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Feasibility of Calcium Peroxide as an Oxygen Releasing Compound in Treatment Walls

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Feasibility of calcium peroxide as an oxygen releasing compound in treatment walls

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Abstract: This research investigates the use of a proprietary formulation of powdered calcium peroxide (PermeOx Plus®) as an oxygen releasing compound in a treatment wall. Laboratory scale column studies evaluated the release of oxygen and the permeability effects resulting from a treatment wall mixture of the calcium peroxide and a representative aquifer sand (40-mesh Unimin sand). The mixtures evaluated ranged from 0.1 to 1.0 percent by weight. Influent water was prepared at an average dissolved oxygen concentration of 3.1 mg/L and pumped into the treatment wall soil at a constant rate of 0.17 cm^3/sec (0.53 ft^3/day) to simulate ground water dissolved oxygen and flow conditions. The average changes in relative permeability for mixtures of 0.1%, 0.5% and 1.0% calcium peroxide by weight were 65.6%, 66.1% and 77.1%, respectively. The peak dissolved oxygen levels in the same mixtures were 5.9, 7.40, and 10.7 mg/L, respectively.

Keywords: Remediation; barriers; treatment walls, calcium peroxide, permeability

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Biographical notes: Lizette Chevalier, Ph.D., P.E., is the Chair of the Department of Civil and Environmental Engineering at Southern Illinois University Carbondale. Her research and teaching expertise includes the fate and transport of non-aqueous phase liquid contaminants in groundwater as well as emerging treatment technologies for groundwater and surface water.

Charles (Chad) D. McCann is a civil and environmental engineer for Florence Hutcheson Inc. in Paducah, Kentucky. He earned a BS and MS degree from Southern Illinois University Carbondale, where he studied civil and environmental engineering.

1 Introduction

The use of treatment walls has been recognized as a potentially cost effective approach for the treatment of contaminated ground water aquifers. The benefits of this technology include the facts that the contaminated soil does not need to be removed, no external energy sources are required to operate these systems once they are in place, there are no above ground facilities, maintenance costs are low, and monitoring costs are reduced. It has been estimated that a cost savings of 50% is common when using these systems in place of pump-and-treat systems (USEPA, 1996). Another potentially viable remediation technology is in-situ bioremediation. One of the major obstacles to this technology is the lack of sufficient oxygen to promote biodegradation. Three potential oxygen releasing compounds that have been considered for the in-situ use are hydrogen peroxide (H_2O_2), magnesium peroxide (MgO_2) and calcium peroxide (CaO_2).

Cassidy and Irvine (1999) reported that hydrogen peroxide is a common oxygen source for oxygenating groundwater for bioremediation applications. They cited several challenges to the in-situ use including the competition for oxygen by metals and humic substances, oxygen released at rates greater than the consumption by microorganisms and the toxics of hydrogen peroxide a concentrations required to achieve biological treatment (Spain et al. 1989; Pardieck et al. 1992). To promote a slower release of oxygen, they also cite the use of sodium percarbonate, magnesium peroxide and calcium peroxide as a solid oxygen source. Magnesium peroxide and calcium peroxide were reported to be orders of magnitude less water soluble than sodium percarbonate (Weast 1998), which allows them to release oxygen over prolonged periods. In the presence of water, magnesium and calcium peroxide produce hydrogen peroxide through the following reactions:

$$MgO_2 + 2H_2O \rightarrow Mg(OH)_2 + \tfrac{1}{2}O_2 + H_2O \qquad (1)$$

$$CaO_2 + 2H_2O \rightarrow Ca(OH)_2 + \tfrac{1}{2}O_2 + H_2O \qquad (2)$$

Borden et al. (1997) reported on the use of concrete briquets to slow the oxygen release of hydrogen peroxide, calcium peroxide and a proprietary formulation of magnesium peroxide (ORC). A batch study indicated that MgO_2 released oxygen for up to 300 days, while the CaO_2 and H_2O_2 were exhausted after 100 and 10 days respectively. A full scale permeable barrier system was then constructed at a gasoline release site using the MgO_2 briquets. The barrier increased the dissolved oxygen from 0.4 to 1.8 mg/L during the first 242 days of operation, but the efficiencies were reported to have declined over time. In addition, the aquifer in the vicinity of the remediation wells was clogged. This was possibly due to precipitation with iron minerals from the soil as a result of the high pH from the concrete and oxygen released. Barcelona and Xie (2001) reported the in-situ use and kinetics of a reductive whey barrier and an oxidative permeable reactive barrier of MgO_2 at the Michigan Integrated Remediation Technology Laboratory. Their study, which used the proprietary formulation of magnesium peroxide used by Borden et al. (1997), concludes that the lifetime of the barrier is a site specific issue.

Dernbach (2001) reported on three field studies using a proprietary formulation of magnesium peroxide in the Lake Tahoe region of California. Two of the three sites were contaminated with gasoline, while the third was contaminated with diesel. The magnesium peroxide was placed in-situ by direct-push borings or placed in socks in a monitoring well. Although initial results indicated a 40% decrease in total petroleum hydrocarbon, almost all of the constituents returned to their original concentration within

6-9 months. Dernback reported that the failure to reach target cleanup levels were most likely due to cold temperatures that inhibited bioremediation.

Commerically, MgO_2 is prepared at a mass purity of only 15-25% as compared with 60-80% for CaO_2. Therefore, commercial CaO_2 can deliver three to four times more molecular oxygen than MgO_2 on a mass basis. It is also reported that CaO_2 is considerably less expensive than MgO_2, and can be easily be produced in the field by heating lime with hydrogen peroxide (Cassidy and Irvine 1999).

Cassidy and Irvine (1999) conducted laboratory studies in solid-phase reactors on a contaminated silt that determined calcium peroxide accelerated ex-situ bioremediation. Kao et al. (2001) conducted a laboratory scale column experiment to evaluate a biobarrier system containing calcium peroxide and peat to remove TCE contaminated groundwater. Results indicated that the continuous release of oxygen and organic substrates enhanced the TCE biotransformation, removing up to 99% of the TCE. This study was extended (Kao et al. 2003) in a laboratory scale column study simulating a bio-barrier treatment of PCE using a series of continuous flow glass columns which included a soil column, a material column, followed by two consecutive soil columns, an oxygen releasing materials column, followed by two other consecutive soil columns. The columns were inoculated with anaerobic and aerobic sludge to provide microbial consortia for contaminant biodegradation. Results showed that up to 99% of PCE removal efficiency was obtained.

More recent studies of on the use of calcium peroxide in remediation are more limited. Park et al (2006) report on the use of calcium peroxide to increase the remediation of soil. In this study, calcium peroxide was used to enhance the ability of shephard's purse roots to remediate soil contaminated with 2,4-dichlorophenol. Hanh et al. (2005) report on the use of calcium peroxide as a slow oxygen release agent for bioremediation of polluted sediments from intensive shrimp farms containing high organic carbon, nitrogen and phosphorus.

In 2002, a proprietary formula of calcium-peroxide based oxygen releasing compound called PermeOx Plus® became available for commercial use. To date, the use of PermeOx Plus® has not been documented outside of laboratory batch and column studies reported by the manufacturer, which have focused on the oxygen releasing capabilities of the compound only.

The objective of this research was to analyze the use of this oxygen releasing compound in treatment walls. In particular, we considered a treatment wall created by a slurry mix of an aquifer soil with the proprietary formula of calcium peroxide. The research focused on 1) measuring permeability effects within the treatment wall due to the initial addition and subsequent chemical reduction of the calcium peroxide and 2) the degree to which dissolved oxygen concentration increased in water flowing out of the treatment wall.

2 Materials and Methods

The fine Unimin sand (Drilling Equipment & Supply Inc., St. Charles, Missouri) was classified according to ASTM standards. The results are summarized in Table 1.

A proprietary formula of calcium-peroxide, PermeOx Plus®, manufactured by FMC Corporation (Philedelphia, PA) was used as the oxygen releasing material. The manufacturer's specifications of PermeOx Plus® are summarized in Table 2.

Three different mixtures of soil and calcium peroxide were evaluated in column studies based on a mass ratio: 99.9% Unimin sand & 0.1% calcium peroxide; 99.5% Unimin sand & 0.5% calcium peroxide; and 99.0% Unimin sand & 1.0% calcium peroxide.

The material was thoroughly mixed until no visible separation of the two samples was apparent. The soil and soil mixtures were packed into glass soil columns in 1-inch increments, followed by tamping with a smooth mallet. The glass soil columns measured 13 cm in height with a 7.5 cm diameter.

Figure 1 is a schematic of the overall experimental set-up, which includes on-line measurements of dissolved oxygen. Tap water was deaired using a vacuum pump and stirrer plate to an average concentration of 3.1 mg/L, which is within the range of dissolved oxygen concentrations of groundwater. This was used for the influent water, and was pumped through the column using a Cole Parmer Masterflex® peristaltic pump fitted with a Masterflex® head no. 7013 and a tubing size of 1/18" I.D. Flow velocities were maintained in the range of 3.5×10^{-7} to 3.5×10^{-6} m/s, which are typically experienced in ground water (Borden et al. 1997). Dissolved oxygen concentrations were measured on-line using a YSI 5010 BOD probe. The temperature and pH of the effluent was also monitored. The temperature remained relatively constant at 22°C. The pH of the effluent was 10.42, 10.56 and 10.81 for 0.1%, 0.5% and 1.0% calcium peroxide respectively. Permeability was determined by the constant head method ASTM D2434-68(2006). Permeability experiments were conducted in triplicate. Turbidity was measured using a DRT 100B Turbidimeter (H.F. Scientific).

3 Results and Discussion

3.1 Permeability

In the construction of treatments walls, the change in permeability is a major factor in the design and operation phases. With the addition of 0.1%, 0.5% and 1% calcium peroxide, the permeability of the soil decreased from 0.00061±0.000019 cm/sec (1.73 ft/day) to 0.00021±0.000048, 0.00021±0.000043 and 0.00014±0.000030 cm/sec, respectively (Figure 2). It is possible that the permeability decreases more rapidly between 0%-0.1%. To evaluate whether this reduced permeability would cause any significant flow to by-pass the treatment wall, we utilized the equation of Wheatcraft and Winterberg (1985):

$$F_{cu} = \frac{2k_r}{(1 + k_r)} \qquad (3)$$

where F_{cu} is the amount of flow that passes through a medium relative to the amount that would pass through the medium when the relative permeability ($k_r = k/k_{sat}$) equals 1. In this application, k_{sat} is the permeability without calcium peroxide, and k is the reduced permeability due to calcium peroxide. The results in Table 3 show that 1% calcium peroxide will initially cause reduced flow as low as 37% (±5.7%) into the treatment wall if the surrounding soil is the same soil used in the treatment wall, whereas the reduced flow for 0.1% and 0.5% is estimated at approximately 50%. To improve the flow of groundwater into the treatment wall, a more permeable soil can be used in the treatment wall mix or hydraulic controls can be designed to promote flow into a region. The next stage of the testing evaluated the permeability change over time.

As shown in Figure 3, the average permeability for each mixture increased over time as the calcium peroxide in the soil mixture was reduced. In this figure, time is scaled to represent the number of pore volumes passing through the soil column. The mixtures of 0.5 and 1.0% calcium peroxide did experience localized points with minor declines in permeability. Noting the error bars, these changes are within the error range. Alternatively, these localized declines in permeability may be due to pathways developed as the calcium peroxide was reduced, and oxygen released. Within the pore, the oxygen may have behaved as a trapped non-aqueous residual phase preventing the flow of water through the pore space until the oxygen was dissolved. On the other hand, pores may have been clogged from the release of non-reactive chemical in the commercial product other than the calcium peroxide. To test this latter hypothesis, additional tests were conducted to monitor the permeability concurrently with monitoring the turbidity of the effluent for the 1% calcium peroxide mixture over time (Figure 4). From this graph, it can be seen that the levels of turbidity measured are generally opposite the trends of the permeability for the test run. As the relative permeability decreased, the levels of turbidity increased, and as the relative permeability began to increase, the levels of turbidity decreased during the same time intervals. Therefore it is reasonable to consider that proprietary chemicals in the commercial product may be transported by the aqueous phase, and are most likely the cause of localized changes in permeability.

3.2 Dissolved Oxygen

The addition of calcium peroxide in soil was expected to enhance the levels of dissolved oxygen in the effluent. Figure 5a shows the average dissolved oxygen concentration (based on a triplicate average) over time, with time scaled to represent the number of pore volumes. With the exception of the control experiment conducted for sand, the column studies were run until the effluent levels of dissolved oxygen approached influent dissolved oxygen levels. Overall, the control experiment indicated that the effluent dissolved oxygen levels were consistent with the influent dissolved oxygen level.

For each addition of calcium peroxide, an increase in the measured levels of effluent dissolved oxygen over time was experienced. In addition, the peak concentration increased (5.9, 7.4 and 10.7 mg/L respectively). The time of the peak concentration for 0.1% and 0.5% calcium peroxide are approximately the same (9 and 8.7 pore volumes). However, the time to reach the peak for 1% calcium peroxide was significantly increased to approximately twenty eight (28) pore volumes. Furthermore, the 1% mixture delivered an increased level of dissolved oxygen for a significantly larger number of pore volumes.

A closer view of the data is provided in Figure 5b to show that at approximately one pore volume, a decrease in the measured levels of dissolved oxygen was observed for all three mixtures. This decrease was not seen in the control experiment. It was hypothesized that this decline was possibly due to oxygen utilization due to either the presence of iron (Fe) or manganese (Mn) in the tap water or microbes present in the soil. A five-day biochemical oxygen demand (BOD_5) test was run on both the tap water and effluent waters collected from a column test without calcium peroxide to test for the presence of microbes. The results from these tests indicate that a BOD of 1.7 and 1.8 mg/L for the tap water and effluent water respectively, indicating that some microbes were added due to the tap water. Without knowing the complete chemical formula of the proprietary calcium peroxide, we also hypothesized that it is also possible that the proprietary product has an initial loading phase or storing of oxygen. During this short time, this could cause the dissolved oxygen levels to decline and then rebound as oxygen is released from the substance. No further analysis of this small and localized drop in dissolved oxygen was conducted.

In Figure 6, we compared the dissolved oxygen concentrations in the aqueous phase to the average permeability of the soil mixtures over time. The data shows a correlation. As the effluent levels of dissolved oxygen increased, the relative permeability increased slightly and then declined during the peak times of oxygen release. Once the effluent levels of dissolved oxygen began to decline, the relative permeability increased fairly linearly with the decline in dissolved oxygen.

For the 0.5% calcium peroxide mixture a pronounced rebound was observed at approximately 125 pore volumes. A similar trend, though not as pronounced, was observed for the 1.0% calcium peroxide mixture at approximately 260 pore volumes. As explained for localized permutations in permeability, it is possible that preferential pathways developed as the calcium peroxide was reduced.

As with the permeability, the amounts of suspended particles present in the effluent were compared to the effluent levels of dissolved oxygen over time. The results for this test are presented in Figure 7.From this preliminary data, a general trend was observed. The effluent dissolved oxygen concentrations rose to a peak level as the turbidity level reached a peak. Additionally, the declining trends in both sets of data are fairly consistent. More importantly, it is apparent that as the levels of dissolved oxygen began to reach equilibrium, or slightly rebound, the same trends were noticed in the turbidity. Therefore, it is possible that localized fracturing within the columns increased levels of oxygen present. On the other hand, this may also be accounted for by statistical variations in the data.

The maximum level of dissolved oxygen saturation (DO_{sat}) that can be obtained in distilled water, within a temperature range of 20ºC to 24ºC, is 9.1 to 8.4 mg/L, respectively (Ray, 1995). As shown in Figure 5a, the measured dissolved oxygen in the 1.0% calcium peroxide mixture reached levels above DO_{sat}. This was made possible due to the oxygen releasing capacity calcium peroxide and the apparatus used for testing. Once the maximum level of saturation was reached, the oxygen simply was forced through fractures in the soil as a separate phase from the water.

4 Summary

The objective of this research was to analyze the use of calcium peroxide in treatment wall applications, specifically focusing permeability and dissolved oxygen. Column studies were conducted mixtures containing 0.1, 0.5 and 1.0 percent calcium peroxide by weight and a uniform 40 mesh Unimin sand. The calcium peroxide used was a commercial product, PermeOx Plus®.

The results from these tests have shown that the addition of calcium peroxide does decrease the permeability and this decrease is a function of the amount of calcium peroxide added to the soil. A decline in the relative permeability of approximately seventy seven percent (77%) (0.00061 to 0.00014 cm/sec) was measured based on the 1% calcium peroxide mixture. The average changes in relative permeability for mixtures of 0.1% and 0.5% calcium peroxide by weight were 65.6% and 66.1%, respectively. Increases in the permeability were observed as the calcium peroxide was reduced due to chemical reactions with the water passing through the soil. During flushing, the amount of dissolved oxygen was significantly increased from an average influent concentration of 3 mg/L to a peak of 5.86, 7.4, and 10.7 mg/L for the 0.1%, 0.5% and 1.0% mixtures, respectively. After 300 pore volumes, the 1.0% mixture still delivered dissolved oxygen above the influent concentration. Localized changes in permeability, dissolved oxygen concentrations and effluent turbidity suggested the presence of preferential pathways and the release of oxygen due to the chemical reaction of water with the calcium peroxide. This preliminary investigation, although not conclusive, supports further investigation into the use of calcium peroxide in treatment walls. The potential for increasing the dissolved oxygen in the water passing through the treatment wall may promote the biodegradation of contaminants by the indigenous microorganisms in the soil matrix.

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Figure Titles

Figure 1: Experimental set up for continuous monitoring of permeability and dissolved oxygen.

Figure 2: The reduction in permeability due to the initial addition of calcium peroxide.

Figure 3: Average permeability of soils mixed with calcium peroxide per pore volume.

Figure 4: Amount of suspended particulates measured in the effluent compared to the average relative permeability over time for a 1.0% calcium peroxide mixture.

Figure 5a: Average dissolved oxygen measured per pore volume.

Figure 5b: Close-up of the average dissolved oxygen measured per pore volume.

Figure 6: Comparison of DO and k_r for 0.5% and 1% calcium peroxide mixtures over time.

Figure 7: Dissolved oxygen and turbidity for 1% calcium peroxide mixture over time.

Table Titles

Table 1: Soil Characteristics
Table 2: PermeOx Plus® Fact Sheet (FMC 2005).
Table 3: Amount of Refraction in Regions of Lower Permeability

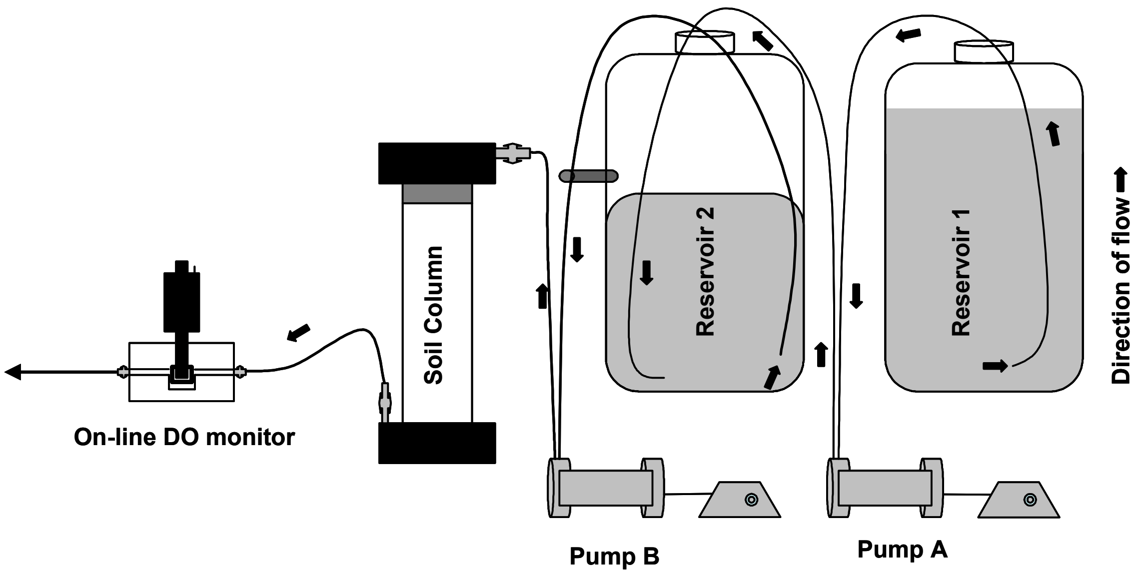

Figure 8: Experimental set up for continuous monitoring of permeability and dissolved oxygen.

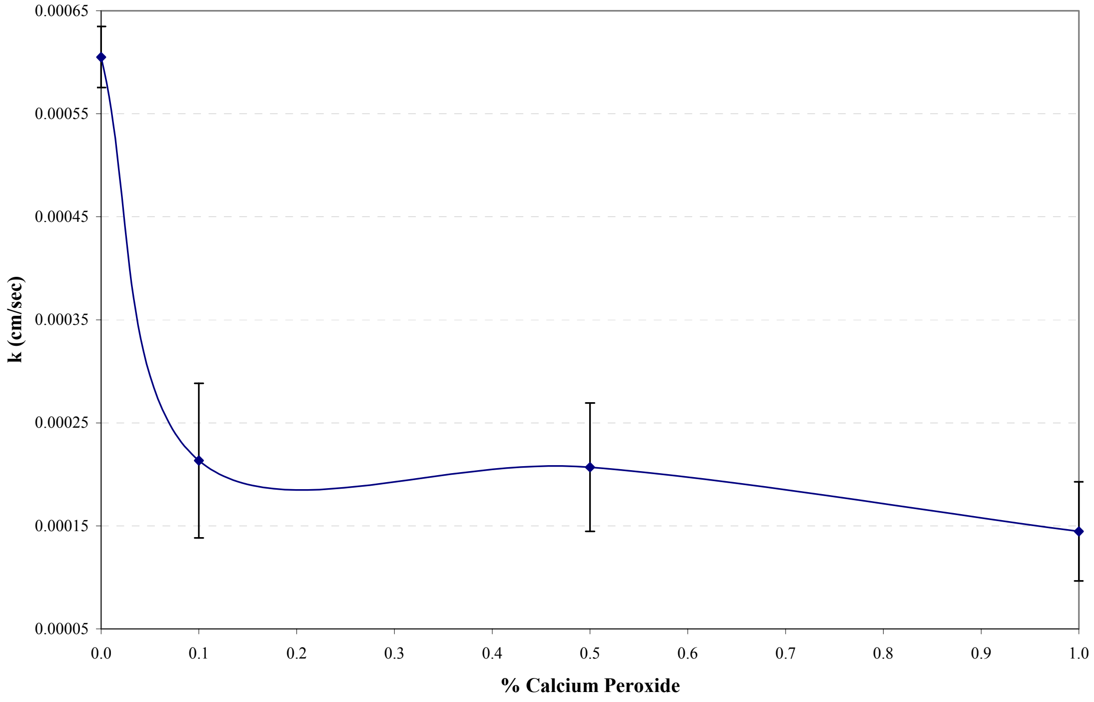

Figure 9: The reduction in permeability due to the initial addition of calcium peroxide.

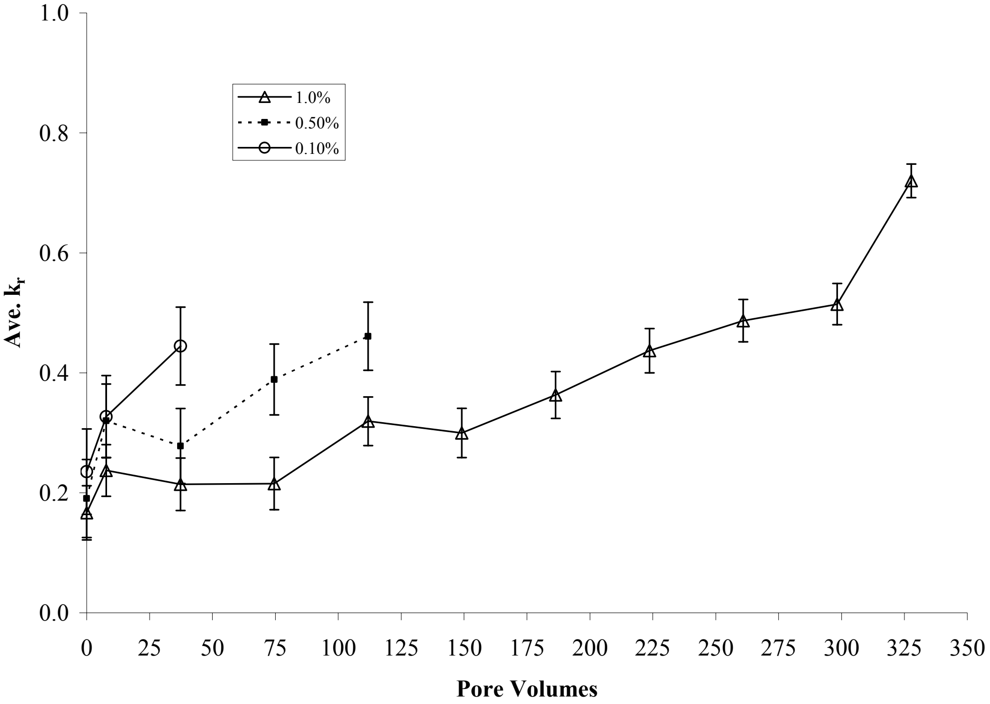

Figure 10: Average permeability of soils mixed with calcium peroxide per pore volume.

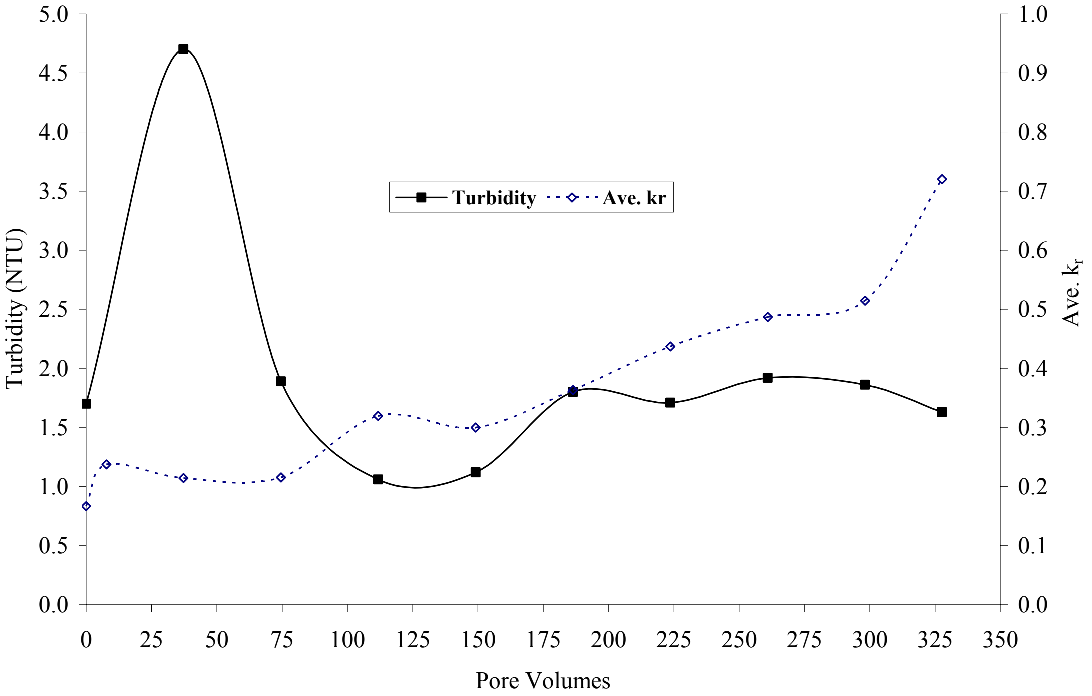

Figure 11: Amount of suspended particulates measured in the effluent compared to the average relative permeability over time for a 1.0% calcium peroxide mixture.

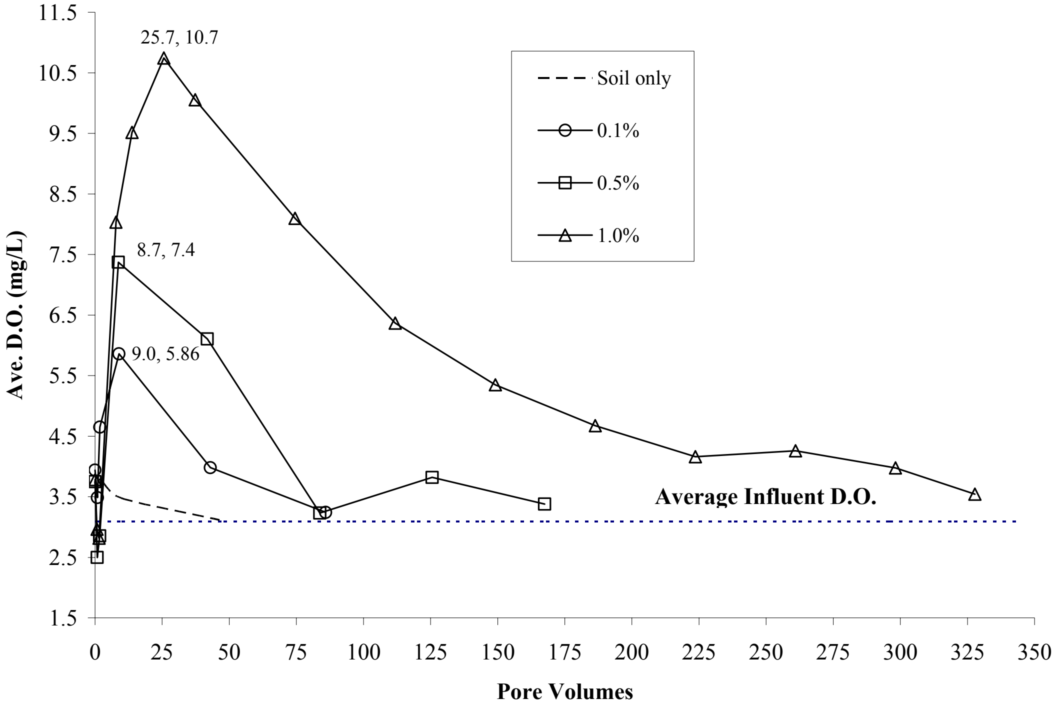

Figure 12a: Average dissolved oxygen measured per pore volume.

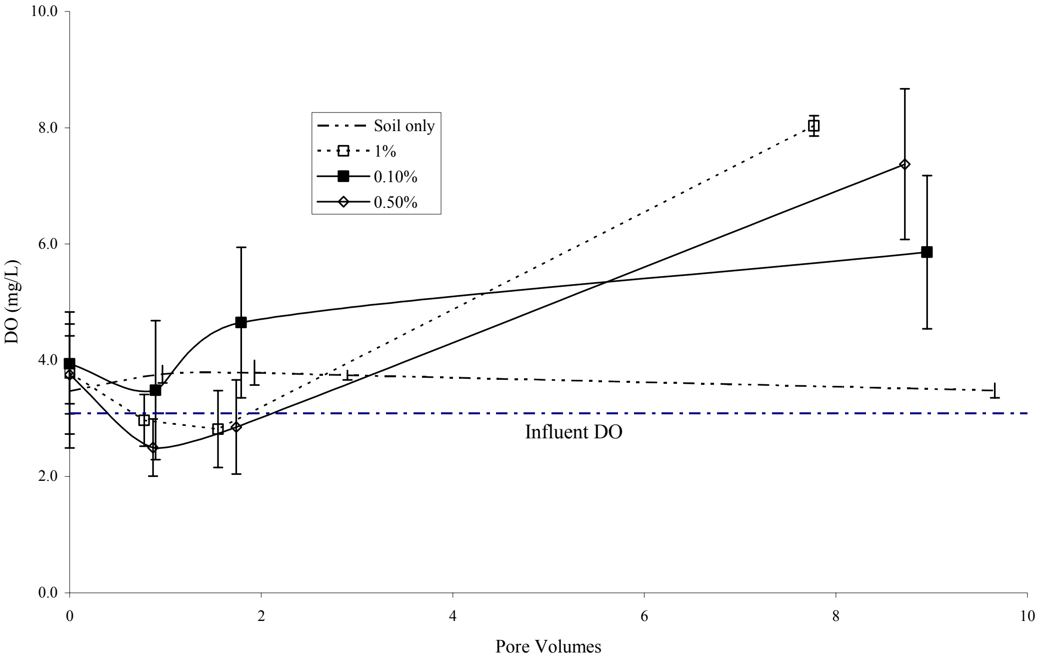

Figure 5b: Close-up of the average dissolved oxygen measured per pore volume.

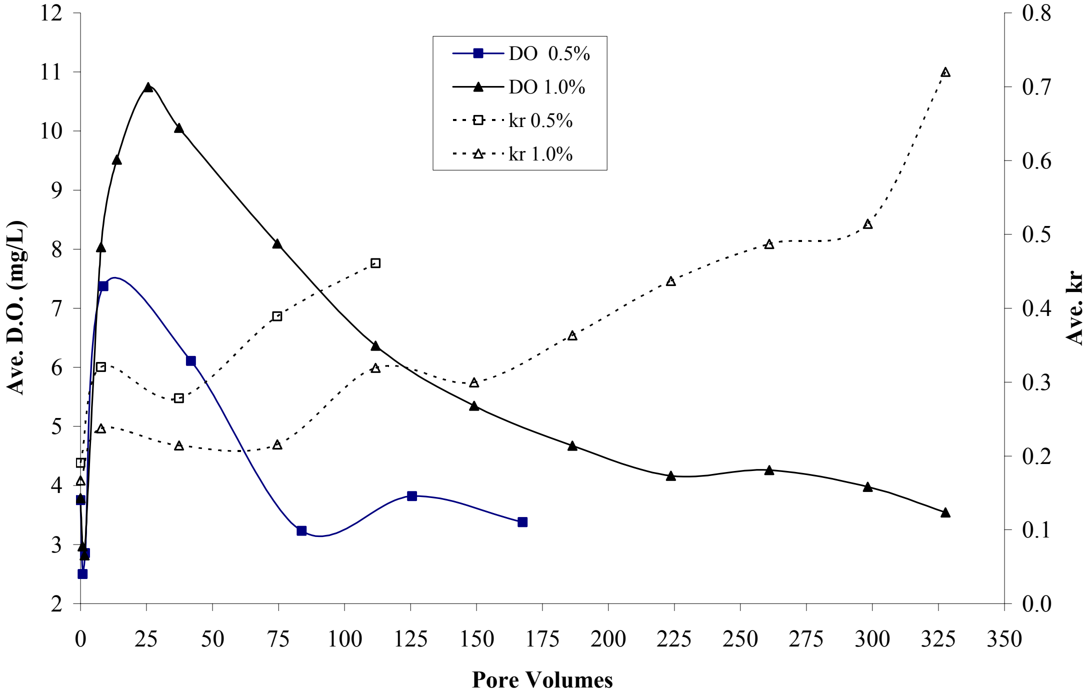

Figure 13: Comparison of DO and k_r for 0.5% and 1% calcium peroxide mixtures over time.

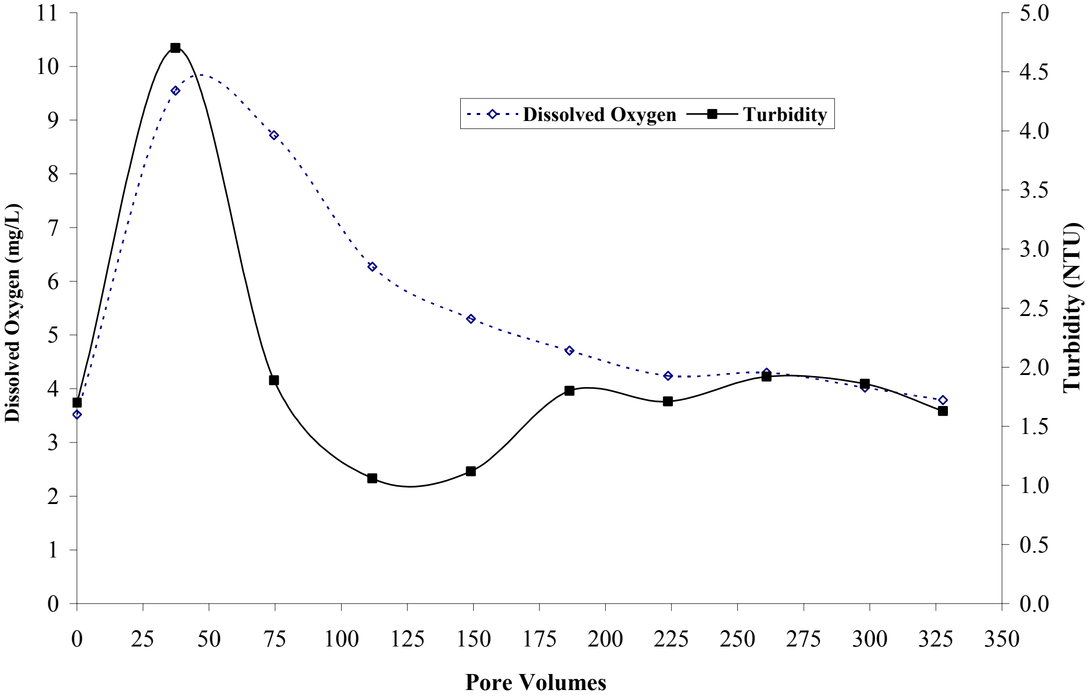

Figure 14: Dissolved oxygen and turbidity for 1% calcium peroxide mixture over time.

Table 1: Soil Characteristics

Parameter	Value
Coefficient of Uniformity, C_u	0.35
Effective Size, D_{10}	0.23 mm
Density of Unimin Sand, ρ_d	1.51 g/cm^3
Porosity, n	0.43
Permeability	0.00061 cm/sec (1.73 ft/day)

Table 2: PermeOx Plus® Fact Sheet (FMC 2005).

Formula:	CaO_2
Molecular Wt:	72g
Description:	Off white granular solid powder
Specifications:	Calcium Peroxide, wt% 75 (min)
	Active Oxygen, wt% 16 (min)
	Other ingredients, wt% 25 (max)
Uses:	Bioremediation
	Petroleum hydrocarbon remediation
	Creosote remediation
	Partially halogenated hydrocarbon remediation
Typical Properties:	Solubility: Slightly soluble in water
	Soluble in acid
	pH of a 1% slurry at 25ºC, approx. 11.4-12.6
	Loose Bulk Density, lb/cu ft 45-66
	Color: Off white
	Odor: None
	Reaction: $CaO_2 + 2H_2O \text{ --> } Ca(OH)_2 + O_2 + H_2O$

Table 3: Amount of Refraction in Regions of Lower Permeability

% Calcium Peroxide	k_r	F_{cu}
0.1	0.344±0.068	0.512±0.075
0.5	0.344±0.060	0.512±0.067
1	0.230±0.043	0.373±0.057