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BIOREMEDIATION OF PETROLEUM HYDROCARBONS A FLEXIBLE, VARIABLE SPEED TECHNOLOGY

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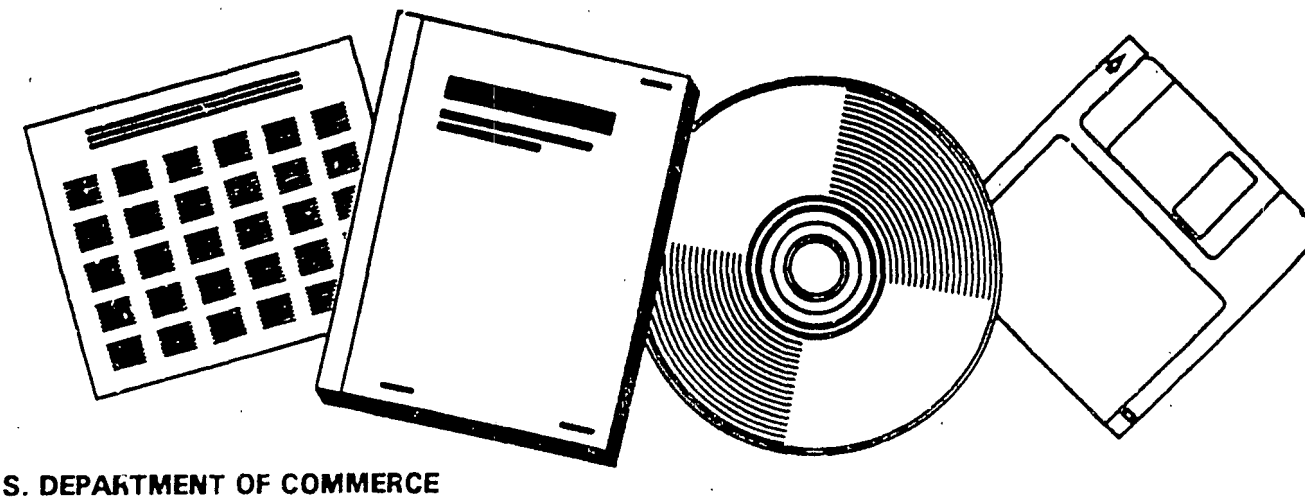

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Bioremediation of Petroleum Hydrocarbons: A Flexible, Variable Speed Technology

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ABSTRACT

The bioremediation of petroleum hydrocarbons has evolved into a number of different processes. These processes include in situ aquifer bioremediation, bioventing, biosparging, passive bioremediation with oxygen release compounds, and intrinsic bioremediation. While these processes are often viewed as competing technologies they are actually part of a continuum of biodegradation processes governed primarily by the interplay between oxygen and carbon availability. Generally the more carbon that needs to be removed per unit time the more oxygen that needs to be supplied. As the carbon availability or desired removal rate decreases, so does the oxygen requirement. By understanding this continuum approach, bioremediation can be applied as a flexible, variable-speed technology, where the effort can be increased or decreased through oxygen supply. This paper will discuss the carbon-oxygen demands of each process and the interplay between processes. The paper will provide operating guidelines for configuring bioremediation systems for maximum flexibility.

INTRODUCTION

The bioremediation of petroleum hydrocarbons was established as a key remediation technology in 1972 when Richard Raymond employed it on a Sun Oil gasoline pipeline in Ambler, PA (Raymond 1976). Raymond demonstrated that the controlled application of oxygen and nutrients could substantially reduce hydrocarbon contamination. Hydrocarbon bioremediation has evolved considerably since that first application. Its evolution has taken two pathways. First, the basic in situ process (the Raymond Process) has become more efficient as both oxygenation systems and nutrient formulations have substantially improved. Early hydrocarbon bioremediation projects often took five years and over a million dollars to remediate a retail gasoline station. Today the process can be accomplished in less than two years at a cost of several hundred thousand dollars. A key factor in this increased efficiency has been the development of aeration systems, such as soil vapor extraction (SVE) and air sparging, which can more easily supply large quantities of oxygen to the biodegradation process than the earlier systems. Second, the

range of application of hydrocarbon bioremediation has evolved from solely the aggressive treatment of soils and groundwater to include slower and/or more subtle processes such as bioventing, passive bioremediation, and intrinsic bioremediation. The focus of early bioremediation development was on achieving lower clean-up levels in shorter periods of time. Today the focus is on processes which accomplish the same level of remediation at lower costs but over a considerably longer period of time. Petroleum hydrocarbon bioremediation, today, represents a continuum of processes that provides a flexibility in effort, time, and cost. On the one end of the spectrum are in situ bioremediation which are cost intensive and aggressive processes that can rapidly treat high levels of soil and/or groundwater contamination. On the other end are intrinsic bioremediation which is an often inexpensive but lengthy process for removing low levels of contamination.

Considering the broad spectrum of hydrocarbon bioremediation processes available, the technology can be classified into essentially four levels of application:

Aggressive (Raymond Process). The Raymond Process is an aggressive source reduction technology. Oxygen (air) is aggressively and continuously supplied, and nutrients are frequently or continuously supplied. Treatment time are typically between one and four years. This process is applied at sites that have a high level of contamination and/or require rapid clean-up. It is effective for both soil and groundwater contamination. The Raymond Process often uses supplemental technologies such as SVE or pump and treat to accelerate clean-up and to control the potential migration of vapors or dissolved contaminants.

Moderate Intensity (Bioventing/Biosparging). These are moderate intensity processes. Bioventing addresses vadose zone (unsaturated) contamination. With bioventing oxygen (air) is supplied at a rate sufficient to support biodegradation while minimizing the transport and recovery of volatile hydrocarbons. Nutrients (and moisture) are generally not applied. Bioventing requires two to ten years to remediate total hydrocarbons, but will address BTEX contamination more rapidly than total hydrocarbons. The process is applied to sites that either have relatively low to moderate levels of contamination or have low levels of volatiles. Bioventing is used to remediate soil contamination. Biosparging addresses contamination in the capillary fringe or below the water table. With biosparging, oxygen (air) is injected into the aquifer. This injection volatilizes and removes VOCs. With biosparging the injection rate is adjusted so that VOCs released into the vadose zone are biodegraded in the soil column before the sparged air reaches the ground surface. Nutrients are generally not applied. Biosparging may require up to eight to ten years to remediate total hydrocarbons. It is applied to sites that have either a relatively low to moderate level of contamination, few volatiles, or a deep vadose zone.

Low Intensity - Passive (Oxygen Releasing Compound - ORC). With passive bioremediation systems oxygen is supplied by a slow release oxygen compound - i.e. magnesium peroxide. Dispersion of the oxygen is largely through advective groundwater flow. Nutrients are generally not applied. ORC systems are primarily used for groundwater control. They may, however, be used to remediate low level dissolved

plumes. Treatment time varies with the degree of contamination but may require eight to ten years.

Intrinsic. Intrinsic bioremediation is the least intensive application of bioremediation. It uses the ambient levels of oxygen (or other electron acceptors) and nutrients. It can be either an aerobic process (using oxygen) or an anaerobic process. Intrinsic bioremediation is effective in controlling and mitigating dissolved plumes. Treatment times vary considerably depending on the level of contamination. In some case, intrinsic remediation may be as fast or faster than more intensive processes. Intrinsic remediation is most effective with low levels of contamination or when the rate limiting factor is the availability of carbon rather than the supply of oxygen or nutrients.

A more detailed description of each level of bioremediation follows. While each level of technology has been developed somewhat independently, there is a common link between them. This link is the interplay between oxygen and carbon availability. Carbon availability represents the mobile fraction of contamination that is available to biodegradation; it is the sum of dissolved and vapor phase carbon.

Aggressive Bioremediation

The Raymond Process is based on the principle that naturally occurring biodegradation processes can be stimulated by supplying enhanced levels of oxygen and nutrients. The early forms of the technology used in-well aeration and the addition of high concentrations of ammonium salts and ortho phosphates. The effectiveness of the early technology was limited by the oxygenation system. These in-well aeration systems were able to sustain dissolved oxygen (DO) levels of 3-5 mg/L at 10-20 feet from the well. Sites with high degrees of contamination or where oxygen transport was limited were slow to respond.

The second phase of development focused on the use of hydrogen peroxide which was a "chemical" carriers for oxygen. By supplying one to two orders of magnitude more available oxygen - 250 to 500 mg/L versus 8 to 10 mg/L - the peroxide based systems shortened the time of treatment and extended the range of bioremediation to more contaminated sites (Brown et.al, 1984). In some cases, the peroxide base systems are able to sustain DO levels of 5-8 mg/L at distances of 20-30 feet from the injection point. The peroxide based system was, however, also limited in effectiveness for highly contaminated sites.

The third phase of development was the use of aeration technologies. First, starting in the mid 1980s with soil vapor extraction and later, from 1989 to 1991 with air sparging, aeration was recognized as an efficient means of supplying oxygen for bioremediation. By 1992 most bioremediation projects employed air based systems rather than chemical based systems (Brown & Jasiulewicz, 1992) resulting in accelerated clean-ups of highly contaminated sites. At some sites, air sparge systems are able to sustain DO levels of 5-8 mg/L over essentially the entire area of treatment.

The practice of in situ hydrocarbon bioremediation involves the controlled application of oxygen and nutrients. There is no upper limit on the amount of available carbon that can be treated. At sites with high levels of available carbon, in situ bioremediation is typically part of a suite of integrated technologies such as NAPL recovery, soil vapor extraction, air sparging, and groundwater recovery. In situ bioremediation is predicated on the assumption that the limiting factors in treatment are the availability of oxygen and nutrients, particularly oxygen. Therefore maximum aeration rates are used. As a result volatilization rates may be in excess of biodegradation rates and, therefore, vapor capture and treatment may be required.

The value of aggressive bioremediation diminishes as the carbon availability decreases. With sites that have less than 20 mg/kg soil - day of carbon availability, less intensive bioremediation processes may be more cost effective. Sites that are contaminated with insoluble and non volatile hydrocarbon mixtures - heavy fuel oils, crude oils, weathered diesel - do not respond any more to aggressive bioremediation than they do to less intensive processes such as bioventing.

Moderate Intensity Bioremediation

Bioventing and biosparging are related, moderate intensity bioremediation technologies. Bioventing is the introduction of air into unsaturated soils; biosparging is the introduction of air into the saturated zone. Both depend upon inducing air flow in-situ to provide oxygen. In most applications this involves the injection of air into the subsurface. Bioventing can also utilize air extraction, allowing air entry from the atmosphere through the ground surface. The rate of air injection is controlled to minimize direct volatilization while enhancing aerobic biodegradation.

Bioventing: The first documented evidence of bioventing was reported by the Texas Research Institute, Inc. in a study of soil vacuum extraction (SVE) for the American Petroleum Institute (Texas Research Institute 1980). It was observed that a portion of the hydrocarbon removed was as the result of aerobic biodegradation and not volatilization. Wilson and Ward (1986) suggested that using air as a carrier for oxygen could be 1,000 times more efficient than water. In a review of soil vacuum extraction processes, (Bennedsen et al 1987) concluded that the SVE process provided large quantities of oxygen and in many cases stimulated biodegradation. The process of bioventing as currently practiced, however, has evolved from parallel development in the late 1980s and early 1990s by Chevron (Ely and Heffner 1988), the U.S. EPA (Kampbell et al 1992), the U.S. Air Force (Dupont et al 1991, Miller et al 1991), and the U.S. Navy (Hoeppel et al 1991). These efforts have led to wide spread commercial application of the technology. One notable example of this is the U.S. Air Force's Bioventing Institute in which the technology has been applied at over 120 U.S. Air Force sites throughout the United States (Leeson et al 1995).

Bioventing has been applied at many different sites to a variety of contaminants. The technology is applicable to any contaminant which degrades more rapidly under aerobic than under anaerobic conditions. To date, most applications have been to petroleum

and petroleum distillate fuels, but success has been reported with PAH compounds and other non-petroleum contaminants (Hinchee and Olfenbuttel 1991).

Bioventing, although potentially applicable to any aerobically degraded compound, has a practical limitation in application to more volatile compounds. If a compound is too volatile it may not biodegrade before it is released into the soil gas. The vapor pressure above which a compound is difficult to biovent is somewhat site specific. On many sites, however, it is not safe or feasible to inject air to biovent highly volatile hydrocarbon mixtures such as gasoline without air extraction to control gas release. In such cases, the process begins to look more like conventional soil vapor extraction because of the need for vapor capture and treatment.

One significant limitation to bioventing is the rate of biodegradation. After overcoming the oxygen limitation, the systems typically become bioavailability limited at rates in the range of 2 to 20 mg/kg-day. Typically the light aromatic fraction, benzene, toluene, and xylenes (BTEX) are most rapidly degraded. At most sites, BTEX is remedied in a year or less. The higher molecular weight hydrocarbons degrade more slowly, frequently resulting in clean up times on the order of 10 years to reach TPH standards.

A variety of techniques have been utilized in attempts to increase bioventing rates. Probably the most successful field demonstrated technique for accelerating bioventing rates is soil warming. Sayles found that by warming soils in Alaska to 20° C bioventing rates increased 2 to 3 fold (Sayles et al 1995). Laboratory testing suggests that nutrification may increase rates; however, field studies have failed to confirm a benefit due to nutrification (Miller et al 1991, Dupont et al 1991, and Leeson et al 1995).

Biosparging: While the use of air sparging to support bioremediation was first suggested by Raymond's use of in-well aerators or spargers to introduce transport oxygen into groundwater, it is likely that in his application the air did not directly enter the aquifer as a separate phase as is common in the current practice of air sparging. Dieter Hiller began applying true air sparging in Germany in the 1980's (Gudemann and Hiller 1988) and its application began spreading in the United States in the late 1980s and early 1990s. Early in its development, it was recognized that air sparging could supply significant oxygen to support biodegradation (Bianchi-Mosquera et al 1994, Brown and Jasiulewicz 1992).

In biosparging air is injected into the aquifer at pressures in excess of the hydrostatic pressure. The air moves in channels from the injection point to the vadose zone. As the air passes through the aquifer materials, oxygen dissolves into water and stimulates biodegradation. If the containment is volatile it may be transported in the air channel to the vadose zone. Once in the vadose zone the contaminant may biodegrade, or it may be extracted by an SVE well. The air flow can be adjusted so that the volatilized contaminant is completely biodegraded by the time it reaches the ground surface.

The physics of air movement in an aquifer are not well understood. A key question is the amount of oxygen that is transferred from the air phase to the water phase. Some

early workers assumed that air transport was in bubble form, and that the aquifer acted like a well mixed system. This lent to overly optimize projections of biosparging's success (Johnson et al 1993). Another problem was that early workers did not understand the presence of monitoring wells or the impact of the air channeling. In some cases air channels intercept monitoring wells resulting in a "clean" well when the air enters the well and forms bubbles which rapidly strip volatiles from and add oxygen to the water in the well. These effects are not necessarily transferred to the surrounding aquifer. The degree of oxygen transferred to the groundwater and volatile organic transfer into air channels is now being studied by a variety of groups, including the API, US EPA, and U.S. Air Force.

Biosparging has the same basic biodegradation rate limitations as bioventing. It appears unlikely that biosparging can result in greater biodegradation rates than bioventing, and in fact, at may sites oxygen transfer may limit biodegradation rates to less than bioventing.

Low Intensity (Passive) Bioremediation

For in situ aquifer remediation using the Raymond method, air sparging and soil vapor extraction are utilized to supply large amounts of oxygen (electron acceptor) to remediate sites with moderate to heavy contamination. However, the conditions at many, more marginally contaminated sites are such that while the total electron acceptor demand is limited, it is not high enough to warrant aggressive effort but is also not low enough to be met through natural recharge processes. Thus, for those sites where there is sufficient contamination to cause concern but where intrinsic bioremediation is not sufficient, or is too slow, or does not provide sufficient control for site owners and regulators, some form of assistance to the indigenous microbial processes is appropriate. In general these efforts focus on providing electron acceptors and possibly nutrients. Nutrient addition, however, is not likely to be necessary because marginally contaminated sites, by definition, have a low level of biodegradable constituents and thus a low level of demand of nutrients. Passive systems that slowly release an electron acceptor offer the potential to provide nearly maintenance free systems. For example, oxygen release compounds represent an approach to providing oxygen as a remedy for aerobically biodegradable contaminants. While relatively small air sparging and bioventing systems can be generally unobtrusive, they both require installation and operation and maintenance of mechanical components. Oxygen release compounds have been field tested and are applicable for use as migration barriers and for source reduction.

Biological Migration Barriers: The introduction of oxygen above ambient recharge levels across the plume will result in decreased concentrations of biodegradable constituents such as BTEX in excess of natural or intrinsic rates. Oxygen addition can be done using a row of air sparging wells, an interceptor trench in which air is release from a slotted horizontal PVC pipe, or a row of wells containing sleeves of a slow release oxygen compound placed perpendicular to the flow of groundwater. The point of interception of the plume is located to meet site objectives such as prevention of migration across property lines. Within a given plume, the closer the barrier is located

to the source area, the greater is the demand for electron acceptors. The location may also be influenced by infrastructure restrictions such as buildings, utility trenches, driveways, etc.

Biological migration barriers have been studied on a pilot scale and implemented successfully at full scale. The choice of barrier is typically between air sparging or oxygen release compounds. Air sparging barriers offer the advantage of relative wide spacing of wells and providing a relative wide oxygenated zone. The disadvantages include the need for ongoing maintenance and the potential for volatile compounds to be transferred to the unsaturated zone and eventually to the atmosphere (in many cases the unsaturated soils may serve as an effective biofilter). The migration of volatile compounds is especially bothersome in the vicinity of utility trenches and buildings with substructures.

Rows of wells containing oxygen release compound require closer spacing than air sparging wells as distribution of oxygen away from the well is dependent on advection, and to a lesser extent, diffusion. However, there is virtually no potential to transfer volatile compounds to the unsaturated zone. Further, once the oxygen release compound is installed, the only maintenance required is periodic replacement of the oxygen release compound. Replacement is required once every four to six months.

Field studies using full scale barriers have been conducted in Alaska (Marlow 1995), North Carolina (Kao and Borden 1994), New Mexico (Johnson et.al, 1995), and at the Borden Landfill in Ontario (Bianchi-Mosquera 1994) using magnesium peroxide (ORC) manufactured by REGENESIS Bioremediation Products. These workers were able to dramatically reduce BTEX levels down gradient of the release.

The Borden Landfill study consisted of a controlled release of benzene and toluene up gradient from a row of ORC containing wells and included the use of several types of controls. Extensive monitoring of wells and piezometers down gradient of the source (ORC) wells showed increases in dissolved oxygen from initial levels of 0.5 mg/l to levels in the range of 8 mg/l to 11 mg/l following introduction of ORC. Benzene and toluene levels were reduced by greater than 97 percent compared to both initial levels and levels in control wells and piezometers.

The most extensive field demonstration is being conducted by GRAM, Inc in close coordination with the New Mexico Environmental Department (NMED) in Belen, New Mexico. Initially, a small scale demonstration was conducted to evaluate the feasibility of using ORC on this site. Increased DO levels and reduced BTEX levels down gradient of the ORC source wells were sufficient to justify installation of a full scale system. GRAM designed and installed a full scale system consisting of twenty 6-inch ORC wells. The vertical distribution of DO and BTEX was measured with probes located 3, 10, and 17 feet below the water table at each of the 54 down gradient monitoring points. Oxygen distribution was estimated by contouring the areal and vertical distribution of initial oxygen concentrations and increased oxygen concentrations at ten sampling times over a three month period. BTEX was evaluated using the same methodology. Within

three to five days oxygen levels increased to levels that could support bioremediation over at least a twenty foot distance down gradient of the source and remained relatively constant. Decreased BTEX levels were also quickly evident.

Source Area Migration Control: In those cases where a source area exists or is under treatment, it may be possible to reduce overall treatment costs by implementing a limited level of bioremediation activity near the source area. This approach has been tried with air sparging wells and with batch addition of electron acceptors to wells located within or immediately down gradient of the source area. Air sparging, however, requires ongoing maintenance and may result in concerns regarding the transfer of volatiles to the unsaturated zone and, subsequently, the atmosphere. Batch additions are generally labor intensive and may be difficult to implement. Placement of an oxygen release compound in one or more wells within or slightly down gradient of the source area has the benefit of requiring little field activity other than monitoring a widely spaced intervals. In some cases, sleeves of oxygen release compounds can be placed in existing wells and thus minimal cost and effort are required beyond continued monitoring and documentation.

Recently, a sixteen site evaluation of the efficacy of ORC for reduction in dissolved phase hydrocarbons has been completed by several independent contractors in conjunction with several major oil companies. In these studies filter socks containing ORC were placed in a single well. The increase in dissolved oxygen and the reduction in dissolved phase benzene, toluene, ethyl benzene, and total xylenes (BTEX) were monitored. Dissolved oxygen (DO) levels, even in the presence of dissolved phase hydrocarbons, generally ranged from 20 to 30 mg/l. The reductions in BTEX levels typically averaged greater than 80 percent and were greater than 95 percent in half of the wells tested. In absolute terms, the reductions in BTEX were as much as 47.5 mg/l.

Additional studies are needed for this and similar application of oxygen release compounds as well as other methods of introducing electron acceptors that are unobtrusive and relatively low cost. Bioremediation methods that can address low levels of contamination will continue to be identified and developed to meet specific niches.

Intrinsic Bioremediation

Intrinsic remediation is the use of ambient natural biodegradation processes to remove low levels of dissolved organics. Natural bioremediation has been used both intentionally and inadvertently as a means to control migration. Intrinsic bioremediation can use a wide range of electron acceptors which are listed in Table 1 (Wilson et al 1994, Borden et al 1994). The table lists the electron acceptors in order of increasing reducing conditions. Of these electron acceptors, oxygen and carbon dioxide are the most readily available being replenished by natural recharge processes. Sulfate, iron, and manganese also occur naturally but are dependent on site mineralogy. The predominant sources of nitrate are anthropogenic activities such as agricultural fertilization. Which of these electron acceptors is used is dependent on the redox conditions (aerobic vs. anaerobic) in the subsurface. In intrinsic bioremediation oxygen is consumed first, then, once anaerobic conditions have been established, nitrate, sulfate, and the other electron acceptors are consumed in order of their redox potentials. Oxygen depletion requires the

presence of a carbon substrate that is readily amenable to aerobic biodegradation (e.g., hydrocarbons). Carbon sources which are resistant to all but methanogenic processes (e.g., PCBs) will not drive the depletion of oxygen and thus will not "activate" other pathways.

Table 1. Common naturally occurring electron acceptors.

Electron Acceptor	Metabolic Pathway	Natural Sources
Oxygen (O_2)	Aerobic	Atmosphere
Nitrate/Nitrite (NO_3^-/NO_2^-)	Facultative Anaerobic	Agriculture/Septic/*Atmosphere*[a]
Sulfate (SO_4^{-2})	Anaerobic	Minerals/*Atmosphere*[a]
Iron (Fe^{+3})	Anaerobic	Minerals
Manganese (Mn^{+4})	Anaerobic	Minerals
Carbon Dioxide (CO_2)	Methanogenic	Atmosphere/*Mineral*[a]

[a] Secondary source (italics)

Intrinsic bioremediation has two uses. The first is to control the leaching of contaminants from untreated or residual sources. The second is to control and mitigate low level dissolved plumes.

The first case study illustrates that intrinsic remediation can adequately reduce the risk of groundwater impact due to residual contamination. Studies of a BTEX plume at a gas plant provide evidence that intrinsic bioremediation processes limited the migration of benzene and other BTEX constituents (Piontek et al. 1994). Groundwater upgradient, within, and downgradient of the NAPL zone was analyzed for BTEX, DO, sulfate, iron, nitrate, methane and bicarbonate. It was observed from this data that the electron acceptors (DO, sulfate, nitrate) decreased in the down gradient direction while the resulting reduced forms (sulfide, iron (+2), bicarbonate, and methane) increased. This paralleled a decrease in the BTEX levels which was in excess of the decrease that would be expected based solely on retardation factors and groundwater flow. The changes in the concentrations of the electron acceptors indicated that sulfate reduction accounted for the majority of the intrinsic remediation. The reduction in BTEX demonstrated that intrinsic remediation could mitigate the impact to groundwater from source areas.

The second application of intrinsic remediation in mitigating low levels of dissolved hydrocarbons is illustrated by the following case history. At the site, groundwater was contaminated by gasoline from a leaking underground storage tank with initial

concentrations exceeding 15 mg/L total petroleum hydrocarbons (TPH). The geology of the site consisted of interbedded highly fractured red shales and pebbly sandstones to a depth of 25 to 30 ft, over a more competent fine-grained sandstone bedrock. Depth to water was 30 to 35 ft near the top of the competent bedrock.

The initial remedial system consisted of a centrally located recovery well. The recovered groundwater was treated by air stripping, amended with nutrients, and reinjected through an infiltration gallery located in the original tank pit where the leak had occurred. Supplemental oxygen was added to the site through a series of six air sparging wells equipped with porous stone diffusers connected to air compressors.

During approximately 2.5 years of operation, the average level of contamination across the site was reduced by approximately 78%, from 4.5 mg/L to 1.1 mg/L. Groundwater concentrations became static after 1.5 to 2 years, indicating that the rate of biodegradation was limited. Dissolved oxygen (DO) levels remained lower than 1 to 2 mg/L in the monitoring wells. The system was then modified to increase the rate of oxygenation by adding hydrogen peroxide at ~500 mg/L continuously through the infiltration gallery and on a batch basis through individual monitoring wells. DO levels increased across the site from 1 to 2 mg/L to 3 to 4 mg/L. The modified system was operated for an additional 1.5 years. The results were an immediate (3 to 4 months) drop in contaminant levels from 1.1 to 0.5 mg/L, a 55% decrease. Over another 6 months of operation, the contaminant level dropped to ~200 to 300 μg/L and stabilized. DO levels began to rise after ~15 months of operation, indicating that the rate of biodegradation was slowing. Because no further benefit was being attained and the cost of continued operation was unacceptable, the remedial system was shut down and the site was monitored on a quarterly basis. As is frequently observed, contaminant levels rebounded after system shutdown. After the rebound, a steady decline in contaminant levels from the rebound level of ~900 μg/L was observed to below the detection limit of 50 μg/L after only five years of monitoring. This continued drop in contaminant levels after the system was shutdown can be attributed to intrinsic bioremediation.

The proper use of intrinsic remediation requires monitoring and evaluation to determine that existing environmental conditions are sufficient for biodegradation to occur and that, indeed, biodegradation is occurring. At minimum there should be documentation that the compounds of interest are decreasing at a rate that is in excess of what would be expected from normal dispersion and dilution. Biodegradation is also indicated by the consumption of electron acceptors (oxygen, sulfate, iron, nitrate) or the presence of by products (reduced iron, sulfide, methane, carbon dioxide, and bicarbonate). Consumption of electron acceptors or the build up of by-products should be evaluated by comparing their concentrations at points up gradient, within and down gradient of the contaminated zone. Additionally general indicators of conditions favorable to degradation should be measured. These include pH, temperature, redox potential, the presence of a viable microbial community, and the presence of low levels of nutrients. Establishing the presence and efficacy of intrinsic remediation is based on the weight of evidence.

SUMMARY AND CONCLUSION

These four levels of hydrocarbon bioremediation can be combined to give more cost effective treatment. The combinations can be done either spatially or temporally. Spatially, as shown in Figure 1, aggressive and moderate intensity bioremediation are best used to treat high levels of contamination, including the source area and high levels of dissolved hydrocarbons. Passive and intrinsic bioremediation are best used to treat dissolved plumes. Low intensity bioremediation is effective for moderate to low levels of dissolved hydrocarbons. Intrinsic bioremediation is best used to treat low levels of dissolved hydrocarbons.

Using a combination of these processes can provide cost effective treatment. Directing the application of aggressive or moderate intensity bioremediation processes at the source area while focussing the application of low intensity and intrinsic processes on the dissolved plume provides a synergistic and cost effective approach. As the aggressive processes reduce the carbon load in the source area, groundwater concentrations will drop as there is less mass to leach into the groundwater. As the groundwater concentrations decrease at the head of the plume, the efficacy of the low intensity or intrinsic processes will increase resulting in a more rapid attenuation of the groundwater plume. This concurrent application of processes gives the fastest remediation.

A second strategy in using the full range of bioremediation systems is to vary their use temporally. This is illustrated in Figure 2. Aggressive remediation is used to address high levels of available carbon. Available carbon is the "sum" of the volatile and dissolved fractions to which adsorbed and NAPL phases will eventually contribute. Aggressive remediation is generally applied in the initial phase of remediation of a highly contaminated site. Once the available carbon level has decreased or if the site has limited available carbon to start, moderate intensity bioremediation (bioventing/biosparging) can be employed. As the source area is removed and the residual problem becomes primarily a low-level, dissolved problem, low intensity and intrinsic bioremediation can be used. This sequential, planned decrease in the level of activity can keep the cost of remediation at a minimum while still attaining low clean up goals. The "hidden cost" is that a sequential remediation will generally take longer than a concurrent approach.

The question to be continually asked in the bioremediation of hydrocarbon site is what is the comparative value of time and money in the remediation effort. The lower the intensity of the bioremediation process the lower the cost, but the longer the time it needs to be applied. If time has limited value, i.e. there is no pressure to clean-up the site within a short time frame, then low intensity and intrinsic processes, or sequential remediation are the most cost effective, provided that long-term monitoring and site management costs do not exceed the difference in treatment costs. If time is important, i.e., there is a need/desire to accomplish clean-up in a defined time period, than aggressive bioremediation or concurrent remediation is warranted.

In reviewing the application of these various levels of bioremediation to hydrocarbon sites, there are two important conclusions that can be drawn. First, all hydrocarbon plumes come to equilibrium. As levels of dissolved hydrocarbons decrease through normal dilution and dispersion, the efficacy of intrinsic remediation will increase. At some distance away from the source area the hydrocarbons will be completely mitigated. Give enough space, intrinsic remediation provides a sufficient and base level of remediation to control hydrocarbon contamination. Second, the size and duration of a hydrocarbon plume can be mitigated by the application of more intensive bioremediation processes. The size of the plume is a function of what is leaching into it and what is being removed from it. As stated above, the plume attains an equilibrium size based on the degree of intrinsic remediation. That equilibrium size can be decreased by reducing the amount of material leaching into the plume, through aggressive or moderate intensity bioremediation of the source area, or by increasing the amount of removal from the dissolved plume by applying low intensity bioremediation.

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