



Project Summary

Enhanced Bioremediation of BTEX Using Immobilized Nutrients: Field Demonstration and Monitoring

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A permeable barrier system was developed to control the migration of dissolved contaminant plumes in ground water. The barrier system consisted of a line of closely spaced wells installed perpendicular to the contaminant plume. Each well contained concrete briquets that released oxygen and nitrate at a controlled rate, enhancing the aerobic biodegradation of dissolved hydrocarbons in the downgradient aquifer.

Laboratory batch reactor experiments were conducted with different concretes to identify mixtures that slowly released oxygen over an extended time period. Concretes prepared with urea hydrogen peroxide were unacceptable, while concretes prepared with calcium peroxide and a proprietary formulation of magnesium peroxide had good oxygen-release rates that slowly declined over a three- to six-month period.

A full-scale permeable barrier system was constructed at a gasoline-spill site near Leland, NC. Initially, increased dissolved oxygen and decreased benzene, toluene, ethylbenzene, and xylene isomer (BTEX) concentrations in the downgradient aquifer indicated that oxygen released from the remediation wells was enhancing biodegradation. Over time, treatment efficiencies declined, suggesting that the barrier system was becoming less effective in releasing oxygen and nutrients to the aquifer. Field tracer tests and soil analyses performed at the end of the project indicated that the aquifer in the vicinity of the remediation wells was being

clogged by precipitation of iron minerals.

This Project Summary was developed by EPA's National Exposure Research Laboratory, Environmental Sciences Division, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The U.S. Environmental Protection Agency (U.S. EPA) is studying the performance of enhanced bioremediation systems to evaluate the effectiveness of the technology. The goal of this study was to design and monitor field performance of a permeable barrier treatment system that enhances the biodegradation of contaminated ground water passing through the barrier. This system could serve as an alternative method for treating contaminated ground water and could be less expensive than the techniques currently employed. The potential advantages of a permeable barrier treatment system include low maintenance requirements, no above-ground facilities, and in-situ biodegradation of contaminants with no requirement for disposal of contaminated treatment media or ground water.

Laboratory batch experiments were conducted to determine the oxygen-release characteristics of several solid peroxide-concrete mixtures. A full-scale barrier system was then installed at an underground storage tank (UST) gasoline-spill site near Leland, NC. Monitoring wells were installed upgradient and downgradient of the barrier in the contaminated portion of the

aquifer. Ground-water samples were monitored and analyzed for dissolved oxygen (DO), individual BTEX components, pH, and other relevant parameters to assess the effectiveness of the barrier system. According to the system design, high DO and low BTEX concentrations should be observed in the remediation wells and the downgradient monitoring wells. At some distance downgradient of the barrier, the BTEX concentration should be degraded below regulatory levels.

The full-scale permeable barrier system examined in this study employs concrete prepared with a proprietary formulation of magnesium peroxide (MgO_2). The concrete is loaded into permeable filter socks and placed in a line of fully screened polyvinyl chloride (PVC) wells (remediation wells) installed perpendicular to the ground-water flow direction. When ground water passes through this line of remediation wells, the MgO_2 in the concrete reacts with water, producing oxygen. Indigenous microorganisms then use the released oxygen to aerobically biodegrade the petroleum hydrocarbons present in the ground water. Sodium nitrate (NaNO_3) may also be added to the concrete, further enhancing biodegradation.

Laboratory Evaluation of Solid Peroxide Concretes

Three solid peroxide compounds, magnesium peroxide (MgO_2), calcium peroxide (CaO_2), and urea hydrogen peroxide [$\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$], were examined for their oxygen-releasing characteristics when incorporated into concrete. Close to 100% of the initial oxygen present in the peroxides was recovered from the MgO_2 and CaO_2 concretes. In contrast, the oxygen recovery for the $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$ concrete was very low (12%). This result indicates that a large portion of the available oxygen in the original $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$ was lost during preparation of this concrete.

Several different types and sizes (concrete cylinders or 4-cm-diameter briquets) of solid peroxide concrete were monitored to determine the volume of oxygen released over time. Results of this work were fitted to a zero-order model of oxygen release versus time. Oxygen release from the $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2$ concrete was too rapid to be useful in field application. Figure 1 shows a comparison of predicted oxygen-release rates over time for different mixtures and sizes of calcium and magnesium peroxide concrete. The 21% MgO_2 concrete cylinders and briquets had the slowest and most uniform release rate, while the 14% CaO_2 briquets had the most rapid release. Where a slow constant re-

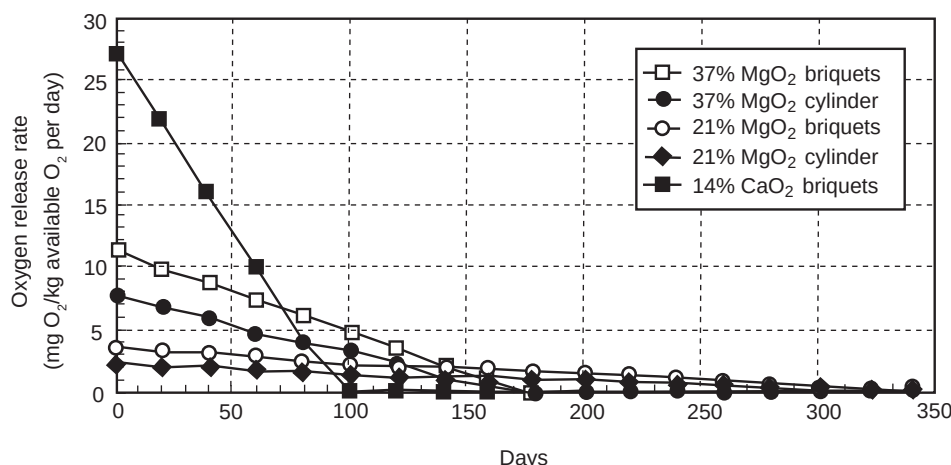


Figure 1. Best fit estimated lines showing variation in oxygen-release rates with time for magnesium peroxide and calcium peroxide concrete mixes.

lease of oxygen is required, the 21% MgO_2 concrete will be most useful.

Field Monitoring of the Permeable Barrier System

Ground water upgradient and downgradient of the barrier was monitored over an 18-month period to determine the barrier system's effectiveness and identify areas where the design could be improved. The permeable barrier was constructed to intersect the BTEX plume approximately 27 m downgradient from the former UST location and initially consisted of a series of 15-cm-diameter (6-in) PVC wells installed approximately 1.5 m (5 ft) on center. Each well was screened from 0 to 3 m (10 ft) below the water table and was designed to release a plume of DO to enhance biodegradation in the downgradient aquifer. Preliminary modeling indicated that plumes from each well would mix over a 6- to 15-m distance, resulting in complete biodegradation of the BTEX plume. Field delineation of the BTEX plume indicated that the barrier would need to be 40 m wide and extend approximately 3 m below the ground-water table. Twenty remediation wells were initially installed in the remediation line perpendicular to the plume at a distance of 1.5 m on center. The nine wells on the eastern half of the plume did not receive concrete and were operated as a control to evaluate the barrier effectiveness. During the course of the project, two major modifications were attempted to enhance the barrier system effectiveness: 1) the use of smaller concrete briquets containing MgO_2 and NaNO_3 , and 2) the installation of additional remediation wells.

The permeable barrier system examined in this project was designed to control the migration of dissolved gasoline components by enhancing the aerobic biodegradation of these compounds in the aquifer immediately downgradient of the barrier. Ideally, all contaminants would be degraded to below regulatory limits before reaching the most downgradient monitoring wells. The permeable barrier examined in this project did not achieve this objective. Table 1 lists average concentrations of benzene, toluene, ethylbenzene, and total xylenes over the entire treatment period. While the average concentrations of all BTEX components decreased substantially with distance downgradient from the barrier, only toluene met water quality standards in Monitoring Well SU5, 25 m downgradient of the barrier system.

Figures 2a and 2b show the average concentrations of total BTEX and DO in monitoring wells SU7, SU13, SU14, and SU5 for the three treatment periods and for the total project. Total BTEX concentrations in wells downgradient of the barrier are significantly lower than upgradient of the barrier for each treatment period at the 95% confidence level, indicating that some loss of contaminants is occurring. The barrier was also effective at increasing the DO concentration in the wells immediately downgradient of the barrier.

Field tracer tests conducted at the end of the project demonstrated that the average specific discharge in remediation wells that received oxygen-releasing concrete were significantly lower than in remediation wells that did not receive concrete. The lower specific discharge is attributed

Table 1. Average Concentrations of BTEX in Monitoring Wells Over the Entire Treatment Period

Well	Distance from Barrier ^a	Benzene (mg/L)	Toluene (mg/L)	Ethylbenzene (mg/L)	Total Xylenes (mg/L)
SU7	-10m	2.419	8.326	1.391	6.060
SU13	+3m	0.757	2.406	0.383	1.627
SU14	+8m	1.123	3.469	0.595	2.366
SU5	+25m	0.877	0.853	0.272	0.745
NC ^b					
Standards		0.001	1.000	0.029	0.400

^a Negative distances are upgradient of the barrier; positive distances are downgradient.

^b North Carolina

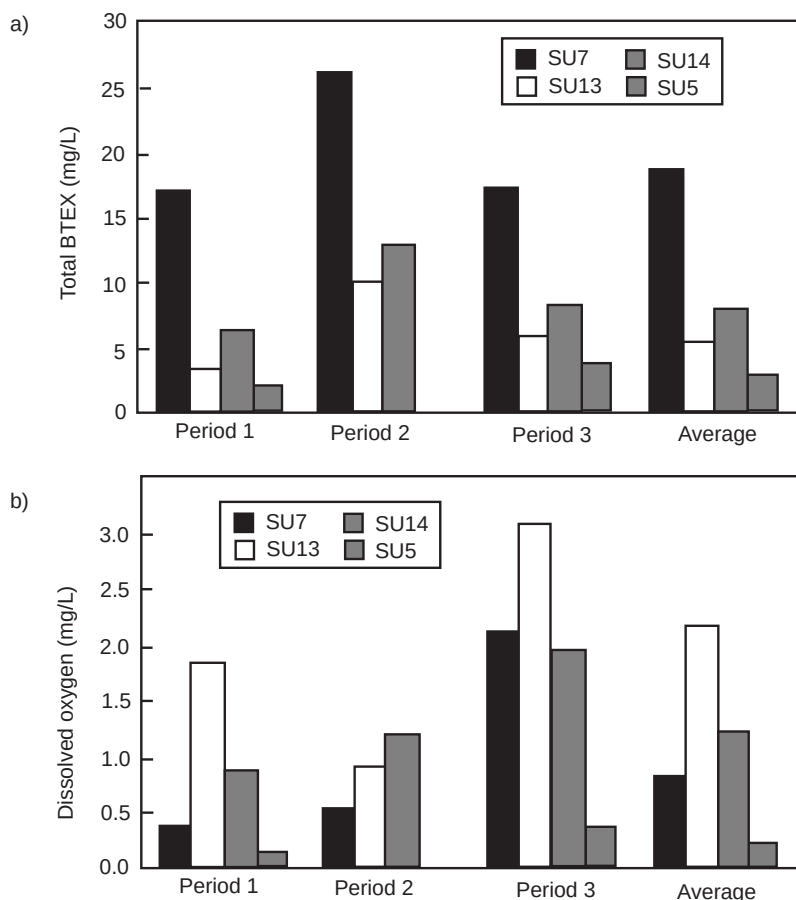


Figure 2. Mean (a) total BTEX concentrations and (b) dissolved oxygen concentrations in monitoring wells for individual treatment periods and entire barrier operational period. (Note: SU5 not included in period 2 graph because only one measurement was taken.)

to the clogging of the aquifer material immediately adjoining the wells by oxidized iron precipitates.

The probable cause of the poor barrier performance was inadequate delivery of DO to the aquifer. Assuming a 3-to-1 mass ratio of oxygen delivered to BTEX biodegraded, the delivered oxygen should be

sufficient to biodegrade approximately 10% of the BTEX entering the barrier. This problem is only partially due to clogging of the remediation wells. Assuming no clogging of the remediation wells, the maximum total BTEX concentration that this barrier could effectively treat would be 6 mg/L.

Conclusions and Recommendations

Concrete briquets containing either calcium peroxide or a proprietary formulation of magnesium peroxide (ORCTM) have desirable oxygen-release characteristics, including high retention of the original oxygen content and slowly declining oxygen-release rates. Magnesium peroxide was used in this study because of its slower and more constant oxygen-release rate compared to calcium peroxide. Concrete prepared with urea hydrogen peroxide was unacceptable for two reasons: 1) chemical assays revealed that most of the original oxygen was lost during the preparation of the concrete; and 2) oxygen-release testing revealed that the oxygen that had been retained by the concrete during preparation was released in less than ten days.

BTEX concentration decreased during passage through the barrier. These reductions were statistically significant but were not sufficient to contain the plume. BTEX reductions on the control side of the barrier were much greater than on the active side. However, the cause of this reduction is unknown. Consequently, it is not possible to determine whether the decline in BTEX was due to the barrier system or due to natural variations in BTEX concentration throughout the site.

Nitrate addition enhanced the aerobic biodegradation of BTEX as in batch reactor experiments using ground water from the site. Incorporating sodium nitrate into the concrete briquets at 0.5 to 0.7% by weight during the second and third treatment periods of the field experiments did not cause regulatory levels for nitrate to be exceeded. This nitrate content should be increased to further enhance aerobic biodegradation and for use as an electron acceptor after the available oxygen is depleted. A small increase in the nitrate content of the concrete should not result in any violations of water quality standards since the maximum nitrate concentration observed in the monitoring wells downgradient of the barrier was 2.9 mg/L NO₃⁻-N, a value well below the current ground-water standard of 10 mg/L NO₃⁻-N.

Significant concentrations of DO were reaching wells immediately downgradient of the permeable barrier towards the end of this project, yet BTEX was not being biodegraded. The lack of biodegradation could be due to stratification within the aquifer, which reduces mixing of oxygenated- and BTEX-contaminated ground water. In future work, variations in oxygen and contaminant concentration with depth should be examined to evaluate the im-

portance of stratification on mixing and subsequent biodegradation.

The oxygen-releasing permeable barrier constructed in this project was not fully effective in containing the hydrocarbon plume due to two factors: 1) the high concentration of BTEX entering the barrier, and 2) the clogging of the barrier wells by oxidized iron precipitates. The high total BTEX concentration entering the barrier resulted in a high demand for oxy-

gen, which was difficult to meet with a reasonable number of remediation wells. The high iron concentration entering the barrier caused clogging of the remediation wells and reduced oxygen delivery to the aquifer. Future work on oxygen-releasing permeable barriers should focus on sites with lower concentrations of biodegradable organics and dissolved iron.

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The complete report, entitled "Enhanced Bioremediation of BTEX Using Immobilized Nutrients: Field Demonstration and Monitoring," (Order No. PB97-186290; Cost: \$21.50, subject to change) will be available only from

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