



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

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
PUBLICATION NUMBER 4671
JULY 1998





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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. ORM 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

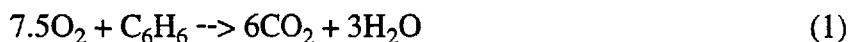
THE ROLE OF OXYGEN IN *IN SITU* BIOREMEDIATION OF PETROLEUM HYDROCARBONS

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 O₂, which can be computed by representing the degradation process as a balanced chemical reaction. For example, the degradation of benzene (C₆H₆) to carbon dioxide (CO₂) and water (H₂O) via an aerobic respiration pathway can be written:



so that 7.5 moles (240 g) of O₂ (the electron acceptor) are required to degrade one mole (78 g) of benzene (the electron donor). The ratio of O₂ 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 O₂ will be required to degrade 1 mg/L dissolved benzene in groundwater and 310 mg O₂/kg will be required to degrade 100 mg benzene/kg in an aquifer sediment matrix. The quantity of O₂ 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 O₂ requirements at contaminated sites.

The stoichiometry described above refers to complete biodegradation of benzene to CO₂ and water (i.e., mineralization). O₂ to benzene ratios less than 3:1 may result in degradation of benzene into less toxic, readily biodegradable compounds. Therefore, some practitioners choose smaller O₂ to contaminant ratios when calculating the ORM requirement to reach a desired site remediation goal.

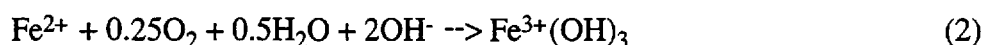
It is important to recognize that microorganisms use a wide variety of organic compounds as electron donors during aerobic respiration, and that all degradable organic compounds create a microbial O₂ demand. It is therefore incorrect to calculate the O₂ required to remediate a petroleum contaminated 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, O₂ requirements should be calculated using concentration measures that represent the sum of all 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 O₂ 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 O₂ thus reducing the amount of petroleum hydrocarbon degraded for a given amount of available O₂. For example, ferrous iron (Fe²⁺) is present in the groundwater and sediment minerals at many hydrocarbon-impacted sites and can react with O₂ to form ferric iron (Fe³⁺) hydroxides:



so that 0.25 moles (8 g or 8 mg/L) of O₂ are consumed by the oxidation of one mole (56 g or 56 mg/L) of Fe²⁺ to Fe³⁺. Similar reactions are possible with reduced forms of sulfur and manganese and should be included when estimating the total quantity of O₂ required to remediate a contaminated site. Although in many cases the O₂ demand created by reduced inorganic compounds is small relative to the O₂ 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 O₂ 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