



Florida Department of Environmental Protection

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

Rick Scott
Governor

Jennifer Carroll
Lt. Governor

Herschel T. Vinyard Jr.
Secretary

February 28, 2012

Robyn T. Price
Advanced Oxidation Technology
4730 Wallace Lane
Fredericksburg, Virginia 22408

Re: **VTX Catalyst**

Dear Ms. Price:

The Division of Waste Management (Division) hereby accepts VTX Catalyst (VTX) for various oxidants, for the remediation of hydrocarbons, chlorinated hydrocarbons, and other suitable contaminants in soil and groundwater. VTX facilitates the generation of hydroxyl radicals that chemically oxidize contaminants. Oxidants with which VTX can be used include but are not limited to ozone, persulfate, permanganate, percarbonate, hydrogen peroxide, calcium peroxide, and magnesium peroxide. The specific ingredients of VTX have been declared proprietary. Therefore, Enclosure 1 contains a proprietary analysis voucher. Enclosure 2 contains regulatory information and Enclosure 3 contains supplemental information.

The Division 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, safety and the protection of public health. For that reason, the Division issues an "acceptance" letter, not an approval. In no way shall an acceptance be construed as a certification of performance. 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. If you have any questions, please contact us at the numbers below.

Sincerely,

X 

Rick Ruscito

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Gary Millington

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enc: (1) Proprietary Ingredients Voucher
(2) Regulatory Information
(3) Supplemental Information

c: Tom Conrardy, P.E. – FDEP/Tallahassee
Rob Cowdery, P.E. – FDEP/Tallahassee

History

PPL #438
INN_186 - 2/28/12

PROPRIETARY INGREDIENTS VOUCHER



Florida Department of Environmental Protection

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Robyn T. Price
Advanced Oxidation Technology
4730 Wallace Lane
Fredericksburg, Virginia 22408

Re: VTX Catalyst Proprietary Ingredients Voucher

Dear Ms. Price:

The Division of Waste Management (Division) hereby acknowledges receipt of a confidential disclosure regarding the proprietary ingredients of VTX Catalyst (VTX), for the remediation of hydrocarbons, chlorinated hydrocarbons, and other suitable contaminants in groundwater and soil, included in your January 11, 2011 Application for Innovative Technology Evaluation.

Having reviewed the confidential disclosure, the Division hereby vouches for its content, and provides advice in Enclosure 2 on how to comply with applicable regulations of the Florida Administrative Code (F.A.C.) when VTX is used for the cleanup of contamination in accordance with a Department-approved, site-specific Remedial Action Plan. The Department, in offering its advice, has been careful to mention only enough general information about the chemical species and parameters that must be monitored by users in order to comply with Underground Injection Control regulations when VTX is used, but not so much information as to compromise the identity of the specific proprietary ingredients.

For Underground Injection Control purposes, injection-type aquifer remediation plans must specify both the volume and the complete chemical composition of the fluid to be injected. But since the details of the ingredients and their proportions in VTX are proprietary, it will suffice to indicate just the volume of the VTX fluid to be injected, and then provide a note that a confidential disclosure of the proprietary details has already been submitted to the Department and accepted. Reference should be made to this voucher, and a copy of it should be included as an appendix to the plan. If you have any questions, please contact us at the numbers below.

Sincerely,

X *Rick Ruscito*

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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, and groundwater permitting and monitoring requirements; Chapter 62-528, F.A.C., for Underground Injection Control (UIC), 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 VTX and oxidants shall comply with all applicable regulations. This includes meeting applicable groundwater cleanup target levels for the contaminants of concern, the residual concentrations of reagent ingredients, and any byproducts of concern produced by chemical and biological reactions induced by those ingredients during the timeframe of the cleanup project. For the ingredients of concern that are present in excess of their groundwater standards, the timeframe is that which is permitted for a temporary injection zone of discharge (ZOD) as described below.

- b. UIC and ZOD permits: 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. And per Rule 62-520.310(8)(c), F.A.C., if a temporary ZOD is necessary, and permissible by way of that rule, then the issuance of the site-specific Remedial Action Plan Approval Order also constitutes the granting of permission for the temporary ZOD.
- c. UIC notification: Remedial Action Plans proposing 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 UIC 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 UIC inventory notification form to the UIC program in Tallahassee.
- d. General information about temporary ZODs: For groundwater remediation, the composition of an injected material must meet the primary and secondary drinking water standards set forth in Chapter 62-550, F.A.C., and the minimum groundwater criteria of Chapter 62-520, F.A.C., pursuant to UIC Rule 62-528.600(2)(d), F.A.C.

Aquifer remediation products that do not meet these requirements must seek relief from water quality criteria by one of two mechanisms. Permission for a temporary ZOD may be obtained via Rule 62-520.310(8)(c), F.A.C. If a ZOD cannot be obtained by rule, it will be necessary to seek a variance from Department rules in accordance with Section 120.542, Florida Statutes.

Rule 62-520.310(8)(c), F.A.C., allows for a temporary ZOD for closed-loop re-injection systems, for the prime constituents of the reagents used to remediate site contaminants, and for groundwater secondary standards. In order to obtain permission for a temporary ZOD by rule, a site-specific Remedial Action Plan must indicate: (a) the chemical ingredients of concern in the fluid to be injected that will be present in excess of groundwater standards; (b) the size of the ZOD that is needed; (c) the amount of time that the ZOD will be needed; and (d) a plan for monitoring the injected chemical ingredients of concern. The size of the temporary ZOD will usually be the injection well radius of influence when the treatment system is a single injection point. For a multiple point system, the ZOD can usually be expressed and illustrated as the total area of the cluster formed by all the injection points, located side-by-side with overlapping radii of influence.

- e. Specific ZOD information for VTX: Site-specific Remedial Action Plans shall indicate the volume of proprietary VTX to be injected, and seek permission for a temporary ZOD by way of Rule 62-520.310(8)(c), F.A.C., as described in paragraph d above, for ammoniacal nitrogen, chloride, iron, pH, sodium, and total dissolved solids. To ensure that the proportions and other specific information about the ingredients of VTX remain proprietary, and also as a prudent regulatory measure, the foregoing six (6) ZOD parameters apply to all concentrations of VTX in the fluid to be injected. VTX is normally injected at a ratio of 1 gallon VTX to between 1,000 and 10,000 gallons of injected water.
- f. ZOD monitoring advice for VTX: For the six (6) ZOD parameters listed in paragraph e above, quarterly monitoring of groundwater should suffice in most cases. The current groundwater standards for those chemical species and parameters are as follows: ammoniacal nitrogen, 2.8 milligrams per liter (mg/L); chloride, 250 mg/L; iron, 0.3 mg/L; pH, range 6.5-8.5; sodium, 160 mg/L; and total dissolved solids, 500 mg/L. Upon expiration of the time period granted for the ZOD, the concentration of each must meet its respective groundwater standard, or its natural-occurring background value at the specific cleanup site, whichever is less stringent.
- g. Oxidants and ZOD: Site-specific Remedial Action Plans shall indicate the type, volume, and concentration of oxidant to be injected. Advanced Oxidation Technology has indicated that hydrogen peroxide is likely to be the most often used oxidant, but others that may be used include and are not necessarily limited to ozone, persulfate, permanganate, percarbonate, calcium peroxide, and magnesium peroxide.

If the Division of Waste Management has already issued a separate acceptance to a supplier for a particular oxidant, then follow the ZOD advice for that oxidant when it is used in conjunction with VTX, otherwise seek ZOD permission by way of Rule 62-520.310(8)(c), F.A.C., or variance if necessary, as discussed in paragraph d above, or consult Table 1 for a conservatively inclusive list of parameters that require ZOD permission and groundwater monitoring for any concentration of the oxidant that is injected to the groundwater.

- h. Utilization of wells: If a remediation site happens to have an abundance of monitoring wells, then the Division has no objection to the use of some wells for the application of VTX and oxidant. However, no “designated” monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used to apply 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.
- i. Avoidance of migration: For injection-type, in-situ aquifer remediation projects, pursuant to Rule 62-528.630(3), F.A.C., injection of VTX and oxidant shall be performed in such a way, and at such a rate and volume, that no undesirable migration of either the ingredients of concern, site contaminants, or remediation byproducts results.
- j. 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.
- k. Open-pit application: Applications of catalyst and oxidant to an open pit in which the groundwater is exposed is not an injection and notification of the UIC Section is not required. However, the applied material must still meet the requirements of paragraph 62-520.310(8)(c), F.A.C., and groundwater in the application area should be monitored in the same manner as if the material had actually been injected.
- l. Additives: If a chemical additive or groundwater conditioner such as a pH adjuster is used with VTX in the future, then a site-specific Remedial Action Plan must include a complete description of its chemical composition and physical properties, the concentration of the additive in the fluid to be injected, the volume of the additive fluid to be injected, and seek permission for a temporary ZOD as described in paragraph d above if the fluid does not meet primary, secondary, and minimum groundwater standards.

Table 1. ZOD Parameters Usually Associated with Oxidants that May Be Used with VTX Catalyst (Note 1)									Florida Groundwater Standard
Oxidant	Ozone	Hydrogen Peroxide	Calcium Peroxide	Magnesium Peroxide	Sodium Percarbonate	Sodium Persulfate	Sodium Permanganate	Potassium Permanganate	
Parameter									
None	X								
pH		X	X	X	X	X	X	X	Range 6.5-8.5
Sodium					X	X	X		160 mg/L
Total Dissolved Solids			X	X	X	X	X	X	500 mg/L
Sulfate						X			250 mg/L
Iron						X	X		0.3 mg/L
Manganese						X	X	X	0.05 mg/L
Aluminum							X	X	0.2 mg/l
Color							X	X	15 color units
Heavy Metals						Note 2	Note 3	Note 3	See 62-550, F.A.C.
									mg/L=milligrams per liter
Note 1.	This conservatively inclusive list of ZOD parameters for regulatory purposes assumes high concentrations of oxidant <u>in the fluid to be injected</u> . As a result of that assumption, it will conservatively over specify the number of parameters for which ZOD permission must be sought and monitored in the receiving groundwater. If the Division of Waste Management has already issued a separate acceptance to a supplier for a particular oxidant that is being used, then follow the ZOD advice for that oxidant at the concentration being used in conjunction with VTX, otherwise use this table as default, or provide the necessary information in a site-specific Remedial Action Plan to obtain ZOD permission by way of Rule 62-520.310(8)(c), F.A.C., or obtain a variance if the oxidant does not qualify for ZOD permission by rule.								
Note 2.	At the time of this publication, only a single supplier of sodium persulfate has sought an evaluation of its assay by the Florida Department of Environmental Protection. For concentrations less than or equal to 20% by weight of that particular supplier's sodium persulfate in the <u>fluid to be injected</u> , ZOD permission can be obtained by way of Rule 62-520.310(8)(c), F.A.C., for pH, sodium, total dissolved solids, sulfate, iron, and manganese, but for concentrations greater than 20% a variance must be obtained for chromium. Since the Division of Waste Management does not restrict the source of any remediation reagent to a single supplier, other suppliers may be used, provided a site-specific Remedial Action Plan includes a guaranteed analysis, product specification or other analysis that includes heavy metals. The presence of heavy metals as impurities in a reagent does not preclude the use of that reagent at injection concentrations in which the heavy metals of concern are not in excess of their Florida groundwater standards, but if they are present in excess of those standards, then it will be necessary to obtain temporary injection ZOD permission for them by way of variance.								
Note 3.	At the time of this publication, two suppliers of permanganate have sought an evaluation of their assays by the Florida Department of Environmental Protection. For the sodium permanganate and potassium permanganate parameters bearing an "X" in the table, ZOD permission can be obtained by way of Rule 62-520.310(8)(c), F.A.C. But since neither source of these permanganates is completely free of heavy metal impurities (for which ZOD permission cannot be obtained by rule) variances have been sought for their heavy metal ZOD permission. Since the Division of Waste Management does not restrict the source of any remediation reagent to a single supplier, other suppliers may be used, provided a site-specific Remedial Action Plan includes a guaranteed analysis, product specification or other analysis that includes heavy metals. The presence of heavy metals as impurities in a reagent does not preclude the use of that reagent at injection concentrations in which the heavy metals of concern are not in excess of their Florida groundwater standards, but if they are present in excess of those standards, then it will be necessary to obtain temporary injection ZOD permission for them by way of variance.								

SUPPLEMENTAL INFORMATION

- a. Configuration: Since contact of VTX and oxidant with the contaminants being remediated is critical, the preferred methods of groundwater remediation are re-infiltration and re-injection. For soil that has been excavated, the preferred method of ensuring contact is a treatment process in which VTX and oxidant are sprayed onto the soil as it passes through a pug mill or a hammer mill.
- b. End products: Carbon dioxide and water are the ultimate products of chemical oxidation in the case of hydrocarbons. Chloride will also be present as an end product when chlorinated hydrocarbons are oxidized. If contaminants of concern other than these are treated by VTX and oxidant, then other end products may be present, depending on the chemical makeup of the contaminants. Groundwater monitoring of these other end product's residual concentrations may be necessary if they are chemical species of concern to the State of Florida as primary, secondary, or minimum criteria groundwater contaminants.
- c. Dosage: Bench-scale testing for dosage determination of both VTX and oxidant is an integral part of this remediation process, and it is site-specific. Measurement of chemical oxygen demand (COD) is used to determine the dosage, taking into account the demand by the contaminants of concern themselves, free radical scavengers and other organics that will compete for those radicals. VTX is normally injected at a ratio of 1 gallon of VTX to between 1,000 and 10,000 gallons of injected water.
- d. Pretreatment parameters: For groundwater treatment, Advanced Oxidation Technology indicates that the following parameters must be known in order to properly develop a treatment process for VTX and an oxidant: COD, pH, concentrations of the contaminants of concern, and the estimated flow rate of groundwater extraction for treatment and re-infiltration or re-injection. For soil, the parameters are soil type, moisture content, concentrations of the contaminants of concern, soil pH, and the quantity of soil to be treated.
- e. Operating parameters: For a VTX and oxidant groundwater treatment process, the key operating parameters (not to be confused with ZOD parameters) are as follows: COD, concentrations of the contaminants of concern, total iron, dissolved oxygen, and pH. For pH, the effective treatment range is 5.0-9.0, with the ideal being 6.5-8.0. The near neutral ideal for the VTX process is in contrast to the low pH that is needed for a classic Fenton's reaction.
- f. Safety reminders: Considerations to keep in mind include but are not necessarily limited to the items below.
 - Use of proper protective clothing.
 - Observe all safety precautions associated with oxidizers.

- Proper handling and storage of VTX and oxidant, and consideration for their compatibility with other chemicals that may be placed alongside them in storage facilities.
- Do not mix VTX with oxidant prior to application, because it is a reactive mixture.
- Use of containers, tanks and piping constructed from materials that are compatible with the chemicals being used.
- Proper disposal of unused or unwanted VTX and oxidant.

Additional safety items to consider for chemical oxidation processes at petroleum cleanup sites are listed in the Bureau of Petroleum Storage Systems' Remedial Action Plan Checklist. The chemical oxidation safety topics in that checklist are general in nature and applicable to hazardous waste cleanup projects as well.

- g. Limitations: Not for free product or completely insoluble contaminants such as heavy oil and grease.