



Florida Department of Environmental Protection

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

Charlie Crist
Governor

Jeff Kottkamp
Lt. Governor

Michael W. Sole
Secretary

September 29, 2009

Andreas D. Jazdanian, Ph.D.
BioManagement Services, Inc.
506 East Summit Street
Crown Point, Indiana 46307

Re: **BIOX™ Process**

Dear Dr. Jazdanian:

The Division of Waste Management (Division) hereby updates its acceptance of the BIOX™ Process for remediation of petroleum, chlorinated hydrocarbons and other suitable contaminants in groundwater and soil, in situ and ex situ. This update supersedes the original February 14, 2005 acceptance with two major changes. First, the acceptance has been converted to a Division of Waste Management format for joint acceptance by the Bureau of Waste Cleanup and the Bureau of Petroleum Storage Systems. Second, a correction has been made to indicate that permission for a temporary injection zone of discharge (ZOD) for ammonia nitrogen is not obtained by way of variance but rather by way of Rule 62-522.300(2)(c), Florida Administrative Code (F.A.C.), in the same way that temporary ZOD permission is obtained for the other four BIOX™ parameters of regulatory concern: iron, sodium, sulfate and total dissolved solids. The ammonia nitrogen is also covered by this rule because it is a prime constituent of the BIOX™ reagents used to remediate site contaminants.

BIOX™ acts first as a chemical oxidation process, in the relatively neutral pH range of 7.0 to 8.5, with a minimal temperature rise of 5 °F or less, and then as a bioremediation process by providing nutrients and oxygen to the indigenous aerobic microorganisms already at the remediation site.

The chemical oxidation aspect of the process is a Fenton-type reaction that uses peroxide and ferrous sulfate to produce hydroxyls. The source of the peroxide can be from any or a mixture of the following: liquid hydrogen peroxide, or solid compounds such as calcium peroxide, magnesium peroxide, and sodium percarbonate. The hydroxyls produced by the Fenton reaction break down the contaminants at a remediation site to intermediate compounds that are more easily degraded by the site's indigenous microorganisms. The ultimate degradation products of petroleum hydrocarbon contaminants are carbon dioxide and water, and the ultimate degradation products of chlorinated hydrocarbon contaminants are carbon dioxide, water and chloride. Enclosure 1 shows the elemental composition of BIOX™; Enclosure 2 contains regulatory

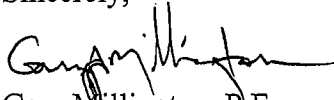
information; Enclosure 3 contains supplemental information; and Enclosure 4 is an Underground Injection Control Notification.

The Division of Waste Management does not provide endorsement of specific or brand name remediation products or processes. It does, however, recognize the need to determine their acceptability in the context of environmental regulations, safety and the protection of public health. For that reason, the Division issues an "acceptance" letter, not an approval. Such acceptance shall not be construed as a certification of performance, nor shall it be construed as approval for uses that are beyond its jurisdiction. Additionally, vendors, upon receipt of an acceptance, must market their product or process on its 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 the 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 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 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 site-specific design details must be provided in a 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@dep.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

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Enclosures: (1) BIOX TM Composition
(2) Regulatory Information
(3) Supplemental Information
(4) Underground Injection Control Notification

c: Tom Conrardy - FDEP/Tallahassee

History:

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9/29/09

BIOX™ COMPOSITION †

Iron, Fe	100 mg/L ▲
Sulfur, S	8,887 mg/L
Nitrogen, N	2,592 mg/L
Phosphorus, P	9,362 mg/L
Sodium, Na	6,417 mg/L
Calcium, Ca	35,297 mg/L
Magnesium, Mg	33,707 mg/L
Potassium, K	8,263 mg/L
Oxygen, O §	125,943 mg/L
Carbon, C	1,285 mg/L

† Maximum concentrations expected in BIOX fluids to be injected.

▲ mg/L (milligrams per liter)

§ Elemental oxygen, not the diatomic molecule.

REGULATORY INFORMATION

- a. Rules: The BIOX™ process shall comply with all applicable regulations. This includes meeting applicable groundwater cleanup target levels during the timeframe of a cleanup project for the contaminants of concern, the residual concentrations of BIOX™ reagents, and any byproducts of concern produced by chemical and biological reactions induced by those reagents.

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 62-522, 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.

- b. Pilot study: In the case of 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. For hazardous waste cleanups, the decision to conduct a pilot study should be made in accordance with applicable rules and regulations.
- c. 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.
- d. 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 4.
- e. Temporary injection zone of discharge (ZOD): Since the BIOX™ fluid to be injected does not meet the minimum groundwater criteria of Chapter 62-520, F.A.C., and the drinking water standards of Chapter 62-550, F.A.C., it will be necessary to obtain permission for a temporary injection zone of discharge by way of Rule 62-522.300(2)(c), F.A.C., prior to its use at a cleanup site. ZOD permission is required for the following five parameters:

ammonia nitrogen, iron, sodium, sulfate and total dissolved solids. Permission for all five can be obtained by way of the rule. None require permission by way of variance.

In order to obtain ZOD permission, each site-specific Remedial Action Plan proposing the use of BIOX™ must: (a) indicate that the concentrations of ammonia nitrogen, iron, sodium, sulfate, and total dissolved solids in the fluid to be injected will be in excess of their groundwater standards; (b) specify a temporary injection zone of discharge size; (c) specify the period of time for which the temporary zone of discharge will be needed; and (d) propose groundwater monitoring of the five ZOD parameters. In most cases, monitoring on a quarterly basis should be sufficient. The number of monitoring wells to be sampled will depend on the size of the area treated with the BIOX™, but for most applications, a minimum of two (2) wells should suffice: one in the center of the treatment area, the other near the downgradient edge.

The current groundwater standards for the BIOX™ zone of discharge parameters are ammonia nitrogen [2.8 milligrams per liter (mg/L)]; iron (0.3 mg/L); sodium (160 mg/L); sulfate (250 mg/L); and total dissolved solids (500 mg/L). Upon expiration of the time requested for the ZOD, each of these five parameters must meet their respective groundwater standard, or their natural-occurring background value at the site, whichever is less stringent.

The issuance of a site-specific Remedial Action Plan Approval Order for a Remedial Action Plan that meets the requirements of Rule 62-522.300(2)(c), F.A.C., constitutes the granting of permission for the temporary injection zone of discharge.

- f. Utilization of wells: If a remediation site happens to have an abundance of monitoring wells, then the Division of Waste Management has no objection to the use of some wells for the application of BIOX™ reagents. However, no "designated" monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used to apply BIOX™ reagents. 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.
- g. Additives: If, in the future, either BioManagement Services Incorporated or a user of the BIOX™ Process decides to augment it with other nutrients and/or chemicals, then the injection of such nutrients and other chemicals into an aquifer must also be in accordance with the underground injection control requirements of Chapter 62-528, F.A.C., which requires that substances injected meet the drinking water standards set forth Chapter 62-550, F.A.C., and the minimum groundwater criteria of Chapter 62-520, F.A.C. If the chemical composition of an additive is such that it cannot meet the injection requirements, then it will first be necessary to obtain permission for a temporary injection zone of discharge.
- h. Underground injection control inventory: Remedial Action Plans proposing injection-type in situ aquifer 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. Only reviewers within the Department, including its district offices, may approve in situ injection-type remediation plans in which the approval constitutes a Class V injection permit; local programs are not authorized to grant such approvals.

- i. Avoidance of migration: For injection-type in situ aquifer remediation projects, injection of BIOX™ 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, pursuant to Rule 62-528.630(3), F.A.C.
- j. Underground injection control operating permit: Although an operating permit is not required for aquifer remediation wells pursuant to Rule 62-528.640(1)(b), and 62-528.640(1)(c), F.A.C., since no movement of the petroleum contamination plume is expected to accompany the treatment process, the Department requests that the information items listed in Rule 62-528.640(1)(b), F.A.C., be considered and included in Remedial Action Plan proposals as a matter of good and thorough design practice. Briefly summarized, they are: quality of water in the aquifer; quality of the injected fluid; existing and potential uses of the affected aquifer; and well construction details. Additionally, each Remedial Action Plan should clearly indicate the total volume of the BIOX™ reagents that will be injected.
- k. 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 they can be removed from the injection well inventory-tracking list.
- l. Phosphate: This element, which is essential for life, occurs naturally in Florida's groundwater and is not a regulated groundwater contaminant. At a Panama City, Florida site, total phosphorus in the groundwater was measured at 800 to 1,100 micrograms per liter (ug/L). At a Volusia County site in Florida, it was measured at 1,200 ug/L, as PO₄. For comparison purposes, the European Community Guide level for phosphorus in drinking water is 400 ug/L, as P₂O₅. While phosphorus may not be a matter of great toxicological concern for in situ injection-type groundwater remediation projects, the Division of Waste Management would like to remind users of the BIOX™ Process that it could become an environmental concern if surface water is very close or present at a remediation site. In that case, if there could be any interaction between the groundwater being remediated and the nearby surface water body, then the state's surface water regulations should be reviewed first for information about phosphorus.
- m. Open-pit applications: While open-pit applications of BIOX™ reagents is not an injection-type application, and notification of the Underground Injection Control Section therefore not required, the user of BIOX™ must still be mindful of groundwater quality. For open-pit

applications, the Division of Waste Management suggests that groundwater in the application area be monitored for the same parameters that would have required monitoring had the application been an injection: ammonia nitrogen, iron, sodium, sulfate, and total dissolved solids.

SUPPLEMENTAL INFORMATION

- a. Dosage and application rate: It is recommended that the dosage and application details of the BIOX™ Process be determined on a site-specific basis, but for information and planning purposes, the following may be helpful:
- Delivery methods: Injection, open-pit application, or overspraying
 - Injection delivery: 1.25-inch diameter direct-push at 2-foot depth intervals
 - Injection rate and pressure: 3 to 5 gallons per minute; 30 to 200 pounds per sq. in.
 - Injection spacing: 3 to 7 ft for free product or low contaminant concentrations, 10 to 15 for low contaminant concentrations
 - Number of injections: One or more may be necessary, depending on conditions
- b. Oxidation reaction: In the first step of the BIOX™ treatment process, reagents partially oxidize contaminants in order to produce intermediates that are more readily biodegradable in the second step. Unlike a conventional Fenton reaction, the BIOX™ Process is not highly exothermic; it generates minimal heat, and does not need to occur at low pH.
- c. Degradation products: Carbon dioxide and water are the ultimate products of aerobic and most anaerobic biodegradations of petroleum hydrocarbons. The intermediate products may include simple acids, alcohols, and fatty acids. Aerobic processes use oxygen as an electron acceptor to produce the carbon dioxide and water.
- d. Indicator parameters and the frequency of their measurement: BioManagement Services Incorporated has provided information about indicator parameters that are important to the BIOX™ treatment process, and the frequency of their measurement. Pre-treatment baseline sampling no earlier than 30 days prior to BIOX™ application is recommended, and post-treatment sampling is recommended at 30, 60 and 90 days as follows:

Soil Analytical Parameters

Contaminants of Concern (COC)
 Chemical Oxygen Demand (COD)
 Biological Oxygen Demand (BOD)
 Total Organic Carbon (TOC)
 Total Heterotrophic Plate Count

Groundwater Analytical Parameters

COC
 COD
 BOD
 TOC
 Total Heterotrophic Plate Count
 Dissolved Oxygen (DO)
 Oxidation-Reduction Potential (ORP)

BioManagement Services Incorporated indicates how these parameters are useful as follows:

- Declining trends in the TOC of soil and concomitant increasing trends in the groundwater can be indicative of the extent of desorption caused by the BIOX™ process.

- Comparison of pre- to post-treatment COD and BOD of soil allows for assessment of the transformation of the soil organic matter, including contaminants, to more biodegradable species.
- Increasing trends in COD and BOD of groundwater are also indicative of desorption processes.
- Comparison of pre- to post-treatment COD and BOD of groundwater allows for the assessment of the biodegradability of the dissolved organic fraction.
- Comparison of trends in post-treatment BOD/COD ratios for soil to trends in post-treatment BOD/COD ratios for the groundwater allows for assessment of the effectiveness of enhanced biodegradation and bioavailability of contaminants over time.
- Analysis of trends in dissolved oxygen concentration, heterotrophic plate counts and biodegradability indicators (BOD, COD, BOD/COD ratio) can be used to derive limiting factors for natural and enhanced biodegradation of a cleanup site.

Memorandum**Florida Department of
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: _____

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: _____
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: _____ 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. %): _____

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 62-522.200(2)(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 62-522.200(2)(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 62-522.200(2)(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:

Cathy McCarty, P.G.
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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.