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TECHNICAL BULLETIN ON OXYGEN RELEASING MATERIALS FOR *IN SITU* GROUNDWATER REMEDIATION

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
PUBLICATION NUMBER 4671
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Technical Bulletin on Oxygen Releasing Materials for *In Situ* Groundwater Remediation

Health and Environmental Sciences Department

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ABSTRACT

Oxygen Releasing Materials (ORMs) are commercially available materials that are being used to treat petroleum hydrocarbon contaminated groundwater aquifers. ORMs release oxygen to groundwater, which stimulates the growth and activity of native microorganisms. The principle questions that must be answered when evaluating a proposed ORM installation are:

1. How much ORM is required and how much will it cost?;
2. What method of ORM installation will distribute oxygen most effectively across the site?; and
3. What type of monitoring will be used to evaluate the effectiveness of the ORM installation in meeting site cleanup goals?

This technical bulletin addresses these questions using a step-by-step design approach intended for practitioners who are evaluating the use of ORMs.

The scientific basis for ORMs is discussed and the current state of knowledge of ORM-based technology is reviewed. A systematic approach is presented for evaluating the utility of ORM treatment for a site and for use in designing ORM installations. Example design calculations are used to illustrate the principles discussed and an annotated bibliography of the technical literature is presented.

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Section 1

INTRODUCTION

The purpose of this technical manual is to provide an introduction to the use of oxygen releasing materials (ORMs) as a method for providing supplemental oxygen to dissolved petroleum hydrocarbon plumes to increase *in situ* bioremediation rates. ORMs are a very new technology, having been commercially available for only the last five years. Nevertheless, ORMs are currently being used at many sites under a wide range of conditions and their use is increasing. Although only limited research data are currently available, the experience of practitioners and researchers with these compounds is growing rapidly. This manual summarizes the current state of understanding of this technology and provides guidance for site managers considering the use of ORMs. Section 2 provides a review of the scientific basis for ORM technology intended for those unfamiliar with the basic principles underlying intrinsic and enhanced bioremediation processes. Section 3 summarizes the current state of knowledge on ORMs including methods of application, mechanisms and timing of oxygen release, and factors affecting oxygen transport and distribution in contaminated aquifers. Section 4 presents an example design approach to assist practitioners in performing a feasibility assessment for the use of ORMs at a particular site, developing a set of alternate designs for ORM installations, and developing preliminary cost estimates. Section 5 presents a set of example design calculations that illustrate the design approach presented in Section 4. Section 6 contains an annotated bibliography of the technical literature, and Section 7 presents additional references cited in this bulletin.

Please note that the information contained in this report is not necessarily intended to supplant any existing practices and that API encourages further development of the ideas presented. In no way should the following information be considered standard practice. However, the information contained herein should provide practical guidance.

Section 2

SCIENTIFIC BASIS FOR THE TECHNOLOGY

THE ROLE OF OXYGEN IN *IN SITU* BIOREMEDIATION OF PETROLEUM HYDROCARBONS

Bioremediation relies on the use of microorganisms to degrade petroleum hydrocarbons ultimately to carbon dioxide and water. Degradation occurs as a consequence of microbial growth and reproduction, which requires a source of organic carbon and nutrients (such as nitrogen, phosphorus, and sulfur). Organic carbon is present in the subsurface as naturally occurring organic matter and as petroleum hydrocarbons and their breakdown products. Energy for microbial growth and hydrocarbon degradation is obtained through oxidation-reduction reactions, which the microorganisms facilitate using specific enzyme systems. In these reactions, electrons are transferred from an electron donor (which is oxidized) to an electron acceptor (which is reduced). A wide variety of compounds may serve as electron donors. These include naturally occurring organic matter in aquifer sediments and the wide range of organic compounds in petroleum-based fuels and lubricants and their intermediate breakdown products. Substantially fewer compounds can serve as electron acceptors.

The most energetically favorable electron acceptor is molecular oxygen (O_2) and, if it is present, microorganisms will preferentially use O_2 as the electron acceptor in a process called aerobic respiration. The energy derived from this process is used for growth and petroleum hydrocarbon degradation. Once the supply of O_2 is depleted, rates of growth and degradation will decrease as organisms use less favorable electron acceptors such as NO_3^-, Fe^{3+}, SO_4^{2-}, or CO_2 in a variety of additional metabolic processes. It is generally accepted that petroleum hydrocarbons are degradable under either aerobic or anaerobic conditions. However, under anaerobic conditions, contaminant degradation rates decrease 10 to more than 100 times compared to degradation rates under aerobic conditions. Thus, increasing dissolved O_2 concentrations in contaminated, anaerobic groundwaters will create conditions favorable for aerobic respiration and therefore increase degradation rates.

OXYGEN REQUIREMENT FOR AEROBIC RESPIRATION

To use an aerobic respiration pathway to degrade organic contaminants requires a minimum quantity of O_2, which can be computed by representing the degradation process as a balanced chemical reaction. For example, the degradation of benzene (C_6H_6) to carbon dioxide (CO_2) and water (H_2O) via an aerobic respiration pathway can be written:

$$7.5O_2 + C_6H_6 \text{-->} 6CO_2 + 3H_2O \qquad (1)$$

so that 7.5 moles (240 g) of O_2 (the electron acceptor) are required to degrade one mole (78 g) of benzene (the electron donor). The ratio of O_2 consumed to benzene degraded (240 g to 78 g or 3.1 to 1) is fixed so that, for example, 3.1 mg/L dissolved O_2 will be required to degrade 1 mg/L dissolved benzene in groundwater and 310 mg O_2/kg will be required to degrade 100 mg benzene/kg in an aquifer sediment matrix. The quantity of O_2 required to degrade other compounds will depend on the number of carbon and hydrogen atoms in the compound's molecular structure. However, the ratio of 3:1 is approximately correct for many petroleum hydrocarbons and is widely used to calculate O_2 requirements at contaminated sites.

The stoichiometry described above refers to complete biodegradation of benzene to CO_2 and water (i.e., mineralization). O_2 to benzene ratios less than 3:1 may result in degradation of benzene into less toxic, readily biodegradable compounds. Therefore, some practitioners choose smaller O_2 to contaminant ratios when calculating the ORM requirement to reach a desired site remediation goal.

It is important to recognize that microorganisms use a wide variety of organic compounds as electron donors during aerobic respiration, and that all degradable organic compounds create a microbial O_2 demand. It is therefore incorrect to calculate the O_2 required to remediate a petroleum contaminated site using only the concentrations of specific contaminants of concern such as benzene, toluene, ethylbenzene, or xylenes (BTEX), which represent only about 15-20 % of most petroleum fuels, even though decreasing the concentrations of these compounds may be the principal objective of remedial action. Instead, O_2 requirements should be calculated using concentration measures that represent the sum of <u>all</u> degradable organic compounds at a site. Some examples of the concentration measures used for this purpose include total petroleum hydrocarbon-gasoline (TPH-G), which represents the combined concentrations of the C_4 to C_{10} hydrocarbons contained in gasoline; total petroleum hydrocarbon-diesel (TPH-D), which represents the combined concentrations of the C_{10} to C_{18} hydrocarbons contained in diesel; biological oxygen demand (BOD), which directly measures O_2 consumption by added "seed" microorganisms as they degrade soluble organic compounds in an oxygen-saturated groundwater sample; chemical oxygen demand (COD), which measures the amount of chemical oxidizing agent consumed (expressed as equivalent O_2) when it is added to a water sample; and total organic carbon (TOC), which measures the combined concentration of all organic carbon containing compounds by burning a sample to produce CO_2. The presence of nonaqueous phase liquids (NAPLs) can complicate O_2 demand calculations because reliable information on the O_2 demand exerted by NAPLs cannot be readily determined. Determining the presence or absence of residual NAPL in the treatment area (Feenstra *et al.*, 1991) is important in determining O_2 demand. NAPL, as either "free product" or residual liquid, may serve as a long-term source of dissolved hydrocarbons (Huntley and Beckett, 1997) and cause long-term oxygen demand. The goals of the remediation project may dictate how the O_2 demand of the NAPL is addressed. If residual NAPL is present within the treatment zone of an ORM installation and the goal is to degrade the available NAPL, it will be necessary to estimate an approximate O_2 demand by converting estimated NAPL volumes to mass and using a simple stoichiometry for NAPL mineralization based on composition (e.g., equation 1). If the objective is to reduce concentrations within a dissolved plume, the longevity and strength of any upgradient or adjacent NAPL source must be considered when determining the O_2 requirements needed to reach the project remediation goal.

It should be noted that naturally occurring organic matter can also create an O_2 demand. Concentrations of naturally occurring dissolved organic carbon in groundwater are typically small (e.g., < 2 mg/L) but may still be substantial relative to petroleum hydrocarbon concentrations at some sites. Dissolved organic carbon concentrations can be determined on groundwater samples from an uncontaminated well (e.g., using a TOC analysis). Concentrations of naturally occurring organic carbon in aquifer sediments are highly variable but can be large in some geologic deposits. However, little information is available on the O_2 demand exerted by these materials. If conditions in the aquifer were aerobic prior to the occurrence of petroleum hydrocarbon contamination, the O_2 demand can probably be neglected. However, some high organic matter content soils and sediments that naturally exist under anaerobic conditions may exert a substantial O_2 demand, which can be determined by analyzing core samples collected from uncontaminated portions of the site.

It is also important to recognize that nonbiological processes "compete" with microorganisms for O_2 thus reducing the amount of petroleum hydrocarbon degraded for a given amount of available O_2. For example, ferrous iron (Fe^{2+}) is present in the groundwater and sediment minerals at many hydrocarbon-impacted sites and can react with O_2 to form ferric iron (Fe^{3+}) hydroxides:

$$Fe^{2+} + 0.25O_2 + 0.5H_2O + 2OH^- \dashrightarrow Fe^{3+}(OH)_3 \qquad (2)$$

so that 0.25 moles (8 g or 8 mg/L) of O_2 are consumed by the oxidation of one mole (56 g or 56 mg/L) of Fe^{2+} to Fe^{3+}. Similar reactions are possible with reduced forms of sulfur and manganese and should be included when estimating the total quantity of O_2 required to remediate a contaminated site. Although in many cases the O_2 demand created by reduced inorganic compounds is small relative to the O_2 demand created by organic contaminants, these reactions are still of concern because the formation of solid hydroxides can cause clogging of well screens and aquifer pores when O_2 is added to promote biodegradation.

ROLE OF OXYGEN IN NATURAL ATTENUATION

Many petroleum hydrocarbons (e.g., benzene, toluene) are only weakly sorbed to aquifer sediments, which suggests that these compounds should be carried long distances by regional groundwater flow and create highly mobile and elongated hydrocarbon plumes. However, at many sites hydrocarbon plumes appear to be stationary and are much smaller than predicted by groundwater transport models. Natural attenuation refers to the reduction in contaminant concentrations that occurs downgradient from a source zone due to dilution and dispersion, volatilization, sorption, and the activity of indigenous microbial populations. The size and shape of untreated hydrocarbon plumes are primarily controlled by interactions among four factors: (1) the rate of hydrocarbon release from the source zone, (2) the rate of regional groundwater flow, (3) heterogeneities in aquifer properties affecting transport and attenuation, and (4) the available supply of electron acceptors and nutrients. Based on extensive surveys of hundreds of petroleum contaminated sites (e.g., Rice *et al.*, 1995; Mace *et al.*, 1997), it is now believed that most hydrocarbon plumes eventually reach a "steady-state" configuration where the rate of contaminant release from the source zone and transport by regional groundwater flow are balanced by a combination of fast degradation along the aerobic plume perimeter and slow degradation within the anaerobic plume interior (Figure 2-1). Because of the important role that O_2 plays in intrinsic bioremediation of petroleum hydrocarbons, it is important to identify and quantify the natural rate of O_2 supply to a plume.

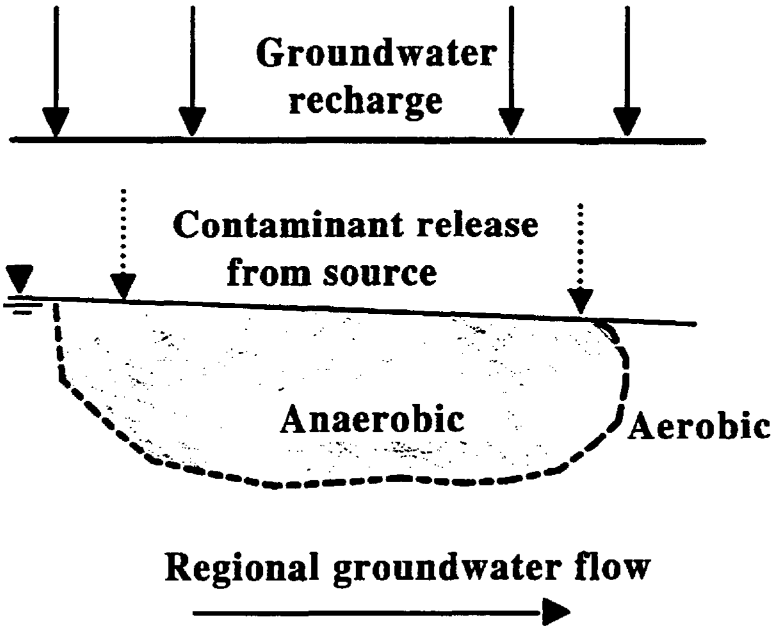

Figure 2-1. "Steady-state" contaminant plume created by balance among several factors: contaminant release from source zone, groundwater flow and transport, and aerobic and anaerobic respiration

NATURAL SOURCES OF OXYGEN

The ultimate source of dissolved O_2 in untreated groundwater is the atmosphere, which contains 21% O_2 on a volumetric basis. Oxygen in the atmosphere dissolves in rain and surface water and is then transferred to groundwater. The maximum dissolved O_2 concentration in untreated groundwater is therefore equal to the O_2 solubility in water in contact with the atmosphere, which in turn is a function of water temperature and salinity (Table 1-1). In most cases, dissolved O_2 concentrations in groundwater are much smaller than the O_2 solubilities in Table 1 because O_2 is continuously removed from solution by aerobic respiration and reaction with reduced inorganic compounds such as ferrous iron and sulfide. At heavily contaminated sites, the abundance of potential electron donors in the form of organic compounds and the presence of a large acclimated microbial population cause aerobic respiration rates to be very fast (and for most purposes can be considered to occur instantaneously) and limited only by the rate at which O_2 is being supplied by the natural processes of groundwater recharge and regional flow.

Table 1-1. Oxygen solubility (mg/L) in water in contact with air

Temperature	Salinity (%)				
(°C)	0	1	2	3	4
5	12.8	11.9	11.2	10.5	9.8
10	11.3	10.6	9.9	9.3	8.7
15	10.1	9.5	8.9	8.4	7.9
20	9.1	8.6	8.1	7.6	7.2
25	8.2	7.8	7.4	7.0	6.6
30	7.5	7.1	6.8	6.4	6.1

The rate of O_2 being naturally supplied to a plume is difficult to determine accurately, but an approximate rate can be calculated using a standard mass balance approach, which treats the plume as a three-dimensional "box " or compartment bounded by two-dimensional surfaces through which O_2 enters or exits. This approach requires estimates for dissolved O_2 concentrations and flow rates for regional flow and recharge. Dissolved O_2 concentrations in regional flow can be measured on groundwater samples collected from monitoring wells located upgradient from the contaminant plume. Regional flow rates are computed using Darcy's Law. Water level elevation contour maps and flow nets, hydraulic conductivity, and porosity data are needed to make the flow rate calculations. Dissolved O_2 concentrations in groundwater recharge can be measured on samples collected from the base of the unsaturated zone using lysimeters or from the top of the saturated zone using multilevel samplers. Recharge rates through the unsaturated zone may be estimated from site-specific information on climate, soil properties, surface conditions, etc. (Stephens, 1996). However, in cases where infiltration is limited by the presence of a surface cover (e.g., buildings, pavement, etc.) it may be reasonable to assume that the amount of O_2 entering the saturated zone via recharge is negligible.

ROLE OF OXYGEN IN ENHANCED BIOREMEDIATION

In most cases the natural rate of O_2 supply is small relative to the microbial O_2 demand created by the petroleum hydrocarbon loading. When this occurs predicted cleanup times for intrinsic bioremediation (i.e., using only natural sources of electron acceptors) sometimes can be unacceptably long (years to decades). For this reason a variety of methods have been developed to increase dissolved O_2 concentrations in groundwater and thus increase rates of hydrocarbon degradation by aerobic respiration pathways. The term enhanced bioremediation is often used to refer to treatment processes designed to stimulate the growth of native microorganisms. These methods include: biosparging (injection of air or O_2 gas into the saturated zone); bioventing (injection of air or O_2 gas into the unsaturated zone); vacuum-enhanced free product recovery (application of vacuum in wells to extract product and to draw air into the unsaturated zone), injection of aerated or oxygenated water (containing dissolved air or pure O_2, hydrogen peroxide, or air or O_2 gas bubbles) into the saturated zone, and various forms of *in-situ* aeration or oxygenation (passive release of aerated or oxygenated water from a well, borehole, or excavation to the saturated zone). The use of oxygen releasing materials (ORMs) is another *in situ* method for increasing the dissolved O_2 content of hydrocarbon-impacted groundwater.

Section 3
OXYGEN RELEASING MATERIALS

WHAT ARE OXYGEN RELEASING MATERIALS?

Oxygen releasing materials (ORMs) are chemicals that release O_2 when immersed in water. A variety of chemicals have been investigated for use in ORM products including magnesium peroxide (MgO_2), calcium peroxide (CaO_2), and sodium carbonate peroxide (sodium percarbonate). The most widely used ORM formulation is MgO_2, prepared by contacting MgO or $Mg(OH)_2$ with hydrogen peroxide (H_2O_2). During production, some ORM manufacturers control the form, structure, and concentration of the reactants; the presence of impurities; product decomposition; and heat evolution to obtain a product with desirable O_2 content and O_2 releasing properties. For example, Regenesis Bioremediation Products, in a patented process, adds small amounts of phosphates to their product ORC® to create a MgO_2 crystal structure that slows O_2 release during hydration.

COMMON MODES OF ORM APPLICATION

ORMs are currently being used in a variety of applications including: treatment of excavated sediments, contaminant source-zone control, on-site treatment of dissolved phase contaminant plumes, and control of off-site migration of contaminant plumes. Depending on the application, ORMs have been used as a dry powder, a dry mixture of ORM powder and silica sand (or other diluent), a water:ORM powder slurry, or as an ORM or ORM-portland cement mixed "concrete" cast into blocks ("briquettes"). Briquettes are no longer used because they have a lower O_2 content than other ORM preparations and a high pH, which may result in undesirable mineral precipitation (Koenigsberg, 1997). Methods of ORM installation include placement in existing wells, direct-push boreholes, augered boreholes, excavation backfill, and interceptor trenches (Figure 3-1).

For use in existing wells, ORMs are typically packaged in cylindrical bags ("socks"), which are lowered into the well casing from the surface (Figure 3-1a). Socks are composed of a woven fabric to retain the ORM powder, which may be mixed with an inert silica sand (e.g., 50 % ORM to 50 % sand), which serves as a diluent. A number of socks may be connected together to place

ORMs in contact with the total screened length of the well within the contaminated zone. Use of ORM socks in existing monitoring wells (converting them to "remediation" or " treatment" wells) is typically the lowest cost ORM application. An additional advantage of this method is that the socks may be easily removed and replaced when the ORMs within the socks are depleted (i.e., when O_2 release rates become small).

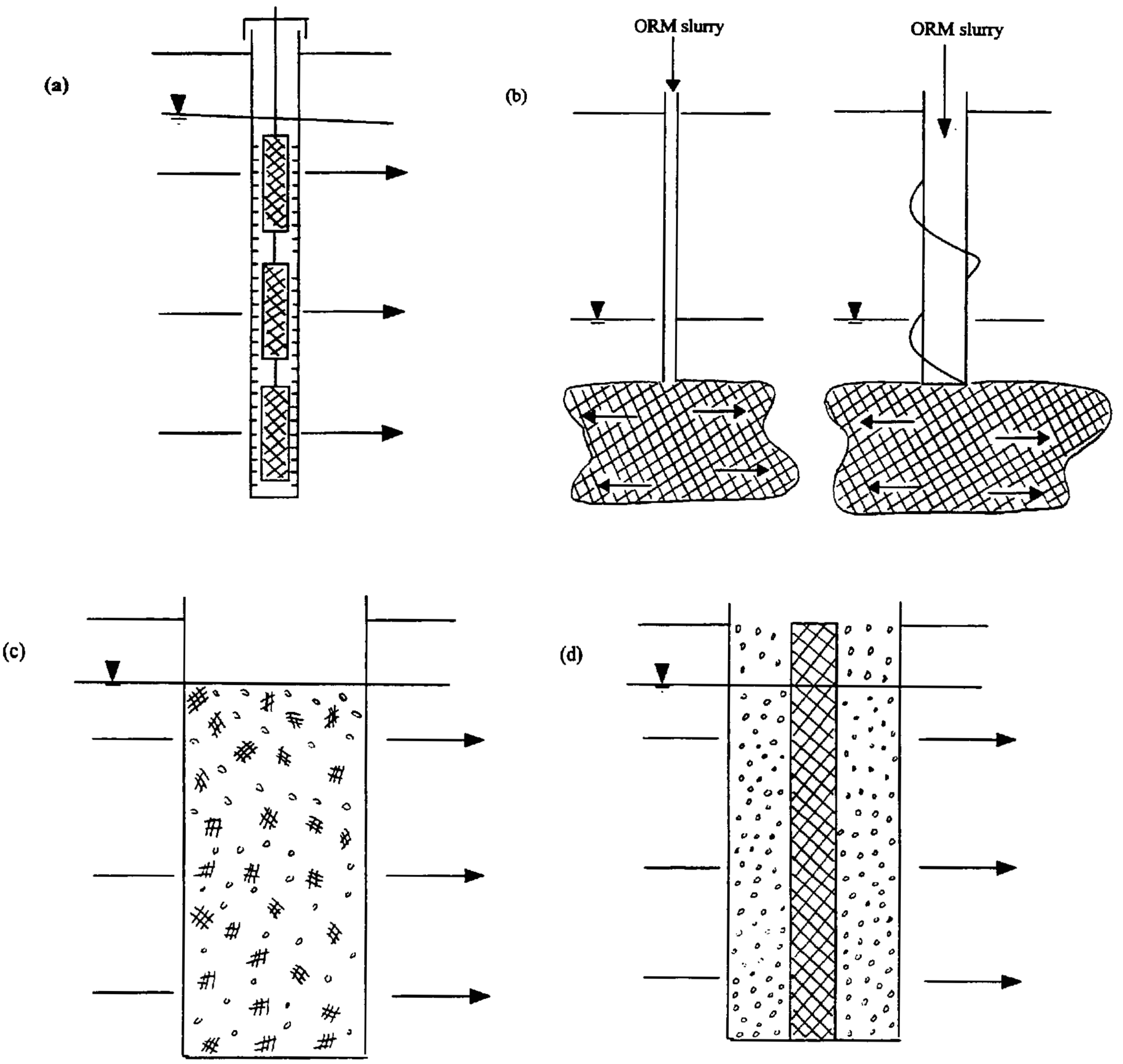

Figure 3-1. Some ORM application methods: (a) ORM socks in wells, (b) ORM slurry injection in direct-push and augered boreholes, (c) powder in interceptor trench, and (d) "funnel and gate" with removable ORM socks or "cassettes"

The potential disadvantage of this method is that existing monitoring wells may not be placed optimally for plume treatment (e.g., well spacings may be too large to provide adequate spatial coverage of the plume) or wells may have too small a diameter or screen length to hold a sufficient volume of ORM to be effective. Additional disadvantages are that unsupported socks may distort upon hardening, making them difficult to remove (Koenigsberg, 1997) and that some regulatory agencies may not allow the conversion of "treatment wells" that once contained ORM socks to be used in the future as monitoring wells.

For use in direct-push boreholes, which typically have a smaller diameter than permanent wells, ORM powder is mixed with water (typically one part water to two parts ORM) to form a liquid slurry, which is injected into the aquifer at high pressure using a grout pump. In one method, the drive-point is first placed at the greatest depth and then the ORM slurry is injected from the tip of a drive-point tool string as it is slowly withdrawn from the soil (Figure 3-1b). The shape of the ORM-treated zone is typically irregular and depends on a number of factors including slurry viscosity and density (a function of the water: ORM powder mix ratio); injection pressure; and the strength, hydraulic conductivity, and pore size distribution of aquifer sediments, which typically vary both vertically within a borehole and laterally from one borehole to the next. The relatively lower cost of direct-push boreholes (compared to the cost of constructing wells or augered boreholes) can allow smaller borehole spacings and thus more intensive ORM treatment, but the injected ORM can only be replenished by additional injections.

When site conditions are not suitable for direct-push boreholes (e.g., high strength or rocky sediments or excessive depths to the contaminated zone), ORM powders and/or slurries can be used to backfill augered boreholes, e.g., through the center of a hollow-stem auger. Depending on the borehole diameter, this method may allow the addition of larger quantities of ORM than either wells or direct-push boreholes, but the ORM is generally not retrievable and can only be replenished by constructing additional borings. In direct-push and augered boreholes the injected slurry may eventually harden into an ORM "concrete," which may reduce the O_2 release rate. In addition, the reduced hydraulic conductivity of the ORM slurry-injected sediment may reduce the groundwater velocity through the ORM treated zone and thus the mixing of contaminated groundwater with the released O_2. Additional field work is needed to understand the distribution and behavior of injected ORM slurries.

When an open excavation is created as part of remedial operations (e.g., to remove an underground storage tank), ORM powder can be distributed on the bottom of the excavation (typically 0.1 to 1% ORM to soil on a weight basis) and/or mixed with the excavation backfill. ORM powder, socks, and/or cast ORM blocks can also be added to interceptor trenches (Figure 3-1c); removable ORM "cassettes" can be used in "funnel and gate" systems (Figure 3-1d) designed to create permeable treatment zones. In this application, O_2 transfer from the ORM to the contaminated groundwater occurs as groundwater flows through the trench thus increasing biodegradation rates in the trench backfill and potentially in the aquifer downgradient from the trench. These installation methods allow the addition of very large quantities of ORM, but the ORM can only be replenished if the design accommodates removable socks or ORM "cassettes."

MECHANISM OF OXYGEN RELEASE FROM ORM

ORMs combine with water in a process called hydration to release molecular O_2 to the water where it exists as a dissolved gas. For example, solid magnesium peroxide (MgO_2) reacts with water to release O_2 and form magnesium hydroxide ($Mg(OH)_2$):

$$MgO_2 + H_2O \dashrightarrow 0.5O_2 + Mg(OH)_2 \tag{3}$$

so that one mole (56 gm) of MgO_2 yields one-half mole (16 gm) of O_2. Similarly, solid calcium peroxide (CaO_2) reacts with water to release O_2 and form calcium hydroxide ($Ca(OH)_2$):

$$CaO_2 + H_2O \dashrightarrow 0.5O_2 + Ca(OH)_2 \tag{4}$$

so that one mole (72 gm) of CaO_2 yields one-half mole (16 gm) of O_2. It should be recognized that although these reactions illustrate the nature of the hydration reaction for pure compounds, O_2 yields from commercial ORM products will be much smaller than those predicted by equations 3 and 4 because commercial products generally are prepared as mixtures of the peroxide and hydroxide forms and other compounds. For example, pure MgO_2 would theoretically yield 16 gm O_2/56 gm MgO_2 or 286 mg O_2/gm MgO_2 (equation 3). However, O_2 yields for ORMs reported in the technical literature range from 1 to 100 mg O_2/gm ORM (e.g., Borden *et al.*, 1997).

Because the O_2 yield determines the mass of ORM that must be used to meet the combined microbial and nonbiological O_2 demand, accurate information on O_2 yields should be obtained prior to designing an ORM installation. This information can be obtained from the ORM manufacturer or by a laboratory test of an ORM sample.

TIMING OF OXYGEN RELEASE

In addition to the ORM's O_2 yield it is also necessary to consider the timing of O_2 release when evaluating the use of ORMs for a particular site. If release rates are too fast, the ORM O_2 content will be rapidly depleted. This may necessitate frequent ORM replacement, and there is a possibility that wasteful "side reactions" will occur at the temporarily very high O_2 concentrations (e.g., evolution of O_2 gas, excessive heating and curing of ORM slurries, rapid precipitation of oxides and hydroxides, oxidation of mineral surfaces, toxicity to native microorganisms, etc.). If release rates are too slow, however, O_2 concentrations will increase only slightly and biodegradation rates will not be enhanced. O_2 release rates are typically determined in laboratory experiments and indicate a two-part behavior: an initial short period of rapid release of a portion of the O_2 content followed by a longer period of slower O_2 release. It should be recognized that O_2 release rates under actual field conditions are difficult to predict accurately because they are determined by complex interactions among: (1) the chemical characteristics of the specific ORM formulation; (2) the physical form of ORM installation (powder, packaged socks, or injected slurry); (3) the presence of silica sand or other diluents; (4) the water:ORM powder ratio of injected slurries; (5) groundwater velocity; (6) degree of subsurface heterogeneities; and (7) the chemistry of the groundwater and sediments in contact with the ORM. In particular, O_2 release rates will be highest whenever the O_2 concentration in the water near the ORM installation is small (e.g., when dissolved hydrocarbon concentrations and aerobic respiration rates are large). This can be seen in equation 3 where removing O_2 from the right hand side increases the hydration rate by the mass action law. Dissolved O_2 concentrations in groundwater directly in contact with ORM particles can be very high (25 - 35 mg/L). Once released, the O_2 is subjected to the normal transport processes of advection, dispersion, diffusion, retardation, and reaction, which all act to reduce dissolved O_2 concentrations downgradient of the ORM installation.

FACTORS AFFECTING O_2 TRANSPORT AND DISTRIBUTION

Advection

Advection transports released O_2 downgradient from the ORM installation by the bulk action of groundwater flowing under either a natural gradient or an induced gradient caused by nearby pumping wells. The rate of O_2 transport by advection is equal to the average pore water velocity (Darcy velocity/porosity). Thus if the Darcy velocity is 0.3 m/d and the aquifer porosity is 0.25, O_2 released from an ORM installation would be expected to move downgradient at a rate of 0.3/0.25 = 1.2 m/d if no other aquifer processes were occurring. However, in most cases, the apparent rate of O_2 transport will be much smaller than the rate predicted from advection calculations alone due to the action of dispersion, diffusion, retardation, and various chemical and biological reactions. In addition, heterogeneity in porosity, hydraulic conductivity, and microbial activity is likely the most important factors controlling O_2 distribution at a given site.

Dispersion

Longitudinal dispersion is the mechanical mixing process caused by pore- and site-scale variations in groundwater velocity and tends to spread the dissolved O_2 front as it moves downgradient. Dispersion also occurs in the transverse (perpendicular to groundwater flow direction) and vertical directions and can help to distribute oxygen across the site. Estimating the magnitude of transverse mixing caused by dispersion is necessary to select well or borehole spacings to ensure adequate spatial coverage of O_2 within the plume. Dispersion effects are quantified using dispersion coefficients computed from the pore water velocity and the aquifer's longitudinal and transverse dispersivities. The longitudinal dispersivity describes the intensity of mixing in the principal flow direction; the transverse dispersivity describes the intensity of mixing in a direction perpendicular to the principal flow direction. The ratio of longitudinal to transverse dispersivity (α_L/α_T) controls the overall shape of the O_2 plume downgradient from an ORM installation (Figure 3-2). Reported values of α_L/α_T range from 6 to 20, with smaller values for homogeneous aquifers (e.g., uniform sands and gravels) and the larger values for heterogeneous aquifers (e.g., fractured rocks). Figure 3-2 shows the effect of this range of values on the length and width of the resulting O_2 plume downgradient of an ORM "point" source with a width of 1 m. This unit can represent for example an augered borehole containing ORM slurry or a 1 m wide slice of an ORM treated excavation. The figure can be scaled to accommodate larger or smaller ORM sources. The plume outlines in the figure can be scaled to larger or smaller ORM sources and to any convenient system of units. For large values of α_L/α_T, plumes are long and narrow with almost no transverse spreading (for $\alpha_L/\alpha_T = 20$, the maximum plume width 7 m downgradient is ~ 1.5 m). In this case, ORM installations will have to be very closely spaced to distribute O_2 adequately within the contaminated zone. For small values of α_L/α_T, plumes are shorter and wider, (for $\alpha_L/\alpha_T = 5$, the maximum plume width 6 m downgradient is ~ 3 m) and ORM installations can be more widely spaced and still distribute O_2 across the contaminated zone.

It is important to note that Figure 3-2 shows the maximum spatial extent of an O_2 plume downgradient of an ORM installation; in almost all cases, the actual spatial extent of O_2 plumes will be much less. In particular, various chemical and biological reactions can limit the zone of increased O_2 concentrations to a very small region downgradient of the ORM installation.

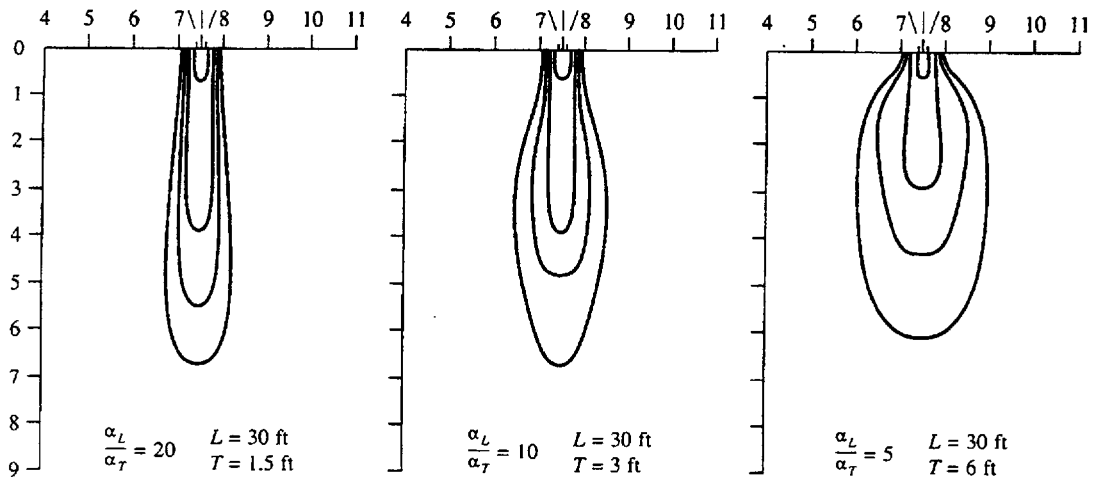

Figure 3-2. **Effect of ratio of longitudinal to transverse dispersivity (α_L/α_T) on length and width of O_2 plume downgradient of ORM source; the plumes are depicted for conditions of no O_2 demand**

Because of the limited amount of transverse spreading that occurs in many aquifers, ORM installations should be designed to maximize spatial coverage of the site to ensure O_2 delivery to all portions of the contaminant plume. For example, direct-push boreholes can be installed in staggered arrays across the site (see Example Calculation No. 4 in Section 5).

Diffusion

Diffusion of dissolved O_2 is caused by the random motion of O_2 molecules and results in a net O_2 transport from locations where dissolved O_2 concentrations are high to where they are low. The rate of oxygen diffusion in water is very slow, only ~ 1 to 2 cm/day, and is much smaller than typical rates of transport by advection and dispersion. Nevertheless, diffusion is an important mechanism for bringing released O_2 from an ORM installation with flowing groundwater to stagnant groundwater in small or dead-end pores. The slow rate of diffusion is also beneficial because it limits the vertical transport of released O_2 from groundwater to the water table, where it can be lost by volatilization to the unsaturated zone.

Retardation

Retardation describes the apparent reduction in solute velocity relative to the average pore water velocity (Darcy velocity/effective porosity) caused by partitioning of the solute to a stationary phase. The effect is conveniently summarized using a retardation factor, R:

$$\text{Retardation factor} = \frac{\text{pore water velocity}}{\text{solute velocity}} \tag{5}$$

Retardation factors are widely used to describe the effect of contaminant sorption to aquifer sediments on apparent contaminant velocity in a plume. Because many petroleum hydrocarbons (including the BTEX compounds) are only weakly sorbed in many aquifers, predicted retardation factors for these compounds are typically close to one (hydrocarbon velocity = pore water velocity). Although it is often assumed that the retardation factor for dissolved O_2 is also one, it is now clear that the presence of small amounts of trapped gas within the saturated zone can cause retardation factors for dissolved O_2 to be greater than one, indicating slowed transport and spreading relative to BTEX. Trapped gas can be created by many processes including evolution of gas by microbial or geochemical reactions, direct gas injection (as in biosparging or air sparging), fluctuating water tables, or by the evolution of gas bubbles due to changing physical or chemical conditions within the aquifer. Although measuring trapped gas saturations in the field is difficult, laboratory studies suggest that up to 20 % of the pore space can contain trapped gas. The effect of trapped gas on retardation factors for dissolved O_2 is given by:

$$\text{Retardation factor for dissolved } O_2 = 1 + H\left(\frac{\text{Fraction of pore space containing trapped gas}}{\text{Fraction of pore space containing water}}\right) \qquad (6)$$

where H is the Henry's Law constant for O_2 (28 at 15°C). For example, equation 6 predicts a retardation factor of 2.5 for dissolved O_2 if only 5 % of the pore space contains trapped gas. The results of field measurements at many sites support the concept of O_2 retardation by this mechanism (Fry *et al.*, 1996; Donaldson *et al.*, 1998).

Chemical and Microbiological Reactions

As discussed previously, a variety of chemical and microbiological reactions may consume dissolved O_2 released from an ORM installation. At heavily contaminated sites with potentially large populations of acclimated microorganisms and high concentrations of reduced inorganic compounds, these reactions occur very quickly (half-lives of hours) and for most purposes can be assumed to occur instantaneously. In any case, chemical and microbial reactions will reduce the spatial extent of dissolved O_2 plumes downgradient of ORM installations from that predicted from advection, dispersion, and diffusion alone. Moreover, at heavily contaminated sites where O_2 reaction rates are large, chemical and microbiological reactions are the dominant processes affecting dissolved O_2 transport and distribution downgradient from ORM installations.

Section 4

DESIGN APPROACH

ON-SITE TREATMENT OF CONTAMINANT PLUME

ORM installations can be designed to meet different remedial objectives. For example, if the objective is on-site treatment of a petroleum hydrocarbon plume, the ORM installation is designed to ensure that the quantity of O_2 released will be sufficient to meet the combined chemical and microbiological O_2 demand exerted by the groundwater and sediment contained within the boundaries of the plume. For example, the design could consist of an array of wells or boreholes that provide complete spatial coverage of the plume. For this type of installation, the design criterion can be written:

$$\begin{array}{l} \text{Quantity of } O_2 \text{ released} \\ \text{by ORM installation} \end{array} = \begin{array}{l} (O_2 \text{ demand of contaminated groundwater and sediment}) \\ \times \quad (\text{total volume of contaminant plume}) \end{array} \qquad (7)$$

The design of an ORM installation using this criterion can be performed as a series of steps:

Step 1

The first step is to estimate the total contaminant mass to be treated. As discussed in Section 1, this calculation can be performed using concentration measures (TPH, BOD, etc.) that best represent the total (combined) concentrations for all petroleum hydrocarbons at the site. This would include petroleum hydrocarbons dissolved in infiltrating recharge water and groundwater, petroleum hydrocarbons sorbed to aquifer sediments, and free product and residual NAPL, if present. Because data are often sparse, and samples can typically be obtained for only a relatively few wells, drive cores, etc., some type of interpolation or spatial averaging procedure will be required to obtain the total contaminant mass. Estimates also will be required for plume and aquifer characteristics and aquifer properties needed to convert measured concentrations to total contaminant mass. These include the location of plume boundaries and aquifer saturated thickness, porosity, and bulk density. Various assumptions also will be required during these calculations (e.g., the aquifer saturated thickness may be assumed to be constant) and it is important that these be documented for subsequent review. In particular, the "patchy" nature of contamination at many sites makes it difficult to accurately define the spatial variation in petroleum hydrocarbon concentrations. For these reasons, there will always be great uncertainty in the estimated total contaminant mass. Despite these uncertainties, a conservative ORM installation design can still be obtained if combinations of concentrations, plume volumes, and aquifer properties are selected to result in a plausible upper estimate for total contaminant mass. Because of these uncertainties, in many cases a hybrid sampling and testing scheme can provide the most cost-effective site characterization information. In this approach a larger number of samples are collected and analyzed for parameters such as BOD which cost less than the petroleum hydrocarbon analyses (e.g., BTEX or TPH). Example Calculation No. 1 in Section 5 shows how to estimate total contaminant mass to be treated at a hypothetical site.

Step 2

The second step is to estimate the quantity of O_2 being supplied to the contaminant plume by natural sources. This will require estimates for flow rates and dissolved O_2 concentrations in recharge and groundwater entering the contaminated zone. It is always conservative to neglect the contribution of natural sources of O_2 when designing an ORM installation. For example, if a substantial portion of the soil surface is covered (e.g., by pavement or buildings) O_2 contributions from surface recharge are probably small and can be neglected. Although considerable uncertainty is involved in quantifying natural O_2 supply rates, the calculations are useful because (1) they provide an estimate for the time required to clean the site in the absence of supplemental O_2 from ORMs, (2) natural O_2 sources may reduce the total quantity of ORM required over the project life, and (3) they serve as a useful check that rates of contaminant degradation at the site are O_2 limited. Example Calculation No. 2 in Section 5 illustrates a method for estimating the rate of O_2 supplied from natural sources.

Step 3

The third step is to estimate the total quantity of O_2 to be supplied by the ORM installation (1) to degrade petroleum hydrocarbons in the plume via aerobic respiration pathways, and (2) to oxidize reduced inorganic species that may be present in groundwater or sediments (e.g., Fe^{2+}). The quantity of O_2 required to meet the microbiological demand exerted by aerobic respiration is obtained by multiplying the total contaminant mass obtained in Step 1 by a factor derived from the mineralization or appropriate degradation reaction (e.g., equation 1). In most cases, a variety of petroleum hydrocarbons will be present at the site and the reaction stoichiometry for the mixture will be unknown. In this case, one could use the ratio 3:1, which is appropriate for the BTEX compounds, and a safety factor or an integrated measure of microbiological O_2 demand (e.g., BOD-ultimate). The quantity of O_2 required to oxidize reduced inorganic species is also obtained using the appropriate reaction stoichiometry (e.g., equation 2) or an integrated measure of chemical O_2 demand (e.g., COD). The required total mass of O_2 is computed by adding the microbial and nonbiological O_2 demands. (If desired, O_2 requirements could be reduced if a site-specific estimate of degradation by anaerobic processes is available.) Often, practitioners multiply the computed total mass of required O_2 by a safety factor to account for uncertainties in site conditions or for anticipated inefficiencies in O_2 delivery and distribution. Safety factors in the range of 8 to 20 have been quoted. However, these factors could be orders of magnitude larger depending on site conditions or the type of ORM. Clearly, the magnitude of the safety factor could have a great impact on the cost effectiveness of this technology. Analyses of a number of different field sites are needed to assess the validity of any quoted safety factors.

Step 4

The next step is to compute the required total ORM mass and volume. The required total mass of ORM is computed by dividing the required total O_2 mass by the ORM's O_2 yield. For example:

$$\text{Required Total Mass of ORM (kg)} = \frac{\text{Required Total } O_2 \text{ Mass(kg)}}{\text{ORM } O_2 \text{ Yield}\left(\frac{\text{mg } O_2}{\text{gm ORM}}\right)\left(\frac{\text{kg } O_2}{10^6 \text{ mg } O_2}\right)\left(\frac{10^3 \text{ gm ORM}}{\text{kg ORM}}\right)} \quad (8)$$

The ORM O_2 yield can be obtained from the manufacturer or can be measured directly on ORM samples. Values reported in the literature range from 1 to 100 mg O_2/gm ORM. It is also useful to estimate the required total volume of ORM by dividing the required total mass of ORM by the density of the specific form of ORM being used:

$$\text{Required Total ORM Volume } (\text{m}^3) = \frac{\text{Required Total ORM Mass (kg)}}{\text{ORM Density} \left(\frac{\text{kg}}{\text{m}^3}\right)} \tag{9}$$

Reported values of ORM density range from approximately 500 kg/m^3 for dry powder to 1,400 kg/m^3 for socks, slurries, and cast ORM.

Example Calculation No. 3 in Section 5 addresses the calculation of the total mass and volume of ORM required for a hypothetical site.

Step 5

Once the required total mass and volume of ORM have been determined, the next step is to select an ORM application method and develop a workable design and cost estimate. If ORM will be added to an excavation or trench, the total mass (or volume) of ORM per unit area of excavation or trench run can be easily computed. If ORM will be installed as socks in existing wells, or if ORM slurry will be injected into direct-push or augered boreholes, the total number of wells or holes required can be determined by dividing the required total ORM volume by the volume of the well, borehole, or the injected slurry zone:

$$\text{Required Number of Wells or Boreholes} = \frac{\text{Total Required ORM Volume } (\text{m}^3)}{\text{Internal Well, Borehole, or Injected Slurry Volume } (\text{m}^3)} \tag{10}$$

An approximate spacing can then be computed by dividing the total area of the plume by the required number of wells, boreholes, or injections:

$$\text{Required Spacing (m)} = \left(\frac{4}{\pi} \frac{\text{Total Area of Plume } (\text{m}^2)}{\text{Required Number of Wells, Boreholes, or Injections}} \right)^{0.5} \tag{11}$$

The required spacing may be reduced to account for uncertainties in the volume of ORM delivered to a unit volume of aquifer by various installation methods. After computing an approximate spacing, it is necessary to arrange the wells or boreholes on the site. Criteria to be considered include physical site constraints (buildings, powerlines, etc.), equipment use efficiency, and providing adequate spatial coverage of the plume. It is also important to consider the potential for only limited transverse mixing of released O_2 downgradient of each well or borehole (see Figure 3-2). To do this, first estimate the ratio α_L/α_T and refer to Figure 3-2 to estimate the approximate width of the dissolved O_2 plume downgradient from each well or borehole. Care should be taken to ensure that the O_2 plumes from all ORM installations overlap and provide complete spatial coverage of the contaminant plume. This will include consideration of the effect O_2 consumption by hydrocarbon degrading microorganisms will have on the O_2 plume. In most cases, a larger number of wells or boreholes is required to meet the requirement of complete site coverage than to deliver the required mass of ORM. Staggered rows of wells or boreholes, with each row offset from the rows on either side, are usually desirable to minimize the required transverse spreading distance of ORM from each well.

In many cases it will be cost-effective to replenish the ORM periodically during the life of the project, and this will reduce the quantity of ORM that will be applied/installed at any one time.

Examples of ORM deployment calculations for a hypothetical site are presented in Example Calculation No. 4 in Section 5.

PREVENTION OF OFF-SITE PLUME MIGRATION

If the objective is to prevent off-site migration of a petroleum hydrocarbon plume, the ORM installation is designed to ensure that the rate of O_2 release will be sufficient to meet the combined chemical and microbiological O_2 demand exerted by groundwater flowing through the treatment zone. For example, the design could consist of an interceptor trench or an array of wells or boreholes installed along the downgradient perimeter of the plume. For this type of installation, the design criteria can be written:

$$\begin{aligned} O_2 \text{ release rate of ORM installation} = & \ (O_2 \text{ demand of contaminated groundwater}) \\ & \times (\text{pore water velocity}) \\ & \times (\text{cross-sectional area of contaminant plume}) \qquad (12) \end{aligned}$$

The design of an ORM installation using these criteria can be performed as a series of steps:

Step 1

The first step is to estimate the O_2 demand that will be exerted by contaminated groundwater entering the treatment zone. As discussed in Section 2, this calculation should be performed using integrated concentration measures (TPH, BOD, etc.). Note that contaminants sorbed to sediments are not included in this calculation because only contaminants in groundwater flowing through the treatment zone will contact the O_2 generated by the ORM. However, oxygen consumption by sorbed sediments, residual NAPL and free product, and reduced species in groundwater or sediment will have to be considered if it is likely that dissolved O_2 released by the ORM will contact these materials.

Step 2

The second step is to estimate the rate of O_2 release required (1) to degrade petroleum hydrocarbons (and perhaps naturally occurring dissolved organic carbon) in the contaminant plume via aerobic respiration pathways, and (2) to oxidize reduced inorganic species in solution (e.g., Fe^{2+}). The rate of O_2 required to meet the microbiological demand is obtained by multiplying the contaminant concentrations by an appropriate stoichiometric coefficient (e.g., equation 1) and then multiplying by the pore water velocity and cross-sectional area of the plume. Similar calculations can be performed to determine the rate of O_2 required to oxidize reduced inorganic species (e.g., equation 2).

Step 3

The next step is to estimate the O_2 release rate of the proposed ORM installation. This is done by multiplying the O_2 release rate of the particular ORM formulation to be used by the total volume of ORM in the interceptor trench, boreholes, etc. The O_2 release rate will be a function of the ultimate O_2 yield of the ORM, the O_2 demand exerted by the groundwater, and the method of application.

COST ESTIMATES FOR ORM INSTALLATIONS

Cost estimates are determined by combining cost for the ORM (calculated using the steps above) with the usual mobilization/demobilization, personnel, equipment use, material, and decontamination costs. Current cost data are best obtained from ORM manufacturers, drilling contractors, etc.

MONITORING PROGRAM

A monitoring program should be designed to collect sufficient data to document ORM installation performance. Typically, the overall objective of the monitoring program is to verify that the selected design will reduce specific contaminant (e.g., BTEX) concentrations or total contaminant mass to applicable regulatory levels in an acceptable time and with an acceptable cost. To meet this objective, sufficient data should be collected (1) to quantify contaminant degradation rates before and after ORM installation, (2) to verify that changes in degradation rates are due to O_2 release, and (3) to predict total time required to meet site cleanup goals. Monitoring data can also be used to modify the design of the ORM installation to improve performance, if necessary (e.g., additional drive-point boreholes may be installed to improve spatial coverage of plume).

Typically the monitoring program consists of periodic groundwater sample collection and analysis from monitoring wells; occasionally these data are supplemented with analyses on sediment cores. Ideally the wells should provide complete spatial coverage of the plume and include wells located in upgradient (uncontaminated) and downgradient positions relative to the regional groundwater flow direction. It is also useful if subsets of the monitoring well array are aligned with the regional flow direction, to simplify rate calculations and to allow approximate mass balances for contaminant and oxygen to be estimated. Sufficient data should be collected prior to ORM installation to establish pre-existing trends. Ideally the same type of data (in the same locations) should be collected after ORM installation to allow direct comparison of the "before-and-after" data. Contaminant degradation rates are best determined by plotting total contaminant mass (determined by integrating individual contaminant concentrations with position throughout the plume) versus time. However, existing monitoring well networks typically contain a limited number of wells and do not provide complete spatial coverage of the plume. It may be necessary to quantify degradation rates by plotting concentration versus time at specific wells or concentration versus distance and time for wells approximately aligned with the regional groundwater flow direction.

As discussed in Section 2, all degradable organic compounds contribute to the microbial O_2 demand and consumption of O_2 released by an ORM installation. The monitoring program should therefore include analyses both for specific contaminants of regulatory concern (e.g., BTEX) and appropriate total concentration measures (e.g., TPH or TOC) since it is not possible to control which specific compounds will serve as electron donors in aerobic respiration. Although not required to demonstrate success of an ORM installation, which is usually determined solely by reductions in petroleum hydrocarbon concentrations, it may be desirable to measure concentrations of other constituents related to ORM performance. For example, measured concentrations of dissolved O_2 and CO_2 can be used to compute rates of O_2 consumption and CO_2 production within the plume. At some sites it may also be desirable to measure concentrations of various reduced inorganic compounds (e.g., Fe^{2+} and S^{2-}), which can be used to compute rates of inorganic O_2 consumption. All of these parameters can be measured at low cost in the field at the time of sample collection for contaminant analyses (e.g., using CHEMetrics or HACH kits) and provide an independent evaluation of ORM installation performance.

Section 5
EXAMPLE DESIGN CALCULATIONS

EXAMPLE CALCULATION NO. 1

Given:

A contaminant plume with approximate dimensions: 100 m (length) x 50 m (width) (Figure 5-1). The thickness of the saturated zone is 5 m and the aquifer porosity and bulk density are 0.25 and 1200 kg/m^3, respectively. The source of contamination was a leaking underground gasoline storage tank and residual product in the unsaturated zone. Average TPH-G concentrations for the groundwater and aquifer sediment within the plume are 20 mg/L and 15 mg/kg, respectively. The average ferrous iron (Fe^{2+}) concentration in groundwater within the plume is 10 mg/L.

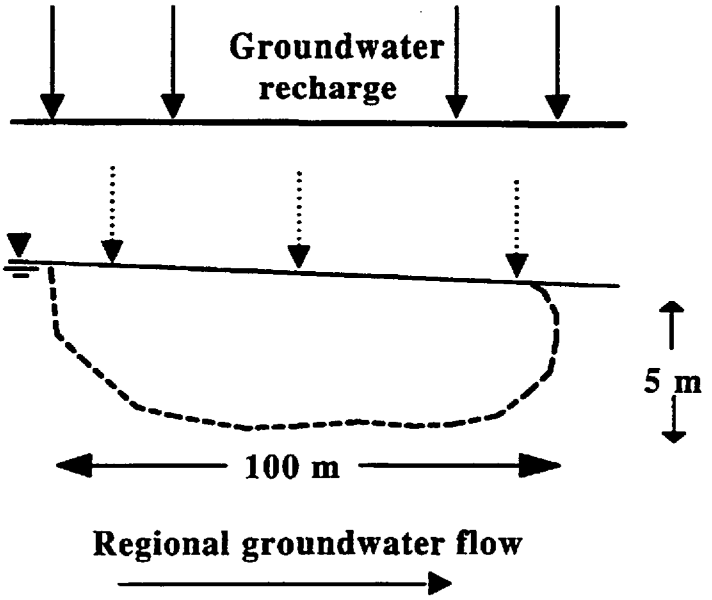

Figure 5-1. Schematic of contaminated site showing overall dimensions of petroleum hydrocarbon plume

Find:

Total quantity of O_2 required to remediate plume using aerobic respiration pathway.

Solution:

$$\text{Volume of contaminated groundwater} = (100\text{ m})(50\text{ m})(5\text{ m})(0.25) = 6250\text{ m}^3$$

$$\text{Mass of contaminated sediment} = (100\text{ m})(50\text{ m})(5\text{ m})\left(1200\frac{\text{kg}}{\text{m}^3}\right) = 3 \times 10^7\text{ kg}$$

Total quantity of TPH–G =

$$\left(20\frac{\text{mg}}{\text{L}}\right)(6250\text{ m}^3)\left(\frac{1000\text{ L}}{\text{m}^3}\right)\left(\frac{\text{kg}}{10^6\text{ mg}}\right) + \left(15\frac{\text{mg}}{\text{kg}}\right)(3 \times 10^7\text{ kg})\left(\frac{\text{kg}}{10^6\text{mg}}\right)$$

$$= 125\text{ kg (groundwater)} + 450\text{ kg (sediment)} = \underline{575\text{ kg}}\text{ total (answer)}$$

$$\text{Mass of Fe}^{2+} = \left(10\frac{\text{mg}}{\text{L}}\right)(6250\text{ m}^3)\left(1000\frac{\text{L}}{\text{m}^3}\right)\left(\frac{\text{kg}}{10^6\text{ mg}}\right) = 62.5\text{ kg}$$

(Assume 3 kg O_2 required to degrade 1 kg petroleum hydrocarbon)

$$\text{Total O}_2\text{ required} = \left(3\frac{\text{kg O}_2}{\text{kg}}\right)(575\text{ kg}) + (62.5\text{ kg Fe}^{2+})\left(\frac{8\text{ g O}_2}{55.8\text{ g Fe}^{2+}}\right)$$

$$= 1725 + 9 = \underline{1734\text{ kg}}\text{ (answer)}$$

EXAMPLE CALCULATION NO. 2

Given:

Regional groundwater flow is aligned with the length of the plume in the previous example and the Darcy velocity is 0.25 m/d. The average dissolved O_2 concentration in upgradient monitoring wells is 4 mg/L. The estimated recharge rate is 0.03 m/y with a dissolved O_2 concentration of 2 mg/L at the depth of the water table (this value is less than the air equilibrated values in Table 1 indicating some O_2 removal in the contaminated soil above the water table).

Find:

Rate of natural O_2 supply to the plume, estimated time required for cleanup using only naturally supplied O_2. Consider only aerobic degradation processes in these calculations.

Solution:

O_2 supply from upgradient groundwater

$$= (50\text{ m})(5\text{ m})\left(0.25\frac{\text{m}}{\text{d}}\right)\left(365\frac{\text{d}}{\text{yr}}\right)\left(4\frac{\text{mg}}{\text{L}}\right)\left(\frac{\text{kg}}{10^6\text{mg}}\right)\left(\frac{1000\text{ L}}{\text{m}^3}\right)$$

$$= 91\text{ kg/yr}$$

O_2 supply from recharge

$$= (50\text{ m})(100\text{ m})\left(0.03\frac{\text{m}}{\text{yr}}\right)\left(2\frac{\text{mg}}{\text{L}}\right)\left(\frac{\text{kg}}{10^6\text{mg}}\right)\left(\frac{1000\text{ L}}{\text{m}^3}\right)$$

$$= 0.3\text{ kg/yr}$$

Total natural O_2 supply = 91 + 0.3 = 91.3 kg/yr

$$\text{Estimated time to clean up} = \frac{(1734\text{ kg})}{\left(91.3\frac{\text{kg}}{\text{yr}}\right)} = \underline{19\text{ yrs}}\text{ (answer)}$$

EXAMPLE CALCULATION NO. 3

Given:

Plume in previous example.

Find:

Total mass and volume of ORM required to remediate site within three years. Assume ORM O_2 content = 85 mg O_2/g ORM. Assume ORM will be installed as a water:ORM powder slurry with density of 1,400 kg/m^3.

Solution:

ORM mass required

$$= \left(1734\text{ kg} - 91.3\frac{\text{kg}}{\text{yr}}(3\text{ yr})\right)\left(\frac{\text{g ORM}}{85\text{ mg }O_2}\right)\left(\frac{10^6\text{mg}}{\text{kg}}\right)\left(\frac{\text{kg}}{10^3\text{g}}\right)$$

$$= \underline{17178\text{ kg}}\text{ ORM (answer)}$$

ORM volume required

$$= 17178\text{ kg}\left(\frac{\text{m}^3}{1400\text{ kg}}\right) = \underline{12.3}\text{ m}^3\text{ (answer)}$$

EXAMPLE CALCULATION NO. 4

Given:

Plume in previous example.

Find:

Trial remedial design using slurry injection in augered boreholes.

Solution:

Assume that, following injection, the effective diameter of ORM slurry filled injection zone is 8 in.

injection zone volume for one borehole

$$= \pi\frac{(8\text{ in})^2}{4}\left(\frac{2.54\text{ cm}}{\text{in}}\right)^2\left(\frac{\text{m}}{100\text{ cm}}\right)^2(5\text{ m}) = 0.162\text{ m}^3$$

number of boreholes required (equation 10)

$$= 12.3\text{ m}^3\left(\frac{1}{0.162\text{ m}^3}\right) = 76$$

approximate borehole spacing (equation 11)

$$= \left(\frac{(4)(100\text{ m})(50\text{ m})}{(\pi)(76)}\right)^{0.5} = 9\text{ m}$$

This is a large number of boreholes. Try boreholes with an effective diameter of 12 in.

injection zone volume

$$= \pi\frac{(12\text{ in})^2}{4}\left(\frac{2.54\text{ cm}}{\text{in}}\right)^2\left(\frac{\text{m}}{100\text{ cm}}\right)^2(5\text{ m}) = 0.365\text{ m}^3$$

number of boreholes required (equation 10)

$$= 12.3\text{ m}^3\left(\frac{1}{0.365\text{ m}^3}\right) = 34$$

approximate borehole spacing (equation 11)

$$= \left(\frac{(4)(100\text{ m})(50\text{ m})}{(\pi)(34)}\right)^{0.5} = 14\text{ m}$$

Now check spacing for effective transverse dispersion. Assume the ratio $\alpha_L/\alpha_T = 10$ for this aquifer. Referring to Figure 3-3, estimate the maximum dissolved O_2 plume width to be ~ 2 m at a downgradient distance of 4 m. If boreholes will be installed in staggered rows offset by one-half the required spacing, an average borehole spacing of 4 m is required, which is smaller than that calculated for either the 8 or 12 inch boreholes. If these size boreholes will be used, the average spacing can be reduced. Alternatively, a larger number of smaller boreholes could be used. For example, if drive-points are used to install ORM slurry and the effective diameter of the ORM treated sediment is 4 in., the required number of boreholes increases to 135 with an approximate borehole spacing of 6.8 m.

Section 6

ANNOTATED BIBLIOGRAPHY

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Describes field experiment to evaluate effectiveness of ORM-concrete briquettes installed in large-diameter wells and cast ORM pencils installed in augered boreholes for increasing dissolved O_2 concentrations and promoting aerobic respiration of benzene and toluene in groundwater flowing through treated portion of the aquifer. O_2 release persisted for ~ 10 weeks in groundwater flowing through the treatment zone. Benzene and toluene concentrations decreased by 50 to 85 percent along a flow path through the treatment zone.

Contaminants:	*benzene and toluene ~ 4 mg/L*
Aquifer type:	*unconfined, fine-to-medium sand (Borden aquifer)*
ORM application:	*ORM briquettes (20 % ORM by weight in concrete) in 10 inch diameter wells; cast-in-place ORM pencils prepared from 60 % ORC: 40 % water slurry*
Monitoring:	*benzene, toluene, dissolved O_2, pH, conductivity, temperature*

Bohan, D.G. and W.S. Schlett. 1997. Enhanced natural bioremediation using a time release oxygen compound. Fourth International *in situ* and On-Site Bioremediation Conference, April 28-May 1, New Orleans, LA, Battelle Press, Columbus, OH.

Describes field demonstration performed to evaluate effectiveness of ORC® for increasing dissolved oxygen concentrations and promoting aerobic BTEX degradation in groundwater. ORC® was installed in a permeable barrier consisting of fifty 10.8 cm diameter boreholes containing cast ORC® cylinders (prepared from 2:1 ORC® powder:water slurry). Numbers of microorganisms in water samples increased approximately 100 times after ORC® installation. Benzene concentrations and total contaminant mass decreased by approximately 75 and 54 %, respectively, in downgradient monitoring wells during the first 316 days after installation.

Contaminants:	*gasoline; maximum total BTEX = 38 mg/L*
Aquifer type:	*unconfined, fine-to-medium sand*
ORM application:	*ORC® cylinders in augered boreholes*
Monitoring:	*BTEX, dissolved O_2, pH, conductivity, total bacteria*

Borden, R.C., R.T. Goin, and C.M. Kao. 1997. Control of BTEX migration using a biologically enhanced permeable barrier. Ground Water Monitoring and Remediation, vol. 17, no. 1, pp. 70-80.

Describes laboratory and field experiments designed to evaluate effectiveness of four ORM formulations for increasing dissolved oxygen concentrations and promoting aerobic BTEX degradation in groundwater flowing through a permeable barrier. Duration of oxygen release in laboratory experiments was longest (300 days) for the 21 % MgO_2 (ORC®). Total BTEX concentrations decreased and dissolved O_2 concentrations increased as groundwater flowed through the field barrier, which was constructed of 6 in diameter wells on 5 ft centers Aquifer clogging was observed downgradient of the remediation wells due to precipitation of ferric-iron containing solid phases. This was believed to have resulted from high pH from the cement and oxygen released by the ORMs.

Contaminants:	*gasoline; maximum total BTEX = 30 mg/L*
Aquifer type:	*medium silty sand*
ORM application:	*four ORM formulations (14 % CaO_2, 21 % MgO_2 [ORC®], 37 % MgO_2 [ORC®], and 21 % Urea-H_2O_2) mixed with portland cement*
Monitoring:	*BTEX, dissolved O_2, pH, anions, iron in sediment cores*

Chapman, S.W., B.T. Byerly, D.J. A. Smyth, and D.M. Mackay. 1997. A pilot test of passive oxygen release for enhancement of *in situ* bioremediation of BTEX-contaminated groundwater. Ground Water Monitoring and Remediation, vol. XVII, no. 2, pp. 93-105.

Describes a field demonstration for increasing dissolved O_2 concentrations and promoting aerobic BTEX degradation in groundwater flowing through a permeable barrier consisting of seven 20 cm diameter, ORM-containing treatment wells located in two staggered rows on 0.6 m centers. Although spatial variability in measured concentrations made interpretations difficult, monitoring over six month period indicated increased dissolved O_2 and decreased BTEX concentrations at wells located 0.6 m downgradient of a line of treatment wells containing ORM, relative to concentrations measured in monitoring wells located 0.6 m upgradient. However, observed BTEX mass loss accounted for less than 10 % of total O_2 released from the treatment wells over the 1.2 m travel path.

Contaminants:	*gasoline; maximum total BTEX = 33 mg/L*
Aquifer type:	*unconfined, fine-to-medium sand*
ORM application:	*socks in wells each containing 50:50 ORC®: # 90 silica*
sand	*54 kg ORM per well for a for total of 378 kg ORM*
Monitoring:	*BTEX, dissolved O_2, pH*

Johnson, J.G. and J.E. Odencrantz. 1997. Management of hydrocarbon plume using a permeable ORC® barrier. Fourth International *In Situ* and On-Site Bioremediation Conference, April 28-May 1, New Orleans, LA, Battelle Press, Columbus, OH.

Describes field demonstration for increasing dissolved O_2 concentrations and promoting aerobic BTEX degradation in groundwater flowing through a permeable barrier consisting of 20 6-in diameter, ORC-containing treatment wells. Monitoring over 12 month period indicated increased dissolved O_2 and decreased BTEX concentrations at wells located ~ 10 ft downgradient of a line of treatment wells containing ORC®, relative to concentrations measured in monitoring wells located ~ 0.8 ft upgradient.

Contaminants:	*gasoline; maximum total BTEX = 33 mg/L*
Aquifer type:	*unconfined, fine-to-medium sand*
ORM application:	*socks in wells each containing 50:50 ORC: # 90 silica sand* *54 kg ORC® per well for a for total of 378 kg ORM*
Monitoring:	*BTEX, dissolved O_2, pH*

Heitkamp, M.A. 1997. Effects of oxygen-releasing materials on aerobic bacterial degradation processes. Bioremediation Journal, vol. 1, issue. 2, pp. 105-114.

Describes laboratory microcosm experiments comparing degradation rates for three ORM products in mixed bacterial cultures. P-nitrophenol and phenol were ~ 50 % degraded within 5 days and ~ 100 % degraded within 10 days in the presence of ORM.

Contaminants:	*p-nitrophenol and phenol ~ 200 mg/L*
Aquifer type:	*laboratory study*
ORM application:	*polyvinylidene chloride-encapsulated sodium percarbonate;* *magnesium peroxide, calcium peroxide*
Monitoring:	*p-nitrophenol, phenol, carbon dioxide*

Section 7
ADDITIONAL REFERENCES

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Feenstra, S., D.M. Mackay, and J.A. Cherry. 1991. A method for assessing residual NAPL based on organic chemical concentrations in soil samples. Groundwater Monitoring and Remediation, Spring, 1991, pp. 128-136.

Fry, V.A., J.D. Istok, and K.T. O'Reilly. 1996. Effect of trapped gas on dissolved oxygen transport - implications for *in situ* bioremediation. Ground Water, Vol, 34, No. 2, pp. 200-210.

Huntley, D. and G.D. Beckett, 1997. Persistence of LNAPL sources and relation to risk. Proceedings: Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, Remediation. November 12-14, 1997. Houston, Texas. pp. 426-441.

Mace, R.E., R.S. Fisher, D.M. Welch, and S.P. Parra. 1997. Extent, mass, and duration of hydrocarbon plumes from leaking petroleum storage tank sites in Texas. Geological Circular 97-1, Bureau of Economic Geology, The University of Texas at Austin, Austin, TX, 52 pp.

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Koenigsberg, S.S. 1997. Personal Communication. Letter of November 19, 1997.

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