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Revision Memo

- 12/01** Discussion of Reaction Walls has been enhanced to include latest developments. Additional information to allow this technology to be considered and designed for ground-water remediation is provided. Discussion of technologies for Free-Phase Hydrocarbon (NAPL) Recovery has been removed, as this is now documented in DP XX-B6.

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SCOPE

This Design Practice provides information on the technical, implementation, and economic feasibility of various ground water remediation technologies. Only those technologies that are proven or are in the late stages of development are discussed. Emerging technologies or those at early stages of research and development are not discussed.

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[Section XX-B6](#) Free-Phase Hydrocarbon Recovery

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DEFINITIONS

Air Sparging - A remedial method which uses air injected below the water table through wells to volatilize hydrocarbons and provide an oxygen source for bioremediation. When air rates are maintained low enough such that only bioremediation, not volatilization, is occurring, the process is called **Biosparging**.

Anisotropy - Having physical properties which vary with direction.

Aquifer - A layer of underground soil or rock in which water collects in quantities sufficient for yields in wells or springs.

Bentonite - A low permeability colloidal clay, made up of the mineral sodium montmorillonite (a hydrated aluminum silicate); used as a surface sealant in well bores and in barrier walls.

Bioremediation - The breakdown of contaminants into by-products through biological processes, particularly microbial metabolism. Also "Biodegradation." Additional information on bioremediation is available in [Design Practice XX-C1](#).

BTEX - Benzene, Toluene, Ethylbenzene, Xylenes.

Capillary Fringe - The zone at the bottom of the vadose zone where ground water is drawn upward by capillary forces. Within the capillary fringe there is a gradual decrease in moisture content with height above the water table.

Cometabolite - A secondary substance which serves as an energy or carbon source during the metabolic transformation of the primary substance.

DNAPL - Dense Nonaqueous Phase Liquids. Organic liquids with densities greater than water that exist as a separate immiscible phase and tend to accumulate below the water surface at physical barriers (e.g., low permeability strata).

Emulsion - A stable suspension of one liquid in a second immiscible, continuous phase liquid, typically containing surfactant and a high percentage of dispersed phase.

Ex Situ - Processes conducted at or above the ground surface.

Hydraulic - A process operated by a fluid under pressure.

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DEFINITIONS (Cont)

gpm - Gallons per minute. A measure of volumetric fluid flow rate.

HDPE - High Density Polyethylene.

Hydraulic Conductivity - A physical property of soil that describes the flow rate of a fluid such as ground water or air, through the soil matrix. Values on the order of 10^{-4} cm/s (cm per second) and greater indicate a highly conductive soil.

In Situ - Processes conducted in or below the ground surface.

LNAPL - Light Nonaqueous Phase Liquids. Organic liquids with densities less than water that exist in a separate, immiscible phase and tend to accumulate on the water surface.

Natural Attenuation - Natural processes such as biodegradation, dispersion, dilution, volatilization, hydrolysis, and adsorption which result in the degradation and attenuation of chemical contaminants in the environment.

Oil/Water Separator - Equipment used to separate the free-phase hydrocarbons from the water in the fluids recovered from the subsurface. Simplest form is a settling tank in which the liquids separate naturally over a period of time.

Oleophilic/Hydrophobic Membrane - A membrane that has an affinity for oil and repels water.

Permeability - A measure of the ability of soil to transmit fluid.

Piezometer - A non-pumping well, generally of small diameter with a short well screen, that is used to measure the elevation of the water table.

Pneumatic - A process using compressed air.

psi - Pounds per square in. Measurement of pressure.

PVC - Polyvinyl Chloride. A rigid plastic used for well and remediation system piping.

Residual LNAPL - LNAPL that is adsorbed to soil particles and thus does not flow.

scfm - Standard cubic ft per minute. Volumetric rate of flow. Standard conditions are air at 1 atmospheric pressure, 36% relative humidity, and 68°F (20°C) having a specific weight of 0.075 lb/ft³ (1.2 kg/m³).

Smear Zone - Depth in the soil profile in which residual hydrocarbons are adsorbed to soil particles due to water table fluctuations.

Surfactant - A substance capable of reducing the surface tension of a liquid in which it is dissolved. Used to improve surface wetting of soil particles and emulsify hydrocarbons.

Unsaturated Zone - Subsurface soil or bedrock, typically above the water table, in which some pore spaces and fractures are not completely filled with ground water.

Vadose Zone - The zone of soil between the water table and the ground surface that includes the unsaturated zone and saturated soil in the capillary fringe.

VOCs - Volatile Organic Compounds. Organic compounds that have a low boiling point or that evaporate readily under typical environmental conditions.

Volatile - Describes a constituent that evaporates readily under normal pressures and temperatures. This process is referred to as "volatilization."

INTRODUCTION

This design practice is organized in the following manner. A description of the criteria that needs to be considered in the selection of a remedial technology is presented in the following section. The following information is presented in sections **In Situ Technology** and **Ex Situ Technology** for selected **In Situ** and **Ex Situ** remedial technologies: an overview of the technology, applicability, limitations, design considerations, and costs. Costs are generally based on 1998 U.S. dollars.

While the primary focus of this design practice is the treatment of ground water, it is important to note that an overall remediation approach almost always involves addressing contamination associated with soils above the water table as well as identification and removal of source materials. This design practice does not address soil remediation or source removal since these topics are discussed in other design practices and technical reports. In addition, one technology should not be regarded as the only solution in many cases. Typically, a combination of technologies will be required to remediate a site. The information contained within this design practice is based on the most recent industry and ExxonMobil experiences. It should also be emphasized that field pilot studies provide valuable information for assessing remedial effectiveness and determining optimal operating parameters for the technology application, and are often a necessary part of technology selection.

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CRITERIA FOR REMEDIAL TECHNOLOGY SELECTION

Selection of a ground water remediation technology is a site-specific process that must account for subsurface characteristics, type of contaminant detected, regulatory requirements and constraints, economic criteria, remedial time objectives, site-specific risks to human health and the environment, and legal issues. In some instances, a site may have one or two contaminants of concern with few potential receptors and impacts limited to a defined area. Under those circumstances, technology selection may be straightforward: a candidate technology can be identified on the bases of successful experience at similar sites. For other cases, such as former manufacturing sites or sites with complex hydrogeology, a comprehensive technology assessment program may be needed. **Figure 1** is a diagram of criteria necessary to evaluate remedial technology selection.

Prior to initiating any remedial effort, the end objectives or clean-up goals should be established. Once these clean-up objectives have been determined, the next step is selection of a basic remediation approach using **Ex Situ** technology, **In Situ** technology, or a combination of both. **In Situ** technologies try to take advantage of subsurface characteristics to treat ground water in the ground. **Ex Situ** technologies incorporate some form of extraction and treatment (water is pumped from the ground and brought to the surface for treatment). As seen in **Figure 1**, there are several considerations that will guide the choice of the basic remediation approach:

1. Subsurface Characteristics

Geological and hydrogeological characteristics of the site will have an impact on the remedial technology selected. For example, soil with intrinsic conductivities of 0.1 darcy or greater (hydraulic conductivities of greater than roughly 10^{-4} cm/sec) may favor **In Situ** approaches.

2. Type of Contaminant

Remedial technology application will be dependent upon the ability of the remedial technology to treat the type of contaminant present. Inorganic, organic, LNAPL, and DNAPL contaminants generally require different remedial technologies. Furthermore, the specific type, concentration, and areal extent of the organic or inorganic contaminant present will also influence technology selection.

3. Regulatory Requirements

Regulatory requirements may limit the type of technology selected. For example, injection of surfactants may not be allowed in certain aquifers. If regulators dictate cleanup levels, then one technology may be favored over another to achieve the required results.

4. Economic Criteria

The funds available for remediating a site may influence technology selection. An acceptable alternative may be a longer duration, less labor intensive, efficient, and less costly remedial action as opposed to a shorter duration, higher effort, more expensive clean-up.

5. Remedial Time Objective

Business or regulatory requirements may limit the time available to achieve cleanup targets. Natural attenuation, for instance, is generally a longer-term solution. Therefore, if a shorter remedial timeframe is required, a more aggressive approach may be necessary.

6. Site Specific Risk Assessment

An assessment of the site-specific risks associated with a zone of contamination will guide the remedial strategy and the appropriate selection of a remedial technology. For instance, if there is an immediate adverse impact to sensitive receptors, then the application of a more aggressive remedial technology would be warranted.

7. Legal Issues

Legal issues may affect the selection of a remedial technology. Examples include remedial action to avoid future liability in property transfer cases or remedial technology selection for third-party sites.

Figure 2 is a technology selection chart which assists the user in selecting among **In Situ** and **Ex Situ** technologies that are considered proven or in the late stages of development. Further guidance is provided based on the phase of contamination present (dissolved phase or LNAPL/DNAPL). Other factors that might influence the choice of technologies are mentioned in the individual technology descriptions below.

Additional testing may be required to establish the feasibility of implementing a technology at a given site. Potential data requirements for each technology are presented with each technology discussion. Technology selection and remedial design for ground water generally require delineation of the horizontal and vertical extent of contaminants and should also be based on a reliable characterization of the hydraulic parameters and chemistry of the aquifer material.

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IN SITU TECHNOLOGY

The remedial technologies discussed in this section address only those technologies that can be performed **In Situ** at the site. These remedial technologies are based on biological, physical, and chemical processes that result in contaminant mass reduction. Some of the technologies involve more than one of these processes. For example, air sparging can be used to physically strip volatile contaminants from the ground water and to introduce oxygen to promote biological growth, both of which can result in contaminant degradation. Most **In Situ** technologies are recently developed. Many continue to be modified and/or combined with other technologies to increase the remedial technology efficiency.

AIR SPARGING

Technology Description

Air sparging is the **In Situ** process of injecting pressurized air below the water table to promote volatilization of contaminants and/or enhance biological growth (see **Figure 3**). Compressed air is injected into the saturated formation via wells specifically designed for sparging purposes. Channels of air tend to move radially outward from the well forming an inverted cone of influence of varying radius, typically 5 to 20 ft (1.5 to 6 m), depending on soil permeability.

Potential migration of fugitive vapors generated from air sparging into surrounding basements is a concern. Thus, air sparging systems are often combined with soil vapor extraction (SVE) technology. Off-gas treatment of collected vapors will depend on local regulations. Generally, the SVE system is designed to recover a greater volume of air than is being injected through air sparging.

Air sparging is most effective for volatile organic compounds. Air sparging is also a means of oxygenating the subsurface to promote biological growth and the subsequent degradation of organic compounds. Air injection rates will dictate whether volatilization or promotion of biological growth predominates. When higher air injection rates are utilized, volatilization is the primary mechanism. Low air injection rates result in more biological growth promotion than volatilization. For instance, a low air injection rate application may be used to degrade heavier, less-volatile hydrocarbon contamination present in the saturated zone. When low air rates are used, such that bioremediation, rather than volatilization, is the primary mechanism, the process is referred to as **Biosparging**.

Applicability

Most effective for volatile and some semi-volatile compounds (generally C₃-C₁₀ hydrocarbons) with Henry's Law constants greater than 10⁻⁴ atm-m³/mole. Not recommended for very low permeability silts and clays.

Limitations

Air sparging may result in non-uniform flow paths through the saturated zone. Researchers have shown that preferential flow paths or channeling of sparged air can be created due to excessive air injection rates. Recovered vapors generally require treatment if the discharge is above local air quality standards. Sparging radius can be relatively small, typically less than 20 ft (6 m). Vapor recovery effectiveness decreases with shallow water tables within 10 ft (3 m) of the ground surface (3 m) due to pressure "short circuiting" to the atmosphere. Injection wells can plug due to biological or inorganic fouling. High injection flow rates without sufficient vapor recovery can result in vapor migration to subsurface utilities, basements, etc.

Design Considerations

Lithological conditions will dictate the success of air sparging at a site. Sandy aquifers are more susceptible to air movement through a formation than a silt or clay. Placement of sparge points is crucial to ensure good areal coverage of contaminated areas. Sparge wells can be screened within or below the zone of contamination depending on the remedial objectives (volatilization or biological growth promotion). Recovery of generated vapors may require treatment and/or an air discharge permit. Most site-specific design information is determined through field testing.

Cost

Costs are moderate and are highly dependent on sparging radius, which will determine the number of sparge/SVE wells, and dependent upon vapor treatment requirements (i.e., incineration, carbon, etc.). Overall costs for a small site (e.g., underground storage tank leak) to a medium size site may range from \$80k to \$500k (U.S. dollars).

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IN SITU TECHNOLOGY (Cont)

IN SITU BIOREMEDIATION

Technology Description

In Situ biological remediation of ground water and saturated soils utilizes a natural process to degrade a variety of organic compounds. Naturally occurring microorganism growth is stimulated through the addition of nutrients, typically nitrogen and phosphorus, and oxygen. **Figure 4** depicts a method whereby the ground water is aerated and reinjected after being pumped from the subsurface. Another method of aerating ground water is to use the **Air Sparging** scheme depicted in **Figure 3**, but at low air rates which provide for biological degradation rather than volatilization. This is referred to as **Biosparging**.

A range of organic compounds is amenable to biodegradation. In general the C₆ to C₂₂ range alkanes and aromatic hydrocarbons typical of motor fuels are readily biodegraded, while longer chains and increasingly complex ring structures tend to be less amenable to biodegradation. Synthetic halogenated compounds, such as the chloroethenes (PCE, TCE, DCE and vinyl chloride), can be degraded either aerobically or anaerobically, and often require more complex bioremediation strategies, such as addition of co-metabolites or use of specific strains of microorganisms that may not be naturally present at a particular site. Bioremediation efforts target dissolved-phase and adsorbed-phase compounds; bioremediation is generally not an effective means of removing separate-phase product, which is usually toxic to microorganisms.

Delivery of nutrients and oxygen to the subsurface is a key consideration in developing an effective bioremediation system. Aerobic biodegradation of petroleum hydrocarbons is generally preferred since the metabolic pathways are more efficient than anaerobic reactions.

Plume containment is usually required during remediation. This can be accomplished with ground water recovery wells that are located to contain the plume. One means of addressing the recovered water is oxygenation, amended with nutrients, and re-introduction to the subsurface either by re-injection, infiltration galleries or irrigation methods (if permitted by the regulatory authorities in the area).

Most bioremediation efforts are limited by the amount of oxygen which can be introduced to the subsurface. Three sources of oxygen are: (1) dissolved air which can result in 8 to 10 mg/L, (2) dissolved pure oxygen which can result in 40 to 50 mg/L, and (3) hydrogen peroxide (H₂O₂) which decomposes to H₂O and 0.5 O₂ (typically applied in the range of 200 to 500 ppm). Dissolved air has cost benefits; however, if substantial contamination is present, this method of introducing oxygen to the system may not be sufficient. The use of hydrogen peroxide as an oxygen source delivers higher levels of oxygen to the subsurface, but at greater expense and with some safety concerns. In addition, at concentrations above 500 mg/L, hydrogen peroxide is toxic to microorganisms.

Applicability

Generally light to mid boiling range hydrocarbons (e.g., gasoline, kerosene, jet fuel, diesel, etc.) are readily degraded. Compounds become less susceptible to degradation as hydrocarbon chain length and aromatic ring number increases. The presence of some metals such as copper, chromium or arsenic may inhibit biodegradation due to their toxicity to microorganisms. **In Situ** bioremediation is typically applied to shallow unconfined aquifers and can be used to treat soil and ground water contamination simultaneously. Oxygen and nutrient delivery is hampered by low permeable soils typical of clays and silts. Soil permeability greater than 0.1 darcy (hydraulic conductivity greater than 10⁻⁴ cm/sec) is optimal.

Limitations

Applying **In Situ** bioremediation as a remedial technology at a site may require several years to meet cleanup criteria. Extremely low cleanup levels may not be feasible. In addition, delivery of oxygen and nutrients in low permeable, heterogeneous soils is difficult. Also, metals may inhibit or be toxic to microorganisms.

Design Considerations

The following information needs to be determined for proper remedial system design: vadose zone water permeability, aquifer permeability, areal extent and depth of contamination, type of contaminant to be degraded, inorganic concentrations (which may inhibit or be toxic to microorganisms). In addition, an assessment of ground water hydrogeology and potential to capture the plume will be necessary.

Cost

Generally low, but variable depending on site conditions, oxygen source, and the delivery system utilized. Cost estimates range from \$80k to \$200k (U.S. dollars) per moderate sized site.

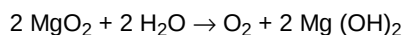
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IN SITU TECHNOLOGY (Cont)

OXYGEN RELEASING COMPOUND (ORC)

Technology Description

Oxygen-releasing compounds (ORC) can be used over an extended period of time to promote biodegradation. For instance, magnesium oxide releases oxygen when hydrated. The following reaction occurs:



Oxygen release stops when the compound is dry or the reaction is complete. ORC can be applied via existing site monitoring wells, deposited as a loose material into soil borings, mixed with backfill/excavated material and returned to the excavation pit, and injected as a slurry. In addition, multiple well application can act to increase the ground water dissolved oxygen concentration across a plume. The biological mechanisms for contaminant mass reduction are identical to the ones described in the **In Situ** biodegradation section (see *In Situ Bioremediation*).

Applicability

ORC is applicable at sites with dissolved-phase hydrocarbons and appropriate aquifer characteristics (i.e., permeable, low BOD, low COD, low organic carbon, etc.). Generally light to mid boiling range hydrocarbons (e.g., gasoline, kerosene, jet fuel, diesel, etc.) are readily degraded. Compounds become less susceptible to degradation as hydrocarbon chain length and aromatic ring number increases. The presence of some metals such as copper, chromium or arsenic may inhibit biodegradation due to their toxicity to microorganisms. Soil permeability greater than 0.1 darcy (hydraulic conductivity greater than 10^{-4} cm/sec) is optimal. ORC has demonstrated success with gasoline plumes in sandy aquifers. Installing ORC in close proximity to the hydrocarbon source is essential.

Limitations

Using ORC may require a fairly long period of time (i.e., years) to meet low cleanup thresholds. Following the completion of ORC application at some sites, a rebound in contaminant concentrations has occurred. Another cause for concern is that delivery of oxygen in low permeability heterogeneous soils is difficult. Also, metals may inhibit or be toxic to microorganisms.

Design Considerations

The type of contamination and project objectives will dictate the delivery method for ORC. The most common application involves the installation of a sock containing ORC in existing monitoring wells. The monitoring wells should be in close proximity to the hydrocarbon source to be optimal points for ORC.

The following information is necessary: ground water chemistry (BOD, COD, DO, organic carbon content, etc.), aquifer permeability, aerial extent and depth of contamination, type of contaminant to be degraded, and inorganic concentrations (which may inhibit or be toxic to microorganisms).

Cost

Generally low, but variable depending on site conditions and type of ORC installation.

SURFACTANT ADDITION

Technology Description

This technology is an **In Situ** process that is typically applied with pump and treat methods. It involves the use of a surfactant or other chemicals to increase the dissolution of hydrocarbons into ground water and reduce capillary forces which retard their transport. The contaminated groundwater is then recovered and treated to remove hydrocarbons and then re-injected or re-infiltrated, creating a closed loop system. When contaminants are present as non-aqueous phase liquid (NAPL), surfactants can promote dissolution by increasing their solubility in the flushing solution, or displacement can be enhanced through a reduction in interfacial tension. In addition, when hydrocarbons are sorbed to aquifer solids, surfactants can promote desorption through decreasing the solid-water partition coefficient. At lower concentrations, these additives can promote the release of soil colloids which may be carrying sorbed hydrocarbons. **Figure 5** illustrates the conceptual design of a pump and treat system with surfactant addition.

Applicability

Surfactant addition is most applicable in heavily contaminated areas, with viscous oils, and in ongoing pump and treat operations to improve recovery and shorten the duration of the process. It is most effective in soils with permeability greater than 1 darcy (hydraulic conductivity greater than 10^{-3} cm/sec), typical of coarse sands and gravels.



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IN SITU TECHNOLOGY (Cont)

Limitations

Technology is typically applicable in homogenous media. Non homogenous soils will cause preferential spreading of the surfactant and may potentially result in minimal contact of the surfactant with the target contaminants. Because contaminants are mobilized, effective hydraulic containment is necessary to limit migration to potential receptors. Regulatory approval for the addition of surfactants to the subsurface environment may be difficult to obtain.

Design Considerations

Care must be taken to ensure that: (1) the surfactant will contact the liquid or sorbed hydrocarbon contaminants, (2) thick emulsions, which would impede NAPL solubilization, do not form at the NAPL-surfactant solution interface, (3) surfactant loss due to precipitation, sorption, or biodegradation is not excessive, (4) there is no offsite migration of surfactant or mobilized chemicals, (5) surfactants do not release excessive soil colloids such that the medium becomes plugged, and (6) the surfactant is recyclable.

Cost

Costs for application of this technology are in the moderate range and are dependent upon the mass of contaminant to be removed, contaminant and aquifer characteristics, and the clean-up criteria.

NATURAL ATTENUATION

Technology Description

Natural attenuation (NA) is a remediation approach that takes advantage of natural processes such as biodegradation, dispersion, dilution, volatilization, hydrolysis, and adsorption to degrade and attenuate chemical contaminants in the environment. For hydrocarbon contaminants, biodegradation is particularly prevalent, and the term "intrinsic bioremediation" is often used interchangeably with NA. Remediation by natural attenuation primarily includes a characterization and monitoring program to prove that these natural processes can meet remedial goals. The American Society for Testing Materials (ASTM) is developing a practical and cost-effective protocol for applying NA (from the perspective of leaking underground petroleum storage tanks such as those found at retail sites) but is flexible enough to apply to more complex multiple-source sites. This protocol is outlined below and in the flowchart on **Figure 6**.

1. Characterize the site to determine the nature and extent of contamination.
2. Evaluate potential receptors to determine whether there is a current risk to human health or environmental resources.
3. Establish remedial goals that are protective of human health and the environment. Include consideration of institutional controls such as deed restrictions or restrictive zoning.
4. Confirm that NA can meet these remedial goals, and is the best option for doing so. Some conceptual and/or analytical modeling may be necessary.
5. Develop a monitoring program to measure progress and compare actual performance to remedial goals.

Once it is established that NA can meet remedial goals and is the most cost-effective approach, then results of the monitoring program are repetitively evaluated to determine whether or not acceptable progress is being made. Ultimately, either remedial goals will be reached, requiring no further action, or NA will have to be reassessed in light of measured results.

Design Considerations

In deciding on the appropriateness of NA, the first and most important step is to characterize the site and use a risk-driven approach like the ASTM Risk-Based Corrective Action (RBCA) methodology to confirm that no immediate threat to human health or the environment exists. If the risk is low, then NA may be appropriate as a stand-alone option for remediating or mitigating the effects of the ground-water plume.

Remedial goals may take the form of target concentration levels or performance criteria, such as demonstration of containment. Institutional controls, such as limiting access or constraining site usage, may also be considered to provide additional assurance that environmental risks can be avoided. A site conceptual model is typically developed to test assumptions about migration pathways and potential receptors.

In determining the applicability of NA, the following lines of evidence are typically pursued, as described below in decreasing order of preference.