

Florida Department of Environmental Protection

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Tallahassee, Florida 32399-2400

Rick Scott
Governor

Jennifer Carroll
Lt. Governor

Herschel T. Vinyard Jr.
Secretary

May 25, 2011

Suzanne Schomer, P.E.
AECOM Technical Services, Inc.
320 East South Street
Orlando, Florida 32801

Re: **PHOSter Nutrient Injection Technology**

Dear Ms. Schomer:

The Bureau of Petroleum Storage Systems (Bureau) hereby reaffirms and updates its recognition of AECOM Technical Services Incorporated (formerly Earth Tech Inc.) as a provider of the PHOSter vapor-phase nutrient injection technology for in situ bioremediation of petroleum hydrocarbons and other suitable contaminants in soil and groundwater. The technology was developed by the U.S. Department of Energy (DOE) and the Savannah River Technology Center in 1995. This update supersedes all previous revisions of PHOSter acceptance letters issued to date by the Bureau of Petroleum Storage Systems to all providers of the PHOSter technology.

The PHOSter process is a pulsed injection system that stimulates the growth of indigenous microorganisms by supplying an optimum quantity of oxygen and phosphorous. Compressed air passes through a vessel containing liquid triethylphosphate (TEP) and emerges as an air/TEP mixture. If nitrous oxide is needed as an additional nutrient, or propane is needed as an additional carbon source, then the process includes an option to include them in the injection mixture as well. Indigenous microorganisms utilize the injected air and nutrients to aerobically degrade petroleum contamination, producing biomass, carbon dioxide and water. Enclosure 1 contains regulatory information; Enclosure 2 contains supplemental information about the PHOSter technology; and Enclosure 3 is an Underground Injection Control (UIC) Notification.

This acceptance applies to the jurisdiction of the Bureau of Petroleum Storage Systems, but other government agencies may choose to recognize it if their needs and regulations are similar. This Bureau is not responsible for applications beyond its jurisdiction,

May 25, 2011

which is the cleanup of petroleum pursuant to Chapter 62-770, Florida Administrative Code (F.A.C.).

The Bureau of Petroleum Storage Systems recognizes PHOSter as a viable technology for the bioremediation of petroleum contaminated sites in Florida. There are no objections to its use provided the considerations of this letter are taken into account and a site-specific Remedial Action Plan is prepared in accordance with Chapter 62-770, F.A.C., for review and approval by the Department.

While the Florida Department of Environmental Protection does not provide endorsement of 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 and safety. The Department does not approve products and processes but rather issues a regulatory acceptance. Vendors, upon receipt of an acceptance letter, must market the product or process on its own merits regarding performance, cost, and safety in comparison to competing alternatives in the marketplace. In no way shall this regulatory acceptance be construed as Department certification of performance.

Site-specific Remedial Action Plans that propose the use of the PHOSter technology should include a copy of this letter as an appendix. It is not a requirement that a particular remediation product or process have an official acceptance letter in order for it to be proposed in a site-specific Remedial Action Plan, provided the plan contains sufficient information about the product or process to show that it meets all applicable rules and regulations.

The Department reserves the right to revoke its acceptance of a product or process if 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 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 a Remedial Action Plan. You may contact me at (850)-877-1133, extension 3720 if there are any questions.

Suzanne Schomer, P.E.

PHOSter Nutrient Injection Technology

Page 3

May 25, 2011

Sincerely,



Rick Ruscito, P.E.

Ecology & Environment, Inc.

Petroleum Cleanup Section 6

Bureau of Petroleum Storage Systems



Rebecca Lockenbach

FDEP Section Leader

Petroleum Cleanup Section 6

Bureau of Petroleum Storage Systems

c: T. Conrardy - FDEP/Tallahassee

Enclosures: (1) Regulatory Information

(2) Supplemental Information

(3) Underground Injection Control Notification Memorandum

History:

4/24/01 INN_057.doc PPL #133

8/2/07 INN_057a.doc PPL #330

5/25/11 INN_057b.doc PPL #428

ENCLOSURE 1

REGULATORY INFORMATION

- a. Regulations: Chapters of the Florida Administrative Code (F.A.C.) that may be applicable, either in part or in their entirety, include but are not necessarily limited to 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 62-520, 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; Chapters 62-770, 62-780, 62-782, and 62-785, F.A.C., for cleanup criteria; and Chapter 62-777, F.A.C., for cleanup target levels.

Users of the PHOSter system shall comply with all applicable regulations. This includes meeting applicable groundwater cleanup target levels for the contaminants of concern, the residual concentrations of PHOSter ingredients, and any byproducts of concern produced by chemical and biological reactions induced by the ingredients during the timeframe of the cleanup project.

- b. Underground Injection Control permit: Per Rule 62-528.630(2)(c), F.A.C., Class V injection-type aquifer remediation wells are exempt from the permitting requirements of Rule 62-528.635, F.A.C., when authorized by a Department-approved Remedial Action Plan or other enforceable mechanism, provided the requirements of the rules governing the remediation project, as well as the construction, operation, and monitoring requirements of Chapter 62-528, F.A.C., are met. Per Rule 62-528.630(2)(c), F.A.C., the issuance of an enforceable, site-specific Remedial Action Plan Approval Order by the Department for injection-type aquifer remediation constitutes the granting of a Class V injection well construction/clearance permit.

- c. Temporary injection zone of discharge (ZOD): Two factors must be taken into account when establishing a temporary injection ZOD for the PHOSter system, and requesting site-specific permission for it. First, it is not possible to directly identify the ZOD chemicals of concern when the fluid to be injected is a gas, *i.e.*, it is not possible to directly compare the gas phase concentrations of those chemicals to the liquid phase concentrations that the Florida injection regulations set forth as injection criteria. Second, even though nitrous oxide and triethylphosphate (TEP) are not regulated as specific groundwater contaminants in Florida, it may be prudent to at least track the fate of the nitrogen from the nitrous oxide to verify that nitrate and nitrite (which are regulated) do not remain after a cleanup at concentrations in excess of their groundwater standards. The fate of the triethylphosphate and any phosphate that may be liberated is less of a concern in

groundwater (but not surface water) because phosphate is not a regulated groundwater contaminant in Florida, and it is naturally present in abundance at some places in the state.

Based on the considerations cited above, the Bureau of Petroleum Storage Systems advises that no ZOD is needed for the triethylphosphate or any phosphate that may be liberated from it when the PHOSter system is used. But if the option to include propane and/or nitrous oxide in the injection is selected, then permission for a temporary injection ZOD for the propane and/or the nitrate and nitrite should be obtained by way of Rule 62-520.310(8)(c), F.A.C. The issuance of a site-specific Remedial Action Plan Approval Order for a remediation plan that meets the requirements of Rule 62-520.310(8)(c), F.A.C., constitutes the granting of permission for a temporary injection ZOD.

Site-specific Remedial Action Plans, in order to meet the requirements of Rule 62-520.310(8)(c), F.A.C., if propane and/or nitrous oxide are included in the injection must: (1) indicate that the parameters associated with the ZOD are propane, and nitrate and nitrite in the case of nitrous oxide; (2) specify the size of the ZOD; (3) specify the amount of time for which the ZOD is requested; and (4) propose adequate groundwater monitoring for the propane, and the nitrate and nitrite if nitrous oxide is injected. Zone size for a single injection point can usually be expressed as its injection radius of influence, and the zone size for a cluster of injection points can usually be expressed as the total area of all their overlapping radii of influence. For the groundwater monitoring of the ZOD parameters propane, nitrate, and nitrite during the period of active remediation by injection, sampling on a quarterly basis should be sufficient.

- d. Post injection remediation monitoring of ZOD parameters: Monitor the groundwater for propane (if propane was injected) and nitrate and nitrite (if nitrous oxide was injected) upon cessation of PHOSter injections. Take samples quarterly for a minimum of one (1) year. After one (1) year, the monitoring can be terminated only if the parameters being sampled have met their groundwater standards or their natural-occurring background levels at the site, whichever is less stringent, for at least the last two (2) consecutive quarters. If not, then continue the monitoring until 2 such consecutive quarters are achieved.

Compare the sampling results for propane to whichever of the following is less stringent: the site's natural-occurring background concentration of propane, or the minimum groundwater criterion of 8,700 micrograms per liter (ug/L) maximum, which was calculated using the method provided in Chapter 62-777, F.A.C. For the nitrate and nitrite, compare the sampling results to their respective drinking water standards of 10,000 ug/L and 1,000 ug/L, or their natural-occurring background levels at the cleanup site, whichever is less stringent.

- e. Underground Injection Control notification: Remedial Action Plans proposing in situ, injection-type aquifer remediation shall include information pursuant to Rules 62-528.630(2)(c)1 through 6, F.A.C., for the inventory purposes of the Underground Injection Control program. Reviewers of those plans, upon issuance of an enforceable Remedial Action Plan Approval Order by the Department, must submit a completed copy of the Underground Injection Control inventory notification memorandum in Enclosure 3.

Advice on filling out the UIC Notification memorandum for the PHOSter system:

1. Notification of injection volumes and flow rates: The UIC Notification memorandum was originally developed for liquid injections, not gas phase injections like those of the PHOSter system. It is therefore permissible for reviewers to modify or annotate appropriate portions of the memorandum, as necessary, to report PHOSter system gas phase injection amounts in terms of pounds or cubic feet of gas instead of gallons, and to report flow rates in terms of cubic feet per minute instead of gallons per minute.
2. Checkbox advice for notification of "no ZOD needed" for triethylphosphate (TEP) and nitrous oxide: Recent revisions of the UIC Notification memorandum include checkboxes under the section heading "Temporary Injection Zone of Discharge (ZOD)" and instruct the reviewer to place a checkmark in the boxes that apply. Reviewers should place a checkmark in the box for "No ZOD needed" for the triethylphosphate, and also for the nitrous oxide when it is injected, and then annotate the memorandum to indicate that they are "not regulated as Florida groundwater contaminants".
3. Checkbox advice for notification of reagent and reagent-related chemical species: When the injection of propane, a PHOSter reagent, is included during the operation of a PHOSter system, the reviewer should check the box that indicates ZOD permission is granted by Rule 62-520.310(8)(c), F.A.C., for the reagent, and indicate in the space provided that the chemical species to be monitored in the groundwater ZOD is propane.

When nitrous oxide, which is also a PHOSter reagent, is injected the reviewer should also place a checkmark in the box for ZOD permission by Rule 62-520.310(8)(c), F.A.C., for a reagent but then indicate in the space provided that nitrate and nitrite are the reagent-related chemical species of concern to be monitored in the groundwater ZOD. While nitrous oxide itself does not require a ZOD because it is not a regulated groundwater contaminant of concern, it is prudent to verify the fate of its nitrogen in the ZOD by

monitoring nitrate and nitrite, both of which are regulated groundwater contaminants of concern.

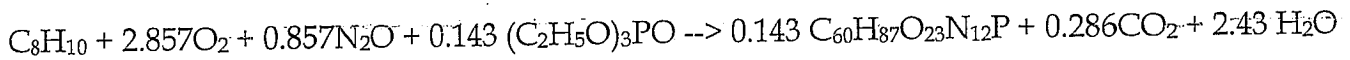
- f. Utilization of wells: If a remediation site happens to have an abundance of monitoring wells, then the Bureau of Petroleum Storage Systems has no objection to the use of some wells for the injection of PHOSter reagents. However, no "designated" monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used to inject reagents. This will avoid a premature conclusion that the entire site meets cleanup goals. By making sure that designated tracking wells are not also used as treatment points, there will be more assurance that the reagents have permeated the entire site and that they did not remain localized to the area immediately surrounding each injection well.
- g. Avoidance of migration: For injection-type, in situ aquifer remediation projects, pursuant to Rule 62-528.630(3), F.A.C., injection of PHOSter reagents shall be performed in such a way, and at such a rate and volume, that no undesirable migration of either the reagents or the contaminants of concern in the aquifer results.
- h. Abandonment of wells: Upon issuance of a Site Rehabilitation Completion Order, injection wells shall be abandoned pursuant to Section 62-528.645, F.A.C., and the Underground Injection Control Section of the Department shall be notified so that the treatment wells can be removed from the injection well inventory-tracking list.

ENCLOSURE 2

SUPPLEMENTAL INFORMATION

- a. Pilot study: For bioremediation, per Rule 62-770.700(2), 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 the rule allows that a proposal explaining the rationale to forego a pilot study may be submitted for review.
- b. Nutrient ratio: The 20:12:1 molar ratio of oxygen, nitrogen, and phosphorus is the cornerstone of the PHOSter technology. The objective is to encourage microorganism growth by supplying these nutrients in a ratio that roughly approximates the molar ratios needed to produce a standard cell of composition $C_{60}H_{87}O_{23}N_{12}P$. The general equations presented for the PHOSter technology that describe the biological oxidation process for a hydrocarbon, and an example of an approximately balanced equation for the oxidation of ethylbenzene (C_8H_{10}), using nitrous oxide (N_2O) as the nitrogen source and triethylphosphate [$(C_2H_5O)_3PO$] as the phosphorus source are:

HYDROCARBON + OXYGEN + NITROGEN + PHOSPHORUS --> CELL MASS + CARBON DIOXIDE + WATER



It should be noted that not all of the carbon in the ethylbenzene is converted directly to carbon dioxide, and that a portion is assimilated as cell mass, which will, in turn, degrade when the microorganisms die.

- c. Pulsing: Injection of vapor-phase nutrients is pulsed on a timed cycle to keep microorganisms fed at an optimum rate. Too little nutrient addition causes them to die, while too much will be wasteful. The strategy of the PHOSter system is to inject vapor-phase nutrients in small enough timed intervals and quantities to keep the microorganisms fed at an optimum rate. Therefore, very little injected material is wasted, and the risk of overdosing is minimal, which in turn minimizes the risk of injecting unnecessary and excessive quantities of nitrogen and phosphorus into the aquifer. Likewise, the same reasoning can be applied to propane when it is used.

- d. Triethylphosphate: This compound is also known as triethyl ester phosphoric acid. Its vapor pressure is 1 millimeter of mercury (mm Hg) at 39°C. It has been indicated to the Department that microorganisms utilize the phosphorus component of this molecule as a nutrient, and consume the ethyl groups as a food source.
- e. Phosphorus: There are no groundwater or primary or secondary drinking water standards for phosphorus in Florida, only a surface water standard. For reference purposes only, it may be helpful to know that the European Economic Community guide level for phosphorus is 400 micrograms per liter (ug/L), as P₂O₅, for drinking water, and that by comparison a surficial aquifer sample at a petroleum remediation site in Volusia County contained 1,200 ug/L of naturally occurring phosphorus, as PO₄. This concentration may not be unusual for Florida.
- f. Nitrous oxide: May be used as a nitrogen source. Nitrous oxide readily dissolves in water. One (1) liter of it dissolves in 1.5 liters of water at 20 degrees Centigrade and 2 atmospheres.
- g. Advantage of vapor-phase injection: Quicker and more thorough dispersal of nutrients can occur if they are injected in the vapor-phase, rather than as liquids or solids, especially at sites where permeability of the soil is low.
- h. Air emissions: No air emissions monitoring is necessary for the PHOSter system since injection gas flow rates are not intended to be high enough to volatilize appreciable amounts of petroleum. If, however, the conditions of a specific cleanup site are such that fugitive air emissions are produced at unacceptable levels, then the PHOSter system flow rates should be adjusted to eliminate the problem, or vapor collection and treatment should be employed.

Florida Department of Environmental Protection

Memorandum

(This version of UIC Notice memo is for use by staff of the BPSS and District offices)

TO: Cathy McCarty, P.G.
Florida Department of Environmental Protection
Bureau of Water Facilities Regulation
Underground Injection Control Section - MS 3530
2600 Blair Stone Road, Tallahassee, Florida 32399-2400

FROM: _____
(An employee of Div. of Waste Management or DEP District Office)

DATE: _____

SUBJECT: **Remediation Product Injection Well(s) for In Situ Aquifer
Remediation at a Petroleum Contaminated Site**

Reminder: This memorandum must be completed by an FDEP employee of the Bureau of Petroleum Storage Systems or an FDEP District Office. A person working for a consultant company preparing a RAP may complete some portions of this memo to expedite the FDEP's review but if so, the "From" and "Date" blanks and the date of RAP approval and phone number should be left blank for the FDEP technical reviewer to complete after verifying other information in the memo is accurate and conforms to applicable rules and procedures.

oOo

Please remove this message box prior to submittal of this memorandum to the Underground Injection Control Section.

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

Facility name: _____

Facility address: _____

City/County: _____

Latitude/Longitude: _____

FDEP Facility Number: _____

Facility owner's name: _____

Facility owner's address: _____

Well contractor's name: _____

Well contractor's address: _____

AFFECTED AQUIFER

Name of aquifer: _____
Depth to groundwater (feet): _____
Aquifer thickness (feet): _____
Areal extent of contamination (square feet): _____

INJECTION WELLS

A site map showing the location and spacing of injection wells, the areal extent of the groundwater contamination plume, and associated monitoring wells is attached. The injection well(s) features are summarized below, and/or a schematic of the injection well(s) is attached.

Direct-push or HSA/Mud rotary (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 land surface
Grouted interval, if applicable: _____ to _____ feet below land surface
Casing diameter, if applicable (inches): _____
Cased depth, if applicable: _____ to _____ feet below land surface
Casing material, if applicable: _____
If a remediation product will be injected as a DP rod is inserted, indicate injection interval: _____ to _____ feet below land surface.

PROJECT DESCRIPTION

The in situ, injection-type aquifer remediation product/process remediates contaminants by:
(check those that apply)

- use of a bioremediation product,
- use of a chemical oxidation product,
- recirculation of partially treated contaminated groundwater, or
- other (describe) _____

Brief description of the project: _____

Summary of major design considerations and features of the project:

Number of injection wells: _____
Injection volume per well (gallons): _____
Single or multiple injection events: _____
Injection volume total (all wells, all events): _____
For continuous recirculation of partially treated water, indicate total daily design flow rate: _____ gallons per day

FLUID TO BE INJECTED

Brand name of remediation product(s): _____

Has an innovative technology acceptance letter been issued for this product by the BPSS:
__ yes __ no (Note: it is not required that an innovative technology acceptance letter be issued for the technology or product to be proposed in a RAP)

If product formula is proprietary then non-disclosure of the formula to the PE reviewing the RAP for the Department is only acceptable if there is an innovative technology acceptance letter issued by the BPSS with an attached proprietary voucher of confidential disclosure and it is verified that the proposed application rates (dosage) is limited to the rates specified in the innovative technology acceptance letter.

Is product formulation proprietary? __ yes __ no.

If product formulation is proprietary are proposed application rates limited to that indicated in innovative technology acceptance correspondence? __ yes __ no __ N/A

Composition of injected fluid (e.g. ingredient, wt. %): _____

TEMPORARY INJECTION ZONE OF DISCHARGE (ZOD)

(check those that apply)

- No ZOD needed. The fluid to be injected meets the primary and secondary groundwater standards of Chapter 62-550, F.A.C., and the minimum groundwater criteria of Chapters 62-520 and 62-777, F.A.C. _____
- ZOD permission by rule 62-520.310(8)(c) †, F.A.C., for reagent chemical species and/or parameter(s) in the fluid to be injected (or re-injected) that exceed secondary groundwater standards. ZOD permission by this rule also applies to chemical species in the fluid to be injected that exceed primary groundwater standards or minimum groundwater criteria, provided those species are prime constituents of the reagents used to remediate site contaminants. The chemical species and parameters for which the approved Remedial Action Plan identifies zone size and duration, and addresses groundwater monitoring are summarized below.

Chemical species & parameters: _____

Zone size (sq. ft.) _____ Duration (mos.) _____ Yes, monitoring addressed.

- ZOD permission by rule 62-520.310(8)(c) †, F.A.C., for the following contaminants of concern that exceed their groundwater standards in the fluid to be re-injected as part of a closed-loop re-injection system for which the approved Remedial Action Plan identifies zone size and duration, and groundwater monitoring:

Contaminants of concern: _____

Zone size (sq. ft.) _____ Duration (mos.) _____ Yes, monitoring addressed.

- ZOD permission by variance because the fluid to be injected contains the following impurities that are not prime constituents of the reagents used to remediate the site's contaminants, and the concentrations of those impurities in the fluid to be injected are in excess of their primary groundwater standards:

Impurities regulated as primary groundwater contaminants: _____

Zone size (sq. ft.) _____ Duration (mos.) _____ Yes, monitoring addressed.

- A variance needs to be granted before the remediation can be conducted.

- A variance has already been granted for the impurities listed above:

Date variance granted: _____

Zone size (sq.ft.): _____

Duration (mos.): _____

- If ZOD permission by rule 62-520.310(8)(c)†, F.A.C., or by variance is checked above, then a figure that delineates the ZOD is attached. (Use the lines below to more fully describe the ZOD if a figure alone will not suffice).

CLEANUP CRITERIA AND ENFORCEABLE APPROVAL ORDER

The in situ injection-type aquifer remediation plan for this contaminated site is intended to meet the groundwater cleanup criteria set forth in Chapter 62-777, 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 reactions induced by those ingredients or the contaminants of concern during their use. Applicable primary and secondary groundwater standards are set forth in Chapter 62-550, F.A.C., and minimum groundwater criteria are set forth in Chapters 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.

† Effective July 12, 2009, rule 62-522.300(2)(c), Florida Administrative Code (F.A.C.), was relocated to Chapter 62-520, F.A.C., and renumbered as rule 62-520.310(8)(c), F.A.C.

