# GEOENVIRONMENTAL ENGINEERING FOR IN SITU REMEDIATION

# Charles D. Shackelford<sup>1</sup> and Stephan A. Jefferis<sup>2</sup>

#### ABSTRACT

An overview of geoenvironmental engineering for *in situ* remediation of contaminated land is presented. After a brief introduction, an historical perspective of remediation in the United States and the United Kingdom is presented as background for the remainder of the presentation, that includes descriptions of the remediation process, including assessment, some technological considerations for remediation, and the existing or potential technologies that may be used for remediation of contaminated land. Emphasis is placed on *in situ* technologies that are separated into four categories: (1) passive containment, (2) active containment, (3) passive treatment, and (4) active treatment. The costs associated with the technologies also are discussed briefly. Finally, the role of geotechnical engineering in geoenvironmental engineering for *in situ* remediation of contaminated land is discussed.

#### **1.0 INTRODUCTION**

Remediation, also commonly referred to as reclamation, of contaminated land may be defined as the process of restoring land that has been contaminated with pollutants from some activity. Although the words 'remediation' and 'reclamation' often are used interchangeably in terms of environmental contamination, it may be argued that the two words have slightly different meanings.

The word "remediation" is derived from the verb, 'remedy', which means "...to restore to the natural or proper condition" (Random House Dictionary). The word 'reclamation' is defined as "...the act or process of reclaiming", and the verb 'reclaim' may be defined alternatively as "...to bring (wild, waste, or marshy land) into a condition for cultivation or other use", or "...to recover (substances) in a pure or usable form from refuse, discarded articles, etc." (Random House Dictionary). Another distinction between the words "remediation" and "reclamation" is that the word "remedy" is used frequently in both medicine (e.g., something such as a medicine or therapy that relieves pain or cures a disease) and law (e.g., a legal means of preventing or correcting a wrong or enforcing a right). Thus, both legal and medical implications are associated with 'remediation', whereas no such implications are necessarily inferred from the use of the word 'reclamation'.

As a result, the goal of reclamation of contaminated land may be inferred as reuse of the land, whereas the goal of remediation of contaminated land may be inferred as a process to prevent or minimize a real (e.g., medical) or perceived (e.g., legal) risk of harm to humans. This distinction is further developed in the United Kingdom (UK) where the term reclamation often is associated with derelict land (e.g., former industrial land which is no longer used) and remediation for land which is contaminated. However, as derelict land also is often contaminated, there are many situations where reclamation involves both minimization and prevention of risk and reuse of the land.

#### 1.1 The Problem

The problem of contaminated land results from a multiplicity of activities. For example, contamination of land can result from relatively localized or 'point' source activities, such as industrial spills, leaking disposal pits, and leaking underground storage tanks, as well as from relatively dispersed or 'non-point' source activities, such as infiltration of pesticides spread over large agricultural areas. In many cases, contaminated land has resulted from controlled activities in the distant past (e.g., more than 20 to 30 years ago) that were

<sup>&</sup>lt;sup>1</sup> Department of Civil Engineering, Colorado State University, Fort Collins, Colorado 80523-1372, USA

<sup>&</sup>lt;sup>2</sup> School of Engineering in the Environment, University of Surrey, Guildford, GU2 7XH, England

not perceived to be a potential threat to the environment and, therefore, were not regulated. In other, more recent cases, contaminated land typically has resulted from negligent or illegal activities, or from uncontrolled activities, such as accidental spills.

For example, as shown schematically in Figs. 1, 2, and 3, liquids sometimes were disposed in unlined disposal pits (surface impoundments) in the United States (US) prior to about 1976 without regard to the potential environmental consequences. As a result, the liquids would migrate downward through the unsaturated, or vadose, zone and into the ground water. Inorganic contamination (Fig. 1) often resulted from unlined surface impoundments that served as evaporation ponds used to concentrate contamination at industrial facilities (e.g., Daniel et al. 1985). In the case of disposal of non-aqueous phase liquids (NAPLs), typically organic solvents, the migrating liquids would either sink to the bottom of the saturated zone (Fig. 2) or float on the surface of the groundwater table (Fig. 3) in essentially pure or 'free-phase' form. These free-phase solvents subsequently represented sources for dissolved-phase contaminants that migrated down gradient and eventually contaminated fresh ground water commonly used for consumption.



Figure 1: Schematic scenario of inorganic contamination from an unlined evaporation pond.



Figure 2 : Schematic scenario of dense, non-aqueous phase liquid (DNAPL) contamination from unlined disposal pit.



Figure 3 : Schematic scenario of light, non-aqueous phase liquid (LNAPL) contamination from unlined disposal pit.

In some cases, recognition of the existence of contamination in an unconfined aquifer has resulted in placement and screening of drinking water wells in underlying, confined aquifers. However, improper sealing of the wells has resulted in subsequent 'cross-contamination' of the underlying, confined aquifer (e.g., Fig. 2). This cross-contamination may also have occurred from natural gaps (e.g., fractures) in the confining layer (aquitard).

The example contamination scenarios illustrated in Figs. 1, 2, and 3 provide only a flavor of the potential subsurface contamination problems that exist worldwide today. The actual possible scenarios are unlimited, and depend on such factors as site-specific conditions, the type of contamination, and the source of the contamination.

### 1.1.1 Objectives

There are at least two limitations associated with presenting an overview on the geoenvironmental engineering aspects of *in situ* remediation of contaminated land to an international audience. First, the social environment and economic conditions in most countries are sufficiently different that the aspirations or goals regarding the process of, or even the need for, remediation of contaminated land vary widely. Second, the nature of contaminated land problem is sufficiently widespread such that most technical solutions to the problem require the expertises of individuals from several different disciplines. The individuals in these varying disciplines often do not have the formal education or training to understand or communicate properly with each other, leading to intimidation and a general reluctance to work in an interdisciplinary setting.

With these limitations in mind, the objectives of this paper are as follows:

- to provide an historical perspective on remediation practice in the US;
- to consider UK practice where it differs significantly from that in the US;
- to review the basic components of the overall *in situ* remediation process;
- to define commonly used terminology;
- to identify some important technological considerations for *in situ* remediation;
- to provide general descriptions of current and potential in situ remediation technologies; and
- to comment on the role of geotechnical engineering in the geoenvironmental engineering aspects of *in situ* remediation of contaminated land.

# 2.0 HISTORICAL PERSPECTIVES ON REMEDIATION IN THE UNITED STATES AND THE UNITED KINGDOM

A brief historical perspective on factors affecting the practice of remediation in the US is presented as background information for the remaining discussion. This is followed by a brief description of the development of concerns regarding contaminated land in the UK.

The US perspective begins in the early 1970s and proceeds chronologically at approximately five-year intervals. Some of the time frames are based on personal recollection and, therefore, are approximate.

- Early to Middle 1970s: The public becomes increasingly aware of the potential risks associated with contaminating the human body by foreign substances (e.g., cancer from smoking) and the unsightliness of polluting the environment (e.g., litter on highways). The government takes action (e.g., Surgeon General, fines for litter). The public begins to connect the human health risks with environmental pollution. The government takes action by forming the US Environmental Protection Agency (EPA). An assessment of the nation's environmental policy and problems begins in earnest.
- Middle to Late 1970s: The Resource Conservation and Recovery Act (RCRA) legislation governing the disposal of newly generated wastes is passed in 1976. Technical considerations governing the design of new disposal facilities begins.
- Early to Middle 1980s: Emphasis is placed on waste disposal (i.e., prevention of new contamination problems). The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) legislation, also known as Superfund, governing the cleanup of contaminated sites is passed. Remediation of existing contaminated sites becomes important, and a National Priorities List (NPL) of sites requiring cleanup is established. Pump-and-treat (PT) technology is a common choice for remediating the sites, in part, because the use of wells for pumping ground water as a resource for distribution and use was well established, and several *ex situ* techniques for treating water already had been developed.
- Middle to Late 1980s: The number of sites on the NPL is growing significantly faster than the number of sites being remediated to completion. Experience indicates that the stringent requirements of the regulations are incompatible with the existing technologies for site cleanup. In particular, pump and treat (PT) as a remediation technology begins to become in disfavor. Aside from the costs associated with the continuous pumping, handling, and treating of large quantities of water for indefinite periods, the conclusion is being reached that the existing PT technology cannot restore aquifers to any health-based standards as required by the Superfund authorization (Mott 1992). The development of alternative remediation technologies begins in earnest, and technical concerns regarding new disposal facilities are de-emphasized. The Superfund Amendments and Reauthorization Act (SARA) legislation is passed in 1986 with a greater emphasis on spending more money for actual site-cleanups versus for research.
- Early to Middle 1990s: The emphasis on development of alternative remediation technologies increases. The ability to achieve remediation goals comes into question due to rising costs and the increasing number of sites on the NPL. There seems to be increasing willingness by regulating authorities and legislature (not necessarily the public) to consider increased risk in view of the rising costs to industry and taxpayers. The use and development of potentially less costly passive containment (e.g., vertical cutoff walls, caps) and treatment (e.g., reactive walls) technologies gains momentum. The Superfund program is not re-authorized (*circa* 1994).
- Middle to Late 1990s: The pressure to reduce rising costs (inflation, increasing number of sites on NPL) associated with remediation is intense. *In-situ* containment becomes a viable option because containment is less expensive relative to many other treatment options, and containment delays the need for immediate expenditure, typically a popular option with elected officials. Also, a re-evaluation of remediation goals is undertaken, and the Brownfields program, which gives more cleanup authority to individual states, is started. Interest in and study of the use of alternative containment systems (reactive barriers, capillary barriers) increases. The option of 'doing nothing' in the form of monitored natural attenuation (MNA) gains momentum, but there is increasing concern regarding costs associated with monitoring.

At least two conclusions can be drawn from this brief historical perspective on remediation of contaminated land in the US. First, remediation in the US has been and will continue to be an ever-

changing, or dynamic, process. Second, in an effort to reduce remediation costs and improve the 'success rate', the objectives of the remediation process have come almost full circle, i.e., from significant involvement of technology to the concept that almost no involvement of technology is necessary in selected cases (MNA).

- In the UK, the situation with respect to contaminated land has been characterized by a very slow implementation of the regulatory framework, and a framework that was focused on clean-up as being part of redevelopment rather than solely for pollution prevention.
- In the 1970s, some Local Authorities began to experience problems in relation to the redevelopment of former industrial sites, such as the site of the former Woolwich Arsenal (Cairney 1987). Inquiries were made to two government departments: the Department of the Environment (DoE) and the Department of Health and Social Security (DHSS) and, in response, it was decided to set up a committee to co-ordinate information and promulgate advice.
- In 1976, the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) was formed with representation from the DoE, DHSS, the Health and Safety Executive, the Ministry of Agriculture Fisheries and Food, the Welsh office, and later the Scottish Development Department. The terms of reference for the committee included: 'to develop and co-ordinate advice and guidance on human health hazards arising in connection with the re-use of contaminated land, to develop and co-ordinate advice regarding possible remedial measures; to make such advice available to local authorities; to advise the Department of the Environment as to the appropriateness of the methods selected by Local Authorities; and to identify research needs'.
- Over the years, the ICRCL produced a number of guidance papers, starting in 1979. In 1987, ICRCL Guidance Note 59/83, 'Guidance on the assessment and redevelopment of contaminated land, 2nd edition' was published. This document included tables setting out trigger levels for a number of inorganic and organic contaminants. Trigger levels were defined as levels below which soil could be assumed as not contaminated but above which the soil was not necessarily unsafe. Action levels were included for a very few of the chemical species, but the form of the action was not specified. The tables were for guidance and had no legal force.
- In 1990, the Environmental Protection Act was published and included a new framework for the management of contaminated land. However, much of the legislation in relation to contaminated land was not brought into force. The Act provided for statutory guidance to be produced on contaminated land. A long period of public consultation followed and several versions of the guidance were produced. In 1995, a revised framework for the identification and remediation of contaminated land was inserted into the 1990 Act by the 1995 Environment Act. This framework and the guidance were finally brought into force on April 1, 2000.
- The fundamental concept of the UK legal framework is that the land should be suitable for use and that this suitability should be assessed following risk-based procedures.
- A major source of complexity and confusion with the UK system is that the law relating to ground water is not aligned with that for soil. The water law predates that for soil and does not include any suitable procedures for assessing use or risk. Fundamentally, it is an offence to cause or knowingly permit the entry into controlled waters (effectively all waters, including ground water and surface water) of any poisonous, noxious, or polluting matter or any solid waste matter.

Finally, it should be noted that the law and procedures relating to the management of contaminated land are not homogeneous across the UK. Scotland always has had a separate legal system, and contaminated land legislation differs between Scotland and England. Wales now has some separate legislative powers and may not exactly follow the English system.

# 3.0 COMPONENTS OF THE REMEDIATION PROCESS

In the US, the process of remediation of contaminated land commonly involves several steps, as outlined in Fig. 4. After contamination is discovered at the site, an emergency response and abatement phase typically is initiated to provide an initial assessment of the nature of the contamination, and rapid measures to abate or prevent further contamination are taken. After this initial assessment, a more detailed site characterization is undertaken to provide more accurate assessment of the problem (e.g., stratigraphy, concentrations of the contaminants of concern, or COCs), followed by a detailed exposure assessment, and a review of the outcomes of these assessments by the governing regulatory authority, a process which is ongoing and interactive.



Figure 4 : Flow chart of remediation process in US.

After the site and exposure assessment is approved, a decision regarding the necessity of remediation is made. This decision typically results in one of three outcomes: (1) there is no need for further action; (2) remediation must be implemented; or (3) the site should be monitored to determine whether or not natural attenuation processes will remediate the site, with the potential for implementation of a more aggressive remediation technology some time in the future.

If remediation is required, the next phases of the remediation process involve defining the remediation objectives (e.g., concentration levels, containment versus treatment, etc.), screening possible remediation technologies that can achieve the objectives, choosing the most appropriate technology, and designing and installing the chosen remediation technology and system. Finally, monitoring of the performance of the system is required to ensure that the chosen technology is working to achieve the stated objectives. If the desired objectives cannot be achieved with the chosen technology, either the design of the chosen technology must be re-evaluated and modified, and/or an additional technology must be used. This process is repeated until the desired remediation objectives are achieved.

In the UK, the process is broadly similar to that set out in Fig. 4, but the role and powers of the regulator are rather different. Also, the standard of remediation is defined in terms of pollutant linkages, i.e., linkages between a contaminant and a receptor via a pathway. The standard to which the relevant land or waters as a whole should be remediated is to be established by considering separately each significant pollutant linkage identified on the land in question. To be significant, a pollutant linkage must:

• result in significant harm being caused to the receptor in the pollutant linkage;

- present a significant possibility of harm being caused to that receptor;
- result in pollution of controlled waters which constitute the receptor; or
- be likely to result in such pollution.

For each such linkage, the standard of remediation should be that which would be achieved by the use of a remediation package which forms the best practicable techniques of remediation with respect to

(a) ensuring that the linkage is no longer a significant pollutant linkage, by (i) removing or treating the pollutant, (ii) breaking or removing the pathway, and/or (iii) protecting or removing the receptor; and

(b) remedying the effect of any significant harm or pollution of controlled waters which is resulting, or has already resulted, from the significant pollutant linkage.

The process may be started by the landowner voluntarily investigating his land or as a result of the Local Authority serving a notice on the landowner to remediate the land. It may be noted that under the April 1, 2000, Statutory Guidance, Local Authorities are under a duty to cause the land in their area to be inspected for contamination. Discovery of contamination is unlikely to be followed by any emergency response or abatement in the UK unless there is evidence of immediate risk to human health or controlled waters.

Having considered regulatory frameworks, the remainder of this section will focus on discussion of various aspects associated with the site characterization (investigation), exposure assessment, and the relationships among concentration, risk, and technology, and monitoring. This discussion then will be followed by more detailed presentations regarding the technological considerations associated with choosing a remediation technology, and brief descriptions of some of the individual remediation technologies.

# 3.1 Site Characterization

The site characterization, or site investigation, for remediation of contaminated land may be separated into two main components: (1) a background review, and (2) a subsurface exploration. The background review is used to help identify the contaminants of concern (COC), probable source(s) of release, zone(s) of contamination, and potential impacted areas and receptors (neighbors, drinking water supplies, etc.). This review includes such steps as collecting and reviewing historical records of the site, and interviewing site personnel.

The subsurface exploration includes delineation of soil stratigraphy or site geology (e.g., using cone penetrometers), location of the groundwater table, recovery of soil samples (e.g., borings), and determination of standard physical (index) properties of the soil samples (e.g., water content, grain-size distribution, Atterberg limits, specific gravity, classification). All of these components of the subsurface exploration are similar to traditional geotechnical engineering practice for uncontaminated land applications (e.g., foundations). However, the subsurface exploration for contaminated land differs from more traditional geotechnical engineering four ways:

- determination of the chemical properties (e.g., soil pH, cation exchange capacity, exchangeable cations, soluble salts), and atypical compositional properties of the soils (e.g., organic matter, organic carbon, carbonate content, clay mineralogy, etc.) may be required;
- delineation of the distribution of contaminants in the saturated and unsaturated (vadose) zones is required;
- installation of monitoring wells, and recovery and analyses of groundwater samples are required; and
- characterization of the site hydrogeology, including determining the site heterogeneity, determining or estimating the groundwater gradient and aquifer permeability, and possibility determining the air permeability, is required.

The approach to subsurface exploration in remedial investigation also is similar to typical geotechnical engineering practice with the exception of the following additional concerns (Holm 1993):

- health and safety of field personnel due to exposure to toxic chemicals;
- equipment decontamination before, during, and after use;
- handling, shipment, and chain of custody of contaminated samples;
- media cross-contamination; and
- disposal of exploration-derived wastes.

The requirement to provide a high level of accuracy with respect to delineation of the subsurface geology and hydrogeology of contaminated land as well as the need to delineate the extent of contamination typically result in the requirement for an inordinate number of discrete boring locations (sampling points). For example, consider the results of an analysis presented by Benson (1993) as shown in Fig. 5. The target area,  $A_t$ , in Fig. 5 may represent, for example, the location of a contaminant plume, a narrow sand lense, or buried drums containing toxic waste. The results shown in Fig. 5 indicate that the number of sampling points increases as (1) the probability of detection of the target area increases for a given target-area-to-site-area ratio, and (2) the target-area-to-site-area ratio decreases for a given probability of detection.



## Area of Target, At Area of Site, As

Probability of	No. of Sample Points			
Detection (%)	$A_t / A_s = 0.1$	$A_t / A_s = 0.01$	$A_t / A_s = 0.001$	
30	3	30	300	
40	4	40	400	
50	5	50	500	
75	8	80	800	
90	10	100	1000	
98	13	130	1300	
100	16	160	1600	

Figure 5 : Discrete sampling requirements (modified from Benson 1993). [Note: This table is based on a uniform sample grid; for a random selection, the sample numbers must be increased by a factor of 1.6.]

The results shown in Fig. 5 also indicate that the number of borings required to provide a relatively high level of detection (e.g.  $\geq$  90 %) for relatively small targets or relatively large sites (A<sub>t</sub>/A<sub>s</sub> = 0.001) is extremely high ( $\geq$  1000). This need for greater accuracy of delineation may be the reason for the high number of borings, and corresponding excessive costs, that typically have been associated with site characterization of contaminated land relative to more traditional geotechnical engineering activities ( see Table 1).

Table 1 : The evolution in site characterization	: 1960 to 1990 (	modified from Du	plancic and	Buckle 1	.989).
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		No. of	Risk of Failure	
Decade	Activity	Borings	Human Lives	Environment
1960s	High rise buildings	5 - 10	10 - 2000	Low
	Large dams	20 - 50	> 5000	Moderate
1970s	Off-shore platforms	1 –10	10-300	Very High
	Nuclear power-plants	50 - 100	50 - 50,000	Extremely High
1980s	Panoche hazardous waste site	~ 400	?	High
	Rocky Mountain Arsenal	1600 *	?	High

\* Also required 3400 wells.

One possible way to reduce the number of sampling points is to complement the use of discrete sampling methods with less intrusive, surface geophysical methods. A summary of some of the surface geophysical methods that commonly are used for evaluation of natural hydrogeological conditions is provided in Table 2. These techniques typically are more rapid than the more traditional sampling techniques, and tend to provide a more continuous distribution of subsurface features. However, geophysical methods do not

provide any samples, and also are restricted by several limitations (Table 2). Detailed descriptions of these geophysical methods are provided by Benson (1993).

	condi	tions (from Benso	on 1993).	
		Continuous	Depth of	Limitations
Method	Application	Measurements	Penetration	
Radar	Profiling and	Yes	$\leq$ 30 m	Penetration limited by soil
	mapping; highest		(typically	conditions
	resolution		$\leq 10 \text{ m}$ )	
Electromagnetics	Profiling and	Yes	≤60 m	Affected by metal fences,
(frequency domain)	mapping; very	(≤15 m)		pipes, buildings, vehicles, etc.
	rapid			
Electromagnetics	Soundings or	No	$\leq$ few	No measurements < 48 m
(time domain)	profiling and		hundred	
	mapping		meters	
Resistivity	Soundings or	No	Typically	Requires good ground contact
	profiling and		100 to	& long electrode arrays;
	mapping		300 m	Integrates a large volume of
				subsurface; Affected by metal
				fences, pipes, buildings,
				vehicles, etc.
Seismic refraction	Profiling and	No	Typically	Requires considerable energy
	mapping soil and		100 to	for deeper surveys; Sensitive to
	rock		300 m	ground vibrations
Seismic reflection	Profiling and	No	$\leq$ few	Shallow surveys < 30 m are
	mapping soil and		hundred	most critical; Sensitive to
	rock		meters	ground vibrations
Micro gravity	Profiling and	No	Typically	Very slow, requires extensive
	mapping soil and		100 to	data reduction; Sensitive to
	rock		300 m	ground vibrations
Magnetics	Profiling and	Yes	Typically	Only applicable in certain rock
	mapping soil and		100 to	environments; Limited by
	rock		300 m	ferrous metal features

Table 2 : Surface geophysical methods for evaluation of natural hydrogeological
conditions (from Benson 1993)

#### 3.2 Exposure Assessment

The basic components of the exposure (or risk) assessment are outlined in Table 3. The primary focuses of this activity are to assess the potential impact or risk of the contamination on the health of the population and to establish the soil cleanup goals. In general, an inverse relationship between risk of contamination and costs associated with remediation of contamination exists. In the first 15 years or so of regulated remediation activity in the US, there was a general perception among the public and the regulators that there should be essentially no risk associated with the contamination. However, given the increasing costs associated with subsurface contamination, and possibly re-defining the goals of the remediation process to accept more risk in the interest of reducing costs. Thus, there also has been a renewed interest in refining and improving the accuracy of the analysis of risk.

In England, after many years of discussion and consultation, the legislation on soil contamination (which was inserted into the Environmental Protection Act 1990 by the Environment Act of 1995) was finally brought into force only on April 1, 2000. There was therefore ample opportunity to learn from experience elsewhere in the World, and the English statutory guidance on contaminated land is risk focused. It remains to be seen how the risk-based guidance will work in practice now that it has the force of law. A key component of the exposure assessment is determining or predicting the fate and transport of the COCs (in England, a COC would be any contaminant in a significant pollutant linkage) to evaluate the potential time-

dependent impact of the COCs on potential receptors (humans, animals, crops, etc.). In this context, transport refers to the physical processes that affect the extent of migration of the COCs, and fate refers to the susceptibility of the COCs to various chemical and biological reactions that can occur during transport.

The analyses to evaluate the fate and transport of COCs typically are performed using sophisticated numerical models that require significant data input and, consequently, provide further justification for more extensive and accurate site characterization.

Table 3 : Major components in an exposure (risk) assessment to determine soil cleanup goals (modified from Loehr 1993, and Freeze and McWhorter 1997).

Component	Description		
Hazard identification	Identify COC		
	Identify exposed populations		
	Identify sensitive receptors		
	Identify exposure pathways		
Fate-and-transport	Estimate exposure-point concentrations of COC using analytical		
analysis	and/or numerical models		
Exposure assessment	Assess the extent of exposure of people and the environment to a given COC		
Toxicity assessment	Assess adverse health effects from a given COC		
Risk characterization	Characterize the potential for, kind of, and extent of adverse health effects		

Note: COC = Contaminant of Concern

# 3.3 Concentration, Risk, and Technology

The objectives of a remediation activity typically include performance criteria, such as reducing the concentrations of the COCs to some acceptable target levels. The target level in the US typically is the maximum contaminant level, or MCL, for the COC. The MCL is defined as the maximum permissible level of contaminant in water delivered to any user of a public system. A comparison of the US MCLs for selected COCs with target concentrations established in other countries or the World Health Organization (WHO) is provided in Table 4.

Contaminant	Target Concentration (µg/L or ppb)			
	US MCL	WHO	Canada	Netherlands
Trichloroethylene (TCE)	5	70	50	500
Tetrachloroethylene (PCE)	5	40		40
Methyl chloroform (TCA)	200	2000		
Toluene	1000	700		1000
Carbon Tetrachloride (CCl <sub>4</sub> )	5	2	5	
Napthalene				70
Phenathrene				5
Lead (Pb)	15	10	10	75
Cadmium (Cd)	5	3	5	6
Chromium (Cr)	100	50	5	6

Table 4 : Target concentrations for some contaminants of concern (COCs).

Note: MCL = maximum contaminant level; WHO = World Health Organization

As indicated in Table 4, the target concentrations may vary widely, reflecting differences in perceived or calculated risk associated with certain COCs. Also, the target concentrations established for COCs typically are significantly lower than the maximum concentration levels of the COCs in the soil, making the goals of remediation typically very difficult to achieve. For this reason, some consideration is being given to establishing higher, alternative contaminant levels (ACLs), established on the basis of the relevant risk and associated remediation technology, as illustrated in Fig. 6 (Freeze and McWhorter 1997).



Figure 6 : Relationship between concentration level and technology for point-of-compliance (POC) well located down gradient from polluted zone (modified from Freeze and McWhorter 1997).

In England, no mandatory MCLs have been published either for soil or water and indeed it is unlikely that they will be. The concept of an MCL does not fit well with the risk focused approach in England, since it does not explicitly include consideration of the contaminant setting (or more precisely the whole contaminant-pathway-receptor linkage). A tiered approach will be used for both soil and ground water. Contaminant concentrations in the soil may be compared with generic guidance figures (these are yet to be published, although the first few are expected in late 2000). If concentrations are below these levels, then an argument may be advanced that the contamination is acceptable. If levels are exceeded, then progressively more detailed levels of risk assessment will be needed.

For ground water, the English approach will be to estimate groundwater concentrations of contaminants using simple partitioning rules or leaching tests. If the results are acceptable in comparison with drinking water standards or local Water Quality Objectives, then the contamination may be regarded as not significant. However, if this first tier shows that there may be a problem, then more detailed, site specific information may be used, such as sorption onto soil and dispersion. Ultimately, full site-specific contaminant migration modeling may be necessary. The aim of the tiered approaches is to keep costs reasonable and avoid unnecessary investigations.

#### 3.4 Monitoring

Monitoring the performance of the selected remediation technology is vital to ensure that the performance achieves the desired remediation goals. Possible monitoring methods include a network of monitoring wells, the geophysical methods already discussed, and electrochemical, mechanical, and electrical sensors (Inyang 1995).

Three types of monitoring well systems commonly are used for monitoring groundwater (Robison 1989): (1) clustered wells, (2) nested wells, and (3) multipoint wells. Clustered wells are groups or clusters of separate wells with each well in a separate drill hole and reaching a separate aquifer. Nested wells refers to a group or nest of individual wells in each drill hole with each well reaching a separate aquifer. The multipoint well system is constructed in a single drill hole and a single well with isolated, multiple screens. As shown in Table 5, the primary difference in these systems is cost and construction schedules.

Table 5 : Comparative costs and construction schedules for different monitoring well systems for a 10-level aquifer system (data from Robison 1989).

Monitoring Well System	Cost (\$US)	Construction Time (wks)
Cluster of 10 separate wells	300,000	18
Two nests of 5 wells per nest	250,000	6 – 8
A single multipoint well with 10 isolated screens	110,000	2 - 4

Electrochemical sensing systems operate on the principle of changes in the physico-chemical characteristics of the sensor due to contact with a solid or fluid. Methods of determining these changes include detection of a voltage drop along a sensing cable caused by degradation or swelling of the coating upon contact with hydrocarbons, or via detection of changes in a probe signal through an optical fiber.

Mechanical sensors include traditional geotechnical monitoring equipment, such as strain gauges, settlement gauges, inclinometers and extensometers. These sensors are used more commonly in containment applications.

Electrical systems include techniques that involve passage of electrical current through subsurface media or physical interactions between an embedded device and surrounding media that may lead to the transmission of electrical impulse to direct-read systems. These techniques include direct-current (DC) resistivity monitors, vibrating-wire piezometers, infiltrometers, and flow velocity sensors.

Some of these monitoring methods are in common use or are growing in application, whereas other methods are either rare or not feasible for the given monitoring objective. A summary of the applicability of these monitoring methods relative to the monitoring objective is shown in Table 6.

of contaminated land (modified from Inyang 1995).						
Monitoring	Monitoring Objective					
Method	Barrier Integrity	<b>Barrier</b> Permeation	External to Barrier			
Well Network	U	U	С			
Geophysical	G	R	G			
Electro-chemical	R	G	G			
Mechanical & Electro-chemical	С	R	R			
Electrical	G	С	G			

 Table 6 : General application of monitoring approaches for containment technologies for *in situ* remediation of contaminated land (modified from Inyang 1995).

Key: C = conventional; G = growing application; R = rare; U = unfeasible.

# 4.0 TECHNOLOGICAL CONSIDERATIONS

#### 4.1 Attenuation

Attenuation may be defined as the process of immobilizing, retarding, or otherwise degrading chemical constituents that exist in the soil or ground water. Thus, the objective of *in situ* remediation technologies is to attenuate contaminants of concern (COCs) that exist in the ground. This attenuation may take the form of artificially induced process (e.g., treatment technology) or through natural geochemical attenuation.

Geochemical attenuation refers to attenuation that results from geochemical interactions between natural geological material and chemical constituents in ground water (Rouse and Pyrith 1993). Some possible geochemical attenuation mechanisms include cation and anion exchange with clays, adsorption of cations and anions on hydrous metal oxides (e.g., iron and manganese oxides), sorption on organic matter or organic carbon, precipitation of metals from solution, and co-precipitation by adsorption.

An assessment of the extent to which geological materials will attenuate the migration of COCs in soil or ground water is an essential consideration in understanding the potential success or failure of the remediation technology, and requires a knowledge of

- the properties and mineralogy of the geological material (porous medium),
- the properties of the contaminated ground water, and
- the chemical conditions (e.g., pH and Eh) that are established during contact of the leachate or ground water with the geological material.

# 4.2 **Properties of Geological Materials and Liquids**

The properties of the geological materials refer to both physical properties, such as the particle-size distribution and the clay content, as well as chemical properties (e.g., Rouse and Pyrith 1993, Shackelford 1994a), including the

- soil pH and electrical conductivity (EC),
- cation exchange capacity (CEC),

- exchangeable cations,
- soluble salts,
- hydrous metal oxide content,
- organic matter and organic carbon contents, and
- carbonate content of the soil (e.g., calcium carbonate, CaCO<sub>3(s)</sub>, and dolomite, CaMg(CO<sub>3</sub>)<sub>2(s)</sub>) and the acid and base neutralizing potential.

Detailed descriptions regarding the measurement of these parameters are provided by Page et al. (1982) and Mitchell (1993).

The properties of the liquid phase of the porous medium (i.e., pore liquid) will depend on the nature and chemical composition of the pore liquid. As shown in Fig. 7, pore liquids may be categorized as aqueous liquids, i.e., solutions containing contaminants that are miscible in water (also known as hydrophilic or 'water-loving'), or non-aqueous liquids consisting of organic compounds immiscible in water (also known as hydrophobic or 'water-hating'). Also, mixtures of both aqueous and non-aqueous liquids resulting in the formation of two separate liquid phases may occur.

Aqueous liquids contain inorganic chemicals (acids, bases, salts) and/or hydrophilic organic compounds. Hydrophilic organic compounds are distinguished from hydrophobic organic compounds based on the concept of 'like dissolves like', i.e., polar organic compounds usually will readily dissolve in water, a polar molecule, whereas nonpolar organic compounds are repelled by water. A hydrophobic compound also is further separated into either a LNAPL (Light Non-Aqueous Phase Liquid) or DNAPL (Dense Non-Aqueous Phase Liquid) based on whether the density of the compound is lower or greater than water, respectively.



Figure 7 : Classification of liquids (after Shackelford 1994a).

Properties of these pore liquids that are necessary for remediation include (1) the concentration and types of chemicals present in the liquid, (2) the density and viscosity of the liquid, (3) the pH and electrical (or specific) conductance (EC) of aqueous liquids, and (4) the solubility, boiling point, and dielectric constant of organic compounds. Other parameters, such as the redox potential (Eh), total dissolved solids (TDS), total organic carbon (TOC), chemical oxygen demand (COD), and biological oxygen demand (BOD), also may be important.

The pH of solutions ranges from 0 to 14. Neutral solutions are characterized by pH values between about 5 and 9. The pH of a solution often is referred to as the 'master variable' that characterizes chemical

reactions (e.g., dissolution/ precipitation) in the pore liquid as well as affects the soil permeability (hydraulic conductivity). Solutions that are highly reactive with soils include strong acids (pH  $\leq$  2) and strong bases (pH  $\geq$  12).

The specific or electrical conductance (EC) of a solution is a measure of the ability of a solution to carry an electrical current, and varies directly with the number and type of ions in solution. As a result, EC is particularly useful for indicating the relative strength of a solution when a detailed characterization of the concentration and types of chemical constituents is not possible (e.g., see Shackelford et al. 1999).

Liquids also are classified as either low-boiling-point ( $< 100^{\circ}$ C) or high-boiling-point ( $> 100^{\circ}$ C) liquids. The boiling point provides an indication of the volatility of the chemical compound (i.e., the lower the boiling point, the greater the susceptibility to volatilization via heating).

The dimensionless dielectric constant ( $\epsilon$ ) is a measure of the ability of the material to conduct an electric field relative to vacuum, and is defined as the ratio of the capacitance with a dielectric material between two charged plates to the capacitance with a vacuum between the same two charged plates. The dielectric constant of water at 20°C is 80.4, whereas  $\epsilon$  for pure phase organic solvents typically is < ~ 40 (Shackelford 1994a).

#### 4.3 Equilibrium Partitioning

As illustrated in Fig. 8, contaminants in soil may exist in the gas phase, in the aqueous phase, and/or as a separate liquid phase (i.e., DNAPL or LNAPL). In addition, contaminants may be adsorbed or 'attached' to the solid phase. The objective of many of the *in situ* remediation technologies is to increase the amount of contaminant existing in either the aqueous phase or the gas phase to enhance the removal of the contaminant. Thus, the success or failure of any *in situ* remediation process applied to clean up contaminated soil depends to a large extent on the distribution of the contaminants in each of the phases. As a result, knowledge of the partitioning of the contaminants between the individual phases is important.



Figure 8 : Block (phase) diagrams for (a) uncontaminated and (b) contaminated soil.

Equilibrium partitioning between NAPL and aqueous phases (solubility) may be represented by the following expression:

$$c_{a,i} = X_i c_{a,i}^0$$
<sup>(1)</sup>

where  $c_{a,i}$  = aqueous-phase concentration of compound i,  $X_i$  = mole fraction of compound i in solution,  $c_{a,i}^o$  = saturated, dissolved concentration of compound i.

Equilibrium partitioning between the aqueous phase and the gas phase is described in accordance with Henry's Law, or

$$c_{g,i} = K_{h,i} c_{a,i}$$
<sup>(2)</sup>

where  $c_{g,i} = gas$ -phase concentration of compound i,  $K_{h,i} = dimensionless$  Henry's Law constant for compound i, and  $c_{a,i} = aqueous$ -phase concentration of compound i. The greater the magnitude of Henry's Law constant, the greater the volatility of the compound.

Equilibrium partitioning between the NAPL phase and the gas phase is described by Raoult's Law, or

$$p_i = X_i p_i^o$$
(3)

where  $p_i$  = partial pressure of compound i, and  $p_i^o$  = partial vapor pressure of pure compound i. Application of the Ideal Gas Law (pV = nRT) to Eq. 3 results in the following expression for Raoult's Law:

$$c_{g,i} = X_i c_{g,i}^0 \tag{4}$$

where  $c_{g,i} = gas$ -phase concentration of compound i, and  $c_{g,i}^{o} = saturated$ , vapor concentration of pure compound i.

Finally, equilibrium partitioning between the aqueous phase and the solid phase, referred to as sorption, can be described as follows:

$$c_{s,i} = K_{d,i} c_{a,i}$$
(5)

where  $c_{s,i}$  = the solid-phase concentration of compound i, and  $K_{d,i}$  = the distribution coefficient for compound i. For sorption of dissolved organic compounds, the distribution coefficient is correlated with the organic carbon partition coefficient,  $K_{oc}$ , and the fraction of organic carbon,  $f_{oc}$ , in the solid phase as follows:

$$K_{d} = K_{oc} f_{oc}$$
(6)

Values for  $K_{oc}$  derived from empirical correlations with the octanol-water partition coefficient,  $K_{ow}$ , or the solubility of the organic compound can be found in several references (e.g., Grubb and Sitar 1994).

The overall mass balance of a given contaminant under equilibrium conditions may be defined as follows:

$$C_{i} = \theta_{g} c_{g,i} + \theta_{a} c_{a,i} + \theta_{N} c_{N,i} + \rho_{d} c_{s,i}$$
(7)

where  $C_i$  = the total mass of compound i per unit total volume,  $\theta_g$ ,  $\theta$ , and  $\theta_N$  = the volumetric gas-phase, aqueous-phase, and NAPL-phase contents in the soil, respectively, and  $\rho_d$  is the dry (bulk) density of the soil.

In addition, the volumetric gas-phase, aqueous-phase, and NAPL-phase contents in the soil are related as follows:

$$\theta_{\rm g} + \theta_{\rm a} + \theta_{\rm N} = n \tag{8}$$

where n = the total porosity of the soil. Finally, given the relationship among the degree of saturation,  $\theta$ , and n (i.e.,  $\theta = Sn$ ), Eq. 8 may be written as follows:

$$S_g + S_a + S_N = 1 \tag{9}$$

where  $S_g$ ,  $S_a$ , and  $S_N$  = the decimal degrees of saturation with respect to the gas, aqueous, and NAPL phases, respectively.

#### 4.4 Miscible versus Immiscible (Multiphase) Flow or Transport

Bear (1972) separates the simultaneous flow of more than one fluid in a porous medium into either miscible displacement or immiscible displacement. Miscible displacement of fluids in porous media occurs in the case when the fluids are completely soluble in each other. In this case, the interfacial tension between the fluids is zero, and the fluids dissolve in each other. As a result, a distinct fluid-fluid interface does not exist.

Miscible displacement, also referred to as hydrodynamic dispersion, is governed for water saturated porous media (i.e.,  $S_g = S_N = 0$ ) by the following equation (Bear 1972):

$$R_{d} \frac{\partial c}{\partial t} = \frac{\partial}{\partial x_{i}} \left( D_{ij} \frac{\partial c}{\partial x_{j}} \right) - \frac{\partial (v_{i}c)}{\partial x_{i}} - \lambda R_{d}c \quad ; \quad i, j = 1, 2, 3 \quad (10)$$

where  $R_d$  = the retardation factor, c = concentration, x = the generalized spatial coordinate, D = the dispersion coefficient including the molecular diffusion coefficient, v = the seepage (interstitial) velocity,  $\lambda$  = the decay constant for first-order decay, and i, j = the Einstein summation indices. In general, Eq. 10 must be written for each solute species contained in the solvent (water). The retardation factor represents instantaneous, linear, and reversible sorption of solutes, and is correlated with the distribution coefficient for compound i as follows:

$$R_{d,i} = 1 + \frac{\rho_d}{n} K_{d,i}$$
(11)

For the special case of one-dimensional transport of a solute in a homogenous liquid that is undergoing steady-state, uniform flow in a homogeneous and isotropic medium, Eq. 10 reduces to the familiar one-dimensional advection-dispersion-reaction equation (ADRE), or

$$R_{d} \frac{\partial c}{\partial t} = D \frac{\partial^{2} c}{\partial x^{2}} - v \frac{\partial c}{\partial x} - \lambda R_{d} c$$
(12)

where the compound subscript designation has been dropped for simplicity. Numerous analytical and numerical solutions to Eqs. 10 and 12 have been published (e.g., Bear 1972).

Immiscible displacement involves the simultaneous flow of two or more immiscible fluids or phases in the porous medium. Since the fluids are immiscible, the interfacial tension between the two fluids is not zero, and a distinct fluid-fluid interface separates the fluids. For an anisotropic medium, immiscible displacement of a single fluid is described by the following form of Darcy's law (Bear 1972):

$$q_{i} = -\left(\frac{k_{ij}}{\mu}\right)\left(\frac{\partial p}{\partial x_{j}} + \rho g \frac{\partial z}{\partial x_{j}}\right) \qquad ; \qquad i, j = 1, 2, 3 \qquad (13)$$

where  $q_i$  = the liquid flux of fluid in the 'i' direction, k = the 'intrinsic' permeability of the fluid,  $\mu$  = the viscosity of the fluid, p = the pressure on the fluid,  $\rho$  = the density of the fluid, g = the acceleration due to gravity, z = the vertical spatial coordinate, x = the generalized spatial coordinate, and i, j = the Einstein summation indices. In general, Eq. 13 must be written for each fluid in the porous medium.

The migration of two separate fluid phases in fluid saturated soil, referred to as two-phase flow, requires special consideration for the interaction between the two fluid phases. Due to surface and interfacial tension effects, a discontinuity in pressure exists across the interface separating the two fluids, and one of the two fluids preferentially wets the surface of the pores resulting in a characteristic concave curvature of the fluid-fluid interface towards the non-wetting fluid, as illustrated in Fig. 9.



Figure 9 : Capillary tube schematics of wetting versus non-wetting fluids. [NAPL = non-aqueous phase liquid.]

The discontinuity in pressure at the interface of the two fluids is referred to as the capillary pressure,  $p_c$ , defined as

$$\mathbf{p}_{c} = \mathbf{p}_{\mathsf{NW}} - \mathbf{p}_{\mathsf{W}} \tag{14}$$

where  $p_{nw}$  = the pressure in the non-wetting fluid, and  $p_w$  = the pressure in the wetting fluid. As defined by Eq. 14,  $p_c > 0$ . The non-wetting fluid can displace the wetting fluid in the pore space of the soil only after a minimum pressure, known as the entry pressure, for the non-wetting fluid is reached. In the case of air flow through initially water-saturated soil, this minimum pressure is known as the air-entry pressure.

For the two-fluid flow scenario, such as the case of immiscible displacement of a water-saturated soil by a non-aqueous phase liquid (NAPL) that is non-wetting, Eq. 13 can be written for both the wetting and the non-wetting phases as follows (Bear 1972, McWhorter and Kueper 1996, Charbeneau 2000):

$$q_{wi} = -\frac{k_{ij}k_{rw}}{\mu_{w}} \left( \frac{\partial p_{w}}{\partial x_{j}} + \rho_{w}g \frac{\partial z}{\partial x_{j}} \right)$$

$$q_{nwi} = -\frac{k_{ij}k_{rnw}}{\mu_{nw}} \left( \frac{\partial p_{nw}}{\partial x_{j}} + \rho_{nw}g \frac{\partial z}{\partial x_{j}} \right)$$
(15)

where the subscripts w and nw = the wetting and non-wetting phases, respectively, and  $k_r =$  the relative permeability of the respective fluid. The overall process of two-phase flow is described by substituting Eqs. 15 along with Eq. 7 into the continuity expression, and solving the resulting two equations along with the constraints dictated by Eqs. 9 and 14 simultaneously (e.g., see Bear 1972).

Two-phase fluid flow is complicated by the fact that the wetting and non-wetting effective permeabilities  $(= k_{ij}k_r)$  are functions of the degree of saturation of the wetting and non-wetting phases, respectively, and therefore, the permeabilities change with location and time. Thus, the governing system of flow equations typically is highly non-linear requiring the use of numerical methods for the solution. Further details regarding the application of this approach for describing DNAPL migration can be found in McWhorter and Kueper (1996) and Charbeneau (2000).

#### 4.4.1 Flow Rates and Reactions

Another potentially complicating factor is the relationship between the flow rate and the mass transfer reaction rate (i.e., the rate at which mass is transferred between phases, e.g., liquid-gas phases, liquid-solid phases, and gas-solid phases). As shown in Fig. 10, hydraulically driven transport, or advection (also referred to as 'convection'), controls when the flow rate is high, whereas diffusion, or concentration-dependent transport controls at low flow rates. In addition, an increasing reaction rate tends to favor equilibrium mass transfer conditions, whereas slower reaction rates favor non-equilibrium, or kinetic, mass transfer conditions. The fate-and-transport analysis is simplified greatly when equilibrium conditions are assumed. However, many situations in remediation of contaminated land are not governed by equilibrium conditions.



Figure 10 : Effect of (a) flow rate on aqueous miscible contaminant transport, and (b) reaction rate on heterogeneous mass transfer.

#### 4.5 Sub-Classifications of Organic Compounds

Hydrocarbons (HCs) are compounds consisting of hydrogen and carbon. Halogenated hydrocarbons are hydrocarbons that also contain one or more of the halogen elements (i.e., fluorine, chlorine, bromine, iodine, and astatine). Chlorinated hydrocarbons are halogenated hydrocarbons that specifically contain chlorine (Cl), and represent the most prevalent group of COCs in the US, including tetrachloroethylene, also known as perchloroethylene (PCE), and trichloroethylene (TCE).

Organic compounds are categorized as aliphatic, aromatic, or heterocyclic compounds (Sawyer and McCarty 1978). Aliphatic compounds are organic compounds in which the characteristic groups are linked to a straight or branched carbon chain, and include alkanes (e.g., methane, or  $CH_4$ ), alkenes (e.g., ethene or  $C_2H_2$ ), alcohols (e.g., methanol, or  $CH_3OH$ ), aldehydes (e.g., formaldehyde, or HCHO), ketones (e.g., acetone, or  $CO(CH_3)_2$ ), acids (e.g., acetic acid, or  $CH_3COOH$ ), esters, ethers, alkyl halides (e.g., carbon tetrachloride, or  $CCl_4$ ), amines, and cyclic aliphatic compounds (e.g., napthenes).

Aromatic organic compounds are ring-structured compounds that contain only one covalent bond in contrast to the ringed, aliphatic compounds that contain two covalent bonds. For example, the aromatic compound benzene,  $C_6H_6$ , has only 6 hydrogens attached to 6 carbons in a ring structure, whereas the aliphatic compound cyclohexane,  $C_6H_{12}$ , has 12 hydrogens attached to 6 carbons, the difference being that three of the six carbon-carbon bonds in the benzene ring are double bonds, whereas all six of the carbon-carbon bonds in the cyclohexane ring are single bonds.

Aromatic compounds include the benzene series of hydrocarbons (i.e., benzene, toluene, ethylbenzene, and xylene), often referred to as the BTEX compounds, the polyring series of hydrocarbons (e.g., naphthalene, or  $C_{10}H_8$ ) that also are known as polycyclic or polyaromatic hydrocarbons (PAHs), aromatic phenols (e.g., cresol, or  $C_6H_4OHCH_3$ ), and aromatic alcohols, aldehydes, ketones, acids, amines, and nitro compounds. The BTEX compounds are derived from petroleum, are major constituents in gasoline, and represent a common group of aromatic hydrocarbons that are of significant environmental concern with respect to remediation of contaminated land.

The heterocyclic compounds differ from the aromatic compounds in that one or more of the carbons in the ring structure is replaced by another element, such as nitrogen (N). This group of compounds is primarily of concern in the biological fields.

Volatile organic compounds (VOCs) are hydrocarbons with vapor pressures at 20°C greater than 1 mm Hg (1.31 x  $10^{-3}$  atm) (Grubb and Sitar 1994). Semi-volatile organic compounds (SVOCs) are hydrocarbons with vapor pressures between  $10^{-10}$  mm Hg (1.31 x  $10^{-13}$  atm) to 1 mm Hg (1.31 x  $10^{-3}$  atm). Although the lower limit of vapor pressures for semi-volatile organic compounds is  $10^{-10}$  mm Hg (1.31 x  $10^{-13}$  atm),

hydrocarbons with vapor pressures  $< 10^{-7}$  mm Hg ( $< 1.31 \times 10^{-10}$  atm) are not expected to volatilize significantly. Tetrachloroethylene (PCE) and trichloroethylene (TCE) are common VOCs, whereas cresol, phenol, pyrene, 1,2-dichlorobenze and 1,4-dichlorobenzene are examples of SVOCs (Grubb and Sitar 1994).

#### 4.6 Remediation Processes

Remediation processes commonly are categorized as physical, chemical, biological, or thermal processes. Physical processes include interphase mass transfer reactions, such as sorption and ion exchange, as well as binding processes, such as cement fixation of chemicals to soil.

Chemical processes involve chemical reactions. Two chemical processes of relatively recent interest in remediation are the oxidative degradation of halogenated hydrocarbons in the presence of oxides, and reductive dehalogenation of halogenated hydrocarbons in the presence of solid, zero-valent iron metal  $(Fe^{0}_{(s)})$ .

For example, oxidation of TCE ( $C_2HCl_3$ ) by potassium permanganate (KMnO<sub>4</sub>) is described by the following reaction (e.g., Siegrist et al. 1999):

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2KCl + HCl$$
(16)

This reaction is rapid and is described by pseudo first-order kinetics with half-lives on the order of 1 to 2 min. The pH of the system declines to strongly acidic conditions (e.g., pH 2–3) depending on the buffering capacity (acid neutralizing capacity) of the system (e.g., soil).

Reductive dechlorination of TCE to DCE ( $C_2H_2Cl_2$ ) in the presence of solid, zero-valent iron metal (Fe<sup>0</sup><sub>(s)</sub>) is described by the following reaction (e.g., Siegrist et al. 1999):

$$2Fe^{0}_{(s)} + C_{2}HCl_{3} + 3H_{2}O \rightarrow C_{2}H_{2}Cl_{2} + H_{2} + Cl^{2} + 3OH^{2} + 2Fe^{24}$$
(17)

The complete dechlorination of TCE to DCE is described by pseudo first-order kinetics with half-lives normalized with respect to the solid surface area of iron to be on the order of 30 to 60 min. The pH of the system tends to rise and stabilize between 9 and 10 due to iron hydroxide precipitation. The reaction products include other chlorinated hydrocarbons (e.g., DCE) that subsequently degrade to vinyl chloride ( $C_2H_3Cl$ , or VC), ethene ( $C_2H_4$ ), or ethane ( $C_2H_6$ ), hydrogen gas ( $H_2$ ), chloride (Cl<sup>-</sup>), and iron oxide (FeO) and hydroxide (Fe(OH)<sub>2</sub>) precipitates.

In biologically mediated processes, the contaminant, typically a hydrocarbon compound, acts as a carbon source and a source of energy for the bacteria. For example, consider the following reactions for bacteria mediated degradation (i.e., biodegradation) of benzene (from Brubaker 1993):

$$C_{6}H_{6} + 2.5O_{2} + NH_{3} \xrightarrow{Pseudonomas} C_{5}H_{7}O_{2}N + CO_{2} + H_{2}O$$
(18)

and

$$C_5H_7O_2N + 5O_2 \xrightarrow{Pseudonomas} 5CO_2 + 2H_2O + NH_3$$
(19)

The first (top) reaction represents oxidation of benzene ( $C_6H_6$ ) to cell mass whereas the second (bottom) reaction represents complete mineralization to carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O), and ammonia (NH<sub>3</sub>). These reactions also illustrate the need for large quantities of oxygen for aerobic oxidation of hydrocarbons. For example, in this case, 3.1 kilograms of oxygen are required per kilogram of contaminant.

Thermal processes involve heating the contamianted soil to induce volatilization and removal of contaminants (e.g., radio frequency heating), or to melt and solidify the contaminated soil mass (e.g., vitrification).

#### 5.0 **REMEDIATION TECHNOLOGIES**

#### 5.1 Classification of Technologies

Remediation technologies can be classified in numerous ways, such as according to the objective of the technology (containment versus treatment), the process involved in the remediation (i.e., physical, chemical, biological, or thermal), or the location of the remediation process (*in situ* versus *ex situ*). A general classification of remediation technologies using all of these categories is given in Table 7.

Soil Removal?	Technology Category	Technique/ Process	Example(s)	Comment(s)
Yes ( <i>ex situ</i> )	Containment	Disposal	Landfills	On-site vs. Off-site; New vs. Existing
	Treatment	Chemical	Neutralization, Solvent	Treated soil may
			Extraction	require disposal in a
		Physical	Soil Washing, Stabilization/	landfill, or may be
			Solidification, Vitrification	returned to the site.
		Biological	Biopiles, Bioreactors	_
		Thermal	Incineration, Vitrification	
No	Containment	Pump &	Vertical Wells,	Both passive and active
(in situ)		Treat	Horizontal Wells	containment
		Capping	Traditional Covers, Alternative	are possible; In pump
			Covers, Geochemical Covers	& treat, pumping is
		Vertical	Slurry Walls, Grout Curtains,	used to control
		Barriers	Sheet Piling, Biobarriers,	hydraulic gradient and
			Reactive Barriers	collect
		Horizontal	Grout Injected Liners	contaminated water;
		Barriers		treatment is ex situ
	Treatment	Chemical	Oxidation, Chemical Reduction	Technologies with
		Physical	Soil Flushing*, Stabilization/	(*) require removal of
			Solidification, Vitrification,	gas and/or liquid
			Air Sparging (AS)*,	phases and ex situ
			Soil Vapor Extraction (SVE)*,	treatment; Both passive
			Electro-kinetics (EK)*	and active
		Biological	Monitored Natural	treatment are possible.
			Attenuation (MNA), Bioventing,	
			Bioslurping, Biosparging	<u>-</u>
		Thermal	Steam Injection*,	
			Radio Frequency Heating (RF)*,	
			Vitrification*	

Table 7 : Classification of remediation technologies based on soil as the contaminated medium.

# 5.1.1 Containment Versus Treatment

Containment refers to technologies used to prevent the spread of contamination without necessarily resulting in degradation or transformation of the contaminants. Treatment refers to technologies used to degrade or otherwise transform contaminants into less toxic or non-toxic concentrations. Containment has been widely used in the UK for almost two decades but, as discussed previously, interest in containing rather than treating contaminated land has gained momentum in the US only over the past five or so years, primarily because containment

- typically is cheaper than treatment,
- can be used until a more efficient technology is developed,
- can provide a means for evaluating the potential for natural attenuation processes to degrade the contaminants, and
- can present a lower overall risk since major excavation, contaminant exposure, etc., can be avoided.

Many remediation scenarios will involve both containment and treatment. However, in some countries where economic resources are not plentiful, using a remediation technology that requires *ex situ* treatment may not be a viable option, particularly if treatment of wastewater, for example, is not already practiced routinely.

#### 5.1.2 In-Situ Versus Ex-Situ Remediation

*In-situ* versus *ex-situ* remediation refers to the location of the remediation technology. In this context, an important distinction arises relative to the location of the application of the technology versus the location of the treatment. For example, in the pump-and-treat approach to remediation, the pumping occurs *in situ*, but the treatment of the pumped, contaminated water occurs *ex situ*.

#### 5.1.3 Active Versus Passive Technologies

Another distinction that may be made between remediation technologies is whether the technology is an active or a passive technology. The terms passive and active have different meanings depending on whether reference is made to containment or treatment, and may have different meanings in different parts of the World.

For example, in North America, passive containment typically refers to unenhanced containment systems that do not require continuous energy input following construction to achieve the desired result, whereas active containment systems typically are passive containment systems that either are enhanced to improve performance, or require additional energy input after construction to perform properly. These active containment systems are inherently more expensive than passive containment systems.

In Europe, the term passive containment refers solely to containment systems without any form of treatment. For example, the term 'active containment' in Europe is used for the permeable reactive walls of North America, and would not include pump and treat (see Table 8). To reduce the potential for confusion, some authors in Europe use 'reactive' in place of 'active', and permeable reactive walls then translate as reactive treatment zones (RTZs).

Although a distinction between active and passive treatment systems is not always recognized, passive treatment typically refers to treatment systems that clean the contaminated medium (e.g., ground water) without a need for input of energy for the treatment process to be effective, whereas active treatment systems require a energy input to achieve the required level of cleanup. Active treatment systems are inherently more expensive than passive treatment systems.

Tashralasu	Dessive an	Technique	Example(a)
Catagory	Passive	Technique	Example(s)
Category	or Active		
Containment	Passive	Capping	Traditional Covers, Alternative Covers,
			Geochemical Covers
		Vertical Barriers	Slurry Walls, Grout Curtains,
			Sheet Piling, Biobarriers
		Horizontal Barriers	Grout Injected Liners
	Active	Pump & Treat	Vertical Wells, Horizontal Wells
		<b>Reactive Barriers</b>	Sorption Enhanced Slurry Walls
		(Low Permeability)	
Treatment	Passive	Monitored Natural	Natural Biodegradation
		Attenuation (MNA)	
		Reactive Walls	Zero-Valent Iron Filings,
		(High Permeability)	Biowalls
		Reactive Horizontal	Zero-Valent Iron Filings,
		Fractures	Oxidants (e.g., potassium permanganate)
		Phytoremediation	Plants, Trees
	Active	Immobilization	Stabilization/Solidification, Vitrification
		Enhanced Removal	Soil Flushing (SF), Soil Vapor Extraction (SVE),
		(requires ex-situ	Air Sparging (AS), Steam Injection (SI),
		treatment)	Radio Frequency (RF) Heating
		Bioremediation	Bioventing, Bioslurping, Biosparging,
		(Bioaugmentation or	Infiltration Galleries,
		Biostimulation)	Electrokinetics (EK) Enhanced

Table 8 : Passive and active categories for *in situ* containment and treatment technologies.

An example of passive containment versus passive treatment systems, based on the *in situ* containment and treatment technologies listed in Table 8, is illustrated in Fig. 11. A detailed description of these technologies follows.



Figure 11 : Schematic examples of *in situ* passive (a) containment versus (b) treatment.

## 5.2 In Situ Passive Containment

#### 5.2.1 Vertical Containment

#### Slurry Walls

Slurry walls, also known as slurry cutoff walls or vertical cutoff walls, are vertical walls constructed by excavating a trench with a back-hoe or clamshell and simultaneously filling the trench with a stabilizing slurry which is typically prepared from bentonite clay and water or bentonite clay, cement, and water. The slurry forms a thin filter cake (typically < 3 mm for bentonite slurry and perhaps a few tens of mm for cement-bentonite slurry) with a low hydraulic conductivity (typically <  $10^{-8}$  cm/s) on the sides of the trench. The filter cake minimizes slurry loss from the trench, stabilizes native soil on the side-walls of the trench, and provides a plane for slurry stabilization of the excavated trench. Both bentonite and cement-bentonite slurries typically contain from 3 to 7 percent (w/w) sodium bentonite mixed with water.

The three main types of slurry walls, illustrated in Fig. 12, used to contain polluted ground water are soilbentonite (SB) walls, cement-bentonite (CB) walls, and composite slurry walls (CSW). Soil-bentonite slurry walls, more common in North America, are constructed by displacing the bentonite slurry in the excavated trench by backfilling with a mixture of the bentonite slurry and the excavated trench spoils. Cementbentonite (CB) walls, more common in Europe, are constructed simply by using a mixture of cement and bentonite slurry to maintain the stability of the excavated trench and then allowing it to set to form the cutoff; i.e., no backfill materials are required. Therefore, CB walls typically are considered for use when suitable backfill materials are not available. Composite slurry walls (CSW) are constructed by inserting a geomembrane into the slurry in the trench and are used when conditions are especially complex or gas, such as landfill gas, is to be controlled.

The hydraulic conductivity (k) of SB walls is affected significantly by the quality of the backfill material and ranges from ~10<sup>-5</sup> cm/s to ~ 10<sup>-9</sup> cm/s (D'Appolonia 1980). Based on data from D'Appolonia (1980), k  $\leq 10^{-7}$  cm/s is obtained for backfill materials that contain  $\geq 15$  percent plastic fines (% < 0.075 mm, USCS = CH or MH) or  $\geq 60\%$  non plastic or low plasticity fines (USCS = ML or CL).



Figure 12 : The three main types of slurry walls for containment of polluted ground water: (a) soil-bentonite (SB) slurry wall; (b) cement-bentonite (CB) slurry wall ; and (c) composite slurry wall (CSW).

The hydraulic conductivity of CB walls is sensitive to the elapsed time from mixing and the time under permeation. The relationship between permeability and time can be represented as

$$k_{t} = k_{0} \left(\frac{t}{t_{0}}\right)^{-n}$$
(20)

where  $k_t$  and  $k_o$  = the hydraulic conductivities (permeabilities) at time t and  $t_o$ , respectively, and the exponent, n, is the range of about 1 to 2 for most combinations of cement-bentonite material and test water, when permeabilities of  $< 10^{-7}$  cm/s are achieved at 90 days. Equation 20 provides a good overall fit to most CB permeability - time data, but it may slightly overestimate the reduction of permeability with time if it is used to extrapolate early age data. The reduction of permeability with time is a result of (a) continuing hydration of the cement, and (b) reaction of the cement-bentonite material with the test water. For example, lime from the cement will react with the carbonate species in the water to precipitate calcium carbonate that acts to block pores and reduce permeability. As a result, laboratory tests with de-gassed, distilled water may underestimate the reduction in permeability with time as compared with the field situation, where the concentration of carbonate species is typically higher than that of tap water, let alone de-gassed waters.

Important design considerations in terms of the hydraulic conductivity of CB walls are the solids content (cement and/or bentonite) of the slurry, the type of bentonite, and the type of cement. The hydraulic conductivity of CB walls decreases with an increase in the solids content (especially the bentonite content). The use of blast furnace slag as a cement replacement can markedly reduce the permeability of the mixture at constant overall cementitious material content (i.e. cement + slag content). However, to achieve the reduction in permeability, the slag content must be at least 60 to 80 % of the total cementitious material (Jefferis 1997). The mixing sequence of bentonite, water, and cement also influences the properties of the material (Jefferis 1981)

Sodium activated calcium bentonite generally is used as the base clay for CB walls in Europe, since natural sodium bentonite is rare and generally must be imported from Wyoming. Sodium bentonite or sodium activated bentonite is preferred, since both bentonites swell and disperse to very fine particle sizes in water, always provided this water has low dissolved solids contents – especially magnesium ion (e.g., see Doe et al. 1999). Some or all of the sodium bentonite can be replaced by calcium bentonite. However, calcium bentonite is more difficult to disperse and, at equal concentrations, calcium bentonite will give a less stable (more sensitive to bleeding) slurry than sodium bentonite and a higher permeability for the final set material. The use of calcium bentonite is therefore generally appropriate only if a high clay content mixture is required. In this circumstance, the poorer dispersion of calcium bentonite is an advantage, since more clay can be used without the mixture becoming unacceptably viscous.

The hydraulic conductivity of composite slurry walls (CSW) is governed by the quality of the joints between geomembrane panels and leakage under the geomembrane at the toe of the wall. For example, it is seldom practicable to seal the geomembrane into an under-lying aquifer (Fig. 12c), and typically there is a small gap at the base of the wall (see Jefferis 2000). Manassero et al. (1995) propose a relatively simple analytical procedure for evaluating flow through different quality joints in CSWs, and Lee and Benson (2000) recently have evaluated the effects of inadequate keys, windows, and poor joint seals on flow rates

through SB walls, geomembrane (GM) walls, and CSWs. Lee and Benson (2000) report that inadequate keying of the wall essentially renders the wall ineffective with respect to control of flow.

For all containment barriers, there is an important consideration of durability and, hence, compatibility between the contained species and the barrier materials (Jefferis 1992). When assessing the effects of aggressive chemicals on permeability, it is very important to continue the test for a sufficiently long duration such that the cutoff material is fully reacted with the contaminants (e.g., see Shackelford et al. 1999). Short-term tests of a few days or months duration may give a spurious and entirely erroneous indication of material performance (e.g., see Shackelford et al. 2000).

To demonstrate this point, consider, for example, the effects of permeation with an imaginary but particularly damaging fluid that completely destroys the impermeability of all material with which it has reacted. By the time the reaction front for this fluid reaches the middle of the sample, the permeability for the first half of the sample effectively would be infinite. However, the remainder of the sample would still have its original permeability and, thus, the overall permeability would have increased by only a factor of 2. This modest change in permeability could have easily passed unnoticed, or even have been reversed, if the second half of the sample had, in the meantime, undergone a modest time-dependent decrease in permeability something that could easily occur as the permeation time required to react with and destroy half the sample is likely to be of the order of tens of years in a material of permeability  $10^{-7}$  cm/s. For example, it will take 6.3 years for one sample volume to permeate through a sample of length 200 mm under an hydraulic gradient of 10, a reasonable laboratory situation, and the permeation of tens to hundreds of sample volumes may be necessary to fully react with a CB material. Indeed, the time to fully react with the sample may be greater than the design life of the cutoff, in which case the permeability of the reacted material ceases to be a design issue and the permeability of the remaining unreacted material at any time will be the controlling issue. Thus, the concept of a reaction front moving through the material is crucial to the understanding of all contaminant barrier interactions. The recognition that there will not be just one reaction front but many reaction fronts, each of which will change the chemistry and the permeability of the material, also is crucial.

In an experimental program to investigate both damaging and beneficial effects of chemicals on the behavior of cement-bentonite materials, sequential permeation tests were carried out on a number of samples of cement-bentonite. These samples were prepared by mixing a sodium activated bentonite with water, allowing some time for swelling and hydration of the bentonite, and then adding a mixture of ordinary Portland cement and blast furnace slag. The samples were specifically designed to be of high permeability to enable more rapid chemical permeation. The test samples were permeated with water, and then with chemical solutions in specially designed chemically resistant triaxial cells.

Figure 13 shows the results for one of the samples that was permeated with water until the effluent pH had reached a plateau at about 8. The initial pH of the effluent was greater than 12 due to the presence of sodium, potassium, and calcium hydroxides in the cement-bentonite mixture. The figure shows a plot of permeability and pH of the sample as a function of the number of sample volumes of water passed through it. The permeation was interrupted on a number of occasions and, upon the re-establishment of flow, the initial effluent was of slightly higher pH as can be seen from the 'spikes' on the pH curve. The sample showed a continuing reduction in permeability up to about 160 sample volumes of permeant liquid at which point the permeability began to level off.

The reduction in the permeability of cement-bentonite upon leaching has been well established and, thus, the behavior shown in Fig. 13 is as expected. However, the figure contradicts a thesis currently in the literature suggesting that the permeability of cement-bentonite continues to decrease without a discernible limit. The results also provide some information on the factors that may underlie the permeability reduction. These factors may include:

- (a) the deposition of calcium carbonate in the pores of the material as a result of the reaction of calcium (particularly from free lime) in the cement with carbonate ions in the permeating water (this was open atmospheric carbon dioxide);
- (b) the leaching of free lime from the cement;
- (c) the leaching of cement hydrate materials and especially calcium from the calcium silicate hydrates that will change the cementing activity of the cementitious phases; and
- (d) the deposition of any suspended matter present in the water.



Figure 13 : Effect of extended permeation by water followed by permeation with magnesium sulfate on a cement-bentonite material.

Since clean tap water was used, (d) was not expected to be a significant effect. Although algae can develop in the slow moving water of the permeameter pipework if this is exposed to sunlight, there was no visible evidence of algal deposits in the pipework which was protected from sunlight.

Mechanisms (a) and (d) may be expected to decrease the permeability of the material, and mechanism (b) to increase it, as a result of loss of solid volume. Mechanism (c) would be expected to soften the material and also increase its permeability. Softening of the sample, evidenced by consolidation (of order 10%) was indeed observed despite the low confining pressure used in the tests (30 kPa). Mechanism (d) would be expected to cause a continuing reduction in permeability, but it cannot explain the observed plateau in permeability after about 160 sample volumes, although it may have had some effect. It follows that mechanisms (a), (b) and (c) appear to be the important controls, and their combined effect results in a reduction in permeability.

Water leaching is thus beneficial to the permeability of cement-bentonites, and the surprising conclusion is reached that the permeability and thus barrier effectiveness will improve with water permeation, i.e., provided the material is confined (and a barrier in the ground will be subject to confinement). In contrast, magnesium sulfate at high concentrations could be expected to be rather damaging to cement-bentonite materials because of both the expansive effect of the sulfate and the tendency for magnesium ion to replace calcium ion, for example, in lime. Unconfined samples of cement-bentonite materials when immersed in 10 g/liter sulfate are completely destroyed. In confined permeability tests, the effects on unleached samples (i.e. those still with high pH) have been found to be more modest - a permeability increase by a factor of a few times is typical. However, if all free lime is first leached form a sample, then the effects could be quite different.

Therefore, as a test of this hypothesis, the test sample was permeated with magnesium sulfate solution at a concentration of 12.5 g/liter (10 g/liter sulfate ion) after 340 sample volumes of water leaching. Rather than an increase in permeability, there was an immediate and substantial drop in permeability on the order of 300 times. This reduction in permeability was sustained until the test was terminated some months later (see Jefferis (1996) for further details).

The test program showed that there is considerable potential to modify the behavior of barriers once in the ground. This could be to repair them, extend their life, protect them from damaging species, or modify or re-charge their chemical activity. Finally, the work demonstrates that it is quite simplistic to consider cement-bentonites or indeed any barrier material as having a unique permeability – permeability is a dynamic parameter controlled by time, and the history of permeation (permeant sequence). Also, cement-

bentonite materials are especially chemically active. However, if we can learn to exploit this activity, new barriers concepts may be forthcoming.

Compatibility for SB walls also is an important design consideration due to the reactive nature of bentonite and the relatively low confining stresses associated with SB walls (e.g., Mitchell and Madsen 1987). Thus, condition specific compatibility tests should be performed on the SB mixtures. In the case of adverse results, stabilizing materials, such as relatively non reactive clays, organic modifiers, or polymers, may be required to prevent drastic increases in the hydraulic conductivity of the SB wall.

For example, Ryan (1987) describes a project in which attapulgite clay was used in the trench slurry and as dry clay added to the backfill primarily due to incompatibility of both a natural bentonite and a treated bentonite to the leachate being contained (Fig. 14). However, Ryan (1987) notes that attapulgite clay is not routinely used in SB walls because attapulgite clay is less efficient and more expensive than bentonite, and attapulgite clay is more difficult to mix into a slurry and requires special equipment.



Figure 14 : Compatibility of attapulgite and bentonite to a natural organic leachate (replotted after Ryan 1987).

The attenuation capacity of slurry walls is largely governed by the attenuation capacity of the constituent materials. In terms of cation exchange, the total exchange capacity, TEC, per cubic meter of slurry wall can be estimated from the following equation:

$$TEC\left(\frac{eq}{m^3}\right) = \rho_d\left(\frac{kg}{m^3}\right) \times \sum_{i=1}^{j} W_{si}\left(\frac{kg}{kg}\right) \times CEC\left(\frac{eq}{kg}\right)$$
(21)

where  $\rho_d$  is the dry density of the wall,  $W_{si}$  is the solid weight of constituent material i per gram of dry wall material, CEC<sub>i</sub> is the cation exchange capacity of constituent material i, and j is the total number of constituents in the slurry wall. For example, the TEC of a SB wall with a dry density of 1380 kg/m<sup>3</sup> (86 lbs/ft<sup>3</sup>) (total density of 1800 kg/m<sup>3</sup> or 112 lbs/ft<sup>3</sup> and water content of 30%) consisting of 2% bentonite (1 kg of dry bentonite per kg of dry backfill mixture) with CEC = 60 meq/100 g (= 0.60 eq/kg) and 98% backfill soil with CEC = 10 meq/100 g (= 0.10 eq/kg) is 152 eq/m<sup>3</sup>.

However, Eq. 21 does not indicate the propensity for cation exchange of individual cationic species that may exist simultaneously in solution. This propensity must be evaluated on a case-by-case basis by performing batch equilibrium adsorption and/or column tests using site specific materials and conditions (e.g., see Shackelford 1994b). In addition, Eq. 21 probably is not relevant for CB materials, since x-ray diffraction tests suggest that the bentonite clay is destroyed by the high pH environment of the cement and is very likely incorporated into the calcium silicate and aluminum hydrates of the cement. Also, even if the clay persisted, cation exchange would be only a minor component of CB chemical reactivity compared with the potential chemical reactions of the cement.

Several of the processed clay soils, such as bentonite and attapulgite clay, are pre-treated at the processing site with an additive (e.g. CaO) that assists in maintaining a high pH (> 8) when the processed clay soil is mixed with water into a slurry. The purpose of maintaining a relatively high pH is to stabilize the slurry by keeping the clay particles from flocculating and settling out of suspension. Thus, these specially treated processed soils also may assist in precipitating heavy metals during migration through the slurry wall.

Diffusive transport generally will be significant for relatively thin ( $\leq 1$  m) SB or CB slurry walls with k  $\leq 10^{-7}$  cm/s and dominant through thin SB or CB walls with k  $\leq 5 \times 10^{-8}$  cm/s (Shackelford 1988, 1989). Thus, diffusion is an important design consideration with regard to contaminant migration through slurry walls.

With respect to diffusive transport through slurry walls, three possible design scenarios, as illustrated in Fig. 15, have been defined (after Shackelford 1989, Manassero and Shackelford 1994): (a) pure diffusion, (b) diffusion with advection; and (c) diffusion against advection. The pure diffusion scenario represents the limiting case. The diffusion with advection scenario will occur when buildup of polluted ground water is allowed on the upgradient side of the wall. The diffusion against advection scenario occurs when the polluted ground water is drawn down on the polluted side of the wall to induce flow towards the containment side thereby minimizing the outward flux of contaminants.

The diffusion with advection scenario can be analyzed using an analytical approach described by Shackelford (1990). Analyses can be performed to (1) evaluate the significance of diffusion through a given slurry wall, (2) to estimate the amount of draw down required to minimize outward flux of contaminants, and (3) to determine the effect of increasing the adsorption capacity of the wall (i.e., increasing  $R_d$ ) for design. Illustrative examples for each of the three scenarios shown in Fig. 15 are provided by Manassero and Shackelford (1994).

In addition to these simplified scenarios, the contaminants in many practical situations may have to diffuse a considerable distance from their source to the cutoff. Also, any receptors of concern or regulatory boundary, known as the 'point of compliance' or POC in the US, may be some distance downstream of the cutoff. Thus, the effective containment period may be much greater than that based solely on analysis in accordance with the design scenarios shown in Fig. 15.



Figure 15 : Design scenarios for low permeability barriers (Shackelford 1989, Manassero and Shackelford 1994): (a) pure diffusion; (b) diffusion with advection; (c) diffusion against advection.

#### Alternative Passive Vertical Barriers

Aside from slurry cutoff walls, other passive vertical barriers include walls constructed using deep soil mixing or jet grouting using chemical grouts (e.g., silicates, resins, and polymers), grout curtains, and sheet pile walls (Mitchell and Rumer 1997). Although these technologies are used extensively in more traditional geotechnical engineering applications, such as in dams and construction excavations, none of these technologies has been used extensively as passive containment barriers for remediation of contaminated land. The limited application of these alternative barrier approaches is due to concern with the integrity of

the containment system and potential leakage of contaminants through 'windows' in the barriers, such as high permeability zones between the grout in grout curtains, or through the interlocks in sheet piles. Corrosion also is a problem with respect to the use of sheet-pile walls.

A comparison of the typical widths, depths, and construction costs for these vertical barriers is summarized in Table 9. In addition to the greater concern for contaminant leakage from the alternative passive barriers, the costs for these alternative barriers typically are greater and the production rates lower than for the more traditional SB and CB slurry walls.

			/	
Wall Type	Width (m)	Depth (m)	Cost (\$US/m <sup>2</sup> )	Production Rate (m <sup>2</sup> /hr)
Soil Bentonite (SB)	0.6 - 0.9	25	20 - 80	25 - 150
Cement Bentonite (CB)	0.6 - 0.9	25	50 - 180	10 - 80
Deep Mixing (DM)	0.8	27	60 - 150	10 - 80
Jet Grouting (JG)	0.4 - 0.9	60	300 - 800	3 – 25
Grout Curtain (GC)	One row	60	400 - 1000	2-10

 Table 9 : Comparison of passive vertical containment barriers (from Filz and Mitchell 1995, and Mitchell and Rumer 1997).

Although alternative passive vertical barriers are not used extensively for long-term containment, they may be used in conjunction with other remediation technologies to aid in temporary, partial containment. For example, Weaver et al. (1992) describe the design, installation, and performance of a single-row grout curtain that was used to increase the effectiveness of a groundwater recovery-well system at a waste site by reducing the inflow of ground water from outside the site.

#### **Biobarriers**

The concept of using bacteria to form biofilm barriers, or biobarriers, in otherwise highly permeable media (e.g., sands) through plugging, clogging, or fouling the media to contain or reduce the migration of contaminant plumes recently has gained attention (e.g., Mitchell 1997). Reductions in the hydraulic conductivity from one to three orders of magnitude have been reported for a variety of porous media using many types of bacteria and different treatment methods including stimulation of indigenous bacteria (biostimulation), and injection of full-sized living and dead bacteria as well as ultramicrobacteria (bioaugmentation) (Dennis and Turner 1998). A summary of some of these results is shown in Fig. 16.



Figure 16 : Hydraulic conductivity (k) of porous media before and after treatment with bacteria (literature data as summarized by Dennis and Turner 1998).

In general, the results of these studies indicate that

• final values of hydraulic conductivity  $< 10^{-7}$  cm/s generally have not been reported (Fig. 16),

- continuous nutrient stimulation does not appear to be necessary to maintain the reduced hydraulic conductivity value,
- the biofilm can grow to thicknesses sufficient to completely fill pores,
- the biofilm increases diffusivity and can affect adsorption strongly, and
- the physical properties of the biofilm can vary widely depending on the bacterial species and morphology and exopolysaccharide composition (Dennis and Turner 1998).

All of the results shown in Fig. 16 represent tests performed on materials with high initial values of k, ranging from 2.5 x  $10^{-1}$  to 2 x  $10^{-5}$  cm/s. Thus, even reductions in k of one to three orders of magnitude are not sufficient to achieve the low k values required in most applications. However, Dennis and Turner (1998) report results showing that the hydraulic conductivity of a compacted silty sand (SM) decreased from ~  $10^{-5}$  –  $10^{-6}$  cm/s to ~  $10^{-8}$  cm/s after treatment with the biofilm-producing bacterium *Beijerinckia indicica*. In addition, they show that the hydraulic conductivity of ~  $10^{-8}$  cm/s for soil specimens with well-established biofilm barriers was essentially unaffected after permeation with a 0.5 N saline solution, an acidic solution (pH 3), or a basic solution (pH 11). Thus, the results of the study by Dennis and Turner (1998) show promise for the use of biobarriers for passive containment applications. However, a significant amount of additional research must be performed before biobarriers can be used routinely for practical applications.

#### 5.2.2 Caps/Covers

Caps or covers are used as horizontal surface barriers to minimize the leaching of contaminants into the ground water. Two possible scenarios involving applications of caps for *in situ* remediation applications are illustrated in Fig. 17.

As shown in Fig. 17a, a cap may be considered as the only technology needed in cases where the climate is arid, the water table is deep, and the site is relatively isolated. An example of this application is the Hanford Barrier that has been designed to isolate single-shell tank wastes and transuranic-contaminated soil sites for a minimum of 1000 years at the US Department of Energy's (DOE's) Hanford site near Richland, WA (Wing and Gee 1994).

The schematic diagram shown in Fig. 17b depicts the conceptual use of an *in-situ* cap designed and placed to prevent the potential for overtopping of the contaminated ground water within a vertically contained zone due to infiltration, an occurrence known as the 'bathtub effect'. The cap is constructed byexcavating the soil above the containment area, placing or compacting the low-permeability barrier, and back-filling with the native soil to provide a protective surface layer. The backfill is shown to original grade to allow for subsequent use of the site. Special design features include sloping the surface of the barrier layer to promote subsurface runoff down gradient of the containment zone. Also, periodic separations between the horizontal (cap) barrier layer and the vertical containment barrier may be required to allow for venting of volatile organics and/or minimizing the potential buildup of gas pressure beneath the cap and eventual uplift of the cap.

As shown in Fig. 18, caps are composed of six basic components, from top to bottom (Daniel and Gross 1995, Mitchell and Rumer 1997): (1) surface layer, (2) protection layer, (3) drainage layer, (4) barrier layer, (5) gas collection layer, and (6) foundation layer. The primary purposes of the surface layer are to support vegetation, resist erosion, and reduce temperature and moisture extremes in underlying layers. The primary purposes of the protection layer are to store and release water through evapotranspiraton (ET), separate underlying waste from humans, burrowing animals, and plant roots (biointrusion), and protect underlying layers from "environmental" stress (e.g., wet-dry cycles, freeze-thaw cycles). The drainage layer is used to allow drainage of the water from overlying layers, reduce the head and, therefore, gradient on the barrier layer, and increase stability by reducing pore water pressures. The barrier layer functions to impede infiltration of water into the underlying soil, and to restrict the outward migration of gases from the underlying waste or contamination. The gas collection layer serves to collect and remove gases to reduce the potential for detrimental effects (e.g., explosions) and to provide for energy recovery and/or vapor treatment. Finally, the foundation layer provides a surface on which to construct the other layers of the cap.



Figure 17 : Schematic example applications for caps for *in situ* remediation: (a) long-term containment of vadose zone contamination in arid climates; (b) capping of slurry wall containment system for saturated zone contamination.



Figure 18 : Cross section of layering in traditional caps (from Daniel and Gross 1995, Mitchell and Rumer 1997).

The potential materials for each layer are summarized in Table 10. Some layers, such as the hydraulic barrier layer, may consist of more than one material, such as a composite barrier comprising a geomembrane overlying a compacted clay.

All caps require a surface layer, but all of the six layers are not required at all sites. For example, a drainage layer may not be needed at an arid site. However, all of the layers that are used in a cap must have adequate shear strength to ensure stability against slope failure, and must be sufficiently durable to function adequately over the design life of the cap. More detail regarding the design and performance of caps can be found in Daniel and Gross (1995) and Rumer and Ryan (1995).

Table	10 : Cap materials (modified from Daniel and Gross 1995).		
Layer	Materials		
Surface	Topsoil (vegetated)		
	Geosynthetic erosion control layer over topsoil (vegetated)		
	Cobbles		
	Paving material		
Protection	Soil		
	Cobbles		
	Recycled or reused waste (e.g., fly ash, bottom ash, and paper mill sludge)		
Drainage	Sand or gravel		
	Geonet or geocomposite		
	Recycled or reused waste (e.g., tire chips)		
Barrier	Compacted clay		
	Geomembrane		
	Geosynthetic clay liner		
	Recycled or reused waste (low permeability)		
	Asphalt		
	Sand or gravel capillary barrier		
Gas Collection/Removal	Sand or gravel		
	Geonet or geocomposite		
	Geotextile		
	Recycled or reused waste (e.g., tire chips)		
Foundation	Sand or gravel		
	Geonet or geocomposite		
	Recycled or reused waste Select waste		

#### Traditional Caps/Covers

Traditional covers are distinguished in that the design typically is based on minimizing infiltration by minimizing the saturated hydraulic conductivity of the barrier component of the cap. These caps/covers often are referred to as "resistive barriers". In the case of the use of compacted clay as the sole or primary material in the barrier, minimizing the saturated hydraulic conductivity usually requires compacting the clay at water contents that result in degrees of saturation  $\geq 90\%$ . In many cases, subsequent drying of the clay soil, particularly in arid environments, results in desiccation cracking of the clay that may ultimately lead to failure of the cap. As a result, recent emphasis has been placed on the use of alternative caps that offer potentially greater durability at less expense than traditional caps.

#### Alternative Caps/Covers

Interest in the use of alternative covers has increased in recent years due, in part, to the costs associated with the more traditional covers and to other problems (e.g., desiccation) associated with low-permeability covers. In particular, a significant amount of study has been devoted to the use of capillary barriers as final covers for waste disposal and *in situ* remediation (e.g., Khire et al. 1994, and Benson and Khire 1995).

A capillary barrier results when unsaturated flow occurs through a relatively fine layer overlying a relatively coarse layer (e.g., clay over sand, silt over gravel, and sand over gravel). In a capillary barrier, only a small fraction of the flux associated with the wetting front through the finer layer is transmitted into the underlying coarser layer. A capillary barrier effect occurs when (1) the unsaturated hydraulic conductivity of the coarser layer decreases to a lower value than the unsaturated hydraulic conductivity of the finer layer as the matric suction increases (see Fig. 19), and (2) the residual suction in the finer layer after first passage of the wetting front is larger than the gravitational force on the wetting front (Shackelford 1997a). Both of these effects result in an effective 'reflection' of the wetting front at the interface of the finer and coarser layers.

In general, the capillary barrier effect is increased with an increase in the contrast in soil properties (e.g., unsaturated hydraulic conductivity) between the finer and coarser layers, and when the residual suction in the finer soil layer is maximized. In contrast, complete saturation of the finer layer during migration of the

incipient wetting front will destroy any residual suction, and the capillary barrier will fail. Thus, the use of capillary barriers as final covers generally is considered plausible only in regions with relatively small precipitation events, such as in arid and semi-arid climates.



Figure 19 : Layering in a capillary barrier and comparison of general trends in hydraulic conductivity as a function of matric suction in the layers (after Shackelford 1997a).

#### Geochemical Caps/Covers

Blowes et al. (1991) evaluated the formation of cemented (hardpan) layers near the surface of two inactive sulfidic tailings impoundments in Canada to evaluate the potential effect of hardpan layers on reducing the rate and magnitude of sulfide oxidation and  $H^+$ ,  $Fe^{2+}$ , and  $SO_4^{2-}$  production. Blowes et al. (1991) found that the hardpan layer at one of the sites consistently occurred at a depth where there was an abrupt increase in the solid-phase carbonate content.

For example, consider the problem of acid drainage resulting from the oxidation of sulfidic tailings, such as pyrite ( $\text{FeS}_{2(s)}$ ), in accordance with the following chemical reaction (e.g., Nicholson et al. 1989, Evangelou and Zhang 1995, Ribet et al. 1995):

$$\operatorname{FeS}_{2(s)} + \frac{7}{2}O_{2} + H_{2}O \rightarrow 2SO_{4}^{2-} + 2H^{+} + Fe^{2+}$$
 (22)

The result of this chemical reaction is the production of a low pH solution (e.g., pH < 6) containing relatively high concentrations of potentially toxic heavy metals associated with the tailings, such as Fe<sup>2+</sup>. In the presence of sulfate (SO<sub>4</sub><sup>2-</sup>) resulting from dissolution of pyritic tailings (Eq. 22), calcite (CaCO<sub>3(s)</sub>) dissolves resulting in gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O<sub>(s)</sub>) precipitation as follows:

$$\mathrm{SO_4}^{2-} + \mathrm{CaCO_3(s)} + 2\mathrm{H}^+ + \mathrm{H_2O} \rightarrow \mathrm{CaSQ_4} \cdot 2\mathrm{H_2O(s)} + \mathrm{CO_2}$$
(23)

The ferrous iron ( $Fe^{2+}$ ) resulting from dissolution of pyritic tailings (Eq. 22) oxidizes to ferric iron ( $Fe^{3+}$ ) in the presence of *Thiobacillus ferrooxidans* as follows (Blowes et al. 1991):

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$$
 (24)

The abundance of ferric iron from the reaction in Eq. 24 results in a hardpan layer of precipitated iron oxyhydroxide (FeO(OH)<sub>(s)</sub>) and/or ferric hydroxides (Fe(OH)<sub>3(s)</sub>) due to an increase in pH (Eqs. 23 and 24) as follows (Evangelou and Zhang 1995, Chermak and Runnells 1996):

$$Fe^{3+} + 2H_2O \rightarrow FeQ(OH)_{(s)} + 3H^+$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+$$
(25)

The acid can be removed according to Eq. 23 and, thus, the presence of  $CaCO_{3(s)}$  or similar acid reactive material results in precipitation of FeO(OH)<sub>(s)</sub> and/or Fe(OH)<sub>3(s)</sub>.

Based on their investigations, Blowes et al. (1991) concluded that the persistence of hardpan layers near the surface of sulfidic tailings can reduce substantially the rate of sulfide oxidation and the generation of acid drainage. They also noted that the formation of the hardpan layer may be enhanced by adding carbonate minerals to the tailings near the end of disposal operations.

Chermak and Runnells (1996) evaluated the potential for creating a low-permeability geochemical cover by evaluating the effect of the addition of lime (CaO<sub>(s)</sub>) and crushed limestone (CaCO<sub>3(s)</sub>) on the hydraulic conductivity of an acidic sulfide-rich overburden material from a gold mine. The measured hydraulic conductivity values for two columns of overburden material without surface amendment permeated with a simulated rainwater (1.5 x 10<sup>-6</sup> m HCl, pH = 5.80) were 1.4 x 10<sup>-3</sup> cm/s and 1.3 x 10<sup>-4</sup> cm/s. The measured hydraulic conductivity values for various surface amended columns ranged from 1.6 x 10<sup>-5</sup> cm/s to 5.7 x 10<sup>-5</sup> cm/s as the result of the formation of hardpan layers with hydraulic conductivity values ranging from 2.8 x  $10^{-7}$  cm/s to 7.8 x  $10^{-7}$  cm/s.

Chermak and Runnells (1996) also found that an important consideration in the development of the hardpan layer is that the sulfide overburden and limestone and/or lime be in direct contact to allow the chemical reactions to occur. Thus, the addition of solid-phase carbonate minerals to acidic sulfide-bearing tailings shows promise in terms of creating a low-permeability geochemical cover. Also, the hardpan layer formation should be self-perpetuating and self-hardening provided sufficient amounts of carbonate minerals are available.

Organic-rich materials, such as sewage sludge, composted municipal waste, peat, or sawdust, also have been proposed as geochemical cover materials to consume oxygen and prevent the oxidation of the underlying sulfidic tailings (Ribet et al. 1995). The major advantages of this approach are low cost and availability of materials. A potentially significant disadvantage is that aerobic and anaerobic biodegradation of the organic-rich waste can release soluble organic compounds to percolating water that subsequently result in reductive dissolution of ferric-bearing precipitates and subsequent release of metals from the tailings.

#### 5.2.3 Subsurface Horizontal Barriers

Subsurface horizontal barriers include indigenous barriers (aquicludes, aquitards) and artificially emplaced barriers. Artificially emplaced barriers include thin diaphragm walls created by directional and non-directional drilling with jet grouting, conventional jet grouting, and soil freezing technologies (Peterson and Landis 1995).

Indigenous barriers rarely are relied upon for permanent containment because of the uncertainty associated the integrity of the system. Application of the artificially emplaced barriers also is limited for the same reasons that the alternative passive vertical barriers are limited, viz., uncertainty regarding integrity and longevity of the placed system, and costs associated with placement of the technology. Further details on these types of barriers can be found in Peterson and Landis (1995).

#### 5.3 In Situ Active Containment

#### 5.3.1 Pump and Treat

Pump and treat (PT) refers to the process of pumping contaminated ground water to a surface collection system through wells screened in the saturated zone, and then treating the contaminated water with one or more *ex situ* treatment technologies. In this context, PT may be considered to be a treatment rather than containment option. However, in terms of the *in situ* aspects of PT, which is pumping, not treatment, PT typically is categorized as a containment option (e.g., Freeze and McWhorter 1997, Clark 1998).

For example, pumping wells may be located within the contaminated area to provide draw down of the water table that directs flow into the site, thus providing active containment by minimizing or preventing

further migration of the plume away from source or site. Alternatively, pumping wells can be located down gradient from the contamination to provide a drawdown barrier.

As previously mentioned, PT as a remediation technology has been shown to be ineffective in achieving remediation goals. The primary causes for the inability of PT to reach remediation goals are attributed to (1) the physical-chemical subsurface conditions (i.e., aquifer characteristics), and (2) the characteristics and fate of contaminants in the subsurface environment (Mott 1992).

The subsurface conditions that render the PT technology ineffective during groundwater remediation include (a) subsurface heterogeneity and (b) low permeability (hydraulic conductivity) formations or zones in the subsurface. The existence of heterogeneities affects the hydraulic impact of the extraction wells and, therefore, the effectiveness of the pumping. Pump and treat in low-permeability zones is not practical because yields are too low for continuous pumping.

As shown schematically in Fig. 20, the existence of low-permeability zones (e.g., clay lenses) within higher permeability formations or fractured rock results in a process known as matrix diffusion. During initial contamination of the aquifer, the difference in concentration between the contaminated aquifer and the clay lense results in diffusion of contaminants into the porous matrix of the clay lense (Fig. 20a). Also, any fractures existing in the bedrock or other fractured formations are penetrated by the contamination resulting in matrix diffusion from the fractures into the surrounding rock matrix (e.g., Parker et al. 1994). Once pumping commences, the higher permeability portion of the aquifer is flushed relatively quickly resulting in a reversal of the concentration gradient and matrix diffusion effect (Fig. 20b). Since the diffusion process is relatively slow, this reverse matrix diffusion effect can result in the long-term release of residual contamination (e.g., Feenstra et al. 1996).

The two primary contaminant characteristics that affect adversely the PT technology are the aqueous solubility of the contaminants and the existence of contaminants adsorbed to the solid phase of the aquifer materials. As a result of the interfacial forces between NAPLs and the aquifer materials, portions of the NAPLs may be retained or trapped in the pore spaces during initial contamination. The flow rates induced by PT may be too rapid to facilitate aqueous saturation levels of the trapped contaminants near the NAPL-water interface since the NAPL-water partitioning (i.e., solubilization) process is slow. Thus, the contaminated water is pumped away from the trapped NAPL before reaching chemical equilibrium and replaced by water up gradient of the well, leaving the trapped NAPL as residual contamination that will act as a potential source of dissolved-phase contamination for a prolonged period.



Figure 20 : Matrix diffusion and fracture contamination in polluted aquifer (a) before pumping and (b) after pumping.

Contaminants concentrated in the ground water generally are pumped out more easily and more efficiently than contaminants that are adsorbed to the soil. Initially, pumping results in high removal efficiencies since the pumping removes non-adsorbed, aqueous-phase contaminants rather easily. However,

with time, contaminant removal efficiency decreases because larger and larger volumes of increasingly less contaminated water must be pumped to extract the contaminants that are adsorbed.

As illustrated in Fig. 21 the combination of these factors results in two characteristic trends with respect to the efficiency of PT technology. In the case of perpetual pumping (Fig. 21a), PT typically results in large contaminant removal efficiencies but the inability to achieve cleanup to the desired level (e.g., MCL). Even in cases where the desired cleanup level may be achieved, the level is not maintained once the pumps are turned off due to the existence of the residual contamination (Fig. 21b).



Figure 21 : Schematic of typical relationship between aquifer concentration versus time of pumping in pump and treat remediation for well located within the contaminated zone: (a) perpetual pumping period; (b) finite pumping period.

Despite the problems historically associated with the PT remediation technology, PT continues to be used primarily in combination with other technologies (e.g., McKinley et al. 1992). A relatively new and reportedly successful adaptation of the PT approach is the use of horizontal well or drains (Reid et al. 1994, Berry and Frantz 1995, Parmenter and Klemovich 1996, Breh et al. 1997, and Hoffman 1998).

The basis for the use horizontal wells or drains is derived from the petroleum industry where horizontal wells are used to recover oil, and from the public utilities where there is a need to lay horizontal gas and water pipes, particularly in urbanized or crowded areas. The approach requires the use of specialized directional drilling equipment and directional tracking equipment.

One of the reported advantages of the approach is that the number of wells required typically is considerably less than in the case of vertical wells because of a greater coverage of the screened interval. Also, the ability to reach subsurface contamination in crowded or tight confinements, such as beneath buildings, roads, etc., is an advantage. However, the approach does include a number of costly factors. Aside from the need for specialized directional drilling equipment, other costly requirements include dual concentric well screens to reduce clogging and pump maintenance, and double casing along the entire length of the wells to avoid leaking contaminated ground water into uncontaminated or less-contaminated strata (Reid et al. 1994). Also, the approach typically is used only at relatively shallow depths (3 m to 4 m).

#### 5.3.2 Reactive Barriers

Although most low-permeability soil barriers have some intrinsic attenuation capacity, the concept of designing passive barriers with an enhanced attenuation capacity recently has gained momentum. For example, the use of additive barrier materials, such as zeolites, high carbon fly ash, organically modified clays, tire chips and ground rubber, and zero-valent iron has been proposed to enhance the attenuation capacity of waste containment liners and vertical barriers (e.g., Evans et al. 1990, Thornton et al. 1993, Lo et al. 1994, Gray 1995, Smith et al. 1995, Allerton et al. 1996, Park et al. 1996, 1997, Evans and Prince 1997, Kershaw and Pamuckcu 1997, Rabideau et al. 1999).

The design of reactive barriers requires an understanding of the potential attenuation mechanisms for the principal chemical species of interest. Thornton et al. (1993) have identified the principal attenuation mechanisms for many of the inorganic chemical solutions of concern as ion exchange (sorption), precipitation, dilution, and neutralization. However, the two primary attenuation mechanisms with respect to heavy metal migration are ion exchange, or adsorption, and precipitation.

Ion exchange or adsorption can be enhanced in a passive barrier by using additive materials that will increase the overall CEC or adsorption capacity of the liner. For example, consideration of the use of zeolites with CEC as high as 250 meq/100 g as a barrier material has been described by Evans et al. (1990) and Allerton et al. (1996).

The precipitation potential of a passive barrier can be enhanced by adding materials that will increase the pH of the permeant liquid. For example, the addition of quicklime [CaO], hydrated high calcium lime  $[Ca(OH)_2]$ , dolomitic quicklime [CaO· MgO], or monohydrated dolomitic lime  $[Ca(OH)_2 \cdot MgO]$  may aid in increasing the pH of an acid solution during migration thorough the barrier to (a) neutralize the pore solution pH, (b) precipitate metals from solution, (c) clog the pores, and (d) decrease the hydraulic conductivity thereby enhancing the overall performance of the barrier. Processed clay soils, such as bentonite and attapulgite clay, that have been pre-treated to maintain a relatively high pH (> 9) for stability considerations (e.g., for use as drilling muds in high TDS environments), also may be used to enhance the precipitation capacity of the barrier materials. In most cases, laboratory column and/or batch tests will be required with barrier specific materials and site-specific chemical solutions to determine the viability and optimum amounts of reactive materials being considered for use in reactive barriers.

Adsorption of neutral, non polar organic compounds (e. g., benzene) is correlated directly with the amount or fraction of organic carbon,  $f_{oc}$ , in the soil through the well-known "hydrophobic effect" (Eq. 6). Thus, increasing the amount of organic carbon in the barrier, for example, by adding high carbon fly ash, rubber tire chips, ground rubber, or granular activated carbon, may increase the attenuation capacity of the barrier with respect to this important class of organic compounds.

A recent study by Rabideau et al. (1999) has shown the feasibility of amending soil-bentonite (SB) slurry walls with zero-valent iron to degrade chlorinated hydrocarbons, such as TCE. Their laboratory results indicated that less than one percent of added iron would be required to reduce the diffusive flux of TCE across an installed slurry wall by over ten orders of magnitude.

The potential benefits of reactive barriers with respect to attenuation of contaminants can be illustrated with the following analysis. Consider the simplified barrier scenario shown in Fig. 15a. In this case, transport through the barrier is governed only by diffusion with the potential for sorption since there is no head loss across the barrier. This simplifying assumption obviates the need to consider the hydraulic conductivity of the barrier, and represents the limiting case of pure diffusion expected to govern miscible transport of contaminants through low-permeability barriers (e.g., Shackelford 1988).

The time-dependent concentration at the outer extent of the barrier schematic shown in Fig. 15a, c(L,t), resulting from diffusion with reaction for the case of a constant source concentration,  $c_0$ , can be evaluated using the following analytical model:

$$\frac{c(\mathbf{L},t)}{c_{0}} = \operatorname{erfc}(\beta)$$
(26)

where 'erfc' is the complementary error function, and the argument,  $\beta$ , is given as follows:

$$\beta = \frac{R_d L}{2\sqrt{D^* R_d t}}$$
(27)

where L is the thickness of the barrier,  $D^*$  is the effective diffusion coefficient, and  $R_d$  is the retardation factor (Eq. 11). The unique relationship between the relative concentration,  $c(L,t)/c_o$ , and the argument  $\beta$  based on Eq. 26 is shown in Fig. 22.

The relationship shown in Fig. 22 may be used to determine the required attenuation capacity as represented by  $R_d$  for a given thickness, L, or containment time, t, through rearrangement of the definition of  $\beta$  as follows:

$$R_{d} = \frac{4\beta^{2}D^{*}t}{L^{2}}$$
(28)

Thus, for given values of  $\beta$  (i.e., c(L,t)/c<sub>o</sub>) and D\*, R<sub>d</sub> is directly proportional to containment period and inversely proportional to the square of the barrier thickness.



Figure 22 : Analytical solution for diffusion-controlled scenario (from Shackelford 1999).

For example, consider a barrier designed to limit c(L,t) to  $\leq 10$  percent of  $c_0$ . Therefore, from Fig. 22 with  $c(L,t)/c_0 = 0.10$ , the limiting value of  $\beta$  is ~ 1.136. With this value for  $\beta$  and assuming that a representative value for  $D^*$  is 5 x 10<sup>-6</sup> cm<sup>2</sup>/s (= 0.0158 m<sup>2</sup>/yr) given that the typical range of D\* for diffusion through saturated soil is  $1x10^{-6}$  cm<sup>2</sup>/s  $\leq D^* \leq 1 \times 10^{-5}$  cm<sup>2</sup>/s (e.g., Shackelford and Daniel 1991), Eq. 28 may be used to evaluate the required thickness for a given containment time or the required containment time for a given thickness, as illustrated in Fig. 23.

Based on the plots in Fig. 23, the barrier thickness can be halved by increasing the retardation factor (i.e., attenuation capacity) by 4X for a given containment period or, conversely, the containment period can be doubled for a barrier with a given thickness by doubling the retardation factor of the barrier material. Thus, the potential benefits of utilizing the reactive nature of passive containment barriers, particularly for long-term containment, are apparent.

#### 5.4 In Situ Passive Treatment

#### 5.4.1 Monitored Natural Attenuation

Monitored natural attenuation (MNA) is a passive approach to *in situ* remediation in that the approach relies on natural processes to attenuate the contaminants in the soil and ground water without any human intervention. Monitored natural attenuation can be used as a remediation approach when natural processes will reduce the mass, toxicity, mobility, and/or volume of the contaminants. Natural processes resulting in a decrease in or spreading of COCs associated with the unsaturated, or vadose, zone include volatilization, sorption, leaching to ground water, and natural bioventing. Natural processes resulting in a decrease in or spreading of COCs associated with the saturated, or groundwater, zone include sorption, diffusion/dispersion, biodegradation, and dilution. Thus, MNA requires (a) a very thorough understanding of the fate and transport of the COCs, and (b) close monitoring of soil and groundwater samples to verify continuous removal of the COCs.



Figure 23 : Retardation factor as a function of (a) thickness for a given containment time and (b) containment time for a given thickness for the case of pure diffusion (from Shackelford 1999).

Three parameters typically monitored to evaluate the existence and persistence of MNA are

- contaminant concentration.
- dissolved oxygen (DO) content, and
- redox potential (Eh).

In the absence of natural attenuation, contaminant concentrations remain relatively constant over the extent of the contaminant plume, whereas contaminant concentrations typically decrease with distance from the center of the plume when natural attenuation is occurring.

Low DO contents (< 2mg/L) within the plume and high DO contents upgradient of the plume indicate the existence of biodegradation around the perimeter of the plume. The DO content also increases as the contaminant concentrations decrease.

The lower the redox potential of ground water, the more reducing and anaerobic the environment. Thus, for natural attenuation to be occurring, redox values within the plume should be lower (more anaerobic) than outside the extent of the plume. The redox potential of ground water typically ranges from 800 to -400 mV.

#### 5.4.2 Vertical Reactive Walls

The concept of an *in situ* reactive wall for groundwater remediation was first proposed by McMurtry and Elton (1985). This remediation concept has been referred to more recently as permeable reactive walls, passive treatment systems, or *in situ* treatment zones or curtains (e.g., Blowes et al. 1995). A *high permeability reactive wall* (HPRW) incorporates chemical and/or biological reagents or catalysts into the porous medium used for the wall to degrade or otherwise reduce the concentrations of pollutants during passage of the contaminated ground water through the wall.

The major difference between more traditional containment barriers, such as slurry walls, and HPRWs is that the hydraulic conductivity of the HPRW must be sufficiently high to allow timely and efficient processing of the contaminated ground water and to minimize the inducement of additional hydraulic resistance across the wall. Under ideal conditions, the hydraulic conductivity of the HPRW will be equal to the hydraulic conductivity of the surrounding aquifer such that the pollutant migration will proceed through the wall in response to the aquifer hydraulic gradient as shown in Fig. 24. As a result, consideration must be given to both the physical and chemical properties of the HPRW materials including the proper choice and amounts of the chemical and/or physical treatment additives.



Advection and Dispersion

Figure 24 : Schematic cross section through treatment zone for high permeable reactive wall (HPRW) scenario.

The HPRW concept has been evaluated recently for treatment of uranium and molybdenum contaminated ground water using hydrated lime (Ca(OH)<sub>2(s)</sub>) as a precipitating agent and ferrous sulfate (FeSO<sub>4</sub>) and ferric oxyhydroxide (Fe<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O) as redox/complexation/precipitation agents (Morrison and Spangler 1993, Morrison et al. 1996), and for control of acid drainage using anoxic limestone drains (ALDs) to increase the alkalinity of acid water thereby facilitating precipitation of heavy metals (Faulkner and Skousen 1994, Hedin et al. 1994, Kuyucak and St-Germain 1994).

Unlike low permeability reactive walls (LPRWs) in which diffusion likely will be an important, if not dominant, transport process, advection should be the dominant transport process for HPRWs. Thus, several important considerations with respect to hydraulics must be considered in the design of HPRWs. Among these considerations, the most important consideration is to provide for an adequate retention or residence time,  $t_r$ , within the HPRW to allow for successful attenuation of the pollutants.

The required retention time is a function primarily of the hydraulic and transport properties of the wall materials and the time required to facilitate the chemical/biological reaction. Based on the assumption of steady-state, purely advective transport with linear and reversible equilibrium sorption,  $t_r$  is related to the thickness of the permeable reactive barrier, L, the seepage velocity, v, and the sorption properties of the barrier materials for the contaminant as follows:

$$t_r = \frac{R_d L}{v} = -\frac{R_d L n}{ki} = -\frac{R_d L^2 n}{k\Delta h}$$
(29)

where i = the hydraulic gradient across the HPRW, n is the porosity (effective) of the HPRW, and  $\Delta h$  (< 0) is the head loss across the HPRW.

Thus, in accordance with Eq. 29, the requirement for a relatively large retention time can be met by increasing the sorption properties of the wall materials, i.e., increasing  $R_d$  (e.g., Rael et al. 1995, Kershaw and Pamuckcu 1997), increasing the thickness of the HPRW, increasing the porosity of the HPRW, decreasing the hydraulic conductivity of the HPRW, and/or decreasing the head loss across the HPRW. However, a decrease in hydraulic conductivity of the HPRW probably will control over an increase in the porosity of the HPRW since an increase in porosity generally correlates with a logarithmic increase in the hydraulic conductivity. Therefore, the requirement for an excessively long retention time for degrading a given pollutant may require an excessively thick and costly reactive wall in the absence of control of the physical and chemical properties of the wall constituents. However, control of the physical and chemical properties of the conducive to providing an optimal HPRW.

For example, the head loss across the barrier,  $\Delta h (< 0)$ , in an ideal scenario would be the same as the regional groundwater flow to allow for rapid and efficient processing of the polluted ground water and to minimize the hydraulic resistance at the inflow (upgradient) side of the wall. However, if the thickness of the HPRW is restricted for economic or other considerations, then the physical (e.g., k) and chemical (e.g., adsorption capacity) properties of the HPRW may have to be controlled through additive materials (e.g., organic matter) to provide the required retention time. Such control may result in a less than the ideal situation with respect to the head loss across HPRW and the associated processing rates. Therefore, any study of the performance of a HPRW must include an evaluation of the influence of the interactions among the physical, chemical, and biological properties of the HPRW constituent materials.

Additional factors to consider in the approach to the design of HPRWs are that

the flow through an HPRW cannot be higher than that which can be delivered by the upstream geology and dissipated by the downstream geology,

the permeability of an HPRW is likely to reduce over time due to biofouling or chemical precipitation,

permeability reduction may cause the HPRW to act as an unwanted barrier, and

the initial permeability of the HPRW actually should be much higher than that of the surrounding soils so that clogging will not have any significant impact over the design life of the HPRW.

Therefore, based on these factors, the design should be to provide a sufficiently high permeability for the wall with flow controlled by the external geology. This allows much more confident estimation of flow rates and their seasonal variation.

The most important consideration for an HPRW is to provide for an adequate retention time,  $t_r$ , within the wall to allow for successful degradation (or sorption, e.g., by activated carbon, etc.) of the pollutants. The required retention time is a function primarily of the reaction time necessary to provide a certain level of reduction in the initial contaminant concentration of the pollutant.

For example, reductive dechlorination of halogenated aliphatics with zero valent iron filings (Fe<sup>0</sup><sub>(s)</sub>) has been shown to closely approximate a first-order decay process. The measured half-lives,  $t_{1/2}$  (i.e., time required to degrade the contaminant to half the original concentration under the assumption of first-order decay), associated with several halogenated aliphatic hydrocarbons in the presence of Fe<sup>0</sup> are provided in Table 11. The values for  $t_{1/2}$  reported in Table 11 are not normalized with respect to the iron surface area.

Based on the assumption of steady-state, purely advective transport with a first-order decay process, a direct relationship can be developed between the half-life and the retention time for various reduction factors, RF:

$$t_r = 1.44t_{1/2} \ln(RF)$$
 (30)

where RF = the inverse of the relative concentration, or

$$RF = \frac{c(0)}{c(L)} = \frac{c_0}{c}$$
(31)

where  $c_o =$  the initial (inflow) concentration, and c = the final (outflow) concentration corresponding to the required level of treatment following passage through the HPRW. The relationship between t<sub>r</sub> and t<sub>1/2</sub> given by Eq. 30 is shown in Fig. 25 for several different RF values. Thus, as illustrated by this simple analysis, the required retention time increases for a given value of t<sub>1/2</sub> as the required clean up level increases (as RF increases), and for a given value of RF as the value of t<sub>1/2</sub> increases.

Table 11 : Half-lives  $(t_{1/2})$  of some common halogenated aliphatic hydrocarbons for first-order decay in the presence of zero-valent iron filings (from Gillham et al. 1993).

<b>_</b>	Ŭ	
Organic Compounds		t <sub>1/2</sub>
Group	Name	(hrs)

		0.24
Methanes	carbon tetrachloride	0.34
	tribromomethane	0.24
	trichloromethane	33.0
	dichloromethane	No Decline
Ethanes	hexachloroethane	0.22
	1,1,2,2-tetrachloroethane	19.2
	1,1,1,2-tetrachloroethane	4.4
	1,1,1-trichloroethane	5.3
Ethenes	tetrachloroethylene (tetrachloroethene)	17.9
	trichloroethylene (trichloroethene)	13.6
	1,1-dichloroethylene (1,1-dichloroethene)	40.0
	trans-dichloroethylene (trans-dichloroethene)	55.0
	cis-dichloroethylene (cis-dichloroethene)	432.0
	vinyl chloride	106.0

The transport of aqueous miscible pollutants through an HPRW is governed by both advection and mechanical dispersion, i.e., as opposed to the LPRW scenario in which diffusion may dominant contaminant transport through the wall. Thus, design of HPRWs generally is based on solutions to the ADRE as given by Eq. 12 (e.g., Eykholt and Sivavec 1995). However, the following more simplified approach based on steady-state transport conditions may be suitable for long-term treatment scenarios.

For the assumption of purely advective, steady-state transport (i.e., no dispersion), the half-life and reduction factor are related to the thickness of the HPRW through the seepage velocity as follows:

$$L = 1.44vt_{1/2} \ln (RF)$$
 (32)

This relationship is plotted as solid lines in Fig. 26 for a seepage velocity, v, of 0.001 m/hr and several different values of RF. As indicated by the plots for Eq. 32 in Fig. 26, the thickness of the HPRW increases with an increase in treatment level, RF, for a give a contaminant half-life,  $t_{1/2}$ , or with an increase in  $t_{1/2}$  for a given RF.

For the case of steady-state transport with dispersion greater than zero, analytical solutions to the ADRE with  $\partial c/\partial t = 0$  may be used to evaluate the required wall thickness. Many of these solutions are published (e.g., van Genuchten and Alves 1982). For example, based on the assumptions of a constant upgradient source concentration  $[c(0) = c_0]$ , a semi-infinite wall thickness  $[dc/dx(\infty) = 0]$ , and a longitudinal dispersivity,  $\alpha$ , equal to 10 percent of the wall thickness  $[\alpha = 0.1L$ , and  $D = \alpha v = 0.1Lv]$ , the required wall thickness is given by the following relationship (Shackelford 1997):

$$L = 3.61 vt_{1/2} \left\{ \left[ 1 + 0.2 \ln \left( RF \right) \right]^2 - 1 \right\}$$
(33)

This relationship, plotted as dashed lines in Fig. 26 for the same v and RF values as for Eq. 32, indicates that the general effect of dispersion is to increase the wall thickness, all other factors being equal, and the difference between the required wall thickness based on the  $\alpha = 0$  and  $\alpha = 0.1L$  cases increases as RF increases for a given  $t_{1/2}$  (note that the  $\alpha = 0$  line for RF = 1000 almost coincides with the  $\alpha = 0.1L$  line for RF = 100). Also, both Eqs. 32 and 33 indicate that RF  $\rightarrow$  1 as L  $\rightarrow$  0. Finally, if consideration is to be given to the effects of dispersion in the field, it may also be necessary to consider what effect dispersion may have had on the determination of  $t_{1/2}$  in the laboratory, i.e., if this determination was based on using flow through a packed column.



Figure 25 : Half-life versus retention time through high permeable reactive wall (HPRW) for chemicals subject to first order decay (from Shackelford 1997).



Figure 26 : Reactive wall thickness as a function of chemical half-life for steady-state transport through high permeable reactive walls (HPRW) ( $\alpha$  = longitudinal dispersivity) (from Shackelford 1997).

The cross-hatched area shown in Fig. 26 corresponds to 0.5 m  $\leq L \leq 1m$  representing the range of wall thicknesses typically considered practical from a construction standpoint. In the case of values of  $t_{1/2} > \sim 40$  hours, more than one HPRW may be required in series and/or a combination treatment (e.g., combining HPRW with biodegradation) may be required to achieve the desired level of clean-up.

The steady-state transport analyses for the HPRW design procedure presented is attractive in terms of simplicity, but limited by the assumptions. The assumption of a semi-infinite wall domain becomes less critical for HPRWs relative to LPRWs as the hydraulic conductivity of the wall approaches the hydraulic conductivity of the surrounding aquifer. However, aside from the assumption of steady-state transport with or without dispersion, the degradation of one compound results in the production of by- products that may be as harmful, if not more harmful, than the primary compound of interest.

For example, the complete dechlorination sequence of tetrachloroethylene ( $C_2Cl_4$ , or PCE) to relatively harmless ethene (ET, or  $C_2H_4$ ) requires four dechlorination steps as follows:

$$PCE \xrightarrow{1} TCE \xrightarrow{2} DCE \xrightarrow{3} VC \xrightarrow{4} ET$$

where TCE = trichloroethylene (C<sub>2</sub>HCl<sub>3</sub>), DCE = dichloroethylene (C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>), and VC = vinyl chloride (C<sub>2</sub>H<sub>3</sub>Cl). Since each of these compounds has a different  $t_{1/2}$  (Table 11), designing for one  $t_{1/2}$  value is not necessarily appropriate, even if this  $t_{1/2}$  value is the largest value in the degradation chain, since the decay of one chemical species results in production of another chemical species. In such cases, a more general multispecies transport analysis involving the simultaneous solution of a series of ADRE equations, one written for each species, is required (e.g., see Bear and Verruijt 1987, Sevougian et al. 1994). In addition, the common situation is even more complicated than indicated above in that the actual dechlorination process is not sequential, but rather involves degradation to numerous other by-products (e.g., see discussion of Eq. 17).

#### 5.4.3 Horizontal Treatment Zones

A relatively recent development in passive *in situ* remediation is the placement of horizontal treatments zones (HTZs) in low-permeability deposits ( $k_{sat} \le 10^{-5}$  cm/s) by hydraulic fracturing (e.g., Siegrist et al. 1999). The fractures are created by injecting a viscous liquid containing a high content of suspended granular solids. Fractures can be filled with sand either to enhance the recovery of fluids from or aid the delivery of reactive fluids into a deposit. Alternatively, fractures can be filled with chemically reactive media, such as illustrated in Fig. 27, to immobilize or degrade organic contaminants *in situ*.



Fractures filled with reactive media



For example, Siegrist et al. (1999) describe a field test where hydraulic fractures were created to emplace potassium permanganate (KMnO<sub>4</sub>) solids and iron metal ( $Fe^0_{(s)}$ ) in the subsurface to chemically treat TCE *in* 

*situ* in accordance with the reactions given by Eqs. 16 and 17, respectively. The fractures were propagated at nominal depths of 1.8, 2.4, and 3.6 m by injecting slurries containing either 0.2 mm diameter  $\text{Fe}^{0}_{(s)}$  particles suspended in guar gum gel or 0.1 - 0.3 mm diameter KMnO<sub>4</sub> particles suspended in a mineral-based gel. The iron-filled fractures formed a discrete reactive seam < 1 cm thick wherein reductive dechlorination could occur, but effects in the adjacent silty clay soils were negligible. However, the permanganate-filled fractures yielded a diffusive reactive zone that expanded over time, covering a thickness of 40 cm after 10 months. Iron from the fractures degraded dissolved TCE at 0.5 and 1 mg TCE per gram of media at efficiencies of 36 % after only 24-48 hrs of contact. The degradation efficiency of TCE in the 40-cm-thick permanganate oxidizing zone was > 99 % after 2 hrs of contact.

#### 5.4.4 Phytoremediation

Phytoremediation refers to the ability of plants to remediate soils by volatilization, extraction, or stabilization. Plants and trees can treat organic pollutants through different mechanisms, including volatilization (transpiration), oxidation, and degradation. For example, one study showed that poplar trees effectively transpired TCE through the leaves and into the atmosphere, with about 10 % of the TCE being oxidized into carbon dioxide in the plant tissue (Matso 1995). In addition, plants have the ability to degrade organic compounds in the rhizosphere (i.e., the soil surrounding the roots).

Plants treat inorganic contaminants, such as metals, through one of three processes (Matso 1995): (1) phytoextraction, (2) phytostabilization, and (3) rhizofiltration. With phytoextraction, plants with high tolerance and accumulation rates for metals (e.g., Ni, Zn, Cd) are used to bring soil contaminants into the shoots where the metals can be harvested. Thus, the plants effectively act as miniature extraction wells. However, some metals, such as lead (Pb), do not effectively translocate to the top of the plant and, therefore, cannot be harvested. The process of phytostabilization involves the use of plants to keep contaminated soil that has previously been stabilized with alkalizing agents, phosphates, mineral oxides, organic matter, and biosolids in place as well as to reduce erosion. Finally, rhizofiltration involves plants that absorb and precipitate metals from solution. For example, one study showed that sunflower roots drastically reduced levels of chromium (Cr), manganese (Mn), cadmium (Cd), nickel (Ni), and copper (Cu) through rhizofiltration (Matso 1995).

Although phytoremediation can play a role in *in situ* remediation, the role currently seems to be limited to relatively shallow depths ( $\leq 2$  m), as a polishing step after the more severely contamination has been treated, or as a long-term solution for more isolated, less contaminated sites. However, research is being conducted to study the effective use of trees to remediate contamination at depths ranging from 6 m to as deep as 14 m, and some studies have indicated that poplars and weeping willows can reach deep aquifers and pump from 190 to 1330 liters per day per tree (Matso 1995).

#### 5.5 In Situ Active Treatment

#### 5.5.1 Immobilization Technologies

#### Stabilization/Solidification

Stabilization and solidification (S/S) methods are intended to immobilize dissolved contaminants and, in certain cases, DNAPLs (Grubb and Sitar 1994). Stabilization refers to techniques that reduce contaminant hazard potential by converting the contaminants to less soluble, mobile, or toxic forms (Conner 1992). Solidification refers to techniques that encapsulate the contaminant in a monolithic solid of high structural integrity (Conner 1992).

*In situ* application of S/S technology typically involves mechanical mixing of the soil with a drilling fluid that carries a S/S reagent, a process commonly referred to as *in situ* soil mixing (e.g., Day and Ryan 1995). The mixing is performed using a crane-mounted high-torque turntable that turns one or more special mixing augers into the soil without excavation. However, jet mixing using the non-replacement jet grouting technique also recently has been used (Day et al. 1997). The field implementation of the technology typically results in an overlapping pattern of large-diameter mixed soil columns (Grubb and Sitar 1995).

The two most common variations of the method are shallow soil mixing (SSM) and deep soil mixing (DSM) (Day and Ryan 1995). Shallow soil mixing typically is employed at depths  $\leq$  10 m using large-

diameter (1 - 4 m) augers. Deep soil mixing is used at depths up to 35 m and employs multiple (2 to 8) augers with smaller diameters (0.8 - 1.0 m).

Common S/S reagents include cement and other pozzolanic materials, such as lime, fly ash, and slag. These reagents typically result in stabilization (fixation) of the contaminants. A relatively recent field study also has shown that DSM using hydrogen peroxide  $(H_2O_2)$  and potassium permanganate (KMnO<sub>4</sub>) as the reagents in the drilling fluid was successful in oxidizing TCE to the required concentrations (Cline et al. 1997).

The S/S method is largely empirical and requires preliminary treatability studies on a case-by-case basis to evaluate the potential success of the selected reagents with the site soils and site contaminants. Also, post-implementation monitoring typically is required to evaluate the success or failure of the process.

#### Vitrification

*In situ* vitrification (ISV) is a thermal process that results in vaporization and mobilization of organic compounds and solidification and immobilization of inorganic compounds (Arman 1992, Grubb and Sitar 1994, 1995, Clark 1998). However, the technology is classified as an immobilization process here since the primary application of the technology historically has been in immobilizing inorganic, radioactive contaminants (Arman 1992).

The ISV process uses a subsurface electrode array to heat the soil to temperatures as high as 1800°C through the application of large currents resulting in melting of the soil. The melting process initiates at the ground surface and propagates downward resulting in vaporization of organic compounds. The vapors migrate to the ground surface and are collected using a vacuum hood. Upon cooling, the remaining contaminants are solidified within a rock-like mass resembling obsidian (Grubb and Sitar 1995).

The process is limited or restricted by the following factors (Arman 1992, Grubb abd Sitar 1995, Clark 1998):

- vitrifiable materials with insufficient glass forming silica to produce a satisfactory solid matrix;
- rubble in the vitrifiable material in excess of 10% by weight;
- groundwater recharge in permeable soils with hydraulic conductivities greater than  $10^{-4}$  cm/s;
- volume of voids of the vitrifiable material in excess of 4.0 to 4.5 m<sup>3</sup>; and
- combustibles in the contaminated material in excess of 5 to 10% by weight.

Finally, the large energy requirements of the process result in very high costs (>  $300 \text{ US/m}^3$ ) which effectively limits the technology to only special cases.

#### 5.5.2 Enhanced Removal Technologies

#### Soil Vapor Extraction

Soil vapor extraction (SVE), also referred to as *in situ* soil venting (SV), couples vapor extraction (recovery wells) with blowers or vacuum pumps to remove vapors from the vadose zone and, therefore, reduce the levels of residual soil contaminants (Johnson et al. 1990). Some SVE systems may incorporate trenches, air injection wells, passive wells, and surface seals.

Schematic cross-sections of three scenarios depicting the use of SVE to remediate volatile contaminants in the vadose zone are shown in Figs. 28, 29, and 30. The basic scenarios for vapor flow through and over the contaminated zones are shown in Figs. 28 and 29. The scenario in Fig. 30 pertains to the case whereby vapor flow is used to remove contamination from a low-permeability medium. In each case, liquid-phase-to-gas-phase partitioning of the contaminant (i.e., volatilzation) is enhanced as air is drawn towards the extraction well. Thus, the primary pathway for contaminant removal is via vapor flow, and the air permeability of the soil is a major factor affecting the efficiency and ultimate success or failure of SVE.



Figure 28 : SVE scenario for vapor flow through contaminated zone (from Johnson et al. 1990).



Figure 29 : SVE scenario for flow parallel to contaminated zone [ $c_g$  = gas-phase concentration] (from Johnson et al. 1990).



Figure 30 : SVE scenario for vapor flow above contaminated low-permeability soil (from Johnson et al. 1990).

A number of system variables affect the choice and efficiency of SVE as an *in situ* remediation technology, including the contamination volume, the depth to ground water, soil heterogeneity, contaminant location and area development, site soil characteristics, chemical properties, operating variables, and response variables (Hutzler et al. (1990). In general terms, SVE tends to be a more viable option (1) as the volume of contamination and the depth to groundwater table and corresponding depth of contamination increase, (2) when heterogeneity is in the form of horizontally stratified soils, (3) when the contamination extends across property lines, (4) when the soil is relatively dry, (5) when the Henry's Law constant of the chemical is greater than 0.01 or vapor pressure is greater than 25.4 mm of mercury, and (6) as the air flow rate increases. Some conditions at typical vapor extraction sites are summarized in Table 12.

Pneumatic fracturing recently has been used to enhance the removal of VOCs in low permeability media (e.g., clay formations) using SVE (Ding et al. 1998). Pneumatic fracturing involves injecting high-pressure, clean air into the subsurface in a controlled manner to create fractures and increase formation permeability. Ding et al. (1998) report achieving good results from the process for two field studies involving the removal of methylene chloride, 1,1,1-trichloroethane (TCA), TCE, and toluene.

Table 12. Conditions at typical SVE sites (after Hutzler et al. 1990).				
	Site No.			
Parameter	1	2	3	4
Soil type	S/M/G	S	CS	S
GW depth (m)	73	12 - 13	15 -16	> 9
Contaminant vol. (m <sup>3</sup> )	>113	$> 11 \text{ x } 10^3$	?	$> 10 \text{ x } 10^3$
Contaminant type(s)	DCP	A, K, T, X	G	OS
Fresh-air source	Inlet vents	Inlet vents	Surface	Surface
Blowers	3	8	1VP	1
Total flow (m <sup>3</sup> /min)	2.4 - 7.1	?	?	5.9
Initial mass (kg)	$200 \times 10^3$	?	?	?
Mass extracted (kg)	$200 \times 10^3$	$> 170 \text{ x } 10^3$	$>48 \times 10^3$	> 520
Operation (months)	7	>5	7	?

Table 12 : Conditions at typical SVE sites (after Hutzler et al. 1990).

Notes: Soil type: S = sand, G = gravel, M = silt, CS = clayey sand; Contaminant type: DCP = dichloropropene; A = acetone, K = ketone, T = toluene, X = xylene, G = gasoline, OS = organic solvents; VP = vacuum pump

Soil vapor extraction often is used in conjunction with other technologies. For example, SVE may be used in conjunction with pumping to access contamination below the water table. Also, SVE may be used in conjunction with air sparging (AS) to remove contaminants that have migrated into the vadose zone from the AS process.

#### Air Sparging

Air sparging (AS), also known as *in situ* air stripping or *in situ* volatilization, is effective in removing SVOCs and VOCs. As illustrated in Fig. 31a, AS involves injecting air into the contaminated aquifer below the water table. The AS process cleans the contaminated groundwater zone through two processes. First, injection of the air creates a turbulent condition that enhances volatilization of the contaminants. The injected air also may result in a mounding of the water table near the well that may result in migration of contaminants away from the well. Second, the injected, or sparged, air increases the oxygen content of the ground water enhancing aerobic biodegradation of the contaminants.

Air sparging is effective in removing volatile contaminants from highly permeable and homogeneous soils. Homogeneous soils that exhibit anisotropy with the horizontal permeability being greater than the vertical permeability tend to enhance the distribution of the sparged air and enhance the removal efficiency (Clark 1998). However, like most *in situ* treatment technologies, the existence of heterogeneities in the soil tends to reduce the efficiency of the process.



Figure 31 : Schematic diagram of air injection well for *in situ* air sparging: (a) general concept; (b) channeling of bubbles.

Also, as shown in Fig. 31b, the air bubbles typically tend to channel through the soil rather than disperse uniformly reducing the effective exposure of the bubbles and, therefore, the overall efficiency. The process of pulsing the injected air by periodically starting and shutting down the system has been proposed as a method to affect the spatial and temporal distribution of the air channels and improve the removal efficiency. However, laboratory studies indicate the pulsing may not improve the overall removal efficiency relative to continuous air injection, but pulsing does result in substantial reduction in system operating time and, therefore, potential cost (Reddy and Adams 1997).

Nonetheless, AS may be more feasible and more cost effective than other *in situ* treatment processes. For example, at a clean-up site in Carson, CA, air sparging was found to be more cost effective and easier to permit than *in situ* bioremediation even though the microorganisms already were sufficiently present in the ground water (Abbasi 1996). As a result, air sparging was selected as the preferred technology, with an estimated clean-up time for the contaminated ground water of five years.

#### Soil Flushing

Soil flushing (SF) may be defined as the enhanced *in situ* mobilization of contaminants in contaminated soil for recovery and treatment (Anderson 1993). Although the terms *soil flushing* and *soil washing* often are used interchangeably to describe the same technology, the term *soil flushing* generally is used in connection with *in situ* remediation, whereas the term *soil washing* is reserved for *ex situ* remediation.

Soil flushing is used to accelerate one or more of the following geochemical reactions that alter contaminant concentrations:

- adsorption/desorption,
- acid/base,
- dissolution/precipitation,
- oxidation/reduction,
- ion pairing or complexation, or
- biodegradation.

Soil flushing also is used to accelerate subsurface contaminant transport mechanisms found in conventional groundwater pumping, such as advection, mechanical dispersion, diffusion, and depletion via volatilization and solubilization.

Soil flushing is most effective in homogeneous, permeable soils such as sands and silty sands. Soil flushing may be used for organic, inorganic, and radioactive contaminants depending on the matrix.

Flushing fluids may be water, enhanced water, and gaseous mixtures. Typical soil flushing solutions include water, dilute acids and bases, complexing and chelating agents, reducing agents, solvents, and surfactants. The fluids are introduced through spraying, surface flooding, subsurface leach fields, and subsurface injection. A schematic illustration of the use of an injection-withdrawal well system for soil flushing is given in Fig. 32.

Soil flushing component activities include (Anderson 1993)

- site characterization (most effective in homogeneous, permeable sand  $(k > 10^{-4} \text{ cm/s}))$ ,
- injection (surface water flooding, surface sprinklers, leach fields, septic tanks, wells, trench infiltration systems), and
- contaminant mobilization and recovery techniques.

The effectiveness and rate of clean-up are site- and contaminant-specific and are assessed based on (a) laboratory tests (column and batch), (b) field tests, and (c) contaminant transport models. Transport heterogeneities and anisotropy (e.g., rock fractures) are the main limitations.



Figure 32 : Schematic illustration of use of injection/withdrawal system for soil flushing indicating polluted aquifer before remediation and propagation of injected 'cleansing' front after remediation has bugun.

Several relatively recent studies have evaluated the use soil flushing, for removing contaminants from polluted sites (Fountain et al. 1991, O'Neill et al. 1993, Augustijn et al. 1994, van Benschoten et al. 1994, Davis and Singh 1995, Gabr et al. 1995a,b, and Ozsu-Acar et al. 1995, Grubb et al. 1997, and Jawitz et al. 1997). These studies have included evaluation of a number of different extracting solutions (e.g., water, strong acids, chelating agents, surfactants, cosolvents) for removing a number of different contaminants (e.g., metals, radioisotopes, organic solvents) from soils with different properties.

#### **Steam Injection**

In steam injection (SI) technology, also referred to as dynamic underground stripping, or DUS (Yow et al. 1995), steam is injected into the subsurface through a ring of injection wells configured to surround all or part of the subsurface plume to be treated. Liquid and vapor are extracted from one or more wells located near the center of the well pattern while steam is injected into the permeable layers through screened portions of wells constructed around the plume. The steam flood directly heats contaminated permeable

layers in the process zone to lower the viscosity and increase volatility of the contaminants. The contaminants are swept towards the extraction wells as ground water is displaced in advance of the injected steam front.

Thermal conduction of less permeable layers adjacent to the more permeable layers is enhanced by electrical resistance heating using electrodes attached to the injection well in zones of low permeability. Monitoring for operational safety and process control also is an essential part of DUS since large amounts of thermal energy are injected into the subsurface. Monitoring includes tiltmeter measurements, borehole temperature logging, and geophysical underground imaging (tomography) to monitor soil mass deformation, temperature, and *in situ* saturation. A schematic of a DUS system is shown in Fig. 33.



Figure 33 : Schematic diagram of dynamic underground stripping (DUS) system (after Yow et al. 1995).

#### **Radio Frequency Heating**

Radio frequency heating (RFH) involves the use of electromagnetic energy to vaporize hydrocarbons in soil (Dev and Downey 1988). The method involves using a system of electrodes implanted in vertical and/or horizontal holes drilled into the soil. Electromagnetic energy in the radio frequency band is generated using a modified radio transmitter and directed from the electrodes into the ground to heat the soil to a predetermined temperature to volatilize trapped hydrocarbons.

The RFH technique relies on molecular agitation, rather than thermal conduction, to heat the soil in the same way that a microwave oven heats food. However, the frequency of operation in RFH is about 100 times lower than that in microwave heating resulting in an energy penetration of several meters into soil in RFH, i.e., versus the several centimeters of energy penetration into food with microwave heating (Bowders and Daniel 1997). The frequency of operation is based upon the dielectric properties of the soil matrix and the size of the area requiring treatment. Vaporized contaminants and soil moisture are vented to a surface vapor barrier and condensed for subsequent disposal or incineration on site.

Reported advantages of RFH relative to other enhanced removal techniques, such as soil flushing and soil venting, are (1) a greater enhancement of soil venting through increased volatility and more rapid desorption, (2) a more complete decontamination of the heated zone due to more uniform heating, (3) an increase in gas-phase permeability due to vaporization and removal of soil moisture resulting in more uniform movement and collection of volatilized contaminants, and (4) enhanced desorption of adsorbed contaminants through steam distillation (Dev and Downey 1988).

Dev and Downey (1988) describe a pilot test program at Volk Field Air National Guard Base, Camp Douglas, Wisconsin, using RFH to remove contaminants from 14.2  $\text{m}^3$  (1.83 m x 3.66 m x 2.13 m) of soil in an abandoned fire training pit. The fire pit was contaminated over a 25-yr period with petroleum hydrocarbons resulting in an average concentration of 4,000 mg/kg. The soil in the fire pit was heated by

inserting 3 rows of electrodes with 13 electrodes per row. The initial radio frequency power level was 35 kW supplied at a frequency of 6.78 MHz. This power level and frequency were maintained for a period of 4 days during which most of the water boiled out of the heated zone. After this initial period, the power level was reduced to 20 kW for the remaining 8 days of the test. The heating system raised the soil temperature to between 150  $^{\circ}$ C and 160  $^{\circ}$ C during the first 8 days of the test. This temperature was maintained over the final 4 days of the test.

The efficiency of the RFH process was evaluated by comparing analyses of soil samples collected before and after the test at various depths within the heated zone. The results, summarized in Table 13, show very high removal efficiencies for SVOCs and VOCs, with the removal efficiencies for the VOCs being slightly higher. In addition, most of the moisture initially present in the soil was vaporized. Finally, the lower removal efficiency for the hexadecane relative to the VOCs and SVOCs was attributed to the high boiling point of hexadecane. Dev and Downey (1988) indicate that the removal efficiency of hexadecane probably would have been increased with a higher temperature and/or a longer test duration.

Cuird Duse, Cuirip Dougrus, (11 (from Dev and Downey 1900).			
Volatility	Category	Efficiency (%)	
Volatile <sup>(1)</sup>	Moisture	97.2	
SVOCs	Aliphatics	94.3	
	Aromatics	99.1	
	Hexadecane	82.9	
VOCs	Aliphatics	99.3	
	Aromatics	99.6	

Table 13 : Removal efficiencies for RFH for depths from 15 cm to 1.65 m at the Volk Field Air National Guard Base, Camp Douglas, WI (from Dev and Downey 1988).

<sup>(1)</sup>Based on saturated vapor pressure of water at 20  $^{\circ}$ C of 2.3 x 10<sup>-2</sup> atm (Fredlund and Rahardjo 1993).

#### **Electrokinetics**

As illustrated in Fig. 34, electrokinetics (EK) involves the use of an applied electrical gradient to speed the removal of contaminants from contaminated, low-permeability, fine-grained soils (e.g., Shapiro and Probstein 1989, Pamukcu et al. 1990, Alshawabkeh and Acar 1992, Acar and Alshawabkeh 1993, Pamucku and Wittle 1993, Eykholt and Daniel 1994, Yeung 1995, and Alshawabkeh and Acar 1996).



Figure 34 : Schematic of electrokinetic remediation set-up (after Acar and Alshawabkeh 1993).

In general, application of the electrical current results in generation of protons  $(H^+)$  at the anode, due to hydrolysis reactions, that migrate together with the metal cations to the negatively charged cathode for removal and processing. In addition, the migrating metal ions (cations) result in bulk water flow from the anode to the cathode, a process referred to as electro-osmosis.

The results of a pilot-scale test involving electrokinetic extraction of Pb from a spiked kaolinite-sand mixture reported by Alshawabkeh and Acar (1996) are shown in Fig. 35. The results in Fig. 35 indicate that the lead concentrations after EK processing for 50 days are reduced everywhere in the soil except near the cathode where slightly elevated Pb concentrations occur. This trend is typical and results primarily from the existence of acidic conditions (low pH) near the anode and basic conditions (high pH) near the cathode, and the greater mobility of hydrogen ( $H_3O^+$ ) relative to hydroxide (OH) resulting in a precipitation front near the cathode. Differences between the model predictions and measured concentrations were attributed to development of a zone of low electrical conductivity near the cathode after ~25 days of processing, the two-dimensional nature of the test near the soil surface, and the potential for lead complexation and sorption near the cathode.



Figure 35 : Comparison of measured and predicted Pb removal from a pilot-scale test using the electrokinetic remediation process (after Alshawabkeh and Acar 1996).

#### 5.5.3 Bioremediation

Bioremediation may be defined as the process where a biological agent (e.g., bacteria, fungi, plants, enzymes) is used to reduce contaminant mass and toxicity in soil, groundwater, and air. The goal of bioremediation is to reduce toxicity and target contaminant concentrations in water and/or soil through either biodegradation (of organics) or biotransformation (of metals).

Biotransformation is a general term representing any biologically catalyzed conversion of a metal or organic chemical. Biodegradation refers to a single biological reaction or sequence of reactions that result in the conversion of an organic substrate to a simpler molecule. Mineralization, or complete biodegradation, refers to conversion of the target compound to carbon dioxide and water under aerobic conditions, or methane (or ethane or ethene) under anaerobic conditions. Biotransformation and biodegradation of a contaminant do not necessarily result in a decrease in toxicity.

Bioremediation results in degradation of contaminants, as opposed to relocation of contaminants, typically at relatively low cost. Thus, biodegradation is a popular alternative to the other treatment technologies. However, biological approaches for detoxification of certain types of contamination (e.g., metals, high levels of organic compounds, and mixtures of different groups of pollutants) have yet to be developed or field tested. In fact, these situations are problematic for most currently used remediation technologies. Since these types of contamination are commonly found at Superfund sites, cost-effective solutions for truly remediating the contamination have not been possible.

Organic pollutants can be used in microbial metabolism as electron donors or acceptors, and as sources of carbon, nitrogen, sulfur, etc. for growth. Hydrocarbons, including those with relatively few chlorine substituents, act as sources of carbon and energy (electrons) by microorganisms that use oxygen, nitrate, sulfate, or other electron acceptors. Other bacteria ferment (substituted) hydrocarbons, producing hydrogen, carbon dioxide, and organic acids. The reductive dehalogenation of chlorinated alkanes and alkenes, polychlorinated biphenyls (PCBs), and other chlorinated hydrocarbons has been documented in laboratory and field studies. The primary factors affecting bioremediation processes are summarized in Table 14.

Table 14. Factors affecting bioremediation processes (modified from Loehr 1993).		
Factor	Comment(s)	
Microorganisms	Natural organisms are satisfactory	
	Acclimation may be necessary	
	Suitable environmental conditions need to be provided	
Toxicity	Need non-toxic conditions	
Available water	25 – 85 % of water holding capacity desirable for solid-phase systems	
Oxygen (O <sub>2</sub> )	Aerobic conditions desired	
Electron acceptors	$O_2$ (aerobic conditions); $NO_3^-$ , $Fe^{3+}$ , $Mn^{2+}$ , and $SO_4^{-2-}$ otherwise	
pH	5.5 – 8.5 (optimum degradation)	
Nutrients	N, P and other nutrients needed for microbial growth	
Temperature	Affects degradation rates	

Implementation of *in situ* bioremediation can take the form of several technologies, including bioventing, biosparging, infiltration galleries, and bioslurping. Bioventing (BV) is the transfer of oxygen (air) in the vadose zone to enhance aerobic biodegradation of hydrocarbons. Although similar to SVE, BV uses lower air flow rates to stimulate microbial activity without volatilizing the contaminants. The soil moisture and nutrient levels must be managed to maintain high biodegradation rates.

An example of the use of BV for the remediation of soils contaminated with diesel fuel hydrocarbons is reported by Gupta and Marshall (1997). In this case, the BV operations consisted of injecting air periodically (weekly or biweekly), a process referred to as biopulsing, and monitoring the subsurface oxygen levels using *in situ* oxygen sensors.

Biosparging (BSP) is the process whereby air, nutrients, and other essential components for biodegradation are injected into the saturated zone. Infiltration galleries simply supply the nutrients, electron acceptors, microorganisms, etc., via infiltration from some surface source (e.g., gravel-filled trench) into the vadose zone.

Bioslurping (BSL) involves placing an extraction well at the interface between the liquid phase, typically an LNAPL, and the gas-phase of the vadose zone. The LNAPL is drawn up through the well by applying a vacuum and, in the process, aeration is enhanced resulting in the promotion of aerobic biodegradation.

#### 5.6 Combined In Situ Technologies

In practical applications, most of the individual containment and treatment technologies are used in combination with one or more other containment and/or treatment technologies (e.g., Blowes et al. 1995, Cagle et al. 1997, Gwinn and Read 1997, Wessley 1997). Some examples of these applications follow.

#### 5.6.1 Funnel-and-Gate System

As shown schematically in Fig. 36, a highly permeable reactive wall (HPRW) may be combined with a low permeability, passive or active containment barrier to direct or funnel the contaminant plume through the HPRW. This concept is referred to as the 'funnel-and-gate' approach (e.g., Blowes et al. 1995). The HPRW may contain several treatment cells to progressively treat a plume containing one or more different COCs. In the case of the funnel-and-gate system, the design must include consideration of the factors affecting the performance of not only the HPRW (e.g., choice of treatment media, length of treatment zone) but also the containment barrier (e.g., permeability, compatibility, thickness, etc.). Integration of the reactive gate with the barrier can be an important design issue and has led to the use of *in situ* reaction chambers contained within cement-bentonite slurry trench cut-off walls (Jefferis et al. 1997).



Figure 36 : Schematic plan (aerial) view of funnel-and-gate system with multiple gate system for treating complex contaminants (modified after Blowes et al. 1995).

#### 5.6.2 Combined AS and HPRW

The use of air sparging (AS) in highly permeable reactive walls (HPRW) has been proposed (Pankow et al. 1993). The process involves injecting air through a perforated pipe placed horizontally along the bottom of a treatment trench that is backfilled with a highly permeable medium, such as sand or gravel. As the contaminant plume migrates through the trench, the injected air volatilizes the contaminants, and resulting vapors are collected at the ground surface in a vapor hood.

Although conceptually enticing, this approach does not seem to have been adopted readily. One inherent problem with this process is that entrapment of injected air may effectively reduce the hydraulic conductivity of the trench medium resulting in a reduction in the flow rate.

#### 5.6.3 Enhanced SVE with Pumping

As previously indicated, SVE often is used in combination with pumping to enhance removal of both volatile contaminants below the original ground water table via SVE and liquid-phase contaminants via traditional pump and treat (e.g., Gwinn and Read 1997). A schematic of this combined approach is shown in Fig. 37.

Hoffman (1998) describes a case involving groundwater extraction using two horizontal wells in conjunction with soil venting near the source of the groundwater plume. The plume consisted of solvents and VOCs, including TCE and 1,2-dichloroethene, and some fuel, and was located within a thin (1.5 m to 2.4 m) saturated zone at a shallow (1.5-m) depth. The horizontal wells act as a dewatering system draining the saturated zone surrounding the contaminant and drawing ground water to the middle of the site. Remediation of the drawndown area then is carried out via SVE. The operation is still ongoing.

Two-phase vapor extraction (TPVE) is a process similar to SVE, but involves the removal of both gasand liquid-phases simultaneously from a single well screened in both the vadose zone and the saturated zones (Lindhult and Kwiecinski 1996). The process uses equipment similar to SVE, but requires a greater vacuum to remove contaminants and achieve hydraulic control in low-permeability soils at 6 m below ground surface or deeper.



Figure 37 : Schematic diagram illustrating enhancement of SVE below the groundwater table through pumping.

#### 5.6.4 Combined AS and SVE

As a result of the need to collect the vapor, air sparging (AS) commonly is used in conjunction with soil vapor extraction (SVE) as illustrated schematically in Fig. 38. The sparging process results in volatilization of the liquid-phase contaminants beneath the water table into the bubbles that subsequently are 'buoyed' to the vadose zone and collected through the vacuum extraction wells. Also, vapors resulting from liquid-phase to gas-phase partitioning at the interface between the saturated and vadose zones are removed through the extraction wells. An exmaple of the use of AS and SVE is described by Simon (1997).



Figure 38 : Schematic illustration of a combined AS/SVE system.

#### 5.6.5 Enhanced SVE/AS With RFH

Several pilot and field studies have been performed to evaluate the use of radio-frequency heating (RFH) to enhance removal of volatile organic compounds via soil vapor extraction (SVE) or air sparging (AS). For example, Bowders and Daniel (1997) describe a field demonstration involving enhanced SVE removal of petroleum hydrocarbons using RFH. The radio frequency energy is supplied through applicators positioned in vertical wells on either side of centrally located extraction well. Temperatures in the center of the treatment zone reached 140 °C, whereas temperatures at the treatment perimeter (2-m radius) reached 100 °C to 120 °C. The process resulted in removal of 65 kg of petroleum hydrocarbons in the first 77 days of operation.

Kasevich et al. (1997) describe the results of a field demonstration and a bench-scale study to evaluate enhancement of combined SVE/AS removal using RFH. A remotely operated, computer-controlled RFH system was used to supply  $8.28 \times 10^6$  kJ (2,300 kW-h) of radio frequency energy to a BTEX contaminated site over a three-week period. The RFH system significantly increased the removal rate of the BTEX compounds during this period relative to the baseline (ambient temperature) removal rate.

#### 5.6.6 The Lasagna Process

The Lasagna process involves the combination of passive treatment zones and electro-osmotic flow to treat low-permeability deposits, such as clay lenses. A schematic of the horizontal configuration for the Lasagna process is shown in Fig. 39. The low-permeability medium is fractured hydraulically, the inner fractures are filled with a treatment substance (e.g., iron filings, oxidant, microbes, etc.) to create a treatment zone, and the outermost fractures are filled with a granular electrode. This process was named the 'Lasagna process' because the layered structure of the treatment zone and electrodes in the horizontal configuration resembles the layering of pasta in the Italian food dish known as *lasagna*.

A vertical configuration for the Lasagna process also has been developed (Austin 1995). In this case, wick drains inserted using sheet piling methods have been used to establish the treatment zone. The vertical configuration has been installed and tested at a site consisting of clay soil contaminated with TCE at the US Department of Energy's Paducah, KY, Gaseous Diffusion Plant.





#### 5.6.7 Biowalls

Biowalls (BWs), also referred to as permeable reactive biowalls (PRBs) or in line microbial filters, are essentially *in situ* bioreactors or highly permeable reactive walls (HPRWs) that treat contaminants passively

through either biostimulation or bioaugmentation. For example, field testing has been proposed to evaluate the potential for passive bioremediation of BTEX and TCE (Gillham and Burris 1992, Barker et al. 1994, Smyth et al. 1994). Much of the effort has been directed toward the use of oxygen and/or nutrient sources as reagents in BWs to stimulate the activity of indigenous microorganisms (e.g., Gillham and Burris 1992, Bianchi-Mosquera et al. 1994). However, the concept of adding a selected, non-indigenous bacterial population to bioaugment HPRWs has been implemented in some studies (e.g., Burris and Cherry 1992, Kuyucak and St-Germain 1994, Smyth et al. 1994, Eykholt and Sivavec 1995, Thomas and Ward 1995).

For example, Blowes et al. (1994) describe the use of in-line bioreactors for facilitating anaerobic denitrification of agricultural derived nitrate ( $NO_3$ <sup>-</sup>). Oxygen reduction and denitrification were enhanced by providing a source of organic carbon (tree bark, wood chips, and leaf compost) for the facultative heterotrophic bacteria in the bioreactors. The bioreactors were successful in reducing  $NO_3$  - N concentrations ranging from 3 to 6 mg/L to less than 0.02 mg/L at rates ranging from 10 to 60 L/day over a 1-yr period. Blowes et al. (1994) conclude that similar organic-carbon amended bioreactors should be effective in treating other redox sensitive contaminants such as As, Se, and Cr.

Bioaugmented BWs are attractive in situations where (1) the activity of indigenous microorganisms is not sufficient to achieve the required contaminant removal, or (2) the metabolic pathway for the contaminant may be undesirable with the indigenous population (Malusis and Shackelford 1997). With respect to the latter situation, anaerobic reductive dechlorination of TCE by methanogenic cultures results in the production of vinyl chloride (VC), a very toxic compound, whereas biodegradation of TCE by *Pseudomonas cepacia* PR1 occurs under aerobic conditions without the generation of VC.

#### 5.6.8 Electrokinetics-Enhanced Bioremediation

In low-permeability deposits, the application of an electrical potential across the deposit induces the movement of water (electro-osmosis) and charged particles, a process referred to as electrophoresis (e.g., Mitchell 1993). These electrokinetic (EK) phenomena can be used to deliver nutrients, electron acceptors, cometabolic substrates, and microorganisms into low-permeability deposits to promote bioremediation within the deposit. Joule heating resulting from the application of the electrical current, also has been shown to promote bioremediation.

#### 5.7 Costs of Technologies

Several references have reported cost comparisons for various *in situ* remediation technologies. Three of these cost comparisons are provided in Fig. 40, Table 15, and Table 16 reported in 1997, 1995, and 1999, respectively.



Figure 40 : Estimated cost ranges of metals remediation technologies. [CT = containment, S/S = stabilization/solidification; V = vitrification; SF = soil flushing.] (Source: EPA/540/S-97/500).

The cost comparisons shown in Fig. 40 and Tables 15 and 16 were presented in different contexts. The costs reported in Fig. 40 were presented only in the context of metals remediation. However, electrokinetics (EK) is not included in Fig. 40 since the EK technology had not been demonstrated at full scale in the US for metals remediation at the time of the referenced study. The costs shown in Table 15 were presented only in the context of DNAPL remediation. Finally, the costs shown in Table 16 were presented with respect to Brownfields remediation regardless of type of contaminant.

Table 15. Cost comparison of selected in situ technologies (modified after Grubb and Sitar 1995)		
Technology ( $C = containment; T = treatment$ )	$\sim \text{Cost} (\text{\$US/m}^3)$	
Bioremediation (T)	20-80	
S/S–Shallow Soil Mixing (T)	35-85	
Permeable Reactive Walls (T)	65-130	
Water Flooding (T)	65-130	
Soil Vapor Extraction (T)	65-130	
Steam Injection (T)	65-160	
Slurry Walls (C)	75-140/m <sup>2</sup>	
Grouting (C)	80-130	
Radio Frequency Heating (T)	85-210	
Soil Flushing (T)	100-160	
Air Sparging (T)	100-160	
Electro-osmosis (T)	100-200	
Electrokinetics (T)	> \$17/Mg	
S/S–Deep Soil Mixing (T)	170-340	
Vitrification (T)	525+	

Other differences in the cost comparisons are that (1) only treatment technologies are included in Table 16, whereas both the containment and the treatment options are evaluated in Fig. 40 and Table 15, and (2) the units for comparing the costs vary.

Table 10. Cost comparison of <i>in still</i> treatment teenhologies (after Reddy et al. 1999).		
~ Cost (\$US/Mg)		
30-340		
55-110		
100-140		
< 110		
< 110		
$105-215/m^2$		
130-200/m <sup>2</sup>		
385-990		

Table 16 : Cost comparison of *in situ* treatment technologies (after Reddy et al. 1999).

Despite these variations, the following general conclusions can be drawn:

- bioremediation tends to be the cheapest technology;
- vitrification tends to be the most expensive technology;
- stabilization/solidification, especially with respect to deep soil mixing, is relatively expensive;
- containment is the cheapest technology for metals remediation; and
- the costs associated with most of the *in situ* enhanced removal technologies vary by only a factor of ~ 2.

#### 6.0 ROLE OF GEOTECHNICAL ENGINEERING?

A subjective assessment of the role of geotechnical engineering and geotechnical engineers with respect to the *in situ* remediation techniques outlined in Table 8 is provided in Table 17.

Geotechnical engineers currently play a significant role in the remediation process in terms of site characterization and monitoring as a result of past experience with these two areas of endeavor. Thus, geotechnical engineers will continue to play some role, albeit a minor one in several cases, with every remediation technique. In addition, geotechnical engineers have considerable experience in the design and construction of the more traditional *in situ* containment systems, such as slurry cutoff walls, and caps, and, therefore, typically can contribute significantly to the *in situ* containment techniques.

Category	Technique	Probable Role
Containment	Capping/Covers Significant	
	Vertical Barriers	Significant
	Horizontal Barriers	Intermediate
	Pump & Treat	Minor
	Reactive Barriers	Minor to Significant
Treatment	Monitored Natural Attenuation (MNA)	Minor
	Reactive Walls	Minor to Intermediate
	Horizontal Treatment Zones	Minor to Intermediate
	Phytoremediation	Minor
	Immobilization	Significant
	Enhanced Removal	Minor to Intermediate
	Bioremediation	Minor

Table 17 : The role of geotechnical engineers with respect to various in situ remediation techniques.

However, geotechnical engineers frequently are limited in their capability to contribute significantly to the treatment technologies due to a lack of formal education in the necessary chemical and biological fields. Nonetheless, the involvement of geotechnical engineers in these treatment techniques is increasing as more geotechnical engineering students and practitioners make the effort to formalize their education and understanding in these other non-traditional, but important subjects.

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