Calcium Peroxide + Calcium Hydroxide (PermeOx® Plus) for Aerobic Bioremediation:

- 1. Dr. Alan G. Seech, FMC Corporation
- 2. Composed of Calcium Peroxide + Calcium Hydroxide
- 3. MSDS & Technical Data Sheet Attached
- 4. Number of Field-scale Applications to Date: 1,000+ sites.
- 5. Case Studies Attached

6. Technical Summary: PermeOx[®] Plus is a food grade oxygen release compound used to enhance the aerobic bioremediation of impacted soil and groundwater. It is composed of calcium peroxide and calcium hydroxide. When placed in contact with water, in wet soil or groundwater, the product releases oxygen and is converted to calcium hydroxide. The oxygen released to groundwater or the aqueous phase of soil stimulates the activity of native aerobic bacteria that degrade petroleum hydrocarbons, BTEX, and many other contaminants that can be degraded aerobically. The end products of such aerobic biodegradation of hydrocarbons are carbon dioxide and water. It has an effective life in groundwater of approximately one year. This enhances the rate and extent of contaminant removal. The available oxygen is 18% by weight and is released over a period of approximately 12 months, subject to the temperature, and the pH of the environment where it has been placed. The product has been applied by direct ex-situ soil mixing, mixed *in situ* at the base of excavation areas, placed in trenches to form biologically active barriers, and injected using direct push technology. This product has been on the market for over 10 years.

Material Safety Data Sheet PermeOx® Plus

MSDS #: 4365-C Revision Date: 2010-09-29 Version 1



This MSDS has been prepared to meet U.S. OSHA Hazard Communication Standard 29 CFR 1910.1200 And Canadian Workplace Hazardous Materials Information System (WHMIS) requirements.

1. PRODUCT AND COMPANY IDENTIFICATION

Product name Synonyms	PermeOx® Plus PermeOx-Solid Peroxygen, Calcium Superoxide, Calcium Peroxide
Recommended use:	Environmental applications
Manufacturer	Emergency telephone number
FMC CORPORATION FMC Peroxygens 1735 Market Street Philadelphia, PA 19103 Phone: +1 215/ 299-6000 (General Information)	For leak, fire, spill or accident emergencies, call: 1 800 / 424 9300 (CHEMTREC - U.S.A.) 1 703 / 527 3887 (CHEMTREC - Collect - All Other Countries) 1 303 / 595 9048 (Medical - U.S Call Collect)

2. HAZARDS IDENTIFICATION

Emergency Overview

E-Mail: msdsinfo@fmc.com

Oxidizer Contact with combustible material may cause fire Severely irritating (eyes)

Potential health effects

Principle Routes of Exposure	Eye contact Inhalation
Eyes	Severely irritating (eyes).
Skin	Non-irritating during normal use.
Inhalation	Irritating to respiratory system.
Ingestion	Not an expected route of exposure. Low oral toxicity.

Chronic Toxicity

No known effect.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Ingredients

Chemical Name	CAS-No	Weight %
Calcium Peroxide	1305-79-9	>75
Calcium Hydroxide	1305-62-0	<25

4. FIRST AID MEASURES

Eye contact	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. If irritation persists, call a physician.
Skin contact	Wash skin with soap and water. Get medical attention if irritation develops and persists.
Inhalation	Move to fresh air. If symptoms persist, call a physician.
Ingestion	Rinse mouth with water and afterwards drink plenty of water or milk. Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Get medical attention.

5. FIRE-FIGHTING MEASURES

Flammable properties	Not combustible.
Flash Point	Not flammable
Suitable extinguishing media	Use plenty of water - FLOOD IT! If water is not available, use CO ₂ , dry chemical or dirt.
Unsuitable Extinguishing Media	Dry chemical. Foam.
5 5	

Contains a chemical that is an oxidizer

Hazardous combustion products	On decomposition product releases oxygen which may intensify fire.	
Explosion Data Sensitivity to Mechanical Impact Sensitivity to Static Discharge	Oxidizable materials can be ignited by grinding and may become explosive Not available	
Specific hazards arising from the chemical	This is a strong oxidizer and will react vigorously or explosively with many materials including fuels. Cool drums with water spray.	
Protective equipment and precautions for firefighters	As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear. Move containers from fire area if you can do it without risk.	

NFPA	Health Hazard 2	Flammability 0	Stability 1	Special Hazards OX

6. ACCIDENTAL RELEASE MEASURES

Personal precautions	Avoid dust formation. For personal protection see section 8.
Methods for containment	Confine spill and place into container. Do not return product to the original storage container/tank due to risk of decomposition. Dilute with large quantities of water. Keep in suitable and closed containers for disposal.
Methods for cleaning up	Do not flush powdered material to sewer. Runoff to sewer may create fire or explosion hazard. Dispose of waste as indicated in Section 13.

7. HANDLING AND STORAGE

Handling	In case of insufficient ventilation, wear suitable respiratory equipment if release of airborne dust is expected. If compounded with organics or combustible materials be sure to exclude moisture. Avoid contact by using personal protective equipment. Refer to Section 8.
Storage	Keep tightly closed in a dry and cool place. Reacts with moisture. Keep away from heat and sources of ignition i.e., steam pipes, radiant heaters, hot air vents or welding sparks.

8. Exposure controls/personal protection

Exposure guidelines

Ingredients with workplace control parameters.

Chemical Name	British Columbia	Quebec	Ontario TWAEV	Alberta
Calcium Hydroxide	TWA: 5 mg/m ³			
1305-62-0				

Occupational exposure controls

Engineering measures	Provide appropriate exhaust ventilation at places where dust is formed. Ensure that eyewash stations and safety showers are close to the workstation location.
Respiratory protection	Whenever dust in the worker's breathing zone cannot be controlled with ventilation or other engineering means, workers should wear respirators or dust masks approved by NIOSH/MSHA, EU CEN or comparable organization to protect against airborne dust.
Eye/face protection	For dust, splash, mist or spray exposure, wear chemical protective goggles or a face-shield
Skin and body protection	Long sleeved clothing. Rubber or plastic boots.
Hand protection	Rubber/latex/neoprene or other suitable chemical resistant gloves. Wash the outside of gloves with soap and water prior to reuse. Inspect regularly for leaks.

Hygiene measures Handle in accordance with good industrial hygiene and safety practice. Clean water, preferably an eyewash station and a safety shower, should be available for washing in case of eye or skin contamination.

9. PHYSICAL AND CHEMICAL PROPERTIES

Information on basic physical and chemical properties

Appearance	dry, free flowing granules
Color	off-white
Physical state	dry powder
Odor	odorless
Odor Threshold	Not applicable
рН	(1% solution) 10.5 - 11.8 (1% solution)
Melting Point/Range	Decomposes on heating. @ ~275 °C
Freezing point	No information available.
Boiling Point/Range	Not applicable
Flash Point	Not flammable
Evaporation rate	No data available
Flammable properties	Not combustible
Oxidizing properties	Oxidizer
Vapor pressure	No information available.
Vapor density	No information available.
Specific Gravity	2.92
Relative density	~ 2.92
Bulk density	27 lb/cu ft
Water solubility	Slightly soluble
Percent volatile	No information available.
Partition coefficient:	Not applicable
Viscosity	Not applicable
-	
Decomposition Temperature	275 °C

10. STABILITY AND REACTIVITY

Stability	Stable under recommended storage conditions. Decomposition can occur on exposure to heat or moisture.
Conditions to avoid	To avoid thermal decomposition, do not overheat, (275)
Materials to avoid	Heavy metals. Combustible materials
Hazardous decomposition products	Oxygen which supports combustion, Calcium oxides.
Hazardous polymerization	Hazardous polymerization does not occur.
Hazardous reactions	Oxidizable material can be ignited by grinding and may become explosive.

11. TOXICOLOGICAL INFORMATION

Acute effects Eye irritation Skin irritation	Severely irritating, corrosive (rabbit) Non-irritating (rabbit) May cause skin irritation in susceptible persons
LD50 Oral LD50 Dermal LC50 Inhalation:	> 5 g/kg (Rat) > 10 g/kg (Rat) > 17 mg/L 1 hr (Rat)
Sensitization	No information available.
Acute toxicity of over-exposure	Dust is irritating eyes, nose, throat, and lungs.
Chronic Toxicity	
Chronic Toxicity	No known effect.
Carcinogenicity	There are no known carcinogenic chemicals in this product

12. ECOLOGICAL INFORMATION

Ecotoxicity

The environmental impact of this product has not been fully investigated

Persistence and degradability	Biodegradability does not pertain to inorganic substances.
Bioaccumulation	Does not bioaccumulate.
Mobility	No information available.
Other adverse effects	None known

13. DISPOSAL CONSIDERATIONS

Waste disposal methods	This material, as supplied, is a hazardous waste according to federal regulations (40 CFR 261). Dispose of in accordance with local regulations.
Contaminated packaging	Empty remaining contents. Empty containers should be taken to an approved waste handling site for recycling or disposal.
US EPA Waste Number	D001

14. TRANSPORT INFORMATION

DOT		
UN/ID No	1457	
Proper shipping name	CALCIUM PEROXIDE MIXTURE	
Hazard Class	5.1	
Packing group	II	
49 STCC Number	49187717	
TDG		
UN/ID No	1457	
Proper shipping name	CALCIUM PEROXIDE MIXTURE	
Hazard Class	5.1	
Packing group	II	
<u>ІСАО/ІАТА</u>	Oxidizers are prohibited from aircraft.	
IMDG/IMO		
UN/ID No	1457	
Proper shipping name	CALCIUM PEROXIDE MIXTURE	
Hazard Class	5.1	
Packing group	II	
Other information	This material is shipped in 25 lb. plastic pails, and 30 lb. and 100 lb. fiber drums.	

15. REGULATORY INFORMATION

International Inventories	
TSCA Inventory (United States of America)	Complies
DSL (Canada)	Complies
NDSL (Canada)	Complies
EINECS/ELINCS (Europe)	Complies
ENCS (Japan)	Complies
IECSC (China)	Complies
KECL (Korea)	Complies
PICCS (Philippines)	Complies
AICS (Australia)	Complies
NZIoC (New Zealand)	Complies

U.S. Federal Regulations

SARA 313

Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA). This product does not contain any chemicals which are subject to the reporting requirements of the Act and Title 40 of the Code of Federal Regulations, Part 372.

Chronic Health Hazard	no
Fire Hazard	yes
Sudden Release of Pressure Hazard	no
Reactive Hazard	no

CERCLA

This material, as supplied, does not contain any substances regulated as hazardous substances under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) (40 CFR 302) or the Superfund Amendments and Reauthorization Act (SARA) (40 CFR 355). There may be specific reporting requirements at the local, regional, or state level pertaining to releases of this material.

International Regulations		
Mexico - Grade		

No information available.

Canada

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all the information required by the CPR.

WHMIS Hazard Class C Oxidizing materials



16. OTHER INFORMATION

HMIS Health Hazard 2 Flammability 0 Stability 1 Special precautions J					
	HMIS	Hoolth Hozord 2	l Flommobility ()	Stability 1	Special precautions J

NFPA/HMIS Ratings Legend

Severe = 4; Serious = 3; Moderate = 2; Slight = 1; Minimal = 0

Protection=J (Safety goggles, gloves, apron, combination dust and vapor respirator)

Revision Date:	2010-09-29
Reason for revision:	Format Change.

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Prepared By

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Visit our E-Commerce Site at http://www.fmcchemicals.com

PermeOx[®] Plus

CAS NO 1305-79-9

Introduction

PermeOx[®] Plus is an economical, viable and effective oxygen-generating compound for use in odor control, metals removal and bio-remediation. PermeOx[®] Plus is a passive, in situ approach to providing an oxygen source for bio-remediation. Successful bio-remediation depends on proper mix of nutrient, oxygen, and microbes. Often the limiting factor of aerobic degradation of contaminants is oxygen availability. PermeOx[®] Plus is designed for slow releases of oxygen over the pH range of 4 to 9 so that indigenous aerobic microbes may utilize the organic containments as a source of nutrient.

Formula CaO₂ MW 72 Description Off white granular solid **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 25 degrees C., approximate 11.4-12.5 Loose Bulk Density, approximate lb/cu ft 27

Standard Containers

NOTICE

Color

Odor

Reaction:

The information contained herein is, to our knowledge, true, and accurate. However, we make no warranty or representation, expressed or implied, except that FMC products discussed herein conform to the chemical description shown on their labels. Nothing contained herein shall be construed as permission or recommendation to infringe any patent. No agent, representative or employee of this company is authorized to vary any of the terms of this notice.

Off white

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

None



FMC Corporation

Chemical Products Group Environmental Business 1735 Market Street Philadelphia, PA 19103 Phone: 1-866-860-4760 **FMC**

Visit our E-Commerce Site at http://www.fmcchemicals.com

Fiber Drums, polyethylene lined

100 lbs (45.25 kg)

Shipping

PermeOx[®] Plus is shipped in the above standard containers. It is classified by DOT as "Oxidizer - 5.1" and containers carry the yellow oxidizer label.

Safety/Handling/Storage

PermeOx[®] Plus is one of the safest to handle of the peroxygen compounds. It represents no significant hazards with regards to skin contact, absorption, inhalation, or ingestion. Airborne dust is irritating to eyes, nose, throat, and lungs. PermeOx[®] Plus should be handled in well ventilated, dust controlled areas. When handling large quantities, the use of dust mask, goggles, and gloves is recommended.

PermeOx[®] Plus is an oxidizer, thus contact with combustible materials (paper, cotton, organics, wood, leather, reducing agents, and other oxidizers) should be avoided.

PermeOx[®] Plus is not flammable but will contribute oxygen to feed a fire. Contamination, heat, and humid conditions will enhance and accelerate decomposition. Fires involving calcium peroxide are best controlled by using large quantities of water. However, unlike most oxidizers, decomposition is endothermic.

PermeOx[®] Plus should be stored in a clean, dry place. Do not expose to heat sources or high humidity. Store away from combustible materials. Keep containers closed when not in use. Handle spills by dilution with water.

(Refer to the MSDS for more detailed information)

Customer Service

To place orders, request samples or obtain general information, please call the marketing office or visit our website at www.fmcchemicals.com

FMC Corporation Active Oxidants Division, Environmental Business 1735 Market Street Philadelphia, PA 19103 Tel 866-860-4760

For technical assistance, please call one of the offices below.

Applications and Chemistry of Peroxygens

FMC Research and Development Center Chemical Products Group Princeton, NJ 08543 (609) 951-3657 Systems for Storage and Handling

FMC Technical Services and Engineering Tonawanda, NY 14240 (716) 876-8306

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Extended oxygen release for enhanced aerobic bioremediation of petroleum contaminants

PermeOx[®] Plus is a specially formulated grade of calcium peroxide, engineered to extend the rate of oxygen release to enhance the aerobic bioremediation of petroleum hydrocarbons in soil and groundwater.

The limiting factor in aerobic metabolism of hydrocarbons is often oxygen, which functions as a terminal electron acceptor. To help address this concern PermeOx[®] Plus provides a slow release of oxygen via the reaction of calcium peroxide and water. Extensive field and laboratory studies have shown that PermeOx[®] Plus releases more oxygen into the subsurface environment over extended periods as compared to other soil remediation products. These studies have demonstrated that PermeOx[®] Plus can continually release oxygen for over 350 days, thus providing a useful and cost-effective tool for enhancing the aerobic bioremediation of petroleum hydrocarbons.

Benefits include:

Higher Active Oxygen

Contains >18% AO, which is higher than other grades of calcium peroxide

Extended Oxygen Release

Releases oxygen for up to one year

High Purity Raw Materials

Produced to ensure a high purity product with minimal heavy metals. The same is not true for all imports

Potential Applications:

Direct application in an excavation Direct push injection Leading edge barriers

For more information and detailed case studies, please visit our website.



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Examples of Contaminants of Concern

BTEX

PETROLEUM HYDROCARBONS GRO, DRO, ORO, MTBE

ORIN Remediation Technologies

Introduction:

A large volume of petroleum related products had leaked from a major oil refinery pipeline in West Texas. The leak impacted an area of 1.2 acres. Both soil and groundwater were contaminated with TPH with benzene being the regulatory driver. Because the spill occurred near a residential area and an active rail line, cleanup efforts had to be quick and non-invasive.



Objective:

After several other technologies and products failed to lower site-wide benzene concentrations, ORIN Remediation Technologies (ORIN) was asked to design a treatment approach to remediate the contamination. ORIN proposed using PermeOX® Plus, a slow release oxygen chemistry to stimulate aerobic bioremediation. The objective of the treatment was to reduce the bulk of the contamination in the soil and groundwater.



Site Characteristics:

Site: Oil refinery in Western Texas

Geology: - Fine Grained, Silty, Calcareous Sand

Groundwater velocity: variable (10-3 to 10-5 cm/sec) Contaminants: 4,700 ppb benzene in groundwater

Size of plume treated: 60.000 ft3

IN-SITU BIOREMEDIATION AT AN OIL REFINERY USING PERMEOX[®] PLUS

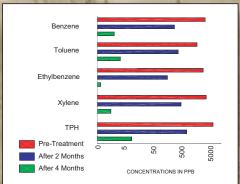
Remediation Approach:

Treatment chemistry: PermeOx® Plus.

Treatment application: Chemical injection through direct push points.

Dosage Rate: Chemical was injected as a 25% slurry at a rate of 2 to 6 gallons per minute

Dosage Volume: A total of 2,500 gallons was injected at the site



Treatment Results:

The dissolved oxygen (DO) levels in the groundwater rose (0.19 mg/L to 18.40 mg/L) immediately after injection and remained elevated after 120 days. After two months, the average benzene concentration in groundwater across the site dropped 90%, to an average concentration of 458 µg/L. The most dramatic decrease in benzene concentrations occurred after four months, where concentrations dropped from roughly 460 µg/L to 3.3 µg/L. The application of PermeOx[®]. Plus as a slurry had increased the DO in groundwater to over 20 mg/L stimulating the aerobic biodegraders across the site.



Summary

ORIN successfully remediated a pilot study area by injecting PermeOx® Plus over a five-day period. Performing the pilot study demonstrated the effectiveness and feasibility for full-scale injection at this site. Compared to alternative cleanup approaches, using chemical injection not only reduced site disruption, PermeOx® Plus was more efficient and cost effective. Full-scale implementation using ORIN's injection design will save the client hundreds of thousands of dollars compared to alternative injection chemistries and other remediation approaches such as dig and haul, soil vapor extraction or pump and treat systems.





Former UST Leakage

Summary ORIN successfully treated petroleum contaminated soil and groundwater with an enhanced bioremediation chemistry. Unsaturated contaminant levels were reduced from 2,900 ug/L to less than detection over a four-month period. ORIN's approach saved the client approximately \$20K to \$48K over traditional remediation approaches.

Site Characteristics:

Geology – clayey silt with intermittent sand lenses Groundwater velocity – variable (10⁻⁴ to 10⁻⁶ cm/sec) Size of plume treated – 41,200 ft³ Contaminants – 1,400 ppb benzene in soil 500 ppb toluene in soil 300 ppb ethylbenzene in soil 700 ppb xylene in soil

Remediation Approach:

Treatment chemistry - PermeOx[®] Plus **Treatment application** – Chemical injection through a series of direct push points

Chemistries used during injection

Successful bioremediation of petroleum contamination via aerobic microbial respiration depend on a number of factors including the presence of appropriate microbes, nutrients, electron donors and terminal electron acceptors. In the aerobic metabolism of petroleum contaminants, oxygen acts as a terminal electron acceptor and petroleum contaminants act as electron donors, which are oxidized. Often, the limiting factor in aerobic bioremediation of petroleum contaminants is oxygen. PermeOx[®] Plus provides oxygen through a reaction of calcium peroxide and water:

 $\begin{aligned} \text{CaO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{H}_2\text{O}_2 \\ 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \end{aligned}$

Summary of Implementation

The chemistry was designed for the enhanced bioremediation of BTEX compounds found in the soils and groundwater at this site. The targeted injection area at the site was down gradient of a former leaking UST. Forty direct push injection points received 25 gallons of PermeOx[®] Plus, at a rate ranging from 1 to 5 gallons per minute.

Two permanent points within the former UST basin were also utilized at this site. Each of the permanent points received 300 gallons of 15% PermeOx[®] Plus, at a rate ranging from 5 to 15 gallons per minute.

Evidence of oxidant influence was observed during the injection by the increase of key groundwater parameters such as DO, ORP, pH and conductivity in monitoring wells within the plume. Chemical was visually observed in down and side gradient wells.

Effectiveness

Three months following the injection, soil samples were taken within the targeted plume area. Benzene concentrations were reduced from 1,400 ug/l to 1.8 ug/l in the highest impacted soils within the plume. Down and side gradient groundwater monitoring wells were purged and sampled and also showed a significant reduction.

The Bottom Line

ORIN successfully remediated the site by injecting PermeOx[®] Plus through a series of direct push points over a three-day period. Compared to alternative cleanup approaches, using chemical injection not only reduced site disruption, but also was quicker and cheaper. Performing chemical injection saved the client over \$20,000 compared to competitive injection chemistries and over \$48,000 for a dig and haul approach.

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Oil Refinery Pipeline Release

Summary ORIN successfully treated petroleum contaminated groundwater with an enhanced bioremediation chemistry. Contaminant levels were reduced from 4,700 ug/L to less than detection over a four-month period. ORIN's approach saved the client approximately \$28K to \$50K over traditional remediation approaches.

overcome this problem by using a specialized high-pressure pump to break open the soil formation and continue with the injection.

Evidence of oxidant influence was observed during the injection by the increase of key groundwater parameters such as DO, ORP, pH, TDS and conductivity in monitoring wells within the plume. Chemical influence was also observed in down gradient

wells where water elevation mounding was found.

Effectiveness

Four month following the injection, monitoring wells were purged and sampled for BTEX constituents. Benzene concentrations were reduced from 4,700 ug/l to 3.3 ug/l in highest impacted well within the plume. Down gradient wells outside

of active injection area also showed a significant reduction.

The Bottom Line

ORIN successfully remediated the site by injecting a sodium persufate and PermeOx[®] Plus chemistry through a series of direct push points over a five-day period. Compared to alternative cleanup approaches, using chemical injection not only reduced site disruption, but was quicker and cheaper. Performing chemical injection saved the client over \$28,000 compared to competitive injection chemistries and over \$50,000 for a dig and haul approach.

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Site Characteristics:

Geology - fine grained, silty, calcareous sand. **Groundwater velocity** – variable (10⁻³ to 10⁻⁵ cm/sec) **Contaminants** – 4,700 ppb benzene in groundwater. **Size of plume treated** – 60,000 ft³

Remediation Approach:

Treatment chemistry – Sodium persulfate and PermeOx[®] Plus **Treatment application** – Chemical injection through a series of direct push points

Chemistries used during injection

An initial bench level treatability study performed at ORIN's treatability laboratory found that a combination of sodium persulfate and PermeOx[®] Plus effectively reduced the concentrations of benzene. PermeOx[®] Plus is chemical oxidant and a slow oxygen release chemistry that stimulates indigenous aerobic microbes to breakdown petroleum compounds.

Summary of Implementation

The chemistry was designed for the chemical oxidation and enhanced bioremediation of BTEX compounds found in the soils and groundwater at this site. The targeted injection area at the site was down gradient of a former pipeline release. Twenty-five direct push injection points received 50 gallons of sodium persulfate followed by 100 gallons of PermeOx[®] Plus, at a rate ranging from 2 to 6 gallons per minute.

In some instances during injection, fluid refusal was present and the chemical was forced to the surface. ORIN was able to





Former Municipal Maintenance Facility

Summary ORIN successfully treated petroleum contaminated groundwater with enhanced bioremediation chemistry. Saturated contaminant levels were reduced from 4,250 ug/L to less than detection over a two-month period. ORIN's approach saved the client approximately \$27K to \$60K over traditional remediation approaches.

Site Characteristics:

Geology – silty clay with trace fine sand Groundwater velocity – 10⁻⁴ to 10⁻⁵ cm/sec Size of plume treated – 50,400 ft³ Contaminants – 2,400 ug/L benzene 120 ug/L toluene 130 ug/L ethylbenzene 1,600 ug/L xylene

Remediation Approach:

Treatment chemistry - PermeOx[®] Plus **Treatment application** – Chemical injection through a series of direct push points

Chemistries used during injection

An initial bench level treatability study performed at ORIN's treatability laboratory found that PermeOx® Plus, a slow, oxygen releasing compound, effectively reduced the concentrations of BTEX found at this site. Successful bioremediation of petroleum contamination via aerobic microbial respiration depends on a number of factors including the presence of appropriate microbes, nutrients, electron donors and terminal electron acceptors. In the aerobic metabolism of petroleum contaminants, oxygen acts as a terminal electron acceptor and petroleum contaminants act as electron donors, which are oxidized. Often, the limiting factor in aerobic bioremediation of petroleum contaminants is oxygen.



Summary of Ex-situ Implementation

The chemistry was designed for the enhanced bioremediation of BTEX compounds found in the groundwater at this site. The majority of the targeted injection area at the site was down gradient of the maintenance building. Twenty-eight direct push injection points received 50 gallons of PermeOx[®] Plus. Ten direct push points were also cored through the floor of the maintenance building each of these points received 50 gallons. Evidence of oxidant influence was observed during the injection by the increase of key groundwater parameters such as DO, ORP, pH and conductivity in monitoring wells within the plume.

Chemical was visually observed in down and side gradient wells.

Effectiveness

Two months following the injection, monitoring wells were purged and sampled for BTEX constituents. Benzene concentrations were reduced from 2,400 ug/l to 19 ug/l in the highest impacted well within the plume. Down and side gradient

groundwater monitoring wells were purged and sampled and also showed a significant reduction.

The Bottom Line

ORIN successfully remediated the site by injecting PermeOx[®] Plus through a series of direct push points over a three-day period. Compared to alternative cleanup approaches, using chemical injection not only reduced site disruption, but also was quicker and cheaper. Performing chemical injection saved the client over \$27,000 compared to competitive injection chemistries and over \$60,000 for a dig and haul approach.

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Department of Civil and Environmental Engineering

Publications

Southern Illinois University Carbondale

Year 2008

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 cm³/sec (0.53 ft³/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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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 (H₂O₂), magnesium peroxide (MgO₂) and calcium peroxide (CaO₂).

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 as a solid oxygen source. Magnesium peroxide 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:

$$MgO_2 + 2H_2O \to Mg(OH)_2 + \frac{1}{2}O_2 + H_2O$$
 (1)

$$CaO_2 + 2H_2O \rightarrow Ca(OH)_2 + \frac{1}{2}O_2 + H_2O$$
⁽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 MgO₂ released oxygen for up to 300 days, while the CaO₂ and H₂O₂ were exhausted after 100 and 10 days respectively. A full scale permeable barrier system was then constructed at a gasoline release site using the MgO₂ 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 MgO₂ 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, MgO₂ is prepared at a mass purity of only 15-25% as compared with 60-80% for CaO₂. Therefore, commercial CaO₂ can deliver three to four times more molecular oxygen than MgO₂ on a mass basis. It is also reported that CaO₂ is considerably less expensive than MgO₂, 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 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):

$$F_{cu} = \frac{2k_r}{\left(1 + k_r\right)} \tag{3}$$

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 (BOD₅) 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 20°C to 24°C, 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.

5 References

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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 $k_{\rm r}$ 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

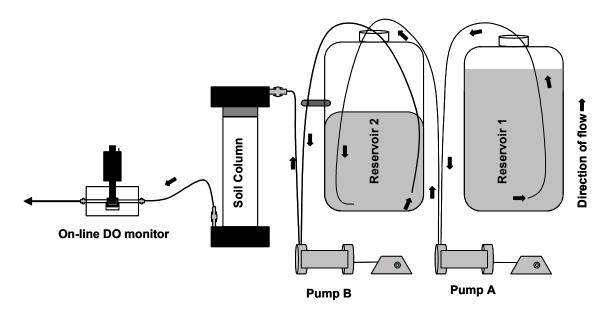


Figure 8: Experimental set up for continuous monitoring of permeability and dissolved oxygen.

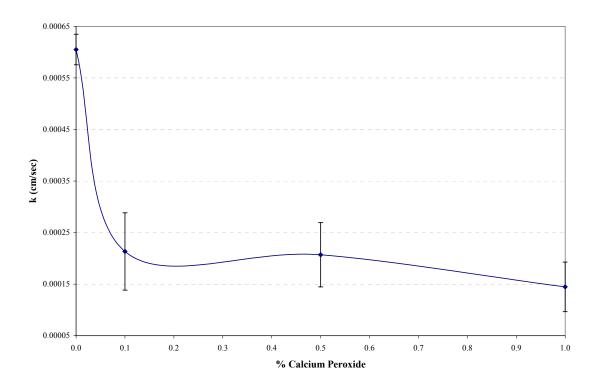


Figure 9: The reduction in permeability due to the initial addition of calcium peroxide.

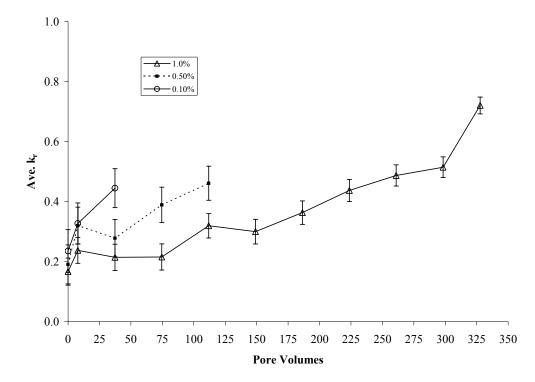


Figure 10: Average permeability of soils mixed with calcium peroxide per pore volume.

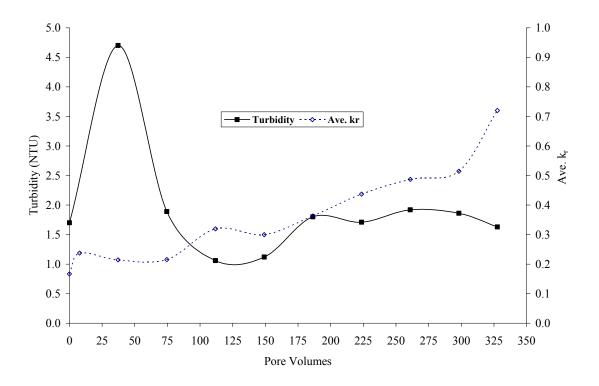


Figure 11: Amount of suspended particulates measured in the effluent compared to the average relative permeability over time for a 1.0% calcium peroxide mixture.

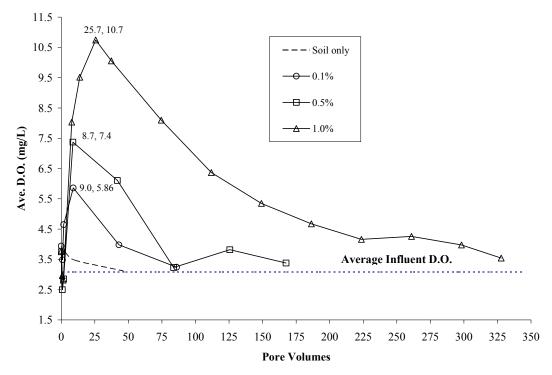


Figure 12a: Average dissolved oxygen measured per pore volume.

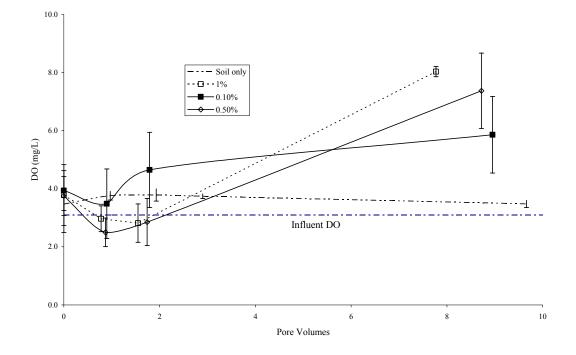


Figure 5b: Close-up of the average dissolved oxygen measured per pore volume.

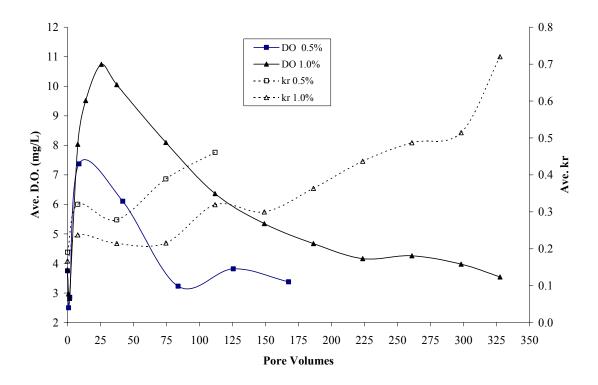


Figure 13: Comparison of DO and k_r for 0.5% and 1% calcium peroxide mixtures over time.

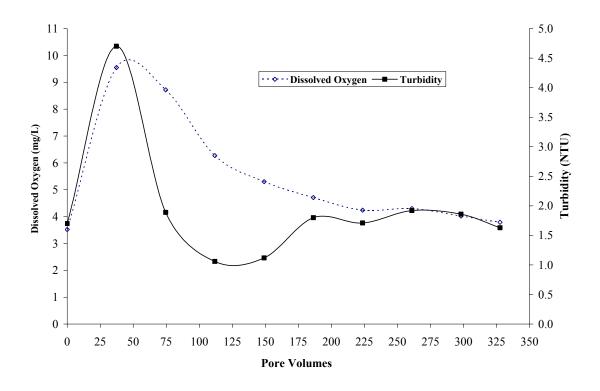


Figure 14: Dissolved oxygen and turbidity for 1% calcium peroxide mixture over time.

Table 1: Soil Characteristics

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

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 25°C, approx. 11.4-12.6	
	Loose Bulk Density, lb/cu ft 45-66	
	Color: Off white	
	Odor: None	
	Reaction: $CaO_2 + 2H_2O \rightarrow Ca(OH)_2 + O_2 + H_2O$	

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

% 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	$0.373 {\pm} 0.057$

Table 3: Amount of Refraction in Regions of Lower Permeability