groundwater		
Influencing Factors			
pH	Depend on contaminants to be treated and the sorbents used.	Generally require high pH.	Depend on particular degradation reactions.
Natural Organic Matter (NOM)	Dissolved organic matter can remobilize contaminants.		
Depth	Typically used at shallower depths (3 to 12 m)		
Potential Detrimental Effects	The immobilized (sorbed or precipitated) contaminants may be re-mobilized upon environmental condition changes. Toxic degradation intermediates can also be generated.		
References	Vidic and Pohland (1996); http://www.rtdf.org/barrdocs.htm		

[1] In this report, permeable chemical treatment wall refers to a physical wall built by excavation followed by re-emplacement with reactive materials as filling.

2.0 TECHNOLOGY DESCRIPTION

In recent years, *in situ* treatment of contaminated groundwater and soils has been demonstrated to be a very promising alternative to conventional *ex situ* techniques. Compared to *ex situ* techniques, *in situ* technologies pose less environmental risk because there is no need for excavation, transport to treatment facilities, or disposal of hazardous waste (Ahlert and Kosson, 1983; Ghassemi, 1988). Many *in situ* treatment technologies also feature faster and more complete contaminant removal or destruction in contrast to conventional pump-and-treat techniques. Several *in situ* technologies, including biological, chemical, physical, and thermal treatment have been investigated on both laboratory and field scales. This report reviews the current status of *in situ* chemical treatment. The theoretical background, technical design and performance of various *in situ* chemical treatment technologies, as well as their applicability and limits, are reviewed with relevant features highlighted. Based on the reaction chemistry and method of implementation, the techniques were classified into two categories, i.e., chemical injection and permeable chemical treatment wall. Chemical injection includes oxidation, reduction/immobilization, and *in situ* chemical flushing of contaminants by injected liquid and gaseous chemicals. Permeable chemical treatment wall refers to a physical wall built by excavation followed by re-emplacement with reactive materials as filling.

In situ oxidation is achieved by delivering chemical oxidants to contaminated media so that the contaminants are either completely oxidized into CO_2 or converted into innocuous compounds commonly found in nature. *In situ* reduction/immobilization is based on redox manipulation of subsurface into a reductive environment. When the contaminants migrate through the reduced zone, they can be either reductively degraded or immobilized by formation of precipitates. In the case that degradation occurs, the contaminants can be directly converted into CO_2 or less toxic intermediates. *In situ* chemical flushing of organic contaminants usually employs surfactants or cosolvents. Surfactants can readily trap hydrophobic compounds into their micelle structure, while cosolvents can increase contaminant solubility by forming soluble complexes or reducing interfacial tension between the contaminants and water. *In situ* flushing of metal contaminants employs acidic or chelate solutions. Acidification of soils or groundwater can significantly increase metal desorption from solid surfaces. Addition of chelating agent can mobilize metal contaminants from soils by forming multi-dentate soluble complexes between metal contaminants and the chelating agent.

Treatment walls are effective for interception of plumes to remove mobile organics and metals from groundwater. When contaminants pass through the treatment wall in groundwater, they can react with the reactive materials and be immobilized by sorption onto the surfaces of the reactive materials or by forming precipitates. The contaminants can also be degraded into non-toxic gaseous products, such as CO_2 or N_2, or converted into less toxic intermediates. The detailed chemical principles behind these *in situ* chemical treatment technologies are described below.

2.1 CHEMICAL INJECTION - CHEMISTRY ASPECTS

2.1.1 Oxidation

Chemical oxidation processes have been widely used for treatment of organic contaminants in waste waters. Because they are aggressive and applicable to a wide variety of compounds, the use of these processes coupled with delivery technologies for *in situ* remediation of contaminated groundwater or subsurface soils has received increasing attention. The oxidants that have been frequently used for this purpose are hydrogen peroxide, permanganate, and ozone.

2.1.1.1 Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is typically used together with Fe(II) to form Fenton's reagent. In Fenton's reagent, H_2O_2 is decomposed by Fe(II) to produce highly reactive hydroxyl radicals as expressed by Equation 1 (Walling, 1975):

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH\bullet + OH^- \qquad (1)$$

The hydroxyl radical can non-selectively attack the C-H bonds of organic molecules and is capable of degrading many solvents, haloalkanes, esters, aromatics, and pesticides (Haag and Yao, 1992). Huang et al. (1993) summarized the major advantages of using Fenton's reagent over other oxidation processes to treat hazardous wastes: 1) there are no chlorinated organic compounds formed during the oxidation process as in chlorination; 2) both iron and hydrogen peroxide are inexpensive and non-toxic; 3) there are no mass transfer limitations because the reaction is homogeneous; 4) no light is required as a catalyst and, therefore, the design is much simpler than ultraviolet light systems; 5) and, H_2O_2 can be electrochemically generated *in situ*, which may further increase the economic feasibility and effectiveness of this process for treating contaminated sites. During the treatment, particulates can be generated and the pore size and continuity can, therefore, be modified within fine-grained media. As a result, the permeability can be significantly reduced (Hargett et al., 1985; Siegrist, 1998).

Under acidic conditions and with an excess of Fe^{2+}, the hydroxyl radical generated can further react with Fe^{2+} to produce Fe^{3+} (Metelitsa, 1971):

$$Fe^{2+} + OH\bullet = Fe^{3+} + OH^- \qquad (2)$$

By properly controlling experimental conditions, ferric iron can be regenerated back to ferrous iron by a subsequent reaction with another molecule of H_2O_2 (Metelitsa, 1971):

$$Fe^{3+} + H_2O_2 = Fe^{2+} + HO_2\bullet + H^+ \qquad (3)$$

The $HO_2\bullet$ radicals produced (Equation 3) have been shown to also participate in oxidation of some organic compounds, although they are much less reactive than $OH\bullet$.

Based on Equation 1, a low pH range of 2 to 4 is preferred to facilitate the generation of hydroxyl radicals, although the reaction is feasible up to neutral pH (Siegrist, 1998). Almost all organic compounds can be *in situ* treated by this technology. The contaminants of particularly interest include chlorinated solvents (e.g., TCE, PCE), polyaromatic hydrocarbons (e.g., naphthalene), PCP, and petroleum products (e.g., BTEX). All of these chemicals are very difficult to biodegrade or may take exceedingly long in many subsurface settings (Siegrist, 1998).

Major concerns for this technology are related to potential ecological effects and chemical handling. The introduction of acid solution can have potential effects on the ecosystem. During the reactions, both OH^- and H^+ can be produced; however, their quantities are relatively small comparing with the acid introduced and thus would have no significant effect on the pH of the media. Because large quantities of chemicals are required for the treatment, it could be hazardous to handle the chemicals. In addition, special measures may be taken during the delivery process because H_2O_2 can easily break down into H_2O vapor and O_2. This can lead to fugitive emissions of VOCs and pressure buildup. One benefit of decomposition of H_2O_2 is that the released O_2 can stimulate aerobic biological activity.

2.1.1.2 Potassium Permanganate

Potassium permanganate ($KMnO_4$) has been used for treatment of wastewater for decades because it can effectively oxidize many water impurities, including phenol, Fe^{2+}, S^{2-}, and taste and odor-producing compounds (Weber, 1972). Reaction of $KMnO_4$ with organic compounds produces manganese dioxide (MnO_2) and either carbon dioxide (Equation 4) or intermediate organic compounds (Vella et al., 1990; West et al., 1997).

$$R + MnO_4^- \rightarrow MnO_2 + CO_2 \text{ or } R_{ox} + \cdots \qquad (4)$$

where; R_{ox} is the oxidized intermediate organic compound.

The compounds that can be oxidized by permanganate include alkenes, aromatics, PAHs, phenols, pesticides, and organic acids. The optimum pH range is 7 to 8, but effective over a wide range (Siegrist, 1998).

Because Mn is an abundant element in the Earth's crust (Greewood and Earnshaw, 1984) and MnO_2 is naturally present in soils, introduction of $KMnO_4$ to soils as well as production of MnO_2 by-product by oxidation would not be an environmental concern. Compared to H_2O_2, $KMnO_4$ is as effective as or more effective in oxidizing organic compounds (Vella et al., 1990; West et al., 1997). Furthermore, $KMnO_4$ is more stable and easier to handle. The potential problem is that MnO_2 particles will be generated and permeability loss is possible.

2.1.1.3 Ozone

Like hydrogen peroxide and permanganate, ozone is a strong oxidant. It can quickly oxidize organic compounds once in contact (Bailey, 1982; Nelson and Brown, 1994; Yao and Masten, 1992; Masten and Davies, 1997). Compared to other technologies, *in situ* ozonation offers several advantages (Masten and Davies, 1997): 1) it is much easier to deliver ozone to the contamination zone than aqueous oxidants; 2) no volatilization of target chemicals is required and, therefore, overcomes mass transfer limitations associated with soil venting; 3) *in situ* ozonation would likely be more rapid than biodegradation or soil venting processes, and thus reduce the remediation time and treatment costs. Ozone is very reactive and corrosive to materials. It must be generated on site. Ozone reacts quickly in the subsurface and does not migrate long distances from the point of delivery.

Ozone can be electrically generated from air on site. *In situ* ozonation is conceptually similar to soil venting processes. Both vertical and horizontal wells can be used to inject ozone. Little degradation of ozone occurs during injection and on-site handling is relatively easy. Similar to H_2O_2 and permanganate, ozone can be used to treat a variety of organic compounds. Currently, ozone is mainly used to *in situ* treat chlorinated solvents, polyaromatic hydrocarbons and petroleum products (U. S. EPA, 1998a).

2.1.2 Reduction and Immobilization

Ground-water contaminants are often dispersed in plumes over large areas, deep below the surface, making conventional types of remediation technologies as well as some other innovative remediation technologies difficult to apply (Williams et al., 1994). An alternative is to create a chemically reactive zone/barrier in which many contaminants can be destroyed or immobilized when they migrate through the reactive zone. It seems a reductive zone/barrier is feasible for this purpose. Based on both laboratory and field studies, an appropriately created reduced zone can remain in reducing conditions for a long time (Amonette et al., 1994; Fruchter et al., 1997). For example, a reduced zone created at the Hanford site by the injection of dithionite has been reported to remain anoxic one year later (Fruchter et al., 1997). Manipulation of subsurface redox conditions can be implemented by injection of liquid reductants, gaseous reductants, or reduced colloids. Several soluble reductants, including sulfite, thiosulfate, hydroxylamine, and dithionite have been studied on bench-scale under anoxic conditions. Dithionite has been found to be the most effective. The gaseous reductant that has been tested is hydrogen sulfide, and the colloidal reductants are Fe(0) and Fe(II) in clays.

2.1.2.1 Dithionite

Injection of dithionite is intended to create a permeable treatment zone in the subsurface for remediating redox-sensitive contaminants in groundwater. The treatment zone is created just downstream of the contaminant plume or contaminant source aquifer fluids and sediments. When the contaminants migrate through the treatment zone, they are either degraded or immobilized.

The reduction treatment zone can be created by reducing, with dithionite, ferric iron to ferrous iron within the clay minerals of the aquifer sediments. The dithionite ion may be conceptualized as two sulfoxyl ($SO_2^{-}\bullet$) radicals joined by a 2.39≈ sulfur-sulfur bond (Amonette et al., 1994). The S-S bond in $S_2O_4^{2-}$ is considerably longer (and hence weaker) than typical S-S bonds (2.00 - 2.15 ≈). Thus, $S_2O_4^{2-}$ tends to dissociate into two free radical $SO_2^{-}\bullet$:

$$S_2O_4{}^{2-} = 2SO_2{}^{-}\bullet \qquad (5)$$

Although direct reduction of high valent structural Fe(III) in clay minerals by dithionite is possible, as proposed by Sevougian et al. (1994) for smectite (Equation 6), it is likely that reduction of Fe(III) in the clay structure is mainly caused by the highly reactive free radicals $SO_2^{-}\bullet$ (Equation 7) (Gan et al., 1992; Amonette et al., 1994; Sevougian et al., 1994).

$$\begin{aligned}&2Ca_{0.3}(Fe_2{}^{(III)}Al_{1.4}Mg_{0.6})Si_8O_{20}(OH)_4\cdot nH_2O\\&\quad+2Na^{+}+S_2O_4^{2-}+2H_2O\\&\quad\Leftrightarrow 2NaCa_{0.3}(Fe^{(III)}Fe^{(II)}Al_{1.4}Mg_{0.6})Si_8O_{20}(OH)_4\cdot nH_2O\\&\quad+2SO_3^{2-}+4H^{+}\end{aligned} \qquad (6)$$

$$\begin{aligned}&Clay-Fe^{(III)}+4SO_2^{-}\bullet\Leftrightarrow Clay-Fe^{(II)}+2S_2O_4^{2-}+H_2O\\&\quad\rightarrow 2SO_3^{2-}+S_2O_3^{2-}+2H^{+}\end{aligned} \qquad (7)$$

From Equation 6, strongly basic solutions are particularly favorable for reduction of clay-Fe(III) into clay-Fe(II). To facilitate the creation of the reduction zone, dithionite is typically injected in alkaline solution buffered with carbonate and bicarbonate. Although H^{+} is produced during the reaction, it will have negligible effect on the solution pH because of the use of buffer. Once the structural Fe(III) is reduced to Fe(II), the reduced Fe(II) would be able to reduce the migrating redox-sensitive contaminants. Redox-sensitive contaminants that can be treated by this technology include chromate, uranium, technetium and some chlorinated solvents (Fruchter et al., 1997). Chromate is immobilized by reduction to trivalent chromium hydroxide or iron chromium hydroxide precipitates, which are not easily reoxidized under ambient environmental conditions. Uranium and technetium are also reduced to less soluble forms, and chlorinated solvents are destroyed by reductive dechlorination. Caution needs to be taken during handling dithionite because of its toxic nature.

2.1.2.2 Gaseous Hydrogen Sulfide

A primary obstacle to applying *in situ* chemical treatment technology for remediation of groundwater and soils is the difficulty of delivering treatment reagent to the contaminated zone. Reactive gas mixtures offer the advantages of ease of delivery and control during treatment, as well as removal of the unreacted agent from the soil after treatment (Thornton and Jackson, 1994). Gaseous hydrogen sulfide has been tested for *in situ* immobilization of chromate-contaminated soils. The H_2S applied reduces hexavalent chromium to the trivalent oxidation state, followed by precipitation as an oxyhydroxide solid phase (Equation 8) (Thornton and Jackson, 1994). The H_2S itself is converted into sulfate during the reaction. Because sulfate is considered non-hazardous, and chromium (III) hydroxide has very low solubility, secondary waste generation is not a problem. Because gaseous H_2S is very toxic, careful measures must be taken in its handling.

$$8\mathrm{CrO}_4^{2-} + 3\mathrm{H}_2\mathrm{S} + 10\mathrm{H}^+ + 4\mathrm{H}_2\mathrm{O} \rightarrow 8\mathrm{Cr(OH)}_3 + 3\mathrm{SO}_4^{2-} \tag{8}$$

2.1.2.3 Zero-valent Colloidal Iron

Zero-valent colloidal iron (Fe^0), a strong chemical reductant, has been shown to be able to reductively dechlorinate a variety of chlorinated solvents (Gillham and O'Hannesin, 1992; Matheson and Tratnyek, 1994; Gillham et al., 1993; Gillham and O'Hannesin, 1994), and to convert many mobile oxidized oxyanions (e.g., CrO_4^{2-} and TcO_4^-) and oxycations (e.g., UO_2^{2+}) into immobile forms (Gould, 1982; Blowes and Ptacek, 1992). Many investigations on the feasibility of remediation of contaminated groundwater by creating a reactive barrier containing zero-valent iron have been conducted. The zero-valent iron can be either placed into a treatment trench perpendicular to and in the flow path of a contaminated plume (Gillham et al., 1993), or injected into natural aquifers as micro-nanometer Fe^0 colloids (Cantrell and Kaplan, 1997). The technology for building a physical treatment wall containing Fe^0 will be discussed later.

Compared with the treatment wall, colloidal injection of Fe^0 provides several advantages (Kaplan et al., 1994). Since no excavation of contaminated soil is needed, the installation and operation are relatively cheaper, and human exposure to hazardous materials is minimized. Injection wells can be installed much deeper than trenches, so remediation of deeper contaminated sites can be accomplished. By generating micro, even, nano-meter Fe^0 colloids, larger reactive surface area can be created and, thus, much less total iron mass may be required to achieve the desired treatment efficiency (Cantrell and Kaplan, 1997). Furthermore, the treatment barrier created this way can be renewed with minimal cost or disturbance to above-ground areas. The disadvantages of colloidal Fe^0 injection is that barrier-integrity verification, effective emplacement, and modeling are more difficult (Kaplan et al., 1994).

2.1.3 *In Situ* Chemical Flushing

In situ treatment of organic compounds largely depends on the solubility and volatility of organic compounds in aquifers and soils. Some organic compounds, such as polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs), are highly hydrophobic and refractory, making direct *in situ* remediation very difficult. An alternative remediation technique is to mobilize the target organic compounds by *in situ* chemical-enhanced flushing followed by further treatment. The chemicals that can be effectively used for flushing include surfactants, cosolvents, alkaline or acidic solutions, as well as chelating solutions and foams.

Table 5. Previous Reports on Chemical Flushing for Remediation of Subsurface Contaminants

I. U. S. DOD Advanced Applied Technology Demonstration Facility Program for Environmental Remediation Technologies (MTDF)
Rice University, Technology Practices Manual for Surfactants and Cosolvents (1st Ed.), TR-97-2.
Rice University, Technology Practices Manual for Surfactants and Cosolvents (2nd Ed.), TR-97-3.
Rice University, MTDF Final Technical Report: Surfactant/Foam Process for Aquifer Remediation, TR 98-1.
Rice University, MTDF Final Technical Report: Laboratory and Field Evaluation for Single-Phase Micromulsions (SPME) for Enhanced In Situ Remediation of Contamination Aquifers. TR-98-2.
Rice University, MTDF Final Technical Report: Laboratory and Field Evaluation for Single-Phase Micromulsions (SPME) for Enhanced In Situ Remediation of Contamination Aqulfers. TR-98-5.
Rice University, MTDF Technology Evaluation Report: Surfactant/Foam Process for Aquifer Remediation. TR-98-6.
Rice University, MTDF Technology Evaluation Report: Surfactant Recovery and Reuse in Surfactant Enhanced Remediation. TR-98-7.
Rice University, MTDF Final Technical Report: Surfactant Recovery and Reuse in Surfactant Enhanced Remediation. TR-98-11.
Rice University, MTDF Final Technical Report: Passive/Semi-Passive Techniques for Groundwater Remediation (2 vol.). TR-98-17.
Rice University, AATDF Final Technical Report: Passive/Semi-Passive Techniques for Groundwater Remediation. TR-98-18.
Rice University, DOD/MTDF Monographs (in press). Lewis Publ., Chelsea, Ml.
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A number of technical reports have been published to address the details of this technology. Representatives of these reports are listed in Table 5 above. In this report, an overview of the chemical and engineering aspects of this technology is provided.

2.1.3.1 Surfactants

Surfactant molecules consist of a hydrophilic head and a hydrophobic tail. In dilute solutions, surfactants exist as free monomers. When the concentration of a surfactant is above a critical micelle concentration (CMC), the hydrophobic tails tend to cluster together to avoid contact with water molecules, while their hydrophilic heads remain toward the solution. As a result, a micelle structure is formed.

When the surfactant is injected into aquifers, the insoluble organic contaminants will be trapped into the hydrophobic center of the micelle structure formed by the surfactants, and thus the solubility of the organic compounds will be increased. The extent by which the solubility of organic compounds is increased is directly proportional to the octanol-water partition coefficient of the organic compounds (Valsaraj et al., 1987; Clarke et al., 1994).

The surfactants used for soil flushing are typically non-ionic or anionic, because cationic surfactants tend to sorb to the surface of the negatively charged soil particles. Non-ionic surfactants are more desirable because they possess lower CMC values and have less tendency to flocculate clay particles in the soil (Chawla et al., 1991). Screening of ideal surfactants can be initially conducted in water without the presence of soil particles. Only those surfactants that can greatly enhance the solubility of the target organic compound in water have the potential of effectively decontaminating soils contaminated by the organic compound.

2.1.3.2 Foam

Foam is a dispersion of gas bubbles separated by thin liquid films containing surfactants (Peters et al., 1994). The surfactant/foam serves as a mobility control agent and allows an efficient sweep of heterogeneous porous media (Hirasaki, et al., 1999). Foams have strong extraction ability for nonaqueous phase liquids (NAPLs). They are currently used by the oil industry to improve crude oil recovery. Foams hold promise for *in situ* decontamination of soils and aquifers contaminated with NAPL. Compared to surfactant flushing, foams provide several advantages (Peters et al., 1994). Only a small amount of surfactant is needed to generate foams, thus the use of foams reduces the cost and minimizes the introduction of potential toxic compounds to the subsurface. Foams tend to float rather than sink, so that pollutant recovery may be simpler. In addition, foams can be designed with different shapes and carry chemicals such as H_2O_2, gases (CH_4, O_2), and bacteria, which may enhance treatability. Under high operational pressure, foams can be delivered to low permeability areas. On the other hand, foam can also block off high permeability zones to allow longer contact time between surfactant and contaminants, which can enhance extraction efficiency (Kovscek and Radke, 1993).

2.1.3.3 Cosolvents

In situ cosolvent flushing is used for remediation of soils and aquifers contaminated with hydrophobic organic contaminants. It uses hydrophilic organic solvents such as alcohols, ethers, and ketones to enhance contaminant removal. Two mechanisms enable *cosolvent*s to promote contaminant removal (U. S. EPA, 1995). The first is to directly chemically react with contaminants to form soluble complexes, and thus increase the solubility of contaminants. The second is to reduce interfacial tension between the contaminants and water, which eventually results in mobilization of contaminants.

2.1.3.4 Alkaline, Acidic, and Chelate Solutions

Removal of soil organic contaminants can also be enhanced by alkali flushing using reagents such as sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), and sodium orthosilicate (Na_4SiO_4). Like cosolvents, alkaline solutions can also increase the aqueous solubility of organic contaminants by direct chemical reaction with the contaminants or by reducing the contaminant-water interfacial tension. In addition, injection of alkaline solutions can alter the porewater salinity and precipitate calcium and magnesium hardness, which enhances alkali-NAPL interactions. In many cases, alkalis are used together with surfactants. This combination provides several advantages. Increases in pH increase the surfactant solubility and reduce the adsorption of surfactants to aquifer solids, which could eventually enhance the extractability of surfactants for contaminants (de Zabala et al., 1982). Co-injection of surfactants may also circumvent NAPL recovery limitations imposed by the finite amount of *in situ* saponification that can be realized (U. S. EPA, 1994).

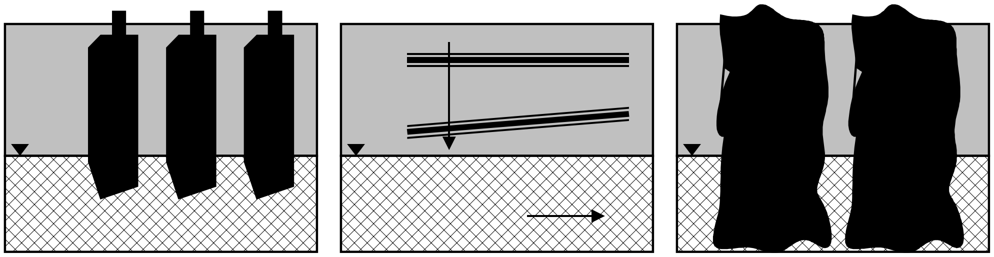
Instead of surfactants, cosolvents, or alkalis which are ideal for organic contaminants flushing, acidic or chelate solutions are effective for *in situ* flushing of metal contaminants. At natural aquifer pH, a large amount of metals is sorbed to aquifer particles (Evanko and Dzombak, 1997; Yin et al., 1999). Injection of dilute acids reduces local pH to very low values, which would result in desorption of metals from solid surfaces because of proton competition. Similarly, injection of chelating agents would pull metals from solid surfaces to the solution phase by formation of very stable soluble complexes between the added chelating agent and the metal contaminants. The most commonly used acids are sulfuric acid, hydrochloric acid, and nitric acid, and the most frequently used chelating agents are ethylenediaminetetraacetic acid (EDTA), citric acid, and diethylenetriaminepentaacetic acid (DPTA) (Smith et al., 1995).

2.2 CHEMICAL INJECTION - ENGINEERING ASPECTS

The feasibility of delivery of chemicals to the contaminated region is the key for successful *in situ* remediation of contaminants via chemical injection. Several conventional delivery systems, namely vertical wells, well points, horizontal or inclined wells, infiltration galleries, treatment fence, etc., have been field- demonstrated to be capable of delivering chemicals into subsurface environments. For soils of low permeability, innovative technologies, such as deep soil mixing and hydraulic fracturing, provide better solutions for the delivery. No matter which chemical delivery technique is used, the materials used for construction of the injection system must be compatible with the chemical to be delivered. The technologies that have been used to deliver different chemicals are described in the following sections.

2.2.1 Injection of Liquid Oxidants

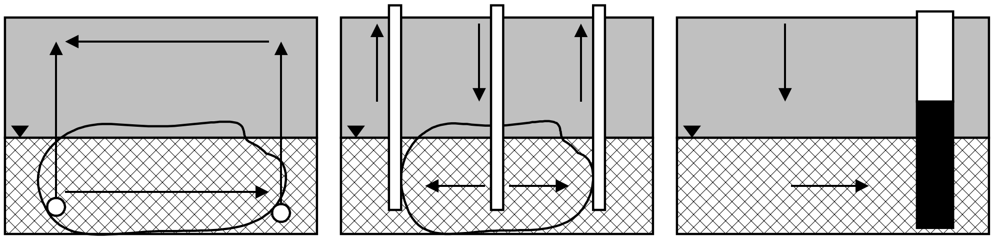
A number of delivery systems have been proposed and field tested for injection of liquid oxidants to the contamination zone. Representatives of these can be found in the work by Siegrist et al., (1995), Cline et al., (1997), Murdoch et al,. (1997), Korte et al., (1997a), West et al., (1997), Jerome et al., (1997), and Siegrist et al., (1999). Figure 1 shows schematics of these delivery systems.



Lance permeation with H_2O_2 or $KMnO_4$

Soil fractures filled with $KMnO_4$ pairs

Soil mixing with $KMnO_4$ or H_2O_2



Horizontal well pair flushing with $KMnO_4$

Vertical well 5-spot flushing with $NaMnO_4$

Treatment fence of $KMnO_4$ solids

Figure 1. Schematic Description of Liquid Oxidant Delivery Systems (Siegrist et al., 1999).

Successful delivery of chemicals relies on careful engineering design of the system and proper construction of the needed delivery equipment. Ho et al. (1995a) developed a pilot-scale model injection system for delivery of H_2O_2 at depth. The injection system is constructed of Teflon® and is similar to devices used for jet grout injection. Two major components of the injection system are a rod and a jet tip perpendicular to the axis of the rod. By rotating the rod about its axis, and thereby rotating the tip, the H_2O_2 can be injected in a plane perpendicular to the rod (Ho et al., 1995a). Based on a preliminary injection feasibility test in a natural sand, the authors concluded that H_2O_2 injection into contaminated soil may be successful in treating inaccessible contaminated sandy soil. Concentration gradients were found after the injection of H_2O_2, which may have resulted from mechanisms similar to the development of chemoclines between salt water and fresh water in aquifers and fresh water lakes.

For soils of low permeability, deep soil mixing has been proposed and tested for delivery of reagents to the contamination zone. This technology uses special augers in series, equipped with mixing paddles that mix soil as they rotate (Gavaskar et al., 1998). With appropriate types of equipment, drilling over 30.5 m has been achieved. To enhance distribution of chemical reagents throughout the mixed region, treatment solutions can be injected into an air stream such that it enters the mixed zone as a fine mist (Siegrist et al., 1993). Deep soil mixing has been used to deliver H_2O_2 to up to 7.5 m into the subsurface to remediate a dense fluvio-lacustrine deposit in southern Ohio (Siegrist et al., 1993).

Hydraulic fracturing is another technique that can be used to deliver reagent to a low-permeability subsurface (Gavaskar et al., 1998; Siegrist et al., 1999). This technique tends to fracture subsurface formations using pumped water or air under high pressure. It has been widely used by the petroleum industry for delivery of flushing reagents or recovery of petroleum hydrocarbons. Only recently has it been adopted by remediation researchers to deliver reagents to the subsurface. A series of horizontally stacked fractures 12 to 15 meters in diameter can create an effective reactive zone to intercept and treat downward migrating contaminants (Gavaskar et al., 1998).

A commercially available injection technology (Geo-Cleanse Technology), developed and patented by Geo-Cleanse International, Inc., has been field tested for delivery of Fentonís reagent to the subsurface (Jerome et al., 1997). The injector is constructed with a mixing head for mixing reagents and components to stimulate ground-water circulation in order to promote rapid reagent diffusion and dispersion. At the beginning of the injection process, air with catalyst solution is injected to ensure the injector is open to the formation prior to injection of Fenton’s reagent. Once an acceptable flow has been established, Fenton’s reagent is simultaneously injected. The injector was designed with a check valve and constant pressure delivery system which prevents mixing of chemicals before they have reached the zone of treatment.

Deep soil mixing technology has been field-demonstrated for delivery of $KMnO_4$ into subsurface regions of low permeability (Siegrist et al., 1993). For soils of high permeability or in the case that physical disruption of contaminated zone is not desirable, an alternative technology of delivering $KMnO_4$ into the subsurface has been proposed and field-tested by researchers at the Oak Ridge National Laboratory (Korte et al., 1997a; West et al., 1997). This technology is referred to as *in situ* chemical oxidation through recirculation (ISCOR). ISCOR involves injection and recirculation of the oxidant solution into a contaminated aquifer through multiple horizontal and vertical wells. The advantages of this technology over other injection technologies were summarized by West et al., (1997): 1) it provides better control of oxidant and contaminant migration within the treatment zone compared to well injections alone; 2) higher volumes of oxidant solutions can be introduced because existing soil pore water is extracted prior to oxidant injection; and 3) it has potentially lower overall cost for treating larger volumes of soil and for multiple oxidant doses compared to deep soil mixing.

2.2.2 Creation of Reductive Zones via Liquid Reductants

A schematic description of the technological design for the creation of a reductive treatment zone is shown in Figure 2 (Fruchter et al., 1997). The treatment process includes three stages, injection, reaction, and withdrawal of reagent or reaction products introduced into the subsurface. The important design factors include; site hydrogeology, well construction and placement, reagent concentration, injection and withdrawal rates, and duration for each stage (Williams et al., 1994; Fruchter et al., 1997).

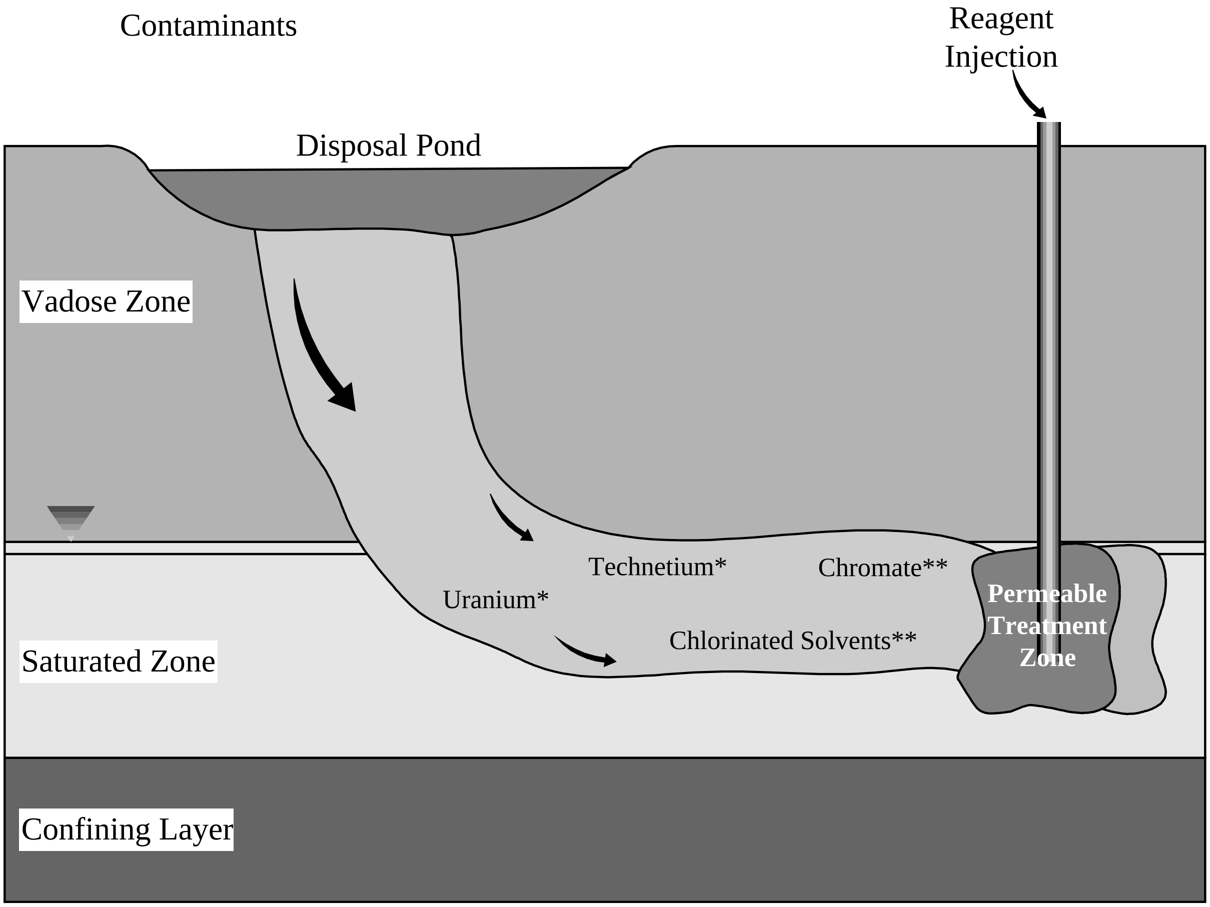


Figure 2. Schematic Description of the Technological Design for The Creation of a Reductive Treatment Zone (from Fruchter et al., 1997).

Due to the complexity and heterogeneity of subsurface materials, unforeseen reactions and interactions can occur during all stages of the treatment. Thus, the final design must be optimized based on carefully planned laboratory and field-scale investigations. Sevougian et al. (1994) proposed a 6-step enhanced design methodology for *in situ* chemical barriers (Figure 3). This methodology includes all phases of rigorous feasibility studies from site characterization to laboratory and field investigations as well as modeling. The screening process used in this methodology is also applicable to other *in situ* treatment techniques.

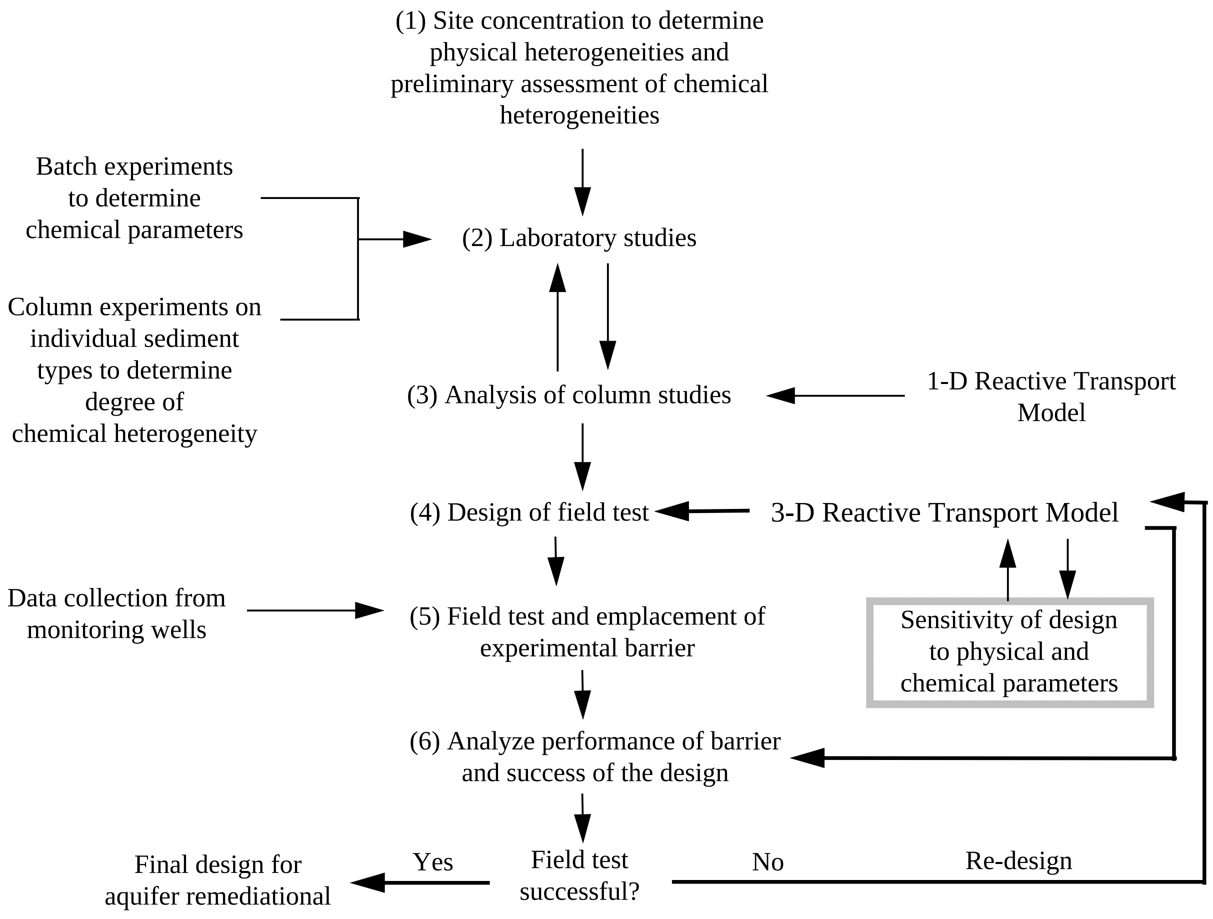


Figure 3. Enhanced Design Methodology for *In Situ* Chemical Barrier (Sevougian et al., 1994).

A primary concern in the injection stage is the feasibility of delivery of reagent to the available ferric iron in the soil to create a long-term reducing condition. Site-specific properties, such as porosity, hydraulic-conductivity anisotropy, and thickness of aquifer, need to be understood, so the volume of reagent required can be determined. A partially screened injection/withdraw well is preferred so the contaminated zone of the aquifer is treated (Williams et al., 1994). The residence stage provides time for the reagent to reach and react with the structural high-valent iron. Residence time achieved depends on the diffusion rate of the reagent in the aquifer and the chemical reaction kinetics for dissociation of dithionite as well as the reaction between the produced free radicals $SO_2^{-}\bullet$ with the high-valent iron in the structure of the clay minerals. Both laboratory and field tests need to be performed to determine the rates of these reactions. Based on the results of these tests, the residence time required to convert clay-Fe(III) to clay-Fe(II) can be determined. The minimum residence time is desired so the volume of water needed to be withdrawn later is minimized. Typically, at least three times the injection volume must be pumped to recover most of the injected reagent and aqueous reaction products. To calculate mass balance, a non-reactive tracer needs to be injected and withdrawn together with the reagent.

2.2.3 Treatment via Gaseous Oxidants and Reductants

In situ treatment via gaseous oxidants and reductants is conceptually similar to soil venting. Researchers at the U. S. Department of Energy (1996) proposed a conceptual design for the construction of injection and withdraw wells for *in situ* gaseous treatment with H_2S (Figure 4). Gaseous reductants are injected in a central borehole. A system of withdrawal wells is constructed at the periphery of the site, which allow removal of excess agent and provide control of gas movement through the site (Thornton and Jackson, 1994). To prevent the escape of treatment gas to the atmosphere, an impermeable cover can be placed on the top of the site. At the end of the treatment, the system is purged with air to remove residual gaseous reductant.

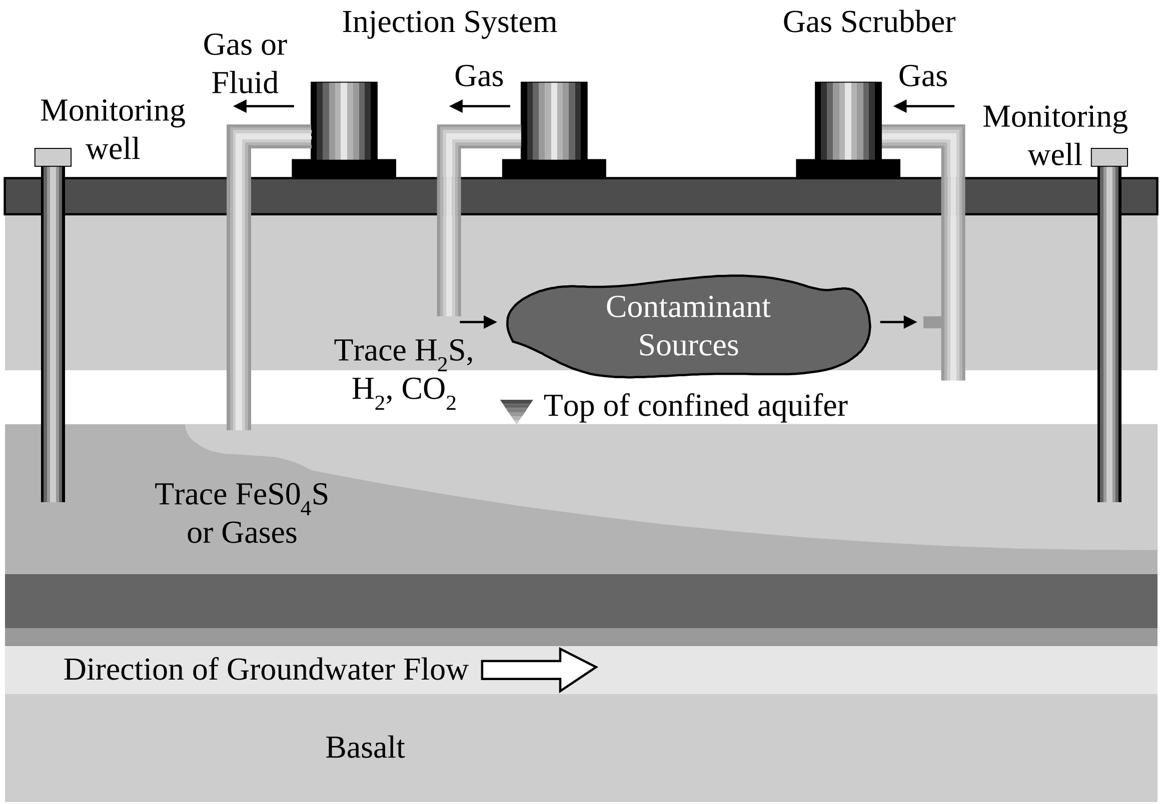


Figure 4. Conceptual Design for Construction of an *In Situ* Gaseous Treatment System (from U. S. DOE, 1996).

Both vertical and horizontal injection wells can be used to inject gaseous reactants into unsaturated soils. Horizontal wells have been claimed to be more effective than vertical wells in delivering ozone into unsaturated soils (Nelson and Brown, 1994).

2.2.4 Injection of Colloidal Fe^0

Both deep soil mixing and fracturing techniques described previously could be used for injection of Fe^0 colloids into the subsurface (Kaplan et al., 1994; Siegrist et al., 1995; Siegrist et al., 1999). A series of wells can be used to create a reactive barrier. Initially, the colloidal Fe^0 is injected into the first well, and the second well is used to withdraw groundwater, so the colloids will be drawn toward the second well. When the media between the first and the second wells is saturated with Fe^0, the second well is then used as the injection well, and the third well as the ground-water withdrawal well to draw the colloidal Fe^0 to the third well. By repeating this process for the rest of the wells, a reactive barrier can be created. It is desired that the colloidal Fe^0 be injected at a high speed and a highly viscous aqueous carrier be used to ensure the colloids are well suspended and quickly delivered to the desired treatment location. Use of surfactants and optimization of solution conditions can also facilitate dispersion and delivery of Fe^0 colloids (Kaplan et al., 1994).

2.2.5 Engineering Related to *In Situ* Chemical Flushing

In situ chemical flushing is conceptually similar to the conventional pump-and-treat technology. Clarke et al. (1994) designed and tested a pilot-scale, *in situ* surfactant flushing system (Figure 5). This system integrates surfactant injection, recovery, regeneration, and reuse into a continuous operational process. Surfactants are injected into soils and aquifers through a surface distribution system. After flushing through the contaminated zone, the surfactant is collected by a serious of extraction wells below the contaminated zone. Volatile organic compounds trapped by the surfactant are removed by air stripping, and non-volatile organic compounds by solvent extraction followed by solvent recovery by a modified commercially available solvent still (Clarke et al.,1994).

To prevent the mobilized contaminants from escaping to the surrounding environment, it is desirable to place an impermeable barrier (e.g., a slurry wall) around the zone of contamination (Clarke et al., 1994). This can be accomplished using advanced jet grouting without excavation of soils. Jet grouting is a technique wherein a high-pressure jet or jets oriented horizontally from the base of a drill stem are used to cut and mix *in situ* soils with pozzalonic or other stabilization materials to create zones of low permeability in the subsurface (Clarke et al., 1994). It has been widely used in Europe to create subsurface cutoff walls and bottom liners for dry-docks and other facilities.

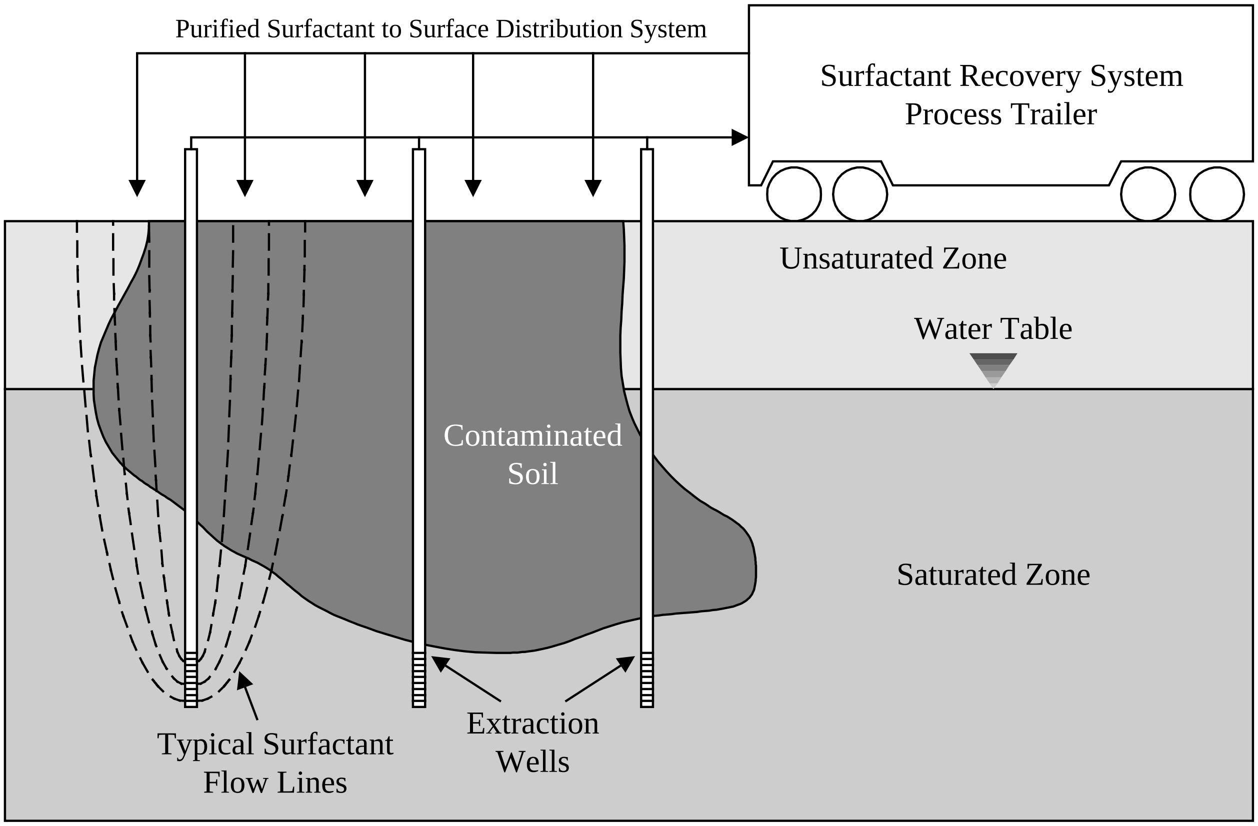


Figure 5. Design of a Pilot-Scale *In situ* Surfactant Flushing System (from Clarke et al., 1994).

Injection and extraction wells for alkaline flushing can be constructed in a similar fashion as those for surfactant and cosolvent flushing. Both horizontal and vertical well configurations have been successfully used (Sale et al., 1989). For extremely corrosive injectates, specialty materials such as stainless steel need to be used for construction of wells.

A conceptual design for delivery of foam to the subsurface is proposed by Peters et al. (1994). The foam is injected underneath the contaminated zone, and the contaminant-saturated foam is extracted from the top of the contaminated zone under vacuum. The surfactant and contaminants are then removed and foam is regenerated. When foams flow through a porous medium, they act as blocking agents to the high permeability regions (Kovscek and Radke, 1993). Thus, the contact time between surfactant and contaminants is increased, which results in higher remediation efficiency. Because of the high operational pressure, foams can also deliver surfactants to areas that would be difficult to reach by surfactant alone.

2.3 PERMEABLE CHEMICAL TREATMENT WALLS - CHEMISTRY ASPECTS

Treatment walls have been widely tested and used to intercept and *in situ* treat migrating contaminants. As mentioned earlier, treatment walls discussed here refer to physical walls built by excavation followed by re-emplacement. The treatment walls can be built by mixing natural materials with one or several types of reactive materials. When contaminants migrate downstream in groundwater through the treatment wall, they will react with the reactive materials contained in the treatment wall. As a result, the contaminants can be either destroyed or *in situ* fixed. Reviews of the knowledge on treatment walls (barriers) have been prepared by Shoemaker et al. (1996), Vidic and Pohland (1996), U. S. EPA (1997, 1998b, 1998c), and Gavaskar et al. (1998).

By using different reactive materials as filling for the reactive treatment wall, various inorganic and organic contaminants can be *in situ* treated. Based on the mechanisms of the chemical reactions between the reactive fillings and contaminants, the following categories of treatment are discussed.

2.3.1 Immobilization of Inorganics and Organics via Sorption

Inorganic and organic contaminants migrating through the installed reactive wall can be passively *in situ* fixed by sorption onto the reactive materials contained in the treatment wall. Depending on the nature of the contaminants, an array of sorbents, including activated alumina, activated carbon, bauxite, exchange resin, ferric oxides and oxyhydroxides, magnetite, peat, humate, lignite, coal, titanium oxide, clays, and zeolite have been investigated for sorption retainment of either inorganic or organic contaminants (Morrison, 1998). The contaminants can be sorbed via different mechanisms; namely, ion exchange, surface complexation or surface precipitation as well as hydrophobic partitioning in case of hydrophobic organic compounds. The details about sorption mechanisms and influencing factors have been reviewed (Sposito, 1985; Dzombak and Morel, 1990; Stumm, 1992; Schwarzenbach et al., 1993).

2.3.2 Immobilization of Inorganics via Precipitation

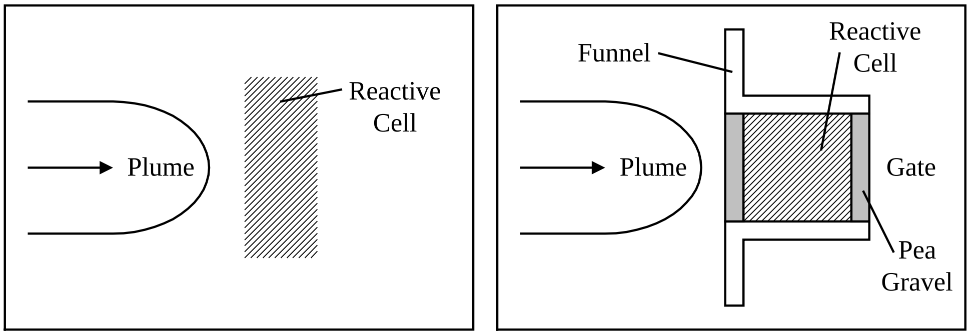
Inorganics can be directly precipitated from the solution phase via chemical reactions with the reactive materials in the treatment wall. The reactive materials contained in the treatment wall can also modify the local environmental conditions, such as pH and redox conditions. Increases in pH can result in the migrating metals being precipitated as metal hydroxides. Changing the local environment into reducing condition can also trigger inorganic species to change into insoluble precipitates. The reactive materials that can be used for these purposes include ferrous salts, phosphate, lime, fly ash, limestone, miscellaneous ($Mg(OH)_2$, $MgCO_3$, $CaCl_2$, $CaSO_4$, and $BaCl_2$), and zero-valent metals (Morrison, 1998).

2.3.3 Degradation of Inorganic Anions and Organics

Both inorganic anions and organic contaminants can be reductively degraded *in situ* by reactive materials in the treatment wall. The chemicals used for degradation of inorganic anions, such as nitrate, include zero-valent metals. Both ferrous minerals and zero-valent metals have been investigated for degradation of organic contaminants.

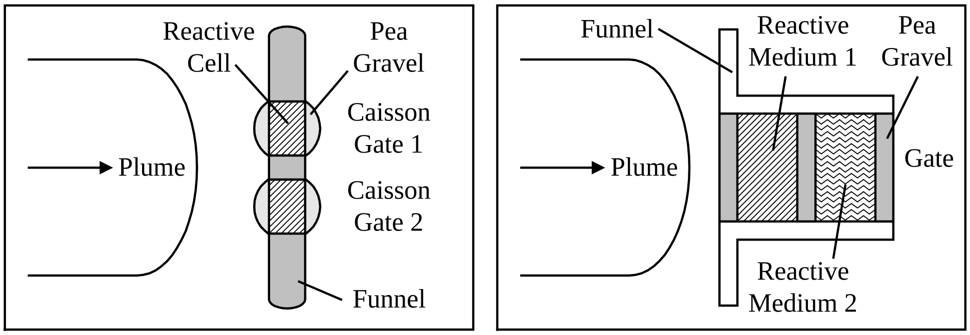
2.4 PERMEABLE CHEMICAL TREATMENT WALL - ENGINEERING ASPECTS

Treatment walls can be installed either as a simple reactive cell or in the funnel-and-gate configuration. Gavaskar et al. (1998) summarized four possible arrangements for construction of the reactive cell (Figure 6). The reactive cell is generally constructed approximately 0.6 m above the water table and 0.3 m keyed into the aquitard (deeper in case of the funnel-and-gate system) (Gavaskar et al., 1998). Such construction would prevent contaminants downstream flowing either from the top or bottom of the reactive cell. In some cases, goetextile fabric or an impermeable intercept floor is constructed to prevent contaminants from escaping through underflow.



(a) Continuous reactive barrier configuration

(b) Funnel-and-gate configuration



(c) Multiple caisson gates

(d) Serial reactive media

Figure 6. Arrangement for Construction of Reactive Treatment Cells (from Gavaskar et al., 1998).

The conventional trench excavation is most frequently used to construct a reactive cell. During the construction process, native materials are excavated and replaced with equal or higher-permeability media containing reactive materials. Several technologies have been used to help stabilize trench walls during construction (Gavaskar et al., 1998). One is to emplace steel sheet piles along the sides of the cell prior to excavation to prevent water from seeping into the reactive cell. The second is to use powdered guar bean slurry to help maintain the integrity of the trench walls during the installation of the cell. The slurry wall can also be simultaneously installed during excavation using a trencher type apparatus. The slurry materials will eventually biodegrade after wall installation. The third is to install a trench box first and then fill the trench box with reactive materials.

Caisson-based and mandrel-based technologies are often used to construct reactive cells. The caisson used for emplacing a reactive cell is a prefabricated, open steel enclosure (Gavaskar et al., 1998). A caisson 2.4 m in diameter or smaller is first pushed or vibrated down into the subsurface, and the soil inside the caisson is then augured out and replaced with a reactive medium. Once the installation of the reactive cell is complete, the caisson is pulled out. A mandrel is a hollow steel shaft with a sacrificial drive shoe at the bottom end. Similar to a caisson, a mandrel can be used to create a void space. After the created space is filled with reactive materials, the mandrel is extracted, leaving the drive shoe and media in the soil. Mandrel-based emplacement is cheaper than is caisson-based, but the void volume created is smaller. During the installation of reactive cells using both technologies, soil compaction could occur along the cell walls, which may lower the permeability of the soil.

In some cases, a continuous trencher, instead of a caisson or mandrel, is used to create a trench. The continuous trencher can simultaneously excavate a narrow, 0.3 to 0.6-m wide trench and immediately refill it with a reactive medium and/or a continuous sheet of impermeable polyethylene liner (Gavaskar et al., 1998). The reactive cell created this way can go down to 10.8 to 12.3 m depth.

Funnel walls are typically constructed in forms of either steel sheet piles or slurry walls (Gavaskar et al., 1998). Steel piles can be installed by either a drop hammer or a vibrating hammer. The commercial steel piles are typically 12.3 m in length, but can be extended by welding two pieces together if necessary. Depending on the subsurface condition, steel piles can last 7 to 40 years. To ensure no leakage is occurring at the interlocks of connecting piles, a sealable-joint sheet piling was developed by the University of Waterloo. The type of sheet pile has very low permeability, is easy for rapid installation, and causes minimum site disturbance. In very rocky soils, installation of steel sheet piles might not be feasible.

Another way to create a funnel wall is to use slurry walls. These are constructed by excavation of a trench which is then refilled with a specific type of slurry. Three types of slurry, soil-bentonite, cement-bentonite, and plastic concrete slurry, have been commercially used (Gavaskar et al., 1998). The soil-bentonite slurry walls are by far the most commonly used. They are less expensive to install, have low permeability, and are suitable for retaining an array of dissolved-phase contaminants. In the case that there is not sufficient surface space for good mixing of the excavated material with bentonite, cement-bentonite slurry walls are often used. Because of the need for disposal of the excavated materials, as well as the higher permeability, the use of cement-bentonite slurry walls are limited. When great strength and deformability are desired, plastic concrete slurry walls can be installed. Slurry walls can be constructed as a single wall, or as multiple-layer walls with increasing chemical resistance and lower permeability.

Besides the conventional technologies, an innovative emplacement technique, jetting (jet grouting), can also be used to construct a funnel wall. With this technique, water and bentonite and/or cement slurry can be directly injected into soils under high pressure, and the soilcrete (grouted soil) columns in series form an impermeable barrier. A high-pressurized jet can form a slurry wall to depths of 40 m (Gavaskar et al., 1998).

2.5 ASSESSMENT OF THE AMENABILITY OF SITE CONTAMINANTS TO CHEMICAL TREATMENT

As indicated in the previous sections, the chemical reactions employed in *in situ* chemical treatment processes include redox reactions, sorption, precipitation, chelating reaction, partitioning, and degradation. The effectiveness of a certain chemical reaction for treatment of a contaminated site depends on the sensitivity of the environmental contaminants to this chemical reaction. To assess the efficiency of a chemical treatment process to a certain contaminant, detailed studies need to be conducted. A three-step process may be followed. First, a laboratory screening study in water without natural matrix present may be conducted to test the ability of a chemical in degrading or immobilizing a contaminant of interest. The optimum conditions, such as pH, temperature, and chemical loading, for treatment of the contaminant can be determined during this study. Second, a batch study with natural matrices present may be conducted to investigate the effect of natural matrix on the treatability of the contaminant with the proposed chemical. Third, a column study may be conducted to evaluate the effect of diffusion on treatability and determine the rate-limiting steps for the chemical treatment.

3.0 PERFORMANCE

The performance of chemical treatment technologies has been investigated by both laboratory and field studies/demonstrations. Laboratory studies can provide insight on reaction chemistry and chemical transport behavior. They are ideal for initial technologies screening. Further field studies are necessary to account for site heterogeneity. Based on laboratory studies, cost indications can be derived, albeit they are uncertain due to uncertainties related to site heterogeneity and technology implementation.

3.1 CHEMICAL INJECTION

3.1.1 Oxidation

3.1.1.1 Laboratory Studies

Fenton's Reagent. Direct oxidation of organic contaminants in soils has been investigated by many researchers (Watts et al., 1990; Kelly et al., 1991; Tyre et al., 1991; Watts et al., 1991; Ravikumar and Gurol, 1994; Stanton and Watts, 1994; Ho et al., 1995a; Gates and Siegrist, 1995; Kakarla and Watts, 1997). These studies were carried out either in soil slurry or columns. Typically, excess H_2O_2 was required over that used in aqueous treatment experiments because naturally occurring organic and inorganic constituents of the soil act to scavenge the $OH\bullet$ radicals present.

Some studies suggested that dissolution (desorption) of organic contaminants into the solution phase is crucial to rapid oxidation of these contaminants by Fenton's reagent (Sheldon and Kochi, 1981; Tyre et al., 1991; Sedlak and Andren, 1994). Sorption of organics to soil particles could either significantly slow down the degradation rate (Sedlak and Andren, 1994) or render the organics unavailable for degradation (Sheldon and Kochi, 1981).

More recent studies, however, have shown that aggressive chemical reactions induced by Fenton's reagent were capable of oxidizing sorbed organic contaminants. Ravikumar and Gurol (1994) demonstrated that pentachlorophenol and trichloro-ethylene adsorbed on sand particles can be oxidized by hydrogen peroxide even without additional iron salt. The hydroxyl radicals were believed to be produced by the interaction of hydrogen peroxide with the natural iron contained in the sand.

Watts et al. (1994) reported that the oxidation of sorbed hexachlorobenzene was more rapid than its desorption by Fenton's reagent at H_2O_2 concentrations greater than 30 mM and H_2O_2:Fe molar ratios of 2:1. They attributed the rapid oxidation to either the direct oxidation of sorbed organic contaminants or the changes in the sorption properties under the redox conditions of the high H_2O_2 concentrations. Watts and Stanton (1994) further investigated oxidation of sorbed hexadecane in batch reactors using high concentrations of H_2O_2 (10-50%). Based on the fact that nearly all added ^{14}C-hexadecane was recovered as ^{14}C-CO_2, it was concluded that high stoichiometric quantities of H_2O_2 are capable of oxidizing sorbed contaminants. Kakarla and Watts (1997) observed that less than 10% of the sorbed hexadecane could be desorbed from soil columns by deionized water, while up to 90% of the sorbed hexadecane was oxidized by H_2O_2 in the parallel soil columns. The results lead to a conclusion that hexadecane oxidation occurred in the sorbed phase.

The above studies indicate that direct oxidation of sorbed organic contaminants on solid surfaces by Fenton's or Fenton-like reagent is feasible. The mechanisms of these reactions are not fully understood. Nevertheless, the rates of these reactions are likely slower than those occurring in the aqueous phase. For example, Tyre et al. (1991) suggested that compound dissolution into solution phase during Fenton's treatment may greatly increase degradability.

A number of environmental parameters affect the treatability of organic contaminants by Fenton's or Fenton-like reagent. Optimum pH conditions to initiate Fenton's oxidation in soil have been found to be between 2 and 3. For example, Watts et al. (1990) investigated oxidation of pentachlorphenol (PCP) in 6.5% H_2O_2-soil slurry at pH 2 to 3. After the first 24 hours of treatment, more than 99% of PCP present was degraded.

The contaminants can be oxidized by Fenton's or Fenton's-like reagents with or without supplemental Fe(II) (Watts et al., 1990; Watts et al., 1994; Ravikumar and Gurol, 1994), although addition of Fe(II) has been found to result in greater oxidation and more extensive reaction (Ravikumar and Gurol, 1994). In the absence of addition of Fe(II), hydroxyl radicals are generated by chemical reactions between H_2O_2 and the Fe(II) contained in soil minerals.

The amount of H_2O_2 applied could have significant effect on treatability by Fenton's reagent. Kelly et al. (1991) explored the treatability of polynuclear aromatic hydrocarbons (PAHs) in soils using Fenton's reagent. Samples of 10 g of virgin sand spiked with ^{14}C-labeled benzo(a)pyrene (BaP) were treated with 2 mL of 33% H_2O_2. A total of 25% of the spiked PAH was recovered as CO_2, 50% as oxidized nonpolar compounds, and 12% polar oxidized products. Increases in H_2O_2 volume from 0 to 4 mL linearly increased mineralization of PAH and decreased mineralization of polar and nonpolar ^{14}C-labeled compounds.

The presence of natural organic matter in soils and groundwater could have significant effects on treatment of organic contaminants by Fentonís or Fenton-like reagents. The organic contaminants could partition into natural organic matter, which would cause the aqueous concentrations of contaminants to decrease. Fenton's reagent applied to groundwater and soils could also be scavenged by the naturally occurring organic matter (Watts et al., 1991; Tyre et al., 1991; Tarr and Lindsey, 1998). In both cases, the presence of natural organic matter would adversely affect treatability. For example, Tyre et al. (1991) investigated oxidation of four compounds, including PCP, trifluralin, hexadecane, and dieldrin, by Fenton's treatment in four soils with naturally occurring organic matter content ranging from 0.2 to 1.6%. Both pentachlorophenol and trifluralin degradation rates decreased with increasing organic matter, suggesting that OH• scavenging by organic matter occurred. The degradation rates of hexadecane and dieldrin in the four soils, however, were not significantly different, and therefore organic matter content of the soils had little effect on the degradation of these compounds. Two possible mechanisms were proposed to explain the difference in the oxidation rates for these compounds. First, reaction of OH• radicals with hexadecane and dieldrin could be slower than that with pentachlorophenol, trifluralin, and soil organic matter. Consequently, the effect of natural organic matter on the oxidation rate was not evident within the experimental time period. Second, the faster oxidation rates for pentachlorophenol and trifluralin probably resulted from a higher percentage of the total pentachlorophenol and trifluralin that were present in the aqueous phase compared to hexadecane and dieldrin.

Similar results were reported by Sherman et al. (1998). The authors observed percentages of TNT desorption of 92, 77, and 62% from three soils with organic matter contents of 0.2, 1.3, and 2.3%, respectively. The corresponding oxidation of TNT in these three soils during the first two hours of reaction time was nearly 60% for the highest organic matter soil and more than 80% for the lowest and intermediate organic matter soils.

The rate of Fenton's or Fenton-like reactions in soils largely depends on temperature. Watts et al. (1991) examined degradation of octachlorodibenzo-p-dioxin (OCDD) in four surface soils at a range of temperatures of 20, 40, 60, and 80°C. The soil organic matter ranged from 0.6 to 6.1%. Degradation of OCDD decreased as soil organic matter increased at a given H_2O_2 concentration. Increases in temperature dramatically increased OCDD oxidation rate. After 30 minutes reaction time, 80 to 90% of OCDD remained in soils treated at 20°C, while less than 20% remained in soils treated above 60°C.

Potassium Permanganate. Although treatment of wastewater by $KMnO_4$ has been well documented, few studies have been conducted to investigate the feasibility of remediation of soils and groundwater using $KMnO_4$. Gates et al. (1995) compared treatability of TCE, PCE, and TCA in soils by $KMnO_4$, H_2O_2, or H_2O_2 plus iron (Fentonís reagent). For contaminant concentrations of 130 mg/kg of TCE, 30 mg/kg of PCE, and 130 mg/kg of TCA, none of the treatments significantly destroyed TCA (less than 2%). Both TCE and PCE were destroyed to a different extent depending on oxidizing agents used. $KMnO_4$ exhibited the highest oxidation efficiency, Fentonís reagent the second, and H_2O_2 alone the third. Application of 20 g $KMnO_4$/ kg soil destroyed nearly 100% of TCE and 90% of PCE; application of 40 g Fentonís reagent (5 mM Fe^{2+}) destroyed nearly 85% of TCE and 70% of PCE; while application of 40 g H_2O_2 per g of soil destroyed nearly 75% of TCE and about 10% of PCE. Increases in initial concentrations of TCE seemed to have no effect on percentage of TCE removal by $KMnO_4$.

The high efficiency of treatment of TCE by $KMnO_4$ was observed by West et al. (1997) in both laboratory and field studies. As a screening test prior to a field demonstration, they observed that 1.5% $KMnO_4$ could reduce the initial TCE concentration from 1000 mg/L to 10 mg/L in 90 minutes in water. The results of a follow-up field study are summarized in section 3.1.1.2.

Ozone. Bailey (1982) observed that ozone directly reacted with aromatic compounds via a 1,3-dipolar addition of ozone across the double bond to yield trioxalane, which was then quickly decomposed to form catechols, phenols, and carboxylic acids. Phenol can be further oxidized by ozone to form organic acids and aldehydes. Oxidation of pyrene with ozone produced a number of byphenyls substituted with carboxylic acid and aldehyde functional groups (Yao, 1997), which have shown to be much less or non-toxic (Upham et al., 1995).

In situ ozonation depends on diffusibility of ozone to the contamination zone. Column studies have indicated that ozone can readily be transported through columns packed with a number of geological materials, including sand, soil, and aquifer materials (Masten and Davies, 1997). All materials studied had a limited ozone demand. Once the initial ozone demand was met, little degradation of ozone was observed. Increases in soil moisture increased ozone degradation rate probably because of dissolution of ozone into soil pore water (Day, 1994).

Day (1994) observed that application of approximately 500 mg/kg ozone could remove 81% of the pyrene from a soil containing 100 mg/kg pyrene. Masten and Davies (1997) reported that more than 95% of the phenanthrene was removed from soil with an ozonation time of 2.3 hours at an ozone flux rate of 250 mg/h, and 91% of the pyrene was removed after 4 hours of ozonation at a flux rate of 600 mg/h. More hydrophobic PAHs were found to react more slowly than would be expected on the basis of their reactivity with ozone, suggesting the partitioning of the contaminant into soil organic matter may reduce the reactivity of the compound.

3.1.1.2 Field Studies/Demonstrations

Table 6 summarizes six field studies for *in situ* chemical oxidation treatment. Two are for hydrogen peroxide (Fentonís reagent), two for potassium permanganate, and two for ozone. For additional field demonstrations, one can refer to a review by U. S. EPA (1998a).

Table 6. Field Studies/Demonstrations for *In Situ* Chemical Oxidation Treatment

No.	Site/Study Name	Pollutants Treated	Treatment Chemicals	Treatment Summary	Contacts	Status & Ref.
1	X-231B Site of the DOE Portsmouth Gaseous Diffusion Plant, Piketon, Ohio. 1993	Volatile organic compounds (VOCs)	Hydrogen peroxide	The demonstration was designed to evaluate the effectiveness of chemical oxidation of VOCs by H_2O_2 coupled with soil mixing. A dilute solution of H_2O_2 (5 wt%) was injected into the air delivery line from an ambient air compressor system. The treatment was conducted for 75 min at a depth of 4.6 m. Approximately 70% of the VOCs were destroyed.	Robert L. Siegrist Colorado School of Mines Environmental Science and Engineering Golden, CO 80401 303-273-3490	Completed. Siegrist et al. (1992); Siegrist et al. (1993).
2	A/M Area of the Savannah River Site.	DNAPL, primarily TCE and PCE	Fentonís reagent	The estimated amount of DNAPL in the treatment zone was 272 kg with PCE ranging from 10 to 150 µg/g. The Fenton's reagent was injected by the Geo-Cleanse process. The treatment was conducted over a 6-day period. Approximately 90% of the DNAPLs in the treatment zone was destroyed, leaving a DNAPL residual of 18 kg in the target zone.	Karen M. Jerome Westinghouse Savannah River Company (WSRC) Savannah River Site Aiken, SC 29808 803-725-2418	Completed Jerome et al. (1997)
3	X-701B Site of DOE Portsmouth Gaseous Diffusion Plant, Piketon, Ohio.	Chlorinated solvent, primarily TCE	Potassium permanganate	The demonstration was performed using the ISCOR technology. Groundwater was extracted from one horizontal well, dosed with $KMnO_4$, and re-injected into a parallel horizontal well approximately 27 m away. The total volume of oxidant solution injected was approximately 77% of the total soil pore volume during 1 month of demonstration. After 21 days, oxidant was detected in all the monitoring wells that were 4.6 m from the injection well. Groundwater monitoring (8 to 12 weeks after treatment operation) indicated that the TCE concentrations were reduced from up to 700,000 µg/L to less than 5 µg/L in all these monitoring wells.	Olivia R. West Oak Ridge National Laboratory P.O. Box 2008 Oak Ridge, TN 37831 423-576-0505	Completed West et al. (1997)

Table 6. Field Studies/Demonstrations for *In Situ* Chemical Oxidation Treatment (Continued)

No.	Site/Study Name	Pollutants Treated	Treatment Chemicals	Treatment Summary	Contacts	Status & Ref.
4	Canadian Forces Base Borden, Ontario, Canada	Primarily TCE, PCE	$KMnO_4$	The treatment was conducted on a sand aquifer of high conductivity with a contaminant concentration of 1200 mg/kg for TCE and 6700 mg/kg for PCE. The source zone was flushed with a 8 g/L $KMnO_4$ solution for almost 500 days. Preliminary analysis showed that 99% of both PCE and TCE was removed. Further monitoring of treatment efficiency is in progress.	Neil Thomson Dept. of Civil Eng. Univ. of Waterloo 200 University Ave. W., Waterloo, Ontario N2L3G1, Canada 519-885-1211	Hood et al. (1998)
5	Dry Cleaning Facilities, Hutchinson, KS	PCE	Ozone	The treatment tests were conducted on an aquifer contaminated with 30-600 µg/L PCE. A C-Sparge™ process was used to inject ozone with an average rate of 3 standard cubic ft per minute (0.085 m^3/min). Monitoring at points 3 m from the ozone injection well indicated that 91% of the PCE was removed.	Leo G. Henning Kansas Dept. of Health & Environ. Bldg 740 at Forbes Field, Topeka, KS 66620 785-296-1914	Completed Dreiling et al. (1998)
6	Former Industrial Facility, Sonoma, CA	PCP and PAHs	Ozone	The treatment was conducted to remediate a contaminated site with an average concentration of 1,800 mg/kg of PAHs and 3,300 mg/kg of PCP. Ozone was injected through wells in the vadose zone at varying rates up to 0.28 m^3/min. After one month of ozonation, sampling from 10 locations indicated that 67-99.5% of PAHs and 39-98% of the PCP were reduced. Soil gas analysis indicated that more than 90% of the injected ozone was consumed.	Chrisopher Nelson Fluor Daniel GTI, Inc. 1527 Cole Blvd. Golden, CO 80401 303-231-8912	Completed Marvin et al., (1998)

3.1.2 Reduction

3.1.2.1 Laboratory Studies

Dithionite: Amonette et al. (1994) investigated the efficiency of dithionite in creating a subsurface reduction zone, and the longevity and reactivity of the reduced iron with soluble inorganic and organic contaminants through laboratory batch and column experiments. They found that one fourth of the ferric iron could be rapidly reduced. The reduction efficiency then declined exponentially with higher degrees of reduction, and up to 75% of the ferric iron could be reduced. Based on the column study, the reduced aquifer barrier created in this way could maintain a reducing environment for about 80 pore volumes before being reoxidized by groundwater. The reduced sediment could rapidly reduce chlorinated hydrocarbon species such as tetrachloromethane (CCl_4). Within a week (168 hours), about 90% of the CCl_4 had been destroyed, while only minor losses of CCl_4 occurred in the oxidized sediment during the same time period. Of the CCl_4 destroyed, less than 10% was converted to trichloromethane, and no dichloromethane was detected.

Fruchter et al. (1997) reported a 18-hour half life of dithionite ion after contacting with on-site sediment. This half life was believed long enough for reduction of high-valent iron in the aquifer, while ensuring that dithionite does not remain as a contaminant in the groundwater for extended periods of time.

Gaseous Hydrogen Sulfide: Thornton and Jackson (1994) investigated the feasibility of *in situ* immobilization of Cr(VI) with hydrogen sulfide in a laboratory column study. Hydrogen sulfide at concentrations of 200 ppm and 2000 ppm in nitrogen was passed through soil columns contaminated with 200 ppm Cr(VI) until a S:Cr mole ratio of 10:1 was achieved. The treated soils were then leached with groundwater or deionized water, and the concentration of Cr in the leachates was analyzed. A total of 90% of the chromium was found to be immobilized and the treatment process was irreversible.

Zero Valent Colloidal Fe^0: Kaplan et al. (1994) investigated the stability of different types of Fe^0 under subsurface conditions. A higher initial colloid concentration resulted in both a higher colloidal settling rate and a higher percentage of colloids settled. Neither ionic strength nor pH exhibit a significant effect on the stability of colloids. Addition of surfactants may affect the stability of colloids in suspensions, depending on the nature and concentrations of the surfactant. For a given surfactant, only at the optimized concentration can the surfactant improve colloid suspension stability.

Cary and Cantrell (1994) suggested that injection of innocuous oil as an additive with Fe^0 could prolong the effective life of Fe^0 without being oxidized by the dissolved oxygen in the liquid carrier. Because microorganisms use the added oil as substrate and oxygen as the electron receptor, the dissolved oxygen would be primarily consumed by microorganisms and the oxidation of Fe^0 by oxygen minimized. A similar idea has been applied for other *in situ* remediation technologies (Streile et al., 1991).

Addition of oil can also create a large immiscible oil-water interface, which acts as a trap for chlorinated hydrocarbons and thus could facilitate reductive dehalogenation of chlorinated hydrocarbons by colloidal Fe^0 (Cary and Cantrell, 1994). In the colloidal suspension, iron colloids are preferentially held in the oil phase and tend to accumulate at the oil-water interface. Consequently, oil injection can facilitate the dispersion of iron colloids in the liquid carrier.

The efficiency of Fe^0 in degradation of organic contaminants and immobilization of inorganic anions will be discussed later in Sections 3.2.2 and 3.2.3.

3.1.2.2 Field Study/Demonstrations

So far, only one field test has been conducted. Two additional field studies are being planned. A summary of these studies is provided in Table 7.

Table 7. Field Studies/Demonstrations for *In Situ* Chemical Reduction Treatment

No.	Site/Study Name & Date	Pollutants Treated	Treatment Chemicals	Treatment Summary	Contacts	Status & Ref.
1	Hanford Site's 100-H Area	Chromate	Dithionite	A 15-m diameter reduced zone was created by injecting 77,000 L of buffered sodium dithionite solution into the aquifer. After a reaction time of 18.5 hr, the spent reagent was withdrawn. It was estimated that 87% of the injected sulfur mass (as dithionite) and 90% of the injected bromide tracer were recovered during the withdrawal phase. One year after the injection, groundwater in the treatment zone remains anoxic. Total hexavalent chromium levels have been reduced from a pre-experiment concentration of about 60 µg/L to below detection limits (8 µg/L).	Jonathan S. Fruchter Pacific Northwest National Laboratory P.O. Box 999, MS K6-96 Richland, WA 99352 509-376-3937	Completed Fruchter et al. (1997)
2	Army Base in Fort Lewis, Washington	TCE	Dithionite	None available.	Jonathan S. Fruchter Pacific Northwest National Laboratory P.O. Box 999, MS K6-96 Richland, WA 99352 509-376-3937	Scheduled Betts (1998)
3	A High Energy Laser System Test Facility (HELSTF) Area within the DOD White Sands Missile Range, South-central New Mexico	Chromate	Hydrogen sulfide	None available.	E. C. Thornton Pacific Northwest National Laboratory P.O. Box 999, MS K6-96 Richland, WA 99352	Scheduled Thornton (1996)

3.1.3 *In Situ* Chemical Flushing

3.1.3.1 Laboratory Studies

Surfactants. After addition of surfactants to soil suspensions or field soils, a portion of the surfactants will be sorbed to soil particles. Thus, the amount of surfactants required for creating micelle structure would be higher than the CMC estimated based on the results of aqueous phase study. For example, Liu et al. (1991) observed that enhancement of anthracene solubility from soil required 0.1% of the non-ionic surfactant Brij 30. This concentration was approximately 40 times higher than the observed CMC determined from aqueous solubility studies. The same trend was observed for other PAH compounds.

Clarke et al. (1994) conducted a column study to determine the feasibility of a surfactant sodium dodecyl sulfate (SDS) in removing biphenyl from contaminated soils. A 90% (± 7%) removal rate was observed for the soil contaminated with 1000 ppm biphenyl with seven pore volumes. The effluent was then recycled to remove the mobilized biphenyl to a residual concentration of 1 to 2 ppm. The recycled surfactant solution was then reused to perform the leaching study, and a removal rate of 94% (± 7%) was observed with seven pore volumes of recycled SDS solution. High removal rate (75%) using surfactant has also been observed for a volatile organic compound, toluene, from a soil containing 3000 ppm toluene (Clarke et al., 1994). An average of 83% of the toluene in the treated surfactant solution was stripped off in the air-stripping column during the surfactant regeneration process.

Comparative batch and column experiments have been conducted by many investigators. It is frequently observed that much less solute can be solubilized from soil columns than from soil suspensions. Pennel et al. (1993) observed that dodecane solubility was increased approximately six orders of magnitude in a non-ionic surfactant, from 3.7 µg/L to 3500 mg/L. Surfactant enhancement of dodecane dissolution from column experiments, however, resulted in a column effluent concentration of 500 mg/L; approximately 7 times less than the equilibrium value determined in batch experiments. Based on a column stop flow study, Pennel et al. (1993) attributed the lower removal of contaminants by surfactant from soil column to the reduction in the rate of solute dissolution into both solution phase and surfactant micelle as well as the decrease in micelles diffusion rate as micelles become saturated with solute. Similar results were observed by Peters et al. (1992) who were able to solubilize more than 97% of No. 2 diesel fuel by a surfactant in batch experiments, but could only remove less than 1% of the contaminant from soil columns. The authors attributed the low efficiency of contaminant removal to channeling of the surfactant solutions to fractures and channeling through cracks.

Peters and Shem (1991) screened 21 surfactants, 6 anionic, 11 non-ionic, and 3 cationic, for possible washing agents to remove No. 2 diesel fuel from soils. Anionic surfactants generally provided the best removal of the total petroleum hydrocarbon

(TPH). The solubility of TPH was increased up to 300% by anionic surfactants over water alone. As high as 90% of the observed alkanes (C12 to C19) could be removed.

Ang and Abdul (1991) investigated the feasibility of removing automatic transmission fluid (ATF) from soils using an alcohol ethoxylate surfactant (Witconol SN 70) at different concentrations. Four soil columns were flushed with 28 pore volumes of 0, 0.5%, 1.0%, or 2% surfactant solutions. A total of 25.5% of the ATF was removed by water, and 55%, 60%, and 72.8% by 0.5%, 1.0%, and 2.0% surfactant solution, respectively.

Kan et al. (1992) reported that commercial surfactant Triton X-100 could significantly enhance solubility of NAPL from soils. They initially flushed a soil column contaminated with aviation gasoline by 21 pore volumes of water. Negligible (< 100 µg/L) aqueous concentrations of NAPL were detected in the water flush. After soil columns were treated with 0.5% or 1.5% surfactant solutions, the leachate concentrations of 2,3,4-trimethylpentane increased to 7 and 123 mg/L for the low and high surfactant solutions, respectively. Greater than 95% of NAPL was removed from soils after 7 to 18 pore volumes of surfactant solution flushing.

Contamination aging tends to make dissolution of contaminants more difficult. Yoem et al. (1993) removed 90% of phenanthrene from soils by a non-ionic surfactant, Brij 30, after soils were contaminated 8 days. For soils contaminated longer period of time (up to 62 days), 5 to 10% less phenanthrene was removed. Dissolution of contaminants from aged contaminated soils followed two time regimes, a fast step followed by a slow step. The slow dissolution was attributed to the binding of contaminants to stronger binding sites or entrapment to soil particles or into the humus structure.

Foams. Peters et al. (1994) tested the feasibility of aqueous-based and ethanol-based foams in solubilizing PAH from contaminated soils. The aqueous foam solution contained 1% (w/v) each of Triton X-100 and Tween-80. A specially synthesized surfactant (IGT FF-1) based on a derivative of polyethylene glycol was used to make the ethanol foam solution because of the difficulty in using commercially available surfactants to make stable foams. The ethanol-based foam was found to be more effective than the aqueous-based foam. After flushing soil columns with 40 foam volumes, less than 20% of the naphthalene was removed from the soil by aqueous-based foam, while nearly 100% of the naphthalene was removed by ethanol-based foam. The authors also tested the possibility of combining *in situ* flushing and biodegradation. The aqueous-based foams showed no adverse effect on naphthalene-degrading microorganisms present in the soil, while ethanol-based foams significantly decreased the microorganism population.

Cosolvents. Much research on cosolvent flushing focused on NAPL. Gatlin (1959) investigated efficiency of alcohol flushing of NAPLs using methanol, isopropanol, and tert-butyl alcohol (TBA) in various combinations. The flushing was performed on 2.7-cm id, 30-m long, galvanized steel pipes packed with Ottawa sand to permeabilities of about 4 darcys. The pipes were oriented vertically and flushed with alcohols at a rate of

1.8 m/hour. It was found that comparable NAPL removal could be achieved at smaller isopropanol expense if methanol was injected prior to the isopropanol slug, because methanol preferentially displaced the residual water.

Boyd and Farley (1990, 1992a) demonstrated that alcohol flooding can be used to mobilize and remove residual light and dense NAPL globules from porous media. They also showed that the injected alcohol concentrations were reduced to biodegradable levels by subsequent flushes with water through the treated zone. In later column studies performed on glass beads and soil, they further observed that residual TCE globules left in a porous medium after water flooding (pump-and-treat) may be removed by injecting an isopropyl alcohol (2-propanol) solution through the contaminated zone (Boyd and Farley, 1992b).

Wood et al. (1992) conducted soil flushing for removal of PCB with ethanol-water mixture in 2.54-cm id, 5-cm long columns. The soils contained low organic matter contents (0.2%) and were contaminated with 2.3 ± 0.3 ppm polychlorinated biphenyl (PCB). By using solvent-water mixtures containing 47.5, 57, 76% ethanol, PCB displacement efficiencies of 85.1, 96.1, and 98.3% were achieved.

Alkaline Solutions. Alkaline flushing, either alkali alone or in combination with surfactants, has been found to be much more effective than conventional water-flooding in recovery of petroleum hydrocarbons (Mayer et al., 1983; Clark et al., 1988). This technique has been widely used in petroleum engineering. Environmental application of alkaline flushing is still in its initial stage. Some field studies will be discussed later.

Acidic and Chelating Solutions. Both acids and chelating agents have been proven effective in extracting heavy metals from soils (Ehrenfeld and Bass, 1984; Rulkens and Assink, 1984). Because acid washing tends to change the soil properties and results in large volumes of liquid that must be treated further before final discharge, extraction with chelating agent is more favored. Peters and Shem (1992) conducted a series of batch experiments to evaluate the extractability of Pb by EDTA. They reported that lead could be removed from spiked soils with efficiencies ranging from 54 to 68%. In other studies using similar batch techniques, Elliott et al. (1989a, 1989b) found that more than 80% of the lead can be removed from contaminated soil by EDTA extraction.

Moore and Matsumoto (1993) investigated the efficiency of *in situ* flushing of lead with three reagents, 0.1 M HCl, 0.01 M EDTA, and 1.0 M $CaCl_2$, based on column studies. Each soil contained 500 to 600 mg/kg lead and was packed in columns under saturated conditions. Flushing with HCl, EDTA, and $CaCl_2$ removed 96, 93, and 78% of lead from soils, respectively. Removal of Pb from soils by HCl was attributed to desorption caused by a decrease in pH, dissolution of $Pb(OH)_2$ or other lead precipitates. The EDTA removed Pb by metal chelation, and the removed Pb by $CaCl_2$ occurred mainly by exchange.

Although highly effective for *in situ* metal flushing, chelating agents like EDTA are very expensive. Thus, it is desired to recycle the chelating agent for reuse in order for this technology to be economically applicable. Allen and Chen (1993) have reported that EDTA and the metal contaminant can be electrochemically recovered.

3.1.3.2 Field Studies/Demonstrations

Many field-scale tests or site treatment using *in situ* chemical-enhanced flushing have been completed, in progress, or are being planned. Table 8 summarizes some of the representative studies. For additional case studies or a more complete description of field studies, one can refer to the technology reports listed in Table 5.

Table 8. Field Studies/Demonstrations for Chemical-Enhanced *In Situ* Flushing

No.	Site/Study Name & Date	Pollutants Treated	Treatment Chemicals	Treatment Summary	Contacts	Status & Ref.
1	Corpus Christi DuPont Site, TX 1991-1993	Carbon Tetrachloride (CTET)	Surfactant	An area of 7.6 x 10.7 m, contaminated with up to 1000 ppm CTET, was selected for the test. The groundwater was initially withdrawn and mixed with surfactant, and then recharged into subsurface to flush CTET. The flushing was conducted in four phases A total of about 276 L of CTET was removed after 12.5 pore volumes of surfactant solution were injected. The CTET concentration was brought down to 219 ppm after the final treatment phase.	John Fountain University of Buffalo Department of Geology 772 Natural Science Complex Buffalo, NY 14260 716-645-6800	Completed Fountain and Waddell-Sheets (1993) Fountain et al. (1995)
2	GE NAO R&D Center, MI 1991	PCBs, oils	Surfactant	The field test was conducted at a site contaminated with polychlorinated biphenyls at 6000 ppm and oils at 67000 ppm. A surfactant solution was applied to a test plot 3 m in diameter and 1.5 m deep. About 10% of the initial contaminants (mass) was removed from the test plot after 5.7 pore volume washing; additional 14% after 2.3 pore volume in the following year. A total of 67% surfactant, 94% PCBs and 89% oils were recovered by membranes.	Abdul S. Abdul GE NAO R&D Center Warren, MI 48090-9055 810-986-1600	Completed Abdul and Ang (1994)
3	Estrie Region, Quebec, Canada 1993-1994	Hydrocarbon	Surfactant	About 1800 m^3 of soils was contaminated with cutting oils with concentrations reaching 200,000 mg/kg. A free floating product phase of hydrocarbon reaching 1 m in free thickness was also observed. A peripheral network was used to hydraulically isolate the contamination, a second zone was used to extract the oils and washing solutions, and a third zone was used to inject and extract materials. A total of 37.6 m^3 of free phase oil was recovered during the first 50 days, and about 160,000 kg oil was recovered during the second extraction period.	Charles Boulanger Ecosite, Inc. 965 Newton Ave. Office 270 Quebec City, Qc. Canada G1P 4M4 1-418-872-3600	Completed Ross et al. (1996)

Table 8. Field Studies/Demonstrations for Chemical-Enhanced *In Situ* Flushing

No.	Site/Study Name & Date	Pollutants Treated	Treatment Chemicals	Treatment Summary	Contacts	Status & Ref.
4	Thouin Sand Quarry, Quebec, Canada 1995	Oil wastes, chlorinated solvents in the form of DNAPL	Surfactant	An area of 4.3 x 4.3 m contaminated with 55,000 mg/kg DNAPL was selected for test. The test plot was flooded sequentially with 1.34 pore volume (PV) water, 0.54 PV polymer, 0.9 PV surfactant, 1.6 PV water. Finally bacteria and nutrients were injected to increase biodegradation of the remaining DNAPL. A total of 86% of the residual DNAPL was recovered.	Richard Martel GREGI Dept. of Geological Eng. Laval University Quebec, Qc, Canada, G1K, 7P4 418-656-2131 x6245	Completed Martel and Gelinas (1996)
5	Traverse City, MI 1995	PCE, TCE, BTEX	Surfactant (Dowfax 8390)	A single borehole was used as both injection well and extraction well. A total of 2044 L of surfactant solution were injected at a surfactant concentration 10 times the CMC value. Recovery of contaminants was enhanced 40 to 90 times higher than that with water alone.	R.C. Knox School of Civil Eng. & Environ. Sci. University of Oklahoma Norman, OK 73019 404-325-4256	Completed Sabatini et al. (1997) Knox et al. (1997)
6	Wood Treating Facility, Laramie, WY 1988	Denser oil	Surfactant /alkali /polymer	Sheet piling was used to create a 8.2 x 8.2 m test cell with about 93,000 ppm oil inside the cell. Two surfactant/alkaline/polymer blends were used for flush. Approximately 95% (wt) of the contaminants was removed.	Tom Sale Colorado State Univ., Dep. Chem. and Bioresource Eng., Fort Collins, CO 80526	Completed Sale et al. (1989)
7	Hill Air Force Base, Test1, Operational Unit 1, UT 1994-1995	NAPL	*Cosolvent* (70% ethanol, 12% n-pentanol, 28% water)	The site contaminated with DNAPL at a content of 7% of the porosity was flooded with *cosolvent*. About 10 pore volume of the *cosolvent* was pumped through the test cell over a period of 15 days. More than 90% of several target contaminants and more than 75% of the total NAPL mass was removed.	P.S.C. Rao Soil Science Dept. 2169 McCarty Hall The Univ. of Florida, Gainesville, FL 32611 904-392-3902	Completed Rao et al. (1997)
8	Province of Utrecht, The Netherlands	Cd	0.001 M HCl	An area about 6,000 m^2, 4 to 5 m deep was estimated to be contaminated with 725 kg Cd. Remediation was conducted by infiltrating acidified water (0.001 M HCl) into the subsurface. The treatment reduced Cd concentration from 5-20 mg/kg to below 2.5 mg/kg in most of the treated area, except a small area where initial Cd concentration was too high.		Completed Otten et al. (1997)

3.2 PERMEABLE CHEMICAL TREATMENT WALL

3.2.1 Immobilization via Sorption and Precipitation

3.2.1.1 Laboratory Studies

Numerous bench- and pilot-scale studies have been conducted to investigate the feasibility of *in situ* immobilization of a variety of contaminants by either synthetic or natural materials via sorption or precipitation. Examples of these studies include activated alumina for treatment of As (Whang et al., 1997); modified and unmodified zeolites for ^{90}Sr, Cd, Hg, Ni, U, As, Cr, Pb, Se, and Ba (Fuhrmann et al., 1995; Cantrell, 1996; U. S. DOE, 1996, Ouki et al., 1993; Bowman et al., 1994; Bowman and Sullivan, 1996); ferric oxides and oxyhydroxides for U and As (Morrison and Spangler, 1993; Whang et al., 1997); and peat, humate, lignite and coal for radioactive elements and metal cations and anions (Thomson and Shelton, 1988; Janecky et al., 1993; Ho et al., 1995b; Whang et al., 1997).

Almost all of the studies showed high retention rates for the contaminants of interest by the employed sorbents at optimized conditions, indicating the potential for field application. Limited information on the sorption mechanisms, however, is available. Sorption can occur by both adsorption and surface precipitation. An understanding of the sorption mechanisms is crucial to evaluate the efficiency of an *in situ* immobilization technique using a specific sorbent. For example, if sorption occurs by inner-sphere complexation or by surface precipitation, the immobilized species tend to be stable and are not easily re-mobilized. If sorption occurs by simple electrostatic interaction, the sorbed species may be re-mobilized upon environmental condition changes.

Many researchers have shown that modification of mineral sorbent surfaces with organics could enhance the ability of the sorbent to immobilize contaminants. Typically, negative charge-bearing 2:1 clay minerals are modified with cationic surfactants. The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the clay (Sparks, 1995). This makes it possible to combine the basic or “positive spots” of the organic cation and the acidic or “negative spots” on the crystal lattice of the clay. The modified organo-clays have been shown to maintain stability under a range of conditions (Smith, 1990; Zhang et al., 1993) and are promising sorbents for *in situ* immobilization of both inorganic and organic contaminants. For example, Haggerty and Bowman (1994) observed that unmodified zeolites sorbed Pb from solution, while surfactant-modified zeolites also sorbed chromate, selenate, and sulfate. Sorption of the anions by surfactant-modified zeolites was suggested to occur by formation of surface-oxyanion complex precipitates. Bowman et al. (1994) observed that unmodified zeolites had no affinity for the organo compounds, while surfactant-modified zeolites could effectively sorb these organic compounds via partitioning. Burris and Antworth (1992) reported that injection of a cationic surfactant (HDTMA) into a aquifer material resulted in the linear sorption coefficients of PCE on the aquifer materials increasing by over two orders of magnitude relative to the original materials.

Most of the studies were conducted in relatively simple systems. The effect of groundwater pH on sorption was generally considered. Few studies examined the effects of other environmental parameters, such as major cations and anions or dissolved organic matter present in groundwater. The competition of major cations for the binding sites and the complexation of contaminants by the dissolved organic matter could significantly affect sorption of these contaminants (Zachara, 1993; Yin et al., 1996). These effects have to be understood before a particular sorbent is applied in field treatment. Another uncertainty is the possibility of remobilization of sorbed contaminants upon environmental condition changes. The long-term stability of the sorbed contaminants is crucial for effective *in situ* immobilization of contaminants by sorption.

Several materials have been investigated for the ability of *in situ* immobilizing contaminants by precipitation or coprecipitation. Among these studies, precipitation of contaminants by lime, phosphates and zero-valent iron have received a great deal of attention and have been extensively investigated. Limestone treatment walls, especially so-called anoxic limestone drain systems, are particularly useful for treatment of groundwater contaminated with acidic mine drainage (Turner and McCoy, 1990; Hedin et al., 1994). Limestone can neutralize acids in the waste and reduce corrosive toxicity. Treatment with limestone also increases the pH of the system, which facilitates precipitation of many metals as hydroxides and also enhances metal sorption on solid surfaces. Furthermore, introduction of lime increases alkalinity of the soil pore water or groundwater, which may precipitate metals as metal carbonates. A number of anoxic limestone drain systems have been commercially installed across the U. S. (Evanko and Dzombak, 1997).

Phosphates are another type of very promising material for *in situ* immobilization of non-redox-sensitive metals, such as Pb, Cu, Cd, and Zn. The treatment is based on the well-known fact that the solubility of some metal-phosphates is extremely low and thus can be considered non-bioavailable. Phosphate-containing minerals, especially apatite and hydroxyapatite, are ideal for the treatment. The chemical reactions involve dissolution of phosphate minerals to release phosphate ligands, followed by formation of insoluble metal phosphate precipitates (Ma et al., 1993; Ma et al., 1994; Ruby et al., 1994; Chen et al., 1997; Lower et al., 1998). Although thermodynamically favorable, the reaction kinetics is the key determining the feasibility of the technique. Recent batch studies performed by Zhang and Ryan (1998) indicated that the added apatite was rapidly dissolved at the initial low pH, and complete transformation of free lead (added as $PbSO_4$) into chloropyromorphite ($Pb_5(PO_4)_3Cl$) precipitate was obtained within 25 min. Most of the studies were performed in pure water-mineral systems. The results obtained from these studies may not directly apply to real soil or ground-water systems. Further studies need to be conducted using natural materials as matrices.

As discussed earlier, zero valent iron can immobilize metal cation and anion contaminants *in situ*. It has been reported that several species, including CrO_4^-, TcO_4^-, UO_2^{2+} and MoO_4^{2-}, can be rapidly removed from aqueous solutions (Blowes et al., 1997; Cantrell et al., 1995; Korte et al., 1997b) by Fe^0. Reductive precipitation was suggested to be the primary mechanism responsible for the removal of these species, although sorption of these species on Fe^0 has likely occurred during the reaction. Gu et al. (1998) further investigated the relative importance of sorption and precipitation in removing metal contaminants by Fe^0 from aqueous solutions by conducting both batch adsorption/desorption and spectroscopic studies. They observed that more than 96% of the UO_2^{2+} removed by Fe^0 from aqueous solution was due to reductive precipitation. Only a small fraction of UO_2^{2+} was removed by adsorption on the corrosion products of Fe^0, and the adsorbed UO_2^{2+} could be replaced by carbonate anions. The study also indicated that the reduced U species could be remobilized upon the local environment changing into more oxidized conditions.

Further studies need to be conducted mimicking real situations. The complex matrices in the natural system could have significant effects on the immobilization of contaminants by Fe^0. For example, Kaplan et al. (1994) investigated the efficiency of several commercial Fe^0 colloids in removal of UO_2^{2+} from groundwater. These Fe^0 colloids vary in size and surface properties. No removal of UO_2^{2+} by three colloids was observed, which was attributed to the presence of trace amount of high-valent Fe and silica that prohibited the reduction reactions. Removal of UO_2^{2+} from 10,000 µg/L to about 1 µg/L was observed for the remaining colloids. The presence of organic matter coating on the surface of Fe^0 colloids resulted in a lag period of several days before a significant amount of UO_2^{2+} was removed from solution.

3.2.1.2 Field Studies/Demonstrations

Table 9 summarizes some of the field studies for *in situ* immobilization of contaminants using different reactive materials.

Table 9. Field Studies/Demonstrations for Chemical Treatment Wall - *In Situ* Immobilization by Sorption and Precipitation

No.	Site/Study Name & Date	Pollutants Treated	Treatment Chemicals	Treatment Summary	Contacts	Status & Ref.
1	Nickel Rim Mine site, Sudbury, Ontario, Canada 1995	Ni, Fe, Sulfate	Organic carbon	A continuous permeable reactive barrier 15 m long, 4.3 m deep, and 3.7 m wide was installed across the ground-water flow path. The barrier consisted of municipal compost, leaf compost, and wood chips. Ground-water monitoring one and nine months after installation of the treatment wall indicated that sulfate concentration was reduced from 2400-3800 mg/L to 110-1900 mg/L, Ni from up to 10 mg/L to < 0.1 mg/L, and Fe from 740-1000 mg/L to < 1-91 mg/L.	David W. Blowes Waterloo Center for Groundwater Research, University of Waterloo, Waterloo, Ontario, Canada 519-888-4878	Installed Benner et al. (1997)
2	U. S. Coast Guard Air Station, Elizabeth City, NC 1996	Cr(VI) and TCE	Zero-valent iron filling	The contaminant plume was estimated to cover a 34,000-ft^2 area with TCE concentration up to 4,320 µg/L and Cr(VI) up to 3,430 µg/L. A full-scale reactive iron treatment wall 45-m long, 5.5 m deep, and 0.6-m wide, was installed using a trencher developed by Horizontal Technologies. The cost for materials and installation of the entire wall was about $500,000. A majority of the multilayer sampling ports show reduction of the TCE concentrations to < 5 µg/L. Treatment efficiency for Cr(VI) is still under investigation.	Robert W. Puls U. S. EPA/National Risk Management Research Lab P.O. Box 1198 Ada, OK 74820 580-436-8543	Installed
3	U. S. Coast Guard Air Station, Elizabeth City, NC 1994	Cr(VI)	Mixture of 25% Fe^0, 25% clean coarse sand, and 25% aquifer material	A treatment wall was created by a series of 21 reactive materials-filled columns created by augured holes. The wall extends to 6.7 m deep with a area of 5.5 m^2. After treatment, Cr(VI) concentration in groundwater decreased from 1-3 mg/L to 0.01 mg/L, DO decreased from 0.6 mg/L to 0.1 mg/L.	Robert W. Puls U. S. EPA/National Risk Management Research Lab P.O. Box 1198 Ada, OK 74820 580-436-8543	Installed Puls et al. (1995)

Table 9. Field Studies/Demonstrations for Chemical Treatment Wall - *In Situ* Immobilization by Sorption and Precipitation (Continued)

No.	Site/Study Name & Date	Pollutants Treated	Treatment Chemicals	Treatment Summary	Contacts	Status & Ref.
4	Y-12 site, Oak Ridge National Lab, TN 1997	U, Tc, HNO_3	Zero-valent iron	A continuous trench and funnel-and-gate system were installed in two areas along the ground-water pathway. Early results indicated that radionuclides (U and Tc) were efficiently removed, while HNO_3 was degraded to NH_4^+, N_2O, and N_2 with a combination of peat and iron fillings.	Baohua Gu Oak Ridge National Lab Envion. Sci. Div. Oak Ridge, TN 37831 423-574-7286	Installed
5	Fly Canyon site, UT 1997	U	Zero-valent iron, amorphous iron oxide (AFO), PO_4^{3-}	The wall has a funnel-and-gate configuration and is comprised of three barriers in series with reactive materials as bone char phosphate, foamed Fe^0, and AFO, respectively. Preliminary results indicated that U was reduced from 3,050-3,920 µg/L to 10 µg/L after traveling 0.6 m into PO_4 barrier; from 1,510-8,550 µg/L to less than 0.06 µg/L 0.15 m into Fe^0 barrier, and from 14,900-17,600 µg/L to less than 500 µg/L 0.6 m into AFO barrier.	David Naftz U. S. Geological Survey 1745 W. 1700 South Salt Lake City, UT 84104 801-975-3389	Installed

3.2.2 Degradation of Inorganic Anions and Organics

3.2.2.1 Laboratory Studies

Feasibility of *in situ* degradation of organic contaminants by zero-valent metals has been and is still being extensively investigated by researchers in academia, government laboratories, and industries. This technology attracted high interest because it is operationally inexpensive and causes minimal environmental damage. Most of these studies focused on degradation of chlorinated solvents by zero-valent iron. The results of these studies indicated that highly chlorinated organic solvents, such as PCE and TCE, could be rapidly degraded by Fe^0 (Gillham and O'Hannesin, 1992, 1994; Matheson and Tratnyek, 1994; Gillham et al., 1993). Some of the lightly chlorinated degradation intermediates (such as cis-1,2-dichloroethelene (cis-DCE) and vinyl chloride), however, are relatively persistent (Orth and Gillham, 1996; Campbell et al., 1997). These intermediates are very toxic and are the primary concern for application of this technology to *in situ* treatment.

Recently, Deng et al. (1997) examined the kinetics of the degradation of intermediate vinyl chloride by Fe^0 as a function of several parameters. The authors observed that ethylene (C_2H_4) is the only degradation product of vinyl chloride. A solid surface reaction is believed to be the primary rate-limiting step. Increases in both temperature and iron loading increased the degradation rate.

Many other zero-valent metals have been demonstrated to be able to degrade chlorinated solvents. Some metals, particularly Zn and Sn, generally yield more rapid degradation rates (Zhang and Wang, 1997). Arnold and Roberts (1997) further indicated that degradation of chlorinated ethylenes by Zn may minimize the formation of undesired products. They observed that approximately 15% of the total PCE degradation occurred by reductive reaction with Zn to produce dichloroacetylene, of which one quarter was ultimately reduced to acetylene through a route that bypassed the production of vinyl chloride. In case of TCE, 20% of the original TCE mass was converted into acetylene. Only traces of vinyl chloride were produced during the reaction.

At present, bimetallic systems based on zero-valent iron for degradation of chlorinated solvents are receiving increasing attention. The bimetallic system is prepared by plating a second metal, such as Pb, Cu, or Ni, onto the iron surface. The second metal serves as a catalyst during the reaction. Coating of iron with the second metal also prevents iron from being oxidized, which otherwise could inhibit degradation reactions. Studies have indicated that the metallic couples can accelerate solvent degradation rates relative to untreated iron metal (Sweeney, 1983; Muttikian et al., 1995; Grittini et al., 1995; Shoemaker et al., 1996; Zhang and Wang, 1997; Liang et al., 1997).

Besides chlorinated solvents, some other organic compounds like herbicides and substituent groups in some nitroaromatic compounds are also degradable by zero-valent metals (Agrawal and Tratnyek, 1994; Eykholt and Davenport, 1997). The available results, however, suggest that straight-chain petroleum hydrocarbons and aromatic compounds such as those found in fuels (e.g., benzene, toluene) are resistant to degradation by Fe^0 (Gates et al., 1996) but can be degraded with a coupled aerobic stage (Baker et al., 1999).

The characteristics of Fe^0 particles could have significant effect on the ability of Fe^0 to degrade contaminants. For example, Zhang and Wang (1997) observed that the laboratory-synthesized nano-meter Fe^0 could much more rapidly degrade TCE and PCBs compared to commercially available larger-sized Fe^0 (< 10 µm). Smaller Fe^0 particles provide greater surface areas and thus facilitate degradation reactions.

The efficiency of Fe^0 or Fe^0-based metal couples in degrading organic contaminants in natural systems needs to be further studied. Interaction of Fe^0 with the complex natural matrices could significantly affect the degradation of the target contaminants by Fe^0. Aging of Fe^0 could also affect the surface properties of Fe^0, which ultimately affect its ability to degrade target compounds.

3.2.2.2 Field Studies/Demonstrations

Table 10 summarizes some of the field studies for *in situ* chemical degradation of inorganic anions and organic contaminants with treatment wall technologies.

Table 10. Field Studies/Demonstrations for Treatment Wall - *In Situ* Chemical Degradation of Inorganic Anions and Organics

No.	Site/Study Name & Date	Pollutants Treated	Treatment Chemicals	Treatment Summary	Contacts	Status & Ref.
1	UMTRA Site, Durango, CO 1996	Nitrate U, Mo	Bi-metallic, zero-valent iron steel wool, zero-valent iron foam	Four treatment walls were installed to treat uranium mill tailing drainage containing 27-32 mg/L NO_3^-, 2.9-5.9 mg/L U and 0.9 mg/L Mo. The first two walls were in baffle style boxes and the other two in horizontal beds. The treatment reduced NO_3^- concentration to 20 mg/L, U to 0.4 mg/L, and Mo to 0.02 mg/L.	Dianne C. Marozas Sandia National Lab P.O. Box 5800 Albuquerque, NM 87185 505-845-9894	Installed
2	Federal Housing Administration (FHA) Facility, Lakewood, CO 1996	TCA, 1,1-DCE; TCE, cDCE	Zero-valent iron (Fe^0)	A funnel-and-gate treatment wall was installed in an unconfined aquifer for treatment of TCE and 1,1-DCE up to 700 µg/L. The system consists of a 317-m funnel section and four reactive gate sections, each 12 m wide. A layer of pea gravel was used to separate the reactive gate from the aquifer materials. After treatment, all contaminants exiting the wall are below 5 µg/L except 1,1-DCE which can be up to 8 µg/L.	Peter McMahon U.S.G.S. Denver Federal Center (MS-415) Denver, CO 80225 303-236-4912	Installed
3	Industrial site, Belfast, Northern Ireland 1995	TCE, 1,2-cDCE	Zero-valent iron	Two 30-m bentonite cement slurry walls were installed to direct water to the inlet of a steel reaction vessel 1.3 m in diameter and containing a 4.8 m vertical thickness of Fe^0. 97% of TCE and 1,2-cDCE were reduced. Vinyl chloride has not been detected in appreciable quantities.	Stephanie OíHannesin EnviroMetal Technol. Inc. 42 Arrow Road Guelph, Ontario N1K 1S6, Canada 519-763-2378	Installed Focht et al. (1996)
4	Industrial site, Coffeyville, KS 1996	TCE, 1,1,1-TCA	Zero-valent iron	The treatment system has a funnel-and-gate configuration with a permeable treatment gate 6 m long and 0.9 m thick installed between two 149-m soil-bentonite slurry walls. Monitoring results indicated that the contaminants in the iron zone are below Maximum Contaminant Levels (MCLs).	Greg Somermeyer SECOR, Inc. 4700 McMurry Drive, Suite 101 Fort Collins, CO 80525 970-226-4040	Installed

Table 10. Field Studies/Demonstrations for Treatment Wall - *In Situ* Chemical Degradation of Inorganic Anions and Organics (Continued)

No.	Site/Study Name & Date	Pollutants Treated	Treatment Chemicals	Treatment Summary	Contacts	Status & Ref.
5	Moffet Federal Airfield, CA 1996	TCE, PCE	Zero-valent iron	A reaction cell 3.2 m wide, 3.2 m thick, and 8.2 m deep was constructed from two layers of 0.6-m pea gravel with 2 m of 100% granular iron in between. Interlocking sheet piles were installed alone the sides of the cell, and a concrete wall was placed at the bottom to prevent groundwater infiltration. TCE was reduced from 850-1180 µg/L in the influent to 11-36 µg/L at a distance 1.3 m into the wall. No VC was detected in the influent, but VC was detected 0.3 m into the wall and not detected within 0.6 m of the wall.	Stephen Chao Dept. of the Navy, Engineering Field Activity West, Naval Facilities Engineering Command, 900 Commodore Drive, Building 208, San Bruno, CA 94066 415-244-2563	Installed
6	Inersil semiconductor site, Sunnyvale, CA 1995	TCE, cDCE, VC, Freon 113	Zero-valent iron	The area is a semiconfined aquifer contaminated with 50-200 µg/L TCE, 450-1000 µg/L cis-1,2-DCE, 100-500 µg/L vinyl chloride and 20-60 µg/L Freon 113. A treatment wall 1.2 m wide, 11 m long, and 6 m deep charged with 100% granular iron was installed. Since installation, VOC concentrations in groundwater were reduced to below the Maximum Contamination Level (MCL) set by the State of California and Primary Drinking Water Standards -- 5 µg/L for TCE, 6 µg/L for cDCE, 0.5 µg/L for VC, and 1,200 µg/L for Freon 113.	Carol Yamane Geomatrix Consultants, Inc. 100 Pine Street San Francisco, CA 94111 415-434-9400	Installed Yamane et al. (1995)
7	Lowry Air Force Base, CO 1995	TCE	Zero-valent iron	The funnel-and-gate system consists of two 4.3-m sheet piling walls and a 3-m wide and 1.5-m thick reactive cell charged with 100% Fe^0. Chlorinated hydrocarbons are being completely degraded within the first foot of the wall. All analytes degrade to their respective analytical limits after 18 hours residence time. The intermediate breakdown products produced during the process are also degraded.	William A. Gallant Versar, Inc. 11990 Grant Street Suite 500 Northglenn, CO 80233 303-452-5700	Installed Duster et al. (1996)

4.0 COST

Unit costs for remediation are affected by several factors, namely reagent cost, desired cleanup level, feasibility of chemical regeneration, characteristics of contamination, and technology implementation costs, such as drilling/infrastructure, monitoring, etc. Depending on the site characteristics, and distribution and quantity of contaminants, the unit cost for treatment of the same contaminants with the same technology at different locations could be quite different. Table 11 lists the estimated costs for some of the case studies.

As indicated in Table 11, the costs for *in situ* treatment via chemical injection primarily depend on reagent cost and expenses for delivery of chemicals to the contamination zone. The unit cost also depends on depth of contamination and quantity of contaminants. For example, Jerome et al. (1997) estimated that the unit cost for *in situ* treatment of DNAPL (mainly TCE and PCE) with Fenton's reagent is greater than \$220/kg for small volumes of DNAPL (less than 1816 kg), and greater than \$1542/kg for even smaller volumes of DNAPL (approximately 454 kg). Gates et al. (1996) estimated that removal of 80% of the TCE with hydrogen peroxide using soil mixing as a delivery method costs \$130-200/m^3, assuming that off-gas treatment constraints are nominal.

Jafvert (1996) listed all basic expenses related to *in situ* chemical flushing under three categories, design costs, capital costs, and operating costs. Each category depended on the specific case. Sale et al. (1996) estimated the cost for *in situ* flushing of a 40 x 40-m hypothetical area contaminated with DNAPL based on the current state of knowledge regarding chemically enhanced recovery. The total cost, including initial bench-scale work, design, installation, operation, maintenance, and post operation monitoring, was \$576,000. More cost estimates can be found in the reports listed in Table 5.

Information on cost for installation of chemical treatment walls is available for many tested or remediated sites. Depending on the size and nature of the treatment walls, the installation cost can range from as low as \$30,000 up to \$1,500,000. More detailed information can be found at the Remediation Technologies Development Forum (RTDF) web site (www.rtdf.org/barrdocs.htm).

Table 11. Capital Costs for Some of the *In Situ* Chemical Treatment Technologies

Technology	Chemical Delivery Technology	Contaminants	Dimensions	Cost	References
Chemical Injection					
Hydrogen Peroxide	Soil mixing with H_2O_2/air injection	TCE, 1,1,1-TCA, 1,1-DCE < 1 to 100 mg/kg	0 to 4.2 m depth	$130/m^3	Siegrist (1998)
$KMnO_4$	Soil Mixing with $KMnO_4$ injection	TCE and 1,2-DCE up to 800 mg/kg	0 to 7.6- or 14.3 m depth	$170/m^3	Siegrist (1998)
$KMnO_4$	Soil fracturing with $KMnO_4$ oxidative particle mixture	TCE Concentration ranged from ppb to ppm	0.5 m to 5 m depth	$40/m^3	Siegrist (1998)
$KMnO_4$	Horizontal well flushing	TCE up to 820 mg/L	7.5 to 9.5 m depth	$240/m^3	Siegrist (1998)
$NaMnO_4$	Vertical well recirculation	TCE 1.5 to 2.0 mg/L in groundwater	7.9 to 10.4 m depth	$77/m^3	Siegrist (1998)
***In situ* Chemical Flushing**					
Surfactant		DNAPL	40 x 40-m area	$576,000	Sale et al. (1996)
Treatment Wall					
Reactive Carbon		Ni, Fe, sulfate	15 m long, 4 m deep, and 3.6 m wide	$30,000	www.rtdf.org/barrdocs.html
Zero valent iron		TCE	3 m wide and 1.5 m thick reactive wall filled with FeO and two 4-m sheet piling walls that were installed to a depth of 5 m.	$530,000	www.rtdf.org/barrdocs.html
Zero valent iron		1,2-DCE, VC	40 m long, 1.8 m wide, and 6 to 10 m deep	$1,500,000	www.rtdf.org/barrdocs.html

5.0 RELATED POLICY AND REGULATORY ISSUES

Despite the fact that innovative technologies, such as the ones discussed in this report, offer significant benefits over conventional pump-and-treat technology, their use is still very limited because of technical uncertainties and regulatory or procedural barriers. For example, in the Superfund programs, fewer than 6% of selected ground-water remedies involve *in situ* methods (U. S. EPA, 1996a). Chemical injection is regulated by the Underground Injection Control (UIC) program under the Federal Safe Drinking Water Act. Injection of chemicals for the purpose of aquifer remediation and experimental technologies are distinguished from hazardous waste injection and are designated as Class V under the UIC program (U. S. EPA, 1996b).

Under the general UIC program, each state has its own policies and regulations, which can be obtained using the Envirotext Retrieval System (ETRS), a Federal database operated by the U. S. Army Corps of Engineers (U. S. EPA, 1996b). Based on this database and discussion and interviews with state regulators, the EPA Technology Innovation Office (TIO) concluded (U. S. EPA, 1996b) that no State has a direct regulatory prohibition on injection technologies for treating contaminated aquifers; few States have policies that discourage use of injection technologies; about two-thirds of the States have allowed some sort of injection incidental to an *in situ* ground-water remediation technology; eleven States have allowed surface injection; several states require closed systems or some other evidence that all injectant will be captured and removed; and fifteen States have not received an application or proposal to review.

To promote application of innovative technologies in waste management, EPA (1996a) has proposed to place a high priority on innovative treatment and characterization technologies. EPA encourages reasonable risk-taking in selecting innovative technologies for treating contaminated soils, sludge, and groundwater. A series of actions have been taken to facilitate and support treatability studies using innovative technologies. For example, in the RCRA context, EPA has revised its Treatability Study Sample Exclusion regulations (40CFR261.4(e)-(f)) to allow treatability studies on up to 10,000 kg of media contaminated with non-acute hazardous waste without the requirement for permitting and manifesting.

EPA (1996) also encouraged reducing impediments to innovative technology development. They encouraged streamlining RCRA permits and orders for innovative treatment technology development and use, encouraged State adoption of and streamlining EPA authorization to administer the treatment study sample exclusion rule. They recommended using Federal facilities as sites for conducting technology development and demonstrations. Finally, EPA is willing to share in risks of using innovative treatment technologies (U. S. EPA, 1996b). Detailed guidelines are being revised based on comments from the individual regions. To encourage prime contractors to use innovative technologies, EPA plans to provide indemnification to both the prime contractor and to its innovative technology subcontractor.

6.0 LESSONS LEARNED

6.1 SELECTION OF TECHNOLOGIES

Selection of a technology for remediation of a contaminated site relies on careful site characterization, laboratory batch and column studies, and pilot and field tests. Issues related to technical bases, design and implementation of these tasks have been addressed by many researchers (NRC, 1994; Sevougian et al., 1994; Lawrence et al., 1995; Freeze, 1997; Anderson, 1997). Site characterization is the first step for any remediation activity. Both regional geological settings and contaminant distributions need to be thoroughly characterized. Geological settings include regional geological structure, stratigraphy, and ground-water hydrogeology. All of these factors affect the distribution and transport of contaminants in the subsurface. General information on geological settings can be obtained from local geological survey departments. Due to the complexity and heterogeneity of subsurface materials, detailed borehole data need to be obtained and analyzed in order to determine the plume and source of contamination as well as the types and forms of contaminants.

Based on site characterization, one or more available technologies can be selected for further feasibility studies. The key factors affecting treatability, including pH, NOM, alkalinity, permeability, and depth, need to be evaluated before a given technology is finally selected. Laboratory batch studies are the best for screening appropriate technologies. Further column studies should be conducted to examine the effects of matrix on the treatability of contaminants by the chosen technology and to determine the optimum treatment conditions. Finally, pilot and field tests may need to be conducted before a final decision is made.

6.2 LIMITATIONS OF TECHNOLOGIES

Although *in situ* treatment technologies provide many advantages, there are limitations for each of these technologies. An understanding of both down and up sides of these technologies are crucial to appropriate application of them for remediation. Treatment via chemical injection doesn’t need excavation and replacement, and thus engineering would be cost-effective. With advanced injection techniques, such as deep soil mixing and soil fracturing, chemicals can be delivered very deep into the subsurface for treatment, which would be impossible using other techniques. Due to diffusion limitation, the area covered by each injection well, however, is relatively small. In some low permeability areas, injection of chemicals to the contaminated region may be very difficult.

In case of oxidation, the oxidants injected are generally non-selective to both organic contaminants and natural organic matter. Thus, the presence of high natural organic matter content in the contaminated site could consume a large portion of the added oxidants (Tyre et al., 1991; Tarr and Lindsey, 1998), making treatment economically infeasible. One of the primary concerns about treatment via injection of reductants is the longevity of the created reduced environment. The inorganic contaminants, such as chromate, immobilized under the reduced conditions could be re-mobilized upon environmental condition changes. Another concern is the toxicity of the degradation products of organic contaminants. Further research is needed to identify the degradation pathway and degradation products.

In situ chemical flushing is very effective to remove DNAPL or other strongly sorbed contaminants. However, measures need to be taken to prevent the mobilized contaminants from escaping to the surrounding area. The introduced chemicals could also have adverse effects on the ecosystem. At present, many of the surfactants tested have been shown to be non-toxic and easily degraded under subsurface conditions. The fate and effects of some surfactants, cosolvents and chelating agents on the ecosystem are not fully understood. Cost is another concern for *in situ* chemical flushing. It seems requisite to regenerate the chemicals in order to make this technology economically feasible.

Chemical treatment walls as a passive treatment technology have the least effect on the ecosystem. The contaminants immobilized by sorption and precipitation, however, could be re-mobilized upon local environmental condition changes. The fate and toxicity of degradation products of organic contaminants and inorganic anions also affect the applicability of this technology. The reactivity of the reactive materials contained in the treatment wall over time is another concern of this technology. Furthermore, due to the technology limitations for building treatment walls, this technology is typically only used for treatment of subsurface contaminants at shallower depths (3 to 12 m).

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