

Application of oxygen-releasing material to enhance in situ aerobic bioremediation

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ABSTRACT: Contamination of groundwater by petroleum-hydrocarbons is a widespread environmental problem. Generally in plumes of petroleum-hydrocarbon contamination, the dissolved oxygen (DO) demand imposed by biodegradation of organic contaminants exceeds the DO available creating anaerobic conditions within the plume core and mid-plume areas. Since the petroleum-hydrocarbons are generally degraded faster under aerobic conditions, aerobic bioremediation can be applied to enhance the biodegradation of petroleum-hydrocarbons within of the plume if oxygen can be provided to the subsurface economically. The objectives of this bench-scale study were to (1) develop an oxygen-releasing materials for continuous oxygen supplement, (2) determine the optimal components of the studied oxygen release material, and (3) evaluate the oxygen release rate and lifetime of this material. Moreover, the potential of using a passive oxygen release material to clean up aquifers contaminated by petroleum hydrocarbons was also studied. Bench experiments were conducted to design and identify the components of the oxygen-releasing materials. The mixtures of the oxygen release material were prepared by blending gypsum, calcium peroxide (CaO_2), sand, and water together at a ratio of 1:0.5:0.14:0.75 by weight. Cement was used as a binder and regular medium filter sand was used to increase the permeability of the mixture. Calcium peroxide releases oxygen upon contact water ($2\text{CaO}_2 + 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{Ca(OH)}_2$). The designed material with a density of 1.1 g/cm^3 was made of 3.5-cm cube for the batch experiment. Results show that the oxygen release rate of the material is 0.025 mg/day/g . The oxygen release material is able to remain active in oxygen release for more than three months. With the application of this developed oxygen release material, the contaminated subsurface can remain an aerobic environment for subsequent aerobic bioremediation. For the future field application, the developed materials can be placed in remediation wells, trenches, horizontal wells, or barriers. Thus, the passive biobarrier system has advantages over conventional system including less maintenance, cost-effectiveness, no above-ground facilities, no groundwater pumping and reinjection, no air pollution problems, and groundwater remediation in situ. The proposed treatment system would be expected to provide a more cost-effective alternative to remediate petroleum-hydrocarbon contaminated aquifers. This technology can also be applied for other hazardous waste contaminated sites.

Keywords: oxygen-releasing material, biobarrier, aerobic bioremediation, petroleum hydrocarbon, biodegradation

1 Introduction

Underground contamination with petroleum-hydrocarbons has been one of the serious environmental problems in several countries, with many industrial sites presenting groundwater contamination. The sources of contaminants may be released from aboveground and underground storage tanks, gasoline pipelines, and industrial wastewater. Petroleum hydrocarbons are mainly composed of benzene, toluene, ethyl-

benzene, and xylems (BTEX), and other constituents such as methyl-t-butylether (MTBE), naphthalene, 1,3,5-trimethyl benzene (1,3,5-TMB), 1,2,4-trimethyl benzene (1,2,4-TMB) [5]. It is generally recognized that petroleum-hydrocarbons have a high risk to biophysical environmental receptors when a hydrocarbon release occurs.

Various biological, physical, and chemical remediation technologies can be used for the

removal of groundwater contaminants, particularly petroleum-hydrocarbons, such as pump and treat, air stripping, chemical oxidation, vapor extraction systems, and bioventing. However, many of these techniques are typically possessed of high costs or have limited applications. Therefore, intrinsic bioremediation or natural bioremediation has been considered as one of the potential methods for the cleanup of petroleum-hydrocarbon contaminated sites. Compare to other traditional technologies, intrinsic bioremediation has a cost-effective advantage.

In general, the most important mechanism of natural attenuation is degradation of pollutants by naturally occurring bacteria. The native bacteria in aquifers need a significant quantity of oxygen to degrade petroleum hydrocarbons [1]. Almost all petroleum hydrocarbons are biodegradable (able to be biodegraded) under aerobic conditions. However, it is reported that aquifers are often anoxic [3,7,8]. In plumes of petroleum-hydrocarbon contamination, the oxygen demand imposed by biodegradation of BTEX and other compounds usually exceeds the available dissolved oxygen in aquifers and results in anaerobic conditions within the plumes. This, aerobic biodegradation may occur only at the plume fringe [2,4,14] (Fig.1). It was often found that the addition of an oxygen source was able to achieve accelerate degradation processes [13]. In general, the addition of oxygen to groundwater using oxygen-releasing material will enhance the rates of natural biodegradation and speed up the plume's destruction [6,9,10]. There are less negative impacts to the naturally occurring processes via the addition of oxygen-releasing material. Alternative methods to add oxygen to aquifer systems include: application of H_2O_2 with UV for generation of hydroxyl radicals ($OH\cdot$), addition of H_2O_2 , injection of pure oxygen, sparging with ambient air via semi-permeable tubing placed in the aquifer [12]. However, these methods were not recommended because of the possible plume mass loss due to volatilization.

Solid containing calcium peroxide mixture rocks, oxygen-releasing material, are used to provide O_2 in bioremediation. Several papers have provided proofs of the concept for

oxygen-releasing material. Kao and Borden [9] have demonstrated that use of oxygen release barriers to passive increase DO in the subsurface enhance the intrinsic biodegradation of dissolved hydrocarbons within the barriers and the downgradient aquifer. Koenigsberg[11] reported that oxygen-releasing material is highly effective in BTEX bioremediation. In addition, artificial oxygen additions via oxygen-releasing material have also been applied to the anoxic aquifer to stimulate the efficiency of natural biodegradation. The results indicate that oxygen-releasing material has effectively enhanced the natural attenuation of the contaminants [1,12]. Applications of oxygen-releasing material include source-area treatments and permeable barriers. Oxygen, moving by advection, dispersion, and diffusion, creates a zone of increasing dissolved oxygen. oxygen-releasing material can also be placed in horizontal well, trenches, injected using geoprobe techniques, or augured into the aquifer.

In this study, bench-scale of oxygen release material was selected to fulfill the following objectives: (1) develop an oxygen-releasing materials for continuous oxygen supplement, (2) determine the optimal components of the studied oxygen release material, and (3) evaluate the oxygen release rate and lifetime of this material.

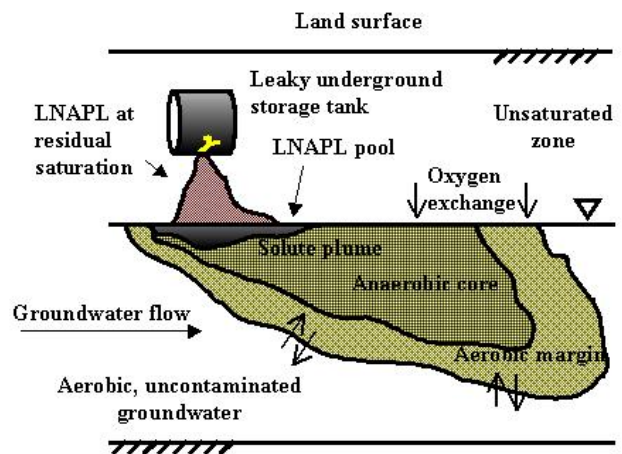


Figure 1. Oxygen supply to petroleum-hydrocarbon release undergoing natural attenuation. [14]

2 Materials and Methods

Laboratory studies were conducted to identify an appropriate oxygen-releasing material mixture and determine the oxygen release rate of oxygen-releasing material. Two wide-mouth bottles (labeled as A and B) were used as batch reactors in batch manometer experiments. A mixture was prepared by blending gypsum, calcium peroxide (CaO₂), sand, and water together at a ratio of 1∓0.5∓0.14∓0.75 by weight. B mixture was the same as A mixture without sand. Gypsum was selected as a binder, sand was used to increase the permeability of the mixture, and CaO₂ was used as the oxygen source. CaO₂ can release oxygen via contact water according to the following reaction:



After the preparation of oxygen-releasing material, the oxygen content of CaO₂ and the fraction of the original oxygen retained in the mixture were determined immediately in triplicates by adding 100 ml of 1M sulfuric acid to 0.5 g of CaO₂ or the mixture, and then titrated with standardized potassium permanganate (0.1 N) to a light pink-purple end point.

The designed oxygen release material with a density of 1.1g/cm³ was made of 3.5 cm cubes. The design of the batch experiments in this study was based on a method for measuring soil respiration. The main difference between this study and the method was that oxygen cubes were used in place of soil. In addition, instead of measuring oxygen adsorption, oxygen release was measured. An enclosed reactor was used to measure the oxygen release according to pressure changes. Fig. 2 presents the schematic diagram showing the oxygen measure reactors. Each reactor contained 80 g of cubes and 300 ml of deionized (DI) water. The control bottles were prepared without the addition of oxygen cubes. Oxygen release from the cubes caused a change in pressure that was recorded by a manometer. Measurements of changes in water height were performed each day, and then the reactors were vented. The released oxygen mass was calculated using the following equation. Results were recorded as mg O₂/d/g of cube versus time.

$$\text{O}_2 \text{ release}(\mu\text{l}) = k(\mu\text{l}/\text{mm}) \times \text{manometer reading}(\text{mm})$$

$$k = (V_g(\mu\text{l}) \times (273/T) + V_f(\mu\text{l}) \times S) / P_0$$

V_g = volume of reactor head space

V_f = volume of fluid added to jar

T = temperature in degrees Kelvin

S = solubility of O₂ in water at temperature of incubation

P₀ = standard pressure (1 atm)

=10336 mm for distilled water

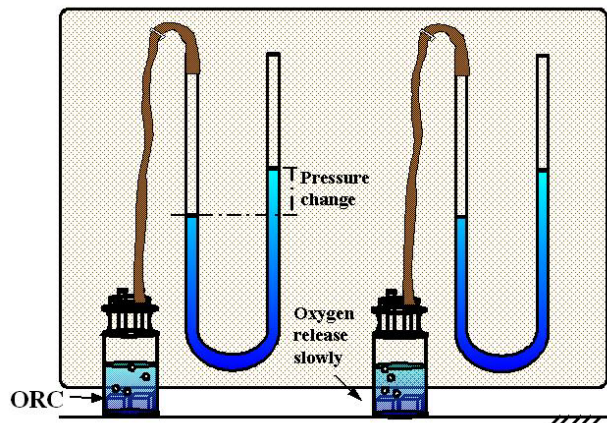


Fig 2. Schematic diagram showing the reactors of oxygen measurement

3 RESULTS AND DISCUSSION

Results from the oxygen analysis show that the oxygen released from CaO₂ was 175 mg O₂ per g of CaO₂. The initial CaO₂ retention in the oxygen mixture was 21∓, which was 37 mg O₂ per g of mixture based on the oxygen content of the CaO₂ used. Figures 3 and 4 present the data of oxygen release from the bench tests A and B, respectively. Fig. 3 shows oxygen release of Test A over time during a 6-month operating period. Results indicate that oxygen release dropped rapidly within 20 days and then declined slowly until the end of the experiment. Fig. 4 presents oxygen release of Test B over time during a 6-month operating period. Because no sand was added to the cubes, Test B has a slower oxygen release rates than Test A. In addition, oxygen release stopped after 150 days. This shows that sand plays an very important role in long-term performance of oxygen-releasing material.

Based on the batch experiment, the average oxygen release rates of Tests A and B were 0.031 mg O₂/d/g oxygen material and 0.025 mg O₂/d/g oxygen material, respectively. The oxygen release rates were calculated based on the period from 20-200 days when the releasing rates reached more stabilized condition. Results (Fig. 5 and 6) indicate that the Test A have a more efficient oxygen release rate than Test B, and the designed material would be able to release oxygen more than six months.

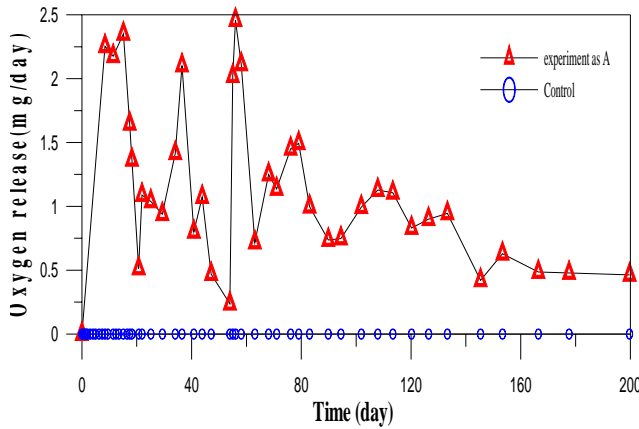


Fig 3. Oxygen release over time from oxygen materials in Test A.

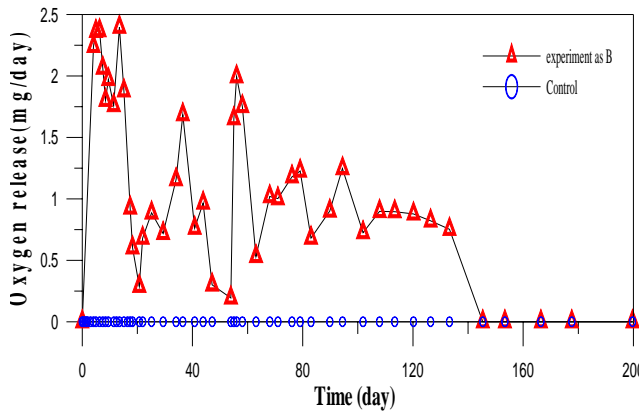


Fig 4. Oxygen release over time from oxygen materials in Test B.

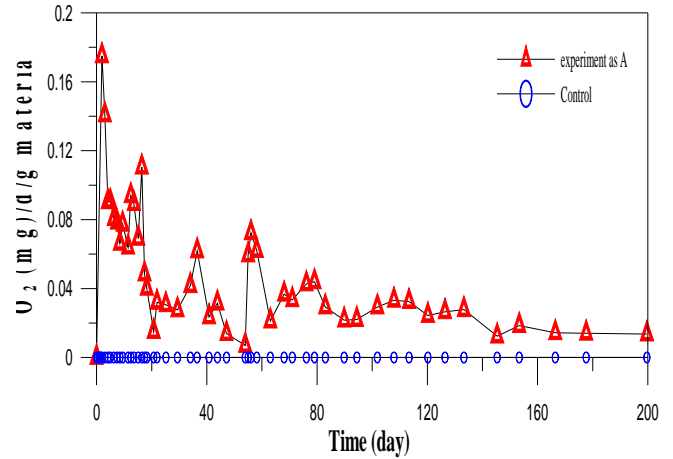


Fig 5. Results of oxygen release rates (test A)

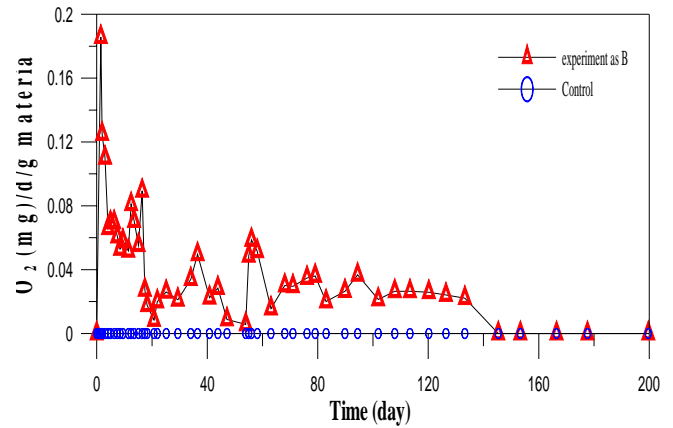


Fig 6. Results of oxygen release rates (test B)

4 CONCLUSIONS

In this study, an oxygen release material was developed to continuously release oxygen for the purpose of enhanced in situ aerobic bioremediation. Results show that the developed material seems to have a good long-term performance in oxygen release.

The following are the conclusions of this study:

1. Oxygen release material can be prepared easily from a mixture of gypsum, calcium peroxide (CaO₂), sand, and water.
2. This material has desirable oxygen release characteristics including high initial oxygen retention and slowly declining oxygen release rate.
3. The optimal components of the studied oxygen release material was to blend gypsum, calcium peroxide (CaO₂), sand, and

water with a ratio of 1:0.5:0.14:0.75 by weight

4. The average oxygen release rate was 0.031 mg O₂/d/g of material during the 6-month batch experiment period.

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