

Department of Environmental Protection

Jeb Bush
Governor

Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Colleen M. Castille
Secretary

March 31, 2004

Mr. Peter J. Palko, P.E.
Panther Technologies, Inc.
220 Route 70 East, Suite B
Medford, New Jersey 08055

Re: **PermeOx Plus**

Dear Mr. Palko:

The Bureau of Petroleum Storage Systems hereby reaffirms its original May 17, 2002 acceptance of PermeOx Plus as a product for in situ and ex situ bioremediation of petroleum and other suitable contaminants in groundwater and soil. PermeOx Plus is a granular calcium peroxide-based product that slowly releases oxygen when wetted, for the purpose of accelerating the growth of microbes that biodegrade contaminants. The chemical composition of PermeOx Plus is shown in enclosure 1.

This letter of reaffirmation supersedes all previous letters of acceptance for Permeox Plus. It is, however, identical in content to those that precede with exception of this paragraph and the two that follow, in order to clarify the effect of a relatively new rule, 62-522.300(2)(c), Florida Administrative Code (F.A.C.). This rule, which became effective August 27, 2001, eliminates in many but not all cases the need for a zone of discharge variance when a remediation product is injected into an aquifer in accordance with an approved Remedial Action Plan. In the case of Permeox Plus, which is mainly calcium peroxide, and a similar chemical, magnesium peroxide, a zone of discharge is now permitted by rule rather than by variance for the secondary drinking water parameters pH and total dissolved solids (TDS).

The only reason why a zone of discharge variance exists for magnesium peroxide, and not for Permeox Plus calcium peroxide is the time at which the marketing of each chemical began in Florida. When a variance was granted for magnesium peroxide on January 5, 1999, there was no other regulatory mechanism available other than a variance to allow a zone of discharge for its injection. By the time Permeox Plus began marketing itself in Florida in 2002, Rule 62-522.300(2)(c), F.A.C., which allows a zone of discharge by rule rather than by variance, had been in effect since August 27, 2001. Therefore, it was not necessary for a variance to be granted in order to inject Permeox Plus. In short, it can be said that magnesium peroxide is allowed its zone of discharge via variance, while Permeox Plus is allowed its zone of discharge via rule. Either way, a zone of discharge is established.

It must also be clearly understood by both state regulators and users of either magnesium peroxide or Permeox Plus calcium peroxide that groundwater monitoring of pH and TDS is necessary when they are used for in situ aquifer remediation. Paragraph 11e of the variance granted for magnesium

peroxide on January 5, 1999 clearly states that groundwater must be monitored for pH and TDS. At no time has a user of magnesium peroxide ever been exempt from the requirement to monitor groundwater for pH and TDS. And regardless of whether the January 5, 1999 variance or new rule 62-522.300(2)(c), F.A.C., is applied to magnesium peroxide, it is a requirement that the groundwater be monitored for pH and TDS.

For vadose remediation where the underlying groundwater will not be affected by leaching of this product, there are no special concerns beyond those which would normally need to be addressed in preparing a Remedial Action Plan and conducting a cleanup in accordance with the petroleum cleanup requirements of Chapter 62-770, F.A.C. For ex situ groundwater treatment, where an aboveground treatment system produces effluent meeting the petroleum cleanup criteria of Chapter 62-770, F.A.C., and the drinking water standards of Chapter 62-550, F.A.C., for disposal via recharge gallery or NPDES permit, there are no special concerns. But for in situ groundwater remediation, via direct injection of PermeOx Plus into an aquifer, there are underground injection control (UIC) regulations that must be observed. Since in situ aquifer remediation via injection is likely to be the most common application of this product, the bulk of the regulatory requirements discussed herein will be directed to that topic.

The bureau recognizes PermeOx Plus as a viable product for the bioremediation of petroleum contaminated sites in Florida. There are no objections to its use provided: (a) the considerations of this letter are taken into account; (b) a Remedial Action Plan is approved by the Department; and (c) applicable and appropriate underground injection control regulations are observed when the product is used for injection-type in situ aquifer remediation. For PermeOx Plus, the major environmental and regulatory considerations are set forth in enclosure 2.

While the Department of Environmental Protection does not provide endorsement of specific or brand name remediation products or processes, it does recognize the need to determine their acceptability from an environmental standpoint with respect to applicable rules and regulations, and the interests of public health, safety, and welfare. Vendors must then market the products and processes on their own merits regarding performance, cost and safety in comparison to competing alternatives in the marketplace. In no way, however, shall this regulatory letter of acceptance be construed as certification of product performance. Additionally, the Department emphasizes a distinction between regulatory "acceptance" and approval. Products and processes are accepted; they are not approved.

Those who prepare Remedial Action Plans may include a copy of this letter in the appendix of plans they submit, and call attention to it in the text of their document. In this way, technical reviewers throughout the state will be informed that you have contacted the Department of Environmental Protection to inquire about PermeOx Plus's environmental acceptability. To aid those reviewers, the Bureau of Petroleum Storage Systems provides supplemental information as enclosure 3.

The Department reserves the right to revoke its acceptance of a product or process if its nature or performance has been falsely represented. Additionally, Department acceptance of any product or process does not imply it has been deemed applicable for all cleanup situations, or that it

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is preferred over other treatment or cleanup techniques in any particular case. A site-specific evaluation of applicability and cost-effectiveness must be considered for any product or process, whether conventional or innovative, and adequate site-specific design details must be provided in Remedial Action Plans prescribing the product or process. You may contact me at (850) 877-1133, extension 29 if there are any questions.

Sincerely,

Rick Ruscito, P.E.
Ecology and Environment, Inc.
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6

Rebecca S. Lockenbach
FDEP Section Leader
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6

c: T. Conrardy - FDEP/Tallahassee

History:

ppl #181
inn_083.doc
5/17/2002

ppl #226
IT 20641
Inn_083a.doc
12/1/03

ppl #232
inn_083b.doc
3/31/04

ENCLOSURE 1

PERMEOX PLUS* CHEMICAL COMPOSITION †

Calcium Peroxide‡ [CaO ₂]	75% by weight §
Calcium Hydroxide [Ca(OH) ₂]	25% by weight §

† Information from Material Safety Data Sheet dated March 19, 2002 by FMC Corporation, Philadelphia, Pennsylvania.

‡ Active ingredient.

§ Percent by weight for product as shipped by the manufacturer: dry, granular solid particles in the size range of 70 to 90 microns with a bulk density of 27 pounds per cubic foot. The specific gravity of the solids alone is 2.92.

* For in situ injection-type remediation projects, Panther Technologies Incorporated indicates that PermeOx will be applied as a 25%-60% aqueous slurry. Since solutions of 1% calcium peroxide can have a pH as high as 11.5 to 12 units, and the total dissolved solids content of the injected slurry is likely to be in excess of 500 milligrams per liter, the Bureau of Petroleum Storage Systems hereby provides a reminder that Rule 62-522.300(2)(c), Florida Administrative Code, applies.

For in situ injection-type aquifer remediation using calcium peroxide, to comply with the rule, a department-approved Remedial Action Plan must: (a) indicate that the fluid to be injected will not meet the secondary drinking water standard of 6.5-8.5 for pH, and that it will not meet the 500 milligrams per liter secondary drinking water standard for total dissolved solids; (b) indicate a zone of discharge size (i.e. a radius of influence for each injection point); (c) indicate the period of time during which the injected fluid could temporarily exceed the secondary drinking water standards for pH and total dissolved solids; and (d) propose adequate groundwater monitoring of pH and total dissolved solids.

ENCLOSURE 2

ENVIRONMENTAL AND REGULATORY INFORMATION

For PermeOx Plus, the major environmental and regulatory concerns are listed below.

- a. Groundwater cleanup standards: The onus shall be on users of PermeOx Plus to ensure that all applicable groundwater contaminant standards will be met at the time of project completion, for the contaminants of concern, any residuals associated with the ingredients of PermeOx Plus, and any byproducts produced as a result of chemical or biochemical reactions involving those ingredients. The following chapters of the Florida Administrative Code are cited: Chapter 62-550, F.A.C., for primary and secondary water quality standards; Chapter 62-520, F.A.C. for groundwater classes and standards; Chapter 62-522, F.A.C., for groundwater permitting and monitoring requirements; Chapter 62-528, F.A.C., for underground injection control, particularly Part V, for Class V, Group 4 aquifer remediation projects; Chapter 62-770, F.A.C., for petroleum cleanup criteria; and Chapter 62-777, F.A.C., for cleanup target levels.

A noteworthy aspect of the minimum criteria set forth in Chapter 62-520, F.A.C., is that it requires groundwater to be free from substances that are harmful to plants, animals, and organisms, and free from substances that are carcinogenic, mutagenic, teratogenic or toxic to human beings. In effect, these "free from" requirements form a catchall. They close what would otherwise be a loophole in the regulations by preventing injection of a potentially harmful product in the event that any of its ingredients is not regulated as a specific primary or secondary drinking water contaminant.

- b. Injection well permit: The issuance of a site-specific Remedial Action Plan Approval Order by either the Bureau of Petroleum Storage Systems or the Bureau of Waste Cleanup, for remediation via injection of PermeOx Plus into an aquifer, constitutes the granting of a Class V injection well permit.
- c. Groundwater injection standards: For in situ aquifer remediation, pursuant to Chapter 62-528, F.A.C., the composition of an injected fluid must meet the drinking water standards set forth in Chapter 62-550, F.A.C., and the minimum groundwater criteria described in Chapter 62-520, F.A.C. The minimum groundwater criteria set forth in Chapter 62-777, F.A.C., also apply. The Bureau of Petroleum Storage Systems knows that the chemical analysis of enclosure 1 for PermeOx Plus will not meet the secondary drinking water standards of 500 mg/L for total dissolved solids and the 6.5 to 8.5 range for pH. Therefore, in order to use PermeOx Plus for injection-type in situ aquifer remediation, rule 62-522.300(2)(c), F.A.C., must be applied to these secondary drinking water parameters that do not meet injection requirements.

Rule 62-522.300(2)(c), F.A.C., effective August 27, 2001, allows a temporary zone of discharge for aquifer remediation purposes, within which a temporary exceedance of the primary and secondary drinking water parameters is tolerated when PermeOx Plus is injected. In order to comply with the rule, a Department-approved site-specific remediation plan proposing PermeOx Plus must: (a) identify the secondary parameters pH and total dissolved solids, whose standards are exceeded by the composition of the fluid to be injected; (b) indicate the size and duration of the temporary zone of discharge; and (c) propose groundwater

monitoring of the secondary parameters in the fluid that do not meet injection requirements.

- d. Utilization of wells: If a remediation site happens to have an abundance of monitoring wells, then the Department has no objection to the use of some wells for the application of PermeOx Plus. However, no "designated" monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used to apply PermeOx Plus. This will avoid premature conclusions that the entire site meets cleanup goals. By making sure that designated tracking wells are not also used for treatment, there will be more assurance that the treatment process has permeated the entire site and that it did not remain localized to the area immediately surrounding each injection well.
- e. Groundwater monitoring:
 - 1. Active remediation monitoring of petroleum: During the period of active remediation, groundwater shall be monitored for petroleum contaminants of concern in accordance with the requirements set forth in Section 62-770.700, F.A.C. For non-petroleum cleanups, the monitoring should be conducted in accordance with the provisions of an approved Remedial Action Plan.
 - 2. Post remediation monitoring of petroleum: During the period of post active remediation, groundwater monitoring for petroleum contaminants of concern shall be conducted in accordance with the requirements set forth in Section 62-770.750, F.A.C. For non-petroleum cleanups, the monitoring should be conducted in accordance with the provisions of an approved Remedial Action Plan.
 - 3. Monitoring for underground injection control purposes: Pursuant to rule 62-522.300(2)(c), F.A.C., groundwater monitoring of the primary and secondary drinking parameters set forth in Chapter 62-550, F.A.C., that are not met by a fluid injected for aquifer remediation must be addressed in a Department-approved Remedial Action Plan. Additionally, if an injected fluid does not meet the minimum groundwater criteria of Chapters 62-520 and 62-777, F.A.C., then groundwater monitoring must be conducted for the specific parameters associated with the necessary temporary zone of discharge variance for the injection of such a fluid. In the case of PermeOx Plus, only secondary drinking water parameters for pH and total dissolved solids are not met by the fluid to be injected, so the groundwater monitoring of those two parameters must be addressed in a Department-approved Remedial Action Plan.
- f. Underground injection control inventory: Remedial Action Plans prescribing in situ aquifer injection-type remediation shall include information pursuant to Rule 62-528.630(2)(c)1 through 6, F.A.C., for the inventory purposes of underground injection control. Per Rule 62-528.630(2)(c), F.A.C., aquifer remediation projects involving injection wells may be authorized under the provisions of a Remedial Action Plan, provided the construction, operation, and monitoring requirements of Chapter 62-528, F.A.C., are met. A memorandum outlining the inventory information about injection-type aquifer remediation plans, to be transmitted by Department reviewers, to the Underground Injection Control Section is provided as enclosure 4.
- g. Avoidance of migration: For in situ injection-type aquifer remediation projects, injection of PermeOx Plus shall be performed in such a way, and at such a rate and volume, that no undesirable migration of either the

product's ingredients or the contaminants of concern in the aquifer results, pursuant to Rule 62-528.630(3), F.A.C.

- h. Operating parameters: Section 62-770.700, F.A.C., sets forth frequency requirements for the measurement of bioremediation operating parameters such as dissolved oxygen levels, rates of nutrient addition, temperature, etc. It also includes an option for reduction in the frequency or discontinuation of some measurements in situations when appropriate.
- i. Abandonment of wells: Upon issuance of a petroleum Site Rehabilitation Completion Order, or a declaration of "No Further Action", injection wells shall be abandoned pursuant to Section 62-528.645, F.A.C. The Underground Injection Control Section of the Department shall be notified so that the injection wells can be removed from the inventory-tracking list.

ENCLOSURE 3

SUPPLEMENTAL INFORMATION

The information below, compiled from several sources, may be helpful to reviewers of Remedial Action Plans prescribing bioremediation.

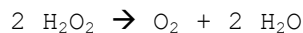
- a. Department of Environmental Protection reviewers of injection-type in situ aquifer remediation plans, regardless of whether in Tallahassee or district offices, must fill in the blanks on the enclosure 4 memorandum, whose subject is "Proposed Injection Well(s) for In situ Aquifer Remediation at a Petroleum Remedial Action Site". The completed form must be submitted to the Underground Injection Control Section at 2600 Blair Stone Road, Tallahassee, Florida 32399-2400.

Only the appropriate bureau chiefs and division directors within the Department and its district offices may sign in situ injection-type remediation plan approval orders that constitute the granting of a Class V injection permit. Local program staff may review such plans but are not authorized to sign the approval orders. Reason: Although an arrangement between the Environmental Protection Agency and the Department delegates underground injection control authority to the Department, it does not allow the Department to delegate that authority any further. This includes delegation to the Department's contracted remediation review agencies such as those operated by the counties and other local governments.

- b. Pilot study: For bioremediation, per Section 62-770.700, F.A.C., a pilot study proposal shall be submitted for review, and a pilot test shall be performed prior to designing a treatment system. If conditions or the situation at a site do not warrant a pilot study, then a proposal explaining the rationale for the decision not to perform a pilot study shall be submitted for review. The state's technical reviewers are encouraged to use judgment in balancing cost and the need for technical information to be obtained from a pilot study.
- c. Bacteria: It is generally reported (on a total weight basis) that bacteria are approximately 70 to 80 percent water. On a dry weight basis, approximately 95 percent of the composition is represented by 5 elements: carbon, oxygen, nitrogen, hydrogen, and phosphorus. At a petroleum remediation site, it is intended that the source of carbon for the growth of bacteria will come from the petroleum hydrocarbons themselves. Natural-occurring organic carbon at a site can also serve as a carbon source for bacteria. Depending on site's specific conditions, the remaining four elements must either be available naturally, or added as macronutrients in order to stimulate bioremediation. Micronutrients must also be present for bacteria to grow.
- d. Degradation products: Carbon dioxide and water are the ultimate products of aerobic and most anaerobic biodegradations of hydrocarbons. In the case of methanogenesis, an anaerobic process, carbon dioxide and methane are produced. The intermediate products of aerobic degradation may include simple acids, alcohols, and fatty acids. Aerobic processes use oxygen as an electron acceptor to produce carbon dioxide and water.
- e. Parameters: The following parameters may be useful in determining the potential for bioremediation at a site, or whether bioremediation is already occurring. They were selected from a list that appears in the publication "In situ Treatment Technology" by E. Nyer et al., Lewis Publishers, 1996. The parameters are dissolved oxygen; redox potential; pH; temperature; specific conductance; volatile organic compounds; nitrate; nitrite; ammonia nitrogen; manganese (total and dissolved); iron

(total, dissolved, and ferrous); sulfate; sulfide; and total organic carbon. Gaseous parameters include carbon dioxide, oxygen, nitrogen, and methane. Other parameters that may be helpful are chemical oxygen demand, biochemical oxygen demand, and total organic carbon. Those who prepare bioremediation plans and their reviewers should determine which parameters, if any should be investigated on a site-specific basis.

- f. Chemical reactions: The chemical reactions that occur when calcium peroxide is mixed with water are shown below. This mechanism of reactions shows how calcium peroxide increases the groundwater's concentration of dissolved oxygen. The notation used is as follows: calcium peroxide, CaO_2 ; calcium hydroxide, Ca(OH)_2 ; hydrogen peroxide, H_2O_2 ; water, H_2O ; and oxygen, O_2 .



- g. Vendor information: Below is some of the information included in the submittal by Panther Technologies for PermeOx that the Bureau of Petroleum Storage Systems would like to pass along to readers of this letter.

Calcium Peroxide (dry granules)	75% by weight, minimum
Molecular Weight of CaO_2	72.8
Calcium Hydroxide (dry granules)	25% by weight
Molecular Weight of Ca(OH)_2	74
Active Oxygen	18.2%, minimum (i.e. there are 18.2 pounds of active oxygen in every 100 pounds of PermeOx Plus)
Solubility	Slightly soluble in water (soluble in acid)
pH of a 1% slurry at 25°C, approximate	11.5 to 12.2
Loose Bulk Density, approximate lb/cu.ft.	45-65
Odor/Appearance	None/Yellow/White granules
Soil Moisture Required for Activation	5%-10%
Theoretical weight ratio of oxygen to hydrocarbon for aerobic degradation	3:1
Factor recommended to apply to theoretical ratio to account for unknown oxygen demands by non-target compounds	Multiply theoretical by up to 8 (therefore provide up to 24 pounds of oxygen for every pound of hydrocarbon to be degraded)
Typical Application Rate	0.1%-1.0% by weight on soil (approx. 2-6 pounds/cubic yard of soil)
Injection Applications	Inject as a 25%-60% slurry

- h. Limitations: Not recommended for free product. Not recommended for chlorinated ethenes and other situations where the contaminant is better suited for anaerobic degradation rather than aerobic.

**Florida Department of
Environmental Protection**

Memorandum

TO: Richard Deuerling, Mail Station 3530
Division of Water Facilities
Underground Injection Control Section
Florida Department of Environmental Protection
2600 Blair Stone Road, Tallahassee, FL 32399-2400

FROM: _____ (Note 1.)

DATE: _____

SUBJ: **Proposed Injection Well(s) for In situ Aquifer
Remediation at a Petroleum Remedial Action Site**

Pursuant to Rule 62-528.630(2)(c), F.A.C, inventory information is hereby provided regarding the proposed construction of temporary injection well(s) for the purpose of in situ aquifer remediation at a petroleum-contaminated site.

Site name: _____

Site address: _____

City/County: _____

Latitude/Longitude: _____

FDEP Facility Number: _____

Site owner's name: _____

Site owner's address: _____

Well contractor's name: _____ (Note 2.)

Well contractor's address: _____

Brief description of the in situ injection-type aquifer remediation project:

Summary of major design considerations and features of the project:

Areal extent of contamination (square feet): _____

Number of injection wells: _____

Composition of injected fluid (Note 3)
(ingredient, wt. %): _____

Injection volume per well (gallons): _____

Single or multiple injection events: _____

Injection volume total (all wells, all
events): _____

Richard Deuerling
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Date: _____

Site name: _____
FDEP facility no.: _____

A site map showing the areal extent of the groundwater contamination plume, and the location and spacing of injection wells and associated monitoring wells is attached.

The following is a summary description of the affected aquifer:

Name of aquifer: _____
Depth to groundwater (feet): _____
Aquifer thickness (feet): _____

The injection well(s) features are summarized below, and/or a schematic of the injection well(s) is attached.

Direct-push or Conventional (*circle the appropriate well type*)
Diameter of well(s) (i.e., riser pipe & screen)(inches): _____
Total depth of well(s) (feet): _____
Screened interval: _____ to _____ feet below surface
Grouted interval: _____ to _____ feet below surface
Casing diameter, if applicable (inches): _____
Cased depth, if applic.: _____ to _____ feet below surface
Casing material, if applic.: _____

The in situ injection-type aquifer remediation plan for this petroleum contaminated site is intended to meet the groundwater petroleum cleanup criteria set forth in Chapter 62-770, F.A.C. Additionally, all other groundwater standards will be met at the time of project completion for any residuals associated with the ingredients of the injected remediation products, and any by-products or intermediates produced as a result of the chemical or biochemical transformation of those ingredients or the contaminating petroleum during their use. Applicable primary and secondary drinking water standards are set forth in Chapter 62-550, F.A.C., and additional groundwater quality criteria are set forth in Chapter 62-520, F.A.C.

The remediation plan estimates that site remediation will take _____ months. We will notify you if there are any modifications to the remediation strategy which will affect the injection well design or the chemical composition and volume of the injected remediation product(s).

The proposed remediation plan was approved on _____ by an enforceable approval order. A copy is attached. The remediation system installation is expected to commence within 60 days. Please call me at _____ if you require additional information.

Note 1. Local programs are not authorized to approve underground injections into aquifers. Reason: Per agreement with EPA, the FDEP cannot delegate this authority. Local programs, after reviewing a Remedial Action Plan or an injection proposal document, should follow the instructions in a March 16, 2000 memorandum to arrange for Department headquarters' execution of an approval order, and then complete this form. This form is primarily for use by state and local program technical reviewers, but petroleum remediation contractors may fill in all blanks except those labeled "FROM", "DATE", and "approval date", and "telephone number" blanks in the last paragraph. Those blanks should be completed only by a state or local program reviewer.

Note 2. If an injection well installation contractor has not yet been selected, then indicate the name and address of the project's general remediation contractor/consultant.

Note 3. Complete chemical analysis of injected fluid is required by Chapter 62-528, Florida Administrative Code. Proprietary formulations shall make confidential disclosure. Injected fluids must meet drinking water standards of Chapter 62-550, F.A.C., unless an exemption or variance has been granted.