Department of
Environmental Protection

Jeb Bush
Governor

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

David B. Struhs
Secretary

February 3, 2003

Mr. William B. Kerfoot, Ph.D, LSP
K-V Associates, Inc. (KVA)
766 Falmouth Road, Unit B
Mashpee, MA 02649

Re: **C-Sparger System® and Perozone ™**

Dear Mr. Kerfoot:

The Bureau of Petroleum Storage Systems (Bureau) hereby accepts KVA's patented in situ chemical oxidation process as an innovative technology for the remediation of petroleum and other suitable contaminants in groundwater and soil. This acceptance applies to both the stand-alone use of ozone gas (C-Sparger System®) and the use of ozone gas and Perozone ™ (hydroperoxide coating). As indicated by the information you submitted, the C-Sparger® system generates and forces a small mass of ozone through microporous diffusors or Spargepoints® into the surrounding formation at a concentration of 6% by volume in air. The micro bubbles (approximately 50 μm in diameter) produced by the Spargepoints® extract dissolved contaminants (stripping) while encapsulated ozone destroys it via oxidation reactions to CO_2 and H_2O (in the case of petroleum products). Use of Perozone™ coats the ozone bubbles with peroxide supplied by pharmaceutical grade hydrogen peroxide. Each C-Sparger ® system consisits of a master control unit and one or more well assemblies. Additional information is provided as enclosure 1.

The Bureau recognizes the KVA C-Sparge System® and the KVA Perozone ™ process as viable methods for the remediation of petroleum and other suitable types of contaminated sites in Florida. There are no objections to its use provided a Remedial Action Plan is submitted pursuant to Chapter 62-770, Florida Administrative Code (F.A.C.), and approved by the Department of environmental Protection (Department). Please note that when using the KVA Perozone™ process, the pH of the injected peroxide may have to be addressed in each site-specific Remedial Action Plan, pursuant to rule 62-522.300 (2) (c), F.A.C.

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

Those who prepare Remedial Action Plans are advised to include a copy of this letter in the appendix of plans they submit, and call attention to it in the text of their document. In this way, technical reviewers throughout the state will be informed that you have contacted the Department to inquire about the environmental acceptability of this process.

The Department reserves the right to revoke its acceptance of any product or process if its nature, performance, or any other aspect has been falsely represented. Additionally, Department

acceptance of a 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 ext. 29 if there are any questions.

Sincerely,

Dona J. Milinkovich, Ph.D.
Ecology and Environment, Inc.
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6

Rebecca Marx
FDEP Section Leader
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6

/djm

enclosures

c: R. Ruscito, P.E. - FDEP/Tallahassee
T. Conrardy, P.E. - FDEP/Tallahassee

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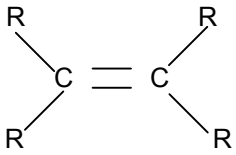
Enclosure 1: ADDITIONAL INFORMATION ABOUT KVA's IN SITU OZONE REMEDIATION PROCESSES - KVA C-Sparge System ® and KVA Perozone ™

K-V Associates, Inc. (KVA) provided most of the information below. The Bureau of Petroleum Storage Systems obtained additional information from the literature, equipment manufacturers, and the Florida Administrative Code.

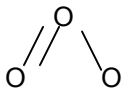
1. Properties: Ozone (O_3) is a molecule composed of three oxygen atoms, with a molecular weight of 48 grams per mole. It is an unstable molecule that degrades rapidly, with a half-life of approximately 2 minutes in air, and approximately 20 minutes when dissolved in water. As small bubbles in aqueous solution, the half-life can be extended to 48 hours in saturated soil solutions. The solubility of ozone in water at 20^{o} C is 600 milligrams per liter, which is approximately 12.5 times the solubility of oxygen. The oxidation potential of ozone is 2.07 volts, which makes it a relatively powerful oxidizer. By comparison, only the hydroxyl radical, with an oxidation potential of 2.8 volts, and fluorine, with 3.06 volts are more powerful. However, ozone, when used for in situ remediation, will also produce some hydroxyl radicals. This enables the process to take advantage of the potential of the hydroxl radical to the extent that this radical is produced. In addition, the ozone gas may be coated with dilute peroxide via the Perozone™ process.

2. Reaction mechanism: An example often used to illustrate the destruction of a hydrocarbon by ozone is that of ethene derivatives [R = 4, 3, 2, and 1. Chloride with perchloroethene (PCE), trichloroethene (TCE), and dichloroethene (DCE), and vinyl chloride (VC), respectively.]

   (a) Ethene (an alkene) to be destroyed is exposed to ozone.

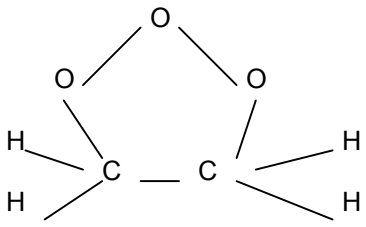


Ethene



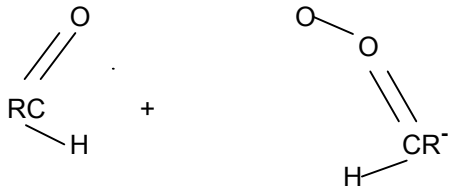
Ozone

   (b) The ozone inserts itself to form an ozonide bridge, which is unstable.



Ozonide
(molozonide or 1,2,3 trioxolane)

(c) The unstable molozonide bridge decomposes into carbonyloxides which are also unstable.



(d) The carbonyls decompose to form an unstable chlorinated aldehyde and chlorinated carboxylic acid, which in the presence of water decomposes to yield CO_2 and Cl^-

3. KVA equipment: The KVA C-Sparger® wallmount ozone system can be installed as a permanent full-scale remediation system at a site, or fabricated as a mobile unit. It produces 2 gm/hr ozone or 6 gm/hr with an oxygen supply. The mobile unit can be used at sites where brief or intermittent treatment is desired for localized areas of high contaminant concentrations or polishing of lower concentrations in order to bring a cleanup project to completion.

   The mobile KVA C-Sparger® unit contains an ozone generator, an electric generator, 10 ozone/air output ports to feed up to 10 Spargepoints®. A vapor control system of 20 cfm may or may not be required. Mobile units with the capacity to generate up to 100 gm/hr may also be used at a given site, and they are available if needed. Tubing can be used to quickly reconfigure the system.

4. Safety: The Department expects appropriate safety practices for the handling and use of equipment and ozone to be observed. KVA has indicated that its ozone systems are engineered to prevent fugitive emissions of ozone gas, including ozone leak detection, soil vapor extraction (SVE) when needed, and destruction of recovered ozone (if any) using ambient air before discharge of SVE off-gas to the atmosphere. An automated shutdown feature is included in the event that an ozone leak is detected. For the purpose of alerting workers at a KVA ozone remediation site to unhealthy levels of ozone, hand-held ozone detectors are used. The Material Safety Data Sheet provided by KVA indicates that the permissible exposure level (PEL) for ozone is 0.1 parts per million. Ozone concentrations near grade are rarely detected with KVA C-Sparge™ and Perozone ™ systems. Groundwater monitoring wells with screens below water table should be equipped with F480 thread tops and o-ring seals (Viton).

5. Utilization of wells: If a remediation site happens to have an abundance of monitoring wells, then the Department has no objection to the use of some wells for the injection of ozone. However, no “designated” monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used as an ozone injection well. This will avoid premature conclusions that the entire site meets cleanup goals. By making sure that designated tracking wells are not used for the introduction of ozone, there will be more assurance that dissolved ozone has permeated the entire site and that it did not remain localized to the area immediately surrounding each injection well. KVA has indicated that the wells used for its ozone process can be installed by either conventional or direct-push methods.

6. Design considerations: As is the case with most in situ remediation strategies, the spacing of injection wells will depend on site-specific conditions. Data for one of the case histories provided by KVA appears to indicate that a practical groundwater radius of influence is approximately 25 to 30 feet from the ozone injection point, although there is evidence that the ozone can travel further. The radius of influence is related to the depth of the unimpeded saturated zone above the Spargepoint®. Spargepoints® can also be nested so that both the saturated and unsaturated zones are treated.

7. Ozone usage: For five petroleum cleanup case histories provided by KVA, the ozone application rate was measured and compared to the hydrocarbon degradation rate. The cleanup times for these sites ranged from 2 to 8 months and involved ozone application rates ranging from 2.5 to 14 pounds per day, per site. Theoretically, the stoichiometric ratio for the mass of ozone to the mass of hydrocarbon degraded should be 3:1, but it was found that actual measured ratios were lower, ranging from 1:1 to 1.8 : 1.

   KVA has prepared a mass balance approach for field engineers (see ACS Preprint: Microbubble Ozone Sparging for Chlorinated Ethene Spill Remediation). After taking into account the difficulties of making such measurements in the field, KVA suggests that other factors may be at work. A possible reason for the observed ratio being lower than the theoretical ratio may be oxidation of the contaminants by hydroxyl radicals that can be formed as a result of introducing ozone to the site. Another reason may be that biodegradation is occurring as a result of increased available oxygen that accompanies the use of ozone. The Bureau agrees with KVA that further study is needed to sort out the effect of other factors, and also believes that it is not necessary to wait for a full explanation in order to take advantage of ozone's ability to clean up contaminated sites.

8. Case histories: For the same five petroleum cleanup projects discussed in paragraph 7 above, KVA indicates that hydrocarbon reductions of 75% to 99% were achieved. Methyl tertiary butyl ether (MTBE) reductions generally represent the upper end of this range. The Bureau of Petroleum Storage Systems considers such a reduction to be reasonably good progress for an operating time range of 2 to 8 months for the sites. BTEX and naphthalene reductions represent the higher end of the range.

9. Air sparge flow rates: To give the reader an idea of the range of flow rates that may be associated with ozone-assisted air sparging, the bureau would like to indicate that a pilot test by KVA involved air sparge rates of 2.5, 5, 10, and 20 standard cubic feet per minute. The first part of the test involved observation of air alone being injected at these rates. The later stages of the test involved the addition of ozone to the air stream.

10. Measurements: The decision regarding which parameters to measure should be made on a site-specific basis. To inform technical reviewers throughout the state, the Bureau of Petroleum Storage Systems would like to pass along information about measurements made by KVA during one of its pilot tests. For the groundwater, measurements of dissolved ozone, dissolved oxygen, pH, and oxidation-reduction potential were made at various radial distances from the point of injection. The dissolved ozone concentrations in the groundwater were as high as 2,000 micrograms per liter (ug/L) at a distance of 5 feet from the Spargepoint®, 500 ug/L at a distance of 10 feet, and 50 ug/L at a distance of 25 feet from the Spargepoint®. The Bureau adds that temperature of the groundwater could also be measured, although the temperature of the groundwater is not likely to vary by much at most sites, and such information may already be available historically in well sampling logs for a site.

    For the vadose zone, measurements of ozone, volatile organic compounds, oxygen, carbon dioxide, and vacuum (or pressure where appropriate) were made.

11. Effect of pH: Information provided by KVA indicates that the reaction kinetics for ozone become slower at lower pH values, and there is a corresponding increase in the half-life of the ozone.

12. Residual vadose zone concentrations: KVA observes that residual concentrations of ozone in the vadose zone are usually less than 1 part per million by volume when ozone concentrations of 6% by volume are being injected into the underlying groundwater. It is also indicated that the residual ozone in the vadose zone generally degrades entirely to oxygen by the time it reaches the surface. In occasional cases where the ozone may not degrade entirely before reaching the surface, a vapor extraction system can be installed.

13. Limitations: As indicated by KVA, the ozone process may be less effective in areas where the thickness of free product is in excess of several inches, and it may not be suitable at all for free product levels greater than one foot in thickness. Additionally, it may not be suitable for adsorbed-phase inorganic contaminants. Lastly, it is not advised that ozone be used for the remediation of trivalent chromium, since it may oxidize into the more toxic hexavalent form.

14. Materials compatibility: Low concentrations of ozone dissolved in water does not pose much of a problem to plastic piping and fittings. However, the Bureau of Petroleum Storage Systems would like to advise reviewers, designers and operators that care should be taken when selecting materials of construction for equipment and piping for the handling of gaseous ozone, including small internal components such as valve seats and seals. Since gaseous ozone can attack system materials and cause a failure, the Bureau advises consulting KVA regarding specific and anticipated ozone concentrations prior to selecting materials and constructing the system.

    The Bureau would like to pass along some information that it has obtained from one manufacturer of hoses and tubing. Currently, HDPE offers reasonable resistance up to 500 ppmv. It is indicated that polyvinylidene fluoride (PVDF) may offer the best resistance, and that Teflon may also be a good choice. Other reasonable choices could be butyl rubber (EPDM), fluorine rubber (Viton), and chlorine sulphonyl polyethylene (Hypalon). PVC, CPVC, and polypropylene may not be as suitable because the pigments and resins can leach, and polypropylene can also stress-crack, although PVC can sometimes be marginally acceptable. Materials susceptible to severe attack are Neoprene and Buna-N or Nitrile.

15. Regulations: The onus shall be on KVA and users of the KVA ozone process to observe all applicable and appropriate regulations in the Florida Administrative Code. Such regulations include but are not limited to Chapter 62-520, F.A.C., for minimum groundwater criteria. Even though the ultimate degradation products of oxidized hydrocarbons are carbon dioxide and water, and chloride in the case of chlorinated hydrocarbons, the onus shall be on KVA and users of the process to ensure that no intermediate degradation products of toxicological concern linger in the environment.

    Another regulation of particular interest when the KVA ozone process is used as part of a closed-loop re-injection type system may be rule 62-522.300(2)(c), F.A.C., which became effective August 27, 2001. A system of this type would be one in which contaminated groundwater is extracted from one end of a contamination plume, and then partially treated by KVA ozone before being re-injected at the other end. The rule allows a zone of discharge for primary and secondary groundwater standards for such a remediation system, provided a Department-approved remedial action plan addresses the duration and size of the zone of discharge, and groundwater monitoring. For example, a remediation plan for such a system should identify: (1) the partially-treated primary and secondary contaminants that will exceed their respective groundwater standards upon re-injection [e.g. benzene, perchloroethylene, chloride, etc.]; (2) the zone of discharge size [i.e. the radius of influence of each injection point]; (3) the duration of the zone of discharge [i.e. the length of time during which the system will re-inject partially treated water that does not meet groundwater standards for the re-injected contaminants]; and (4) appropriate groundwater monitoring to make sure that no unwanted

migration of the contaminants is occurring as a result of operating the closed-loop re-injection type remediation system.