

June 9, 1997

Mr. Kent Cooper
Asset Recovery Group, Inc.
9645 East Colonial Drive, Suite 114
Orlando, Florida 32817

Re: Oxy-Cat Remediation Process

Dear Mr. Cooper:

The Bureau of Petroleum Storage Systems thanks you and your associates for the March 14, 1997 briefing about the Asset Recovery Group's innovative "Oxy-Cat" remediation process, for in situ remediation of petroleum hydrocarbons in groundwater, pursuant to Chapter 62-770, Florida Administrative Code (F.A.C.).

The two-step process involves injection of a ferrous sulfate catalyst solution into a petroleum contaminated aquifer, followed by the injection of hydrogen peroxide. In a Fenton type reaction, the catalyst converts the hydrogen peroxide to hydroxyl radicals, which in turn oxidize petroleum hydrocarbons to carbon dioxide and water. The iron from the spent catalyst precipitates in the form of ferric oxide.

The Bureau recognizes Oxy-Cat as a viable technology for the remediation of petroleum contaminated sites in Florida. There are no objections to its use, provided: (a) the considerations of this letter are taken into account; (b) a Remedial Action Plan is approved by the Department for each site prior to the commencement of work; and (c) an appropriate administrative mechanism is identified, in cooperation with the Underground Injection Control (UIC) Section, to allow the temporary injection of a fluid whose iron concentration exceeds the maximum allowable 300 micrograms per liter (ug/L) secondary water quality standard or the naturally occurring background iron concentration. At this time, it appears that such a mechanism may be the granting of a variance from Rule 62-522.300(2)(a), Florida Administrative Code (F.A.C.), which does not allow a zone of discharge when fluids are directly injected into Class G-I or G-II groundwater. The variance may allow for the establishment of such a zone, where an elevated concentration of iron may be temporarily tolerated, until the cleanup is complete, at which time all

contaminants, including iron, meet applicable groundwater standards. Additionally, the following chapters of the Florida Administrative Code are cited as pertinent, as portions of them are applicable to the Oxy-Cat process: 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; and Chapter 62-528, F.A.C., for underground injection control, particularly Part V, for Class V, Group 4 aquifer remediation projects.

The onus shall be on the Asset Recovery Group to ensure that all applicable groundwater contaminant standards will be met at the time of project completion for any residuals associated with the principal and proprietary ingredients of the injected fluids, and any byproducts produced as a result of the chemical transformation of those ingredients or of the petroleum by the Oxy-Cat process.

While the Department of Environmental Protection does not provide endorsement of specific or 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. Vendor's must then market the products and processes on their own merits regarding performance, cost, and safety in comparison to competing alternatives in the marketplace. For the Oxy-Cat process, the major environmental and regulatory items of interest are below.

- a. Groundwater monitoring: Since the active phase of remediation for Oxy-Cat projects will last only a few days, the bulk of monitoring for the tracking of its effect will occur during the post remediation monitoring period. Like any other petroleum site remediation projects, Oxy-Cat projects shall include at least one (1) year of quarterly post remediation groundwater monitoring at a minimum of two (2) wells, one located in the area of maximum petroleum contamination, the other downgradient of the area of maximum petroleum contamination, pursuant to Section 62-770.750, F.A.C.

Additionally, for Oxy-Cat projects, an injected fluids monitoring schedule shall be implemented to track the fate of the spent ferrous sulfate catalyst. Hydrogen peroxide used in the process,

which quickly decomposes, does not have to be tracked.

The Department has determined that the monitoring schedule for injected fluids, pursuant to Rule 62-528.615(2), F.A.C., shall be a quarterly sampling of at least two (2) wells, one located in the central region of the Oxy-Cat injection points, the other downgradient. For a given remediation site, costs may be kept to a minimum by installing only two monitoring wells, whose locations are such that they may serve as both the petroleum remediation tracking wells, pursuant to Section 62-770.750, F.A.C., and the spent catalyst tracking wells, pursuant to Rule 62-528.615(2), F.A.C. The spent catalyst and Oxy-Cat parameters to be sampled for comparison to their standards (or a site's background concentrations) are as follows: iron [300 micrograms per liter (ug/L) maximum], sulfate (250,000 ug/L maximum), total dissolved solids (500,000 ug/L maximum), and pH (range 6.5 - 8.5). Rules cited from Chapter 62-528, F.A.C., are for the August 10, 1995 issue.

- b. Background samples. Prior to commencement of Oxy-Cat remediation projects, at least one (1) monitoring well located upgradient of the petroleum contamination plume, or at least one (1) non-upgradient monitoring well, safely located beyond the edge of the plume, shall be sampled and analyzed for the following background parameters: iron, sulfate, total dissolved solids, and pH. If more than one well is sampled, then the average value of each parameter can be used as the background value for the site.
- c. UIC Inventory: Oxy-Cat Remedial Action Plans 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 are 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 information to be transferred from the Bureau of Petroleum Storage Systems to the Underground Injection Control Section within the Department is enclosed.

d. Operation:

1. Avoidance of migration: Injection of Oxy-Cat catalyst and hydrogen peroxide shall be performed in such a way, and at such a rate and volume, that no undesirable migration of either Oxy-Cat components or petroleum contaminants in the aquifer results, pursuant to Rule 62-528.630(3), F.A.C.
2. 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 Oxy-Cat 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 Oxy-Cat 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 amount of catalyst and hydrogen peroxide that will be injected, with a breakdown showing at least the number of pounds of ferrous sulfate (on a pure basis) and the number of pounds of hydrogen peroxide (on a pure basis).

- e. Abandonment: Upon issuance of a petroleum Site Rehabilitation Completion Order, or a declaration of "No Further Action", Oxy-Cat injection wells shall be abandoned pursuant to Section 62-528.645, F.A.C. The Underground Injection Control Section of the Department shall be notified so that the injection wells can be removed from the inventory tracking list.

Preparers of Remedial Action Plans for state-funded cleanups may wish 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 and its contracted local reviewing programs will be informed that you have contacted the Department of Environmental Protection to inquire about the environmental

acceptability of this process. To aid those reviewers, the Bureau of Petroleum Storage Systems lists some items below.

- a. A theoretical minimum of 6.5 to 6.7 pounds of hydrogen peroxide (100%) is needed for complete degradation of each pound of BTEX to carbon dioxide and water. The exact amount within that range will depend on the ratio of benzene, ethylbenzene, toluene, and xylene. The actual amount required for a remediation site's specific conditions may be higher, depending on how efficiently the hydroxyl radicals formed by the decomposition of hydrogen peroxide can be contacted with petroleum contaminants in the aquifer, and whether other non-BTEX petroleum hydrocarbons, which will compete for hydroxyls, are also present. In each Oxy-Cat Remedial Action Plan submitted, the Asset Recovery Group should indicate the mass of the petroleum contaminants present at the site, and the prescribed amount of hydrogen peroxide that will be needed to remediate that given mass.
- b. At sites where the concentration of total organic carbon (TOC) is elevated, the amount of hydrogen peroxide needed may increase accordingly, as TOC will compete with the BTEXs for hydroxyl radicals.
- c. Iron is a secondary drinking water contaminant. It may be present in the groundwater at concentrations in excess of the 300 micrograms per liter (ug/L) secondary standard (or in excess of applicable background levels) after the Oxy-Cat treatment. If iron concentrations do not satisfactorily decrease immediately after the initial Oxy-Cat treatment, or during the one year post remediation monitoring period, then the situation may be remedied by subsequent injections of hydrogen peroxide, which can precipitate some of the excess iron out of the groundwater. Another way to avoid excessive amounts of post treatment iron in the groundwater may be to reduce the concentration of ferrous sulfate in the injected Oxy-Cat catalyst.
- d. The Oxy-Cat process is not intended for soil remediation above water table. Remediation of contaminated vadose should be addressed separately by other methods such as vapor extraction, excavation, bioremediation, etc.

- e. For an Oxy-Cat test site, the radius of influence of each Oxy-Cat injection point was determined to be 8 to 10 feet. This could serve as a rule of thumb for future projects, unless there are geological or other indications that a pilot test should be performed to determine a site specific radius. For the test site, thirty-five injection points were used. Oxy-Cat catalyst, as a 1.4% solution by weight, was first injected into the points at 3 gallons per minute (gpm) and allowed to naturally disperse throughout the aquifer for approximately 24 hours. Hydrogen peroxide, as a 25% solution by weight, was then introduced to those same injection points at 1.3 gpm to begin the reaction. In a matter of days, petroleum contaminant concentrations were reduced by approximately 80 to 90 percent. After approximately one week, contaminant reductions as high as 98 to 100 percent were realized at some injection points. Over a period of approximately 5 hours during remediation, the pH of the aquifer dropped from 6 to 3, but by the 48th hour it had returned to its original value. The temperature of the aquifer rose from approximately 25 to 55 degrees Celsius after approximately 5 hours of treatment but returned to its original temperature by the 48th hour.

- f. Although there are no regulations pertaining to the amount of precipitated iron (spent catalyst in the form of solid ferric oxide, commonly known as rust) which may be deposited as immobile, nonsuspended particles in an aquifer, each Remedial Action Plan prescribing the Oxy-Cat process should evaluate the potential impact of this substance on porosity, and whether or not it could hamper the cleanup of future petroleum discharges into the same aquifer at the same site. Based on the catalyst quantity used at the Bradenton test site, it appears that average aquifer porosity was reduced by less than one percent, which is insignificant. It is not known whether the effect is more intense in the immediate area of catalyst injection points. Since the amount of petroleum contamination to be remediated will vary from site to site, and therefore the corresponding amount of catalyst and hydrogen peroxide required for remediation, the effect of ferric oxide on porosity may vary, and should therefore be evaluated from site to site.

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- g. Oxy-Cat catalyst and hydrogen peroxide should not be injected into monitoring wells which are intended to track the progress of remediation at a site, since a premature and false indication of complete remediation may result when those wells are sampled. However, if there is an abundance of monitoring wells at a site, and not all of them are needed for tracking the progress of remediation, then some of the spare monitoring wells can be used as injection points.
- h. No air emissions monitoring is necessary for the Oxy-Cat process since it emits only carbon dioxide and water vapor.
- i. Reviewers of Oxy-Cat Remedial Action Plans, regardless of whether in Tallahassee or district offices, must fill in the blanks on the enclosed memorandum whose subject is "Proposed Injection Well(s) for In Situ Aquifer Remediation at a Petroleum Remedial Action Site". The completed form must be submitted to the Underground Injection Control Section at 2600 Blair Stone Road, Tallahassee, Florida 32399-2400.

The Department reserves the right to revoke its acceptance of a product or process if the nature or composition of either or any of its principal and proprietary ingredients, or the performance of the process, 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 Remedial Action Plans prescribing the product or process. You may contact me at 904/487-3299 if there are any questions.

Sincerely,

Rick Ruscito, P.E.
Bureau of Petroleum Storage Systems

RR/rr

Mr. Kent Cooper
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cc: T. Conrardy - FDEP/Tallahassee
W. Evans - FDEP/Tallahassee

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**Florida Department of
Memorandum**

Environmental Protection

TO: Richard Deuerling
Division of Water Facilities
Bureau of Resource Protection
Underground Injection Control Section

FROM: _____ (Local programs
_____ see Note 1.)

DATE: _____

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

This is to notify you of proposed injection well(s) construction for the in situ remediation of ground-water at a petroleum contaminated site. The following is a description of the site location.

Name: _____
Address: _____
City/County: _____
Latitude/Longitude: _____
FDEP Facility Number: _____

The design of the injection-type aquifer remediation system consists of the following:

Areal extent of contamination (square feet): _____
Number of injection wells: _____
Composition of injected fluid (See note 2)
(ingredient, wt. %): _____

Injection volume per well (gallons): _____
Single or multiple injection events: _____
Injection volume total (all wells, all events): _____

Note 1. Local programs are not authorized to approve underground injections into aquifers. Reason: The Department, per agreement with EPA, has been delegated this authority but is not allowed to delegate it any further. Local programs should arrange with either Department district offices or Department headquarters to approve such injections after reviewing the Remedial Action Plan.

Note 2. Complete chemical analysis of injected fluid is required by Chapter 62-528, Florida Administrative Code (no exceptions). Proprietary formulations shall make confidential disclosure. Injected fluids must meet drinking water standards of Chapter 62-550, F.A.C., unless an exemption or variance has been granted.

Richard Deuerling
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Date:_____

A site map showing the areal extent of the groundwater contamination plume and the location and spacing of injection wells is attached.

Excerpts from the remedial action plan which describe the site lithology are attached. The following is a summary description of the affected aquifer:

Name of aquifer:_____
Depth to groundwater (feet):_____
Aquifer thickness (feet):_____

A schematic of the injection well(s) is attached. The following is a summary:

Depth of well (feet):_____
Screened interval:_____ to _____ feet below surface
Well casing diameter (inches):_____
Bore hole diameter:_____
If direct-push type well(s), describe
diameter (inches):_____ and depth (feet):_____

The in situ injection-type aquifer remediation plan for this petroleum contaminated site is a design intended to meet the groundwater petroleum cleanup criteria set forth in Chapter 62-770, 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 byproducts or intermediates produced as a result of the chemical or biochemical transformation of those ingredients or the contaminating petroleum 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 Chapter 62-520, F.A.C.

The remedial action plan estimates that the 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 system was approved on _____ by a Remedial Action Plan Approval Order (or other enforceable document) signed by the Director of the Division of Waste Management (copy attached). The remediation system installation is expected to commence within 60 days. Please call me at _____ if you require any additional information.