



Florida Department of Environmental Protection

Bob Martinez Center
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Charlie Crist
Governor

Jeff Kottkamp
Lt. Governor

Mimi A. Drew
Secretary

November 30, 2010

Louis LeBrun, P.E.
APTwater, Inc.
3106 NW 116th Ave.
Coral Springs, Florida 33065

Re: **PulseOx[®] Advanced Oxidation Process (PulseOx[®] AOP)**

Dear Mr. LeBrun:

The Division of Waste Management (the Division) hereby accepts the PulseOx[®] Advanced Oxidation Process (PulseOx[®] AOP) by APTwater Incorporated as a system for in situ remediation of petroleum, chlorinated hydrocarbons and other suitable contaminants in groundwater and soil. As APTwater Incorporated has indicated, the AOP process injects timer-controlled pulses of ozone and oxygen, air, and aqueous hydrogen peroxide for the destruction of contaminants by chemical oxidation. Residual oxygen from the process dissolves in the groundwater and stimulates a cleanup site's indigenous microorganisms to provide additional oxidation by aerobic degradation. There is no objection to the use of the AOP process for remediation of contaminated sites in Florida, provided a site-specific Remedial Action Plan is approved by the Department. Regulatory information is provided in Enclosure 1; supplemental information is provided in Enclosure 2; and an Underground Injection Control notification form in Enclosure 3.

The Division of Waste Management does not provide endorsement of specific or brand name remediation products or processes, but it does recognize the need to determine their acceptability in the context of environmental regulations, and the protection of public health and safety. In no way shall this regulatory acceptance be construed as an endorsement or certification of product performance. Additionally, the Division emphasizes a distinction between its regulatory "acceptance" letter and an approval. Products and processes are accepted but they are not approved. Vendors and environmental consulting companies must market the products and processes on their own merits regarding performance, cost, and safety in comparison to competing alternatives in the marketplace.

Remedial Action Plans that propose the use of an accepted product or process should include a copy of the acceptance letter in plan's appendix, and reference it in the text of the document. 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

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Plan. The plan, however, must contain sufficient information about the product or process to show that it meets all applicable rules and regulations.

The Division reserves the right to revoke its acceptance of a product or process if it has been falsely or incompletely represented. Additionally, Division 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 design details must be provided in a site-specific Remedial Action Plan submitted for Department review and approval. Questions about hazardous waste cleanup applications should be directed to Gary Millington, and questions about petroleum cleanup applications should be directed to Rick Ruscito.

Sincerely,

Gary Millington, P.E.
Division of Waste Management
Bureau of Waste Cleanup
Program and Technical Support Section
gary.millington@fdep.state.fl.us
(850)-245-7502

Rick Ruscito, P.E.
Ecology and Environment, Inc.
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6
rruscito@ene.com
(850)-877-1133, extension 3722

c: T. Conrardy - DEP/Tallahassee
R. Cowdery – DEP/Tallahassee

REGULATORY INFORMATION

1. Regulations: Users of the PulseOx® AOP process shall comply with all applicable regulations. This includes meeting all applicable groundwater contaminant standards by the time of project completion for a cleanup site's contaminants of concern; the residual concentrations of chemical and biological agents used to remediate the contaminants; and any byproducts of concern produced by chemical and biological reactions induced by those agents. The following chapters of the Florida Administrative Code (F.A.C.) are cited: Chapter 62-550, F.A.C., for primary and secondary drinking 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; 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.
2. Pilot study: For petroleum cleanup, per Rule 62-770.700(2), F.A.C., it is required that a pilot study proposal be submitted for review, and that a pilot test be performed prior to the design of a full-scale treatment system. If conditions at a site do not warrant a pilot study, then a proposal explaining the rationale to forego it must be submitted for review.
3. Air emissions: In keeping with the approach taken by Rule 62-770.700(5), F.A.C., for in situ destruction of contaminants, a PulseOx® AOP system shall be equipped with a means of air emissions control unless the Remedial Action Plan design is based on an optimum injection rate of air, oxygen, ozone, and hydrogen peroxide that promotes in situ destruction of contaminants with minimal volatilization of hydrocarbons. This objective shall be confirmed by a pilot study or by emissions sampling during startup. A similar approach to air emissions control can be used when PulseOx® AOP is used for in situ destruction of chlorinated hydrocarbons.
4. Ozone, oxygen and air: Florida groundwater regulations do not set concentration limits on the concentration of ozone, oxygen and air, but the absence of specific groundwater criteria for a chemical does not necessarily mean it is of no environmental or toxicological concern. The Division of Waste Management, however, in the case of these gases, does not have any concerns in regard to their residual groundwater concentrations after PulseOx® AOP treatment. The residual groundwater concentration of ozone is not of concern because this gas is unstable and decomposes quickly (the half-life in water is less than 30 minutes). The residual concentration of oxygen is not of concern because its presence is generally considered to be beneficial, and because it is relatively benign from a toxicological standpoint. Air (a mixture of oxygen and nitrogen) is not of concern either, since it is generally considered benign, and the nitrogen component is inert.
5. 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., provided they are authorized under the provisions of a Remedial Action Plan or other enforceable mechanism, and 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. 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.

6. 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 underground injection control. Reviewers of those plans, upon issuance of an enforceable Remedial Action Plan Approval Order by the Department, must complete and submit the Enclosure 3 Underground Injection Control notification. This notification must be submitted by the reviewer, not the environmental consulting company that prepared the remediation plan.

For in situ sparging with relatively benign air and oxygen, it historically has not been imperative to provide Underground Injection Control notification. But when the more reactive ozone will be injected, the Division of Waste Management advises that notification should be provided. Since the standard notification memorandum -- like most injection documents and regulations -- anticipates that the injected fluid will be a liquid, it expresses the injection fluid volumes and concentrations in units that are more suited for liquids than gases. Therefore, for situations in which the notification will be for the injection of ozone and other gases, it will be acceptable to modify the memorandum by crossing out the liquid units and replacing them with those commonly used for gases; for example: volumes in cubic feet; flow rates in cubic feet per minute (cfm); and concentrations either as volume percent or parts per million by volume (ppmv). It is also acceptable to report the amount of ozone to be injected over the life of the project in pounds (on a pure basis) along with its concentration in the ozone/air-carrier gas mixture that is actually injected, and the injection flow rate of the mixture.

7. Temporary injection zone of discharge: Rule 62-520.310(8)(c), F.A.C., allows a temporary injection zone of discharge for the primary groundwater standards that apply to the contaminants of concern, the prime constituents of the reagents used to remediate a site's contaminants (the reagents being air, oxygen, ozone and hydrogen peroxide in the case of PulseOx[®] AOP) and for the secondary groundwater standards. For the injection of air and oxygen, a temporary injection zone of discharge is not needed because they do not violate minimum groundwater criteria. But for the injection of ozone and hydrogen peroxide, which are more reactive in the environment and of toxicological concern, permission for a temporary injection zone of discharge should be sought pursuant to rule 62-520.310(8)(c), F.A.C.

In order to obtain permission for a temporary zone of discharge for ozone via rule 62-520.310(8)(c), F.A.C., a site-specific Remedial Action Plan must: (a) indicate that ozone, a chemical species of concern with respect to the minimum groundwater criteria of Chapter 62-520, F.A.C., will be injected into the aquifer, and that a hydrogen peroxide solution of pH that is not within the 6.5-8.5 range allowed by the secondary drinking water standards will also be injected; (b) specify the size of the zone that is needed; (c) specify the amount of time that the zone will be needed; and (d) provide for the monitoring of pH in the groundwater. It is not necessary to monitor the concentration of ozone in the groundwater since it has a decomposition half-life of less than 30 minutes. As for indicating the size of the

temporary injection zone of discharge in item (b) above, it will usually suffice to indicate just a radius of influence when the treatment system at a contaminated site is no more than a single injection point. For a multiple point system, the zone of discharge can usually be expressed and illustrated as the total area of a cluster formed by all the injection points, located side-by-side with overlapping radii of influence.

8. 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 existing wells as PulseOx[®] AOP injection points for ozone and oxygen, air, and hydrogen peroxide, if their materials of construction are chemically compatible with the AOP oxidizers, and their physical design is similar to the nested Max-Ox[®] injection points developed by APTwater Incorporated, or their design is such that they can be integrated into the AOP treatment process. However, no “designated” monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used as a PulseOx[®] AOP treatment point. This will avoid a premature conclusion that the entire site meets cleanup goals. By making sure that designated tracking wells are not used for the introduction of AOP reagents, there will be more assurance that the reagents have permeated and treated the entire site, and that they did not remain localized to the immediate area surrounding each PulseOx[®] AOP treatment point.
9. Avoidance of migration: Per Rule 62-528.630(3), F.A.C., in situ, injection-type aquifer remediation projects shall be conducted in such a way that there is no undesirable migration of either the remediation agents used or the contaminants of concern.
10. 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.

SUPPLEMENTAL INFORMATION

The Division of Waste Management has selected some of the information provided by APTwater Incorporated to pass along below. It is not an exhaustive list. For more information about the PulseOx[®] AOP system, please refer to APTwater Incorporated publications.

1. PulseOx[®] AOP equipment and reagents: APTwater Incorporated offers cabinet-enclosed and trailer-enclosed PulseOx[®] AOP systems, some with separate hydrogen peroxide dosing skids in order to meet the needs of various size cleanup projects. The range of outputs for the current line of equipment is summarized below.

Atmospheric air: 0.5-18 standard cubic feet per minute (scfm), 120 pounds per square inch (psi).

Oxygen: 15-150 standard cubic feet per hour (scfh) at 90% O₂ produced by a pressure swing adsorption generator. The O₂ is used to generate ozone (O₃).

Ozone: 1-25 lbs/day, 20-45 psi, 10% O₃.

Hydrogen peroxide: 14-75 gallons per day, 5-35% H₂O₂.

2. Residuals: The byproducts of in situ chemical and biological oxidation of hydrocarbon contaminants by the PulseOx[®] AOP process are carbon dioxide and water. If chlorinated hydrocarbon contaminants are treated, then chloride will also be present as a byproduct.
3. Handling of chemicals: The PulseOx[®] AOP system produces ozone in a separate gas stream, and stores the hydrogen peroxide in a separate high density polyethylene (HDPE) container. The two chemicals are not mixed until they are injected into the subsurface.
4. Reactions: The mixing and use of ozone and hydrogen peroxide in the subsurface to chemically oxidize contaminants is an exothermic reaction, but APTwater Incorporated indicates that minimal heat generation has been observed for its process.
5. Materials of construction: As indicated by APTwater Incorporated, the materials of construction for key components of the PulseOx[®] AOP system are selected for compatibility with ozone and hydrogen peroxide. Components in contact with ozone are constructed of either stainless steel, Teflon tubing, ceramic or Viton.
6. Safety: All appropriate safety considerations shall be addressed in the design, construction and operation of a PulseOx[®] AOP system. The Division of Waste Management makes no attempt to provide a detailed, exhaustive list as part of this acceptance. The major items cited by APTwater Incorporated are summarized below.
 - Lower Explosive Level (LEL): The lower explosive level of ozone in oxygen at room temperature and atmospheric pressure is 10-11% by volume.
 - PulseOx[®] AOP systems are constructed by an Underwriters Laboratories (UL) 508 facility for industrial control equipment and use UL listed panels.

- Instruments, controls and interlocks for shutdown of the system in the event of an ozone leak inside the system; alarms for conditions of high or low pressures, flows and temperatures; fault alarms for the air compressor, and trailer cooling fans; and high and low voltage protection.
 - Level D personal protective clothing and equipment.
7. Radius of influence: Depending on site-specific lithology, the PulseOx[®] AOP injection radius of influence may range from approximately 10 feet in clay to approximately 25 feet in sand. Use overlapping radii of influence to ensure thorough coverage.
 8. Underground storage tanks (USTs): When using the AOP process at sites where underground storage tanks are present, it is recommended that the minimum horizontal distance between any UST and an ozone or hydrogen peroxide injection point be based on the site-specific radius of influence. The timer-controlled duration of injection can also be adjusted to prevent prolonged exposure of USTs to the ozone and hydrogen peroxide. The minimum vertical distance between the bottom of a UST and a deeper AOP injection point can be based on the site-specific vertical interval in which the AOP oxidizers are active, approximately 20 feet.
 9. Useful parameter measurements: In addition to the sampling and analysis for contaminants of concern during a Pulse-Ox cleanup project, the pH, temperature, conductivity, oxidation-reduction potential (ORP) and dissolved oxygen (DO) concentration of the groundwater are also measured.
 10. Oxidizer demand: In addition to the contaminants of concern to be remediated, natural-occurring organics, iron and manganese also compete for the AOP oxidizers. If the iron and manganese demand at a cleanup site accounts for more than 50% of the demand, then a different method of remediation should be considered.
 11. Limitations: APTwater Incorporated does not recommend the use of PulseOx[®] AOP for in situ remediation of free product that is greater than 6 inches thick.

UNDERGROUND INJECTION CONTROL NOTIFICATION

Florida Department of
Memorandum Environmental Protection

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, FL 32399-2400

FROM: _____ (Note 1.)

DATE: _____

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

Pursuant to paragraph 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 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: _____ (Note 2.)

Well contractor's address: _____

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Date: _____

Facility name: _____
FDEP facility no.: _____

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: _____ to _____ feet below land surface
Casing diameter, if applicable (inches): _____
Cased depth, if applicable: _____ to _____ feet below land surface
Casing material, if applicable: _____

PROJECT DESCRIPTION

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

- ☐ bioremediation,
☐ chemical oxidation, 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): _____

FLUID TO BE INJECTED

Composition of injected fluid:

(ingredient, wt. %) (Note 3.): _____

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 list of chemical species and parameters for which the approved Remedial Action Plan identifies zone size, duration and groundwater monitoring are as follows:

- ☐ 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, duration and groundwater monitoring:

- ☐ ZOD permission by variance because 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 concentration of those impurities in the fluid to be injected are in excess of their primary groundwater standards:

☐ 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 (feet): _____ Duration (time): _____

..... ◆◆◆

- ☐ 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, or ☐ the ZOD is described as follows:

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Date: _____

Facility name: _____
FDEP facility no.: _____

CLEANUP CRITERIA AND ENFORCEABLE APPROVAL ORDER

In situ injection-type aquifer remediation of the contaminants of concern at this site is intended to meet the groundwater cleanup target levels established for them in accordance with applicable and appropriate chapters of the Florida Administrative Code and cited in the approved Remedial Action Plan. 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 contaminants of concern 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 Chapters 62-520 and 62-777, 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.

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- Note 1. This notification memorandum is primarily for use by state technical reviewers, but remediation contractors may fill in all blanks except those labeled "FROM" and "DATE" on page 1, and the "approval date", and "telephone number" blanks in the last paragraph on page 4. Those blanks are filled only by the regulator. In the case that the memorandum form is partially completed by the remediation contractor, the FDEP technical reviewer must verify that the information provided by the contractor is accurate and complete. 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 the March 16, 2000, memorandum to arrange for Department headquarters' execution of an approval order, and then complete this memorandum.
- 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 the fluid to be injected is required by Chapter 62-528, F.A.C. Some remediation products and processes may have already submitted this information at the time of application for acceptance by the Innovative Technology Acceptance Program. For those situations, when completing the Fluid To Be Injected section of this memorandum, it will suffice to indicate: (1) an Innovative Technology Acceptance letter has been issued; (2) the date of the acceptance letter; (3) the acceptance letter contains the chemical analysis, or a voucher for the confidential disclosure of the injected fluid's chemical composition if it is a proprietary formulation; and (4) the fluid will be injected at concentrations that are less than or equal to those cited in the acceptance letter. For products and processes that do not hold an Innovative Technology Acceptance letter, but for which the site-specific Remedial Action Plan provides a complete description of the chemical composition of the fluid to be injected, it will be necessary to enter this information into the Fluid To Be Injected section of this memorandum.

