Department of
Environmental Protection

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

Jeb Bush
Governor

Colleen M. Castille
Secretary

May 12, 2005

Dr. Kirit D. Chapatwala
Chapatwala Consultancy
236 Ramsey Drive
Selma, Alabama 36701

Re: **BIOBEAD**

Dear Dr. Chapatwala:

The Florida Department of Environmental Protection (Department) hereby accepts BIOBEAD as a groundwater remediation product and method for the biodegradation of hazardous wastes such as acetonitrile and other organic cyanides, amides, polychlorinated biphenyls (PCBs), and other suitable contaminants. As the Chapatwala Consultancy has indicated, BIOBEAD is bacteria and sodium alginate, encapsulated and immobilized in beads of 1 to 2 millimeters in diameter, and hardened in a cold calcium chloride solution. Also, as the Chapatwala Consultancy has indicated, BIOBEAD is for the in situ remediation of groundwater, but we believe that the air-uplift bioreactor (a fluidized-bed) lends itself to ex situ applications as well.

As of this date, we are only aware of bench-scale air-uplift bioreactor tests, and not any field tests or full-scale applications of BIOBEAD. Nevertheless, we would like to convey an opinion that laboratory research papers presented for our review appear technically sound, and that the observed amount of contaminant degradation in relatively short periods of time is worthy of attention.

During in situ aquifer remediation projects involving BIOBEAD, including recirculating/re-injection-type projects, groundwater should be monitored for pH and sodium, and when the contaminants being remediated contain nitrogen atoms, such as the nitriles and the amides for example, it should be monitored for ammonia nitrogen as well. For ex situ treatment of groundwater, should it be employed in the future, with the return of the treated effluent to the aquifer by either infiltration or injection, or discarded to the ground surface, we believe that the bioreactor should be sampled and analyzed for these same parameters and the contaminants of concern prior to discharge, to ensure that the effluent meets the criteria of Chapter 62-777, F.A.C.

The Department recognizes the potential of BIOBEAD to be a viable product and method for the remediation of suitable hazardous waste contaminants. 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; and (c) the requirements of Rule 62-522.300(2)(c), Florida Administrative Code (F.A.C.) are observed for pH and sodium, and when applicable, ammonia nitrogen. For BIOBEAD, the major regulatory considerations are set forth in Enclosure 1.

While the Florida 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 and safety. Vendors must then market the products and processes on their own merits regarding performance, cost and safety against competing alternatives in the marketplace. In no way, however, shall this regulatory letter of acceptance be construed as certification of product performance. Additionally, the Department emphasizes a distinction between its regulatory "acceptance" and an approval. Products and processes are accepted but they are not approved.

Those who prepare Remedial Action Plans may 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 acceptability of BIOBEAD. To aid those reviewers, the Department provides supplemental information as Enclosure 2.

Even though it may be convenient to have an acceptance letter, for inclusion in the appendix of a site-specific Remedial Action Plan as suggested above, the Department would like to emphasize that such a letter is <u>not</u> a requirement. The plan, however, must contain sufficient information about the product or process to show that it meets all applicable and appropriate rules and regulations.

The Department reserves the right to revoke its acceptance of a product or process if it 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 proposing the product or process. You may contact me at (850) 877-1133, extension 29 if there are any questions.

Sincerely,

Rick Ruscito, P.E.
Ecology and Environment, Inc.
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6

Rebecca S. Lockenbach
FDEP Section Leader
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6

enc: (1) Regulatory Information
(2) Supplemental Information
(3) Underground Injection Control Memorandum

c: T. Conrardy - FDEP/Tallahassee

ENCLOSURE 1

REGULATORY INFORMATION

a. Groundwater regulations and cleanup standards: The onus shall be on users of BIOBEAD to ensure that all applicable groundwater standards will be met at the time of project completion, for the contaminants of concern, any residuals associated with the ingredients of BIOBEAD, and any byproducts produced as a result of chemical or biochemical reactions involving those ingredients. The following chapters of the Florida Administrative Code are cited: 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; and Chapter 62-777, F.A.C., for cleanup criteria.

   A noteworthy aspect of the minimum criteria set forth in Chapter 62-520, F.A.C., is that it requires groundwater to be free from substances that are harmful to plants, animals, and organisms, and free from substances that are carcinogenic, mutagenic, teratogenic or toxic to human beings. In effect, these "free from" requirements form a catchall. They close what would otherwise be a loophole in the regulations by preventing injection of a potentially harmful product in the event that any of its ingredients is not regulated as a specific primary or secondary drinking water contaminant.

b. Injection well permit: The issuance of a site-specific Remedial Action Plan Approval Order by either the Bureau of Waste Cleanup, the Bureau of Petroleum Storage Systems, or other bureau or district office of the Florida Department of Environmental Protection, for remediation via direct injection of remediation products into an aquifer, or the insertion of a BIOBEAD reactor into a well for in situ treatment, or the re-injection of partially treated groundwater in a recirculating/re-injection-type arrangement constitutes the granting of a Class V injection well permit. [62-528.630(2)(c) and 62-528.640(1)(c), F.A.C.]

c. Specific groundwater standards that apply to BIOBEAD: The Department, having considered the chemical constituents and physical properties of BIOBEAD, has determined that Rule 62-522.300(2)(c), F.A.C., should apply to pH and sodium, and ammonia nitrogen when nitrogen-containing contaminants are being remediated. pH is of interest because it tends to rise as the bioreactor operates, and ammonia nitrogen could be of interest if enough of it is generated as a degradation product.

   In order to comply with Rule 62-522.300(2)(c), F.A.C., a Department-approved site-specific remediation plan proposing BIOBEAD must: (a) identify pH and sodium (and ammonia nitrogen when applicable) as the parameters whose groundwater standards could be exceeded; (b) indicate the size and duration of the temporary zone of discharge needed; and (c) propose groundwater monitoring for each of these parameters.

The Department would like to encourage those who prepare Remedial Action Plans to use a non-excessive duration time and zone size when complying with Rule 62-522.300(2)(c), F.A.C. Historically, in Florida, most temporary zones of discharge for injection-type aquifer remediation have been for a period of approximately one (1) year and a zone size in the range of 10 to 50 feet radially from each injection point.

d. 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 application of BIOBEAD, either as insertion points for small-diameter air-lift reactors or as re-injection points for a continuous, recirculating/re-injection-type system that only partially treats groundwater in the ex situ portion of the loop. However, no "designated" monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used for BIOBEAD. 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.

e. Groundwater monitoring:

1. Active remediation monitoring for contaminants of concern: Active remediation groundwater monitoring should be conducted in accordance with the provisions of an approved site-specific Remedial Action Plan for the contaminants of concern.

2. Post remediation monitoring for contaminants of concern: During the period of post active remediation, groundwater monitoring for contaminants of concern shall be conducted in accordance with the provisions of an approved site-specific Remedial Action Plan.

3. Monitoring of BIOBEAD parameters for underground injection control purposes: Pursuant to Rule 62-522.300(2)(c), F.A.C., the monitoring of pH and sodium must be addressed in a site-specific, Department-approved Remedial Action Plan that proposes the use of BIOBEAD. For sites where nitrogen-containing contaminants will be remediated, the ammonia degradation product should be monitored as well.

f. 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 3.

g. Avoidance of migration: For injection-type, in situ aquifer remediation projects, BIOBEAD shall be used in such a way that no undesirable migration of either the BIOBEAD

ingredients or the contaminants of concern in the aquifer results, pursuant to Rule 62-528.630(3), F.A.C.

h. Abandonment of wells: Upon issuance of a Site Rehabilitation Completion Order, or declaration of "No Further Action", 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 (or BIOBEAD application wells) can be removed from the inventory-tracking list.

i. Open pit applications: Should the application of BIOBEAD to an open excavation pit prior to backfilling be feasible, then this would not be considered an injection. In such a case, it would not be necessary to notify the Underground Injection Control Section by using the memorandum in Enclosure 3. However, this does not release the user from the responsibility of making sure that no long-term negative groundwater impacts occur as a result of the substances added to the pit. In the case of BIOBEAD, it would be prudent to monitor the groundwater for pH and sodium (and ammonia nitrogen if applicable) prior to application, and at regular time intervals afterward, in order to demonstrate that each of these parameters returns to its respective groundwater standard, or its natural-occurring background level, whichever is less stringent. For pH, the groundwater standard is range 6.5 to 8.5; for sodium the standard is 106 milligrams per liter, maximum; and for ammonia nitrogen, the standard is 2.8 milligrams per liter, maximum.

ENCLOSURE 2

SUPPLEMENTAL INFORMATION

a. Department of Environmental Protection reviewers of injection-type, in situ aquifer remediation plans, regardless of whether in Tallahassee or district offices, must fill in the blanks on the Enclosure 3 memorandum, whose subject is "Proposed Injection Well(s) for In Situ Aquifer Remediation at a Contaminated Site". The completed form must be submitted to the Underground Injection Control Section at 2600 Blair Stone Road, Tallahassee, Florida 32399-2400.

b. Contaminant degradation products: The type of contaminants that are degraded by BIOBEAD will determine the type of degradation end products that are formed. The ultimate degradation products of pure hydrocarbons are carbon dioxide and water. The intermediate degradation products of organic cyanides, such as the nitriles and amides, include ammonia and acetic acid, and the intermediate degradation products of PCBs include benzoic acid (a carboxylic acid). In the case of the organic cyanides, the production of ammonia (NH_3) is evidence that the carbon-nitrogen bond of the cyanide group has been cleaved. These intermediates further degrade in the environment. Also, when chlorinated hydrocarbons are degraded, the products will include chloride.

c. Contaminant degradation rates: Having reviewed several BIOBEAD research papers that were provided on the degradation of nitrile, amide and PCB, the Department notes that the amount of contaminant degradation ranged from 51 to 82 percent in time periods of 48 to 168 hours. The amount of degradation was determined by measuring and taking the sum of the amount of carbon dioxide generated and the amount of biomass produced.

d. Ingredients of BIOBEAD:

   1. Alginate: This substance is a salt or an ester of alginic acid $(C_6H_8O_6)_n$, which in its salt form is found in the cell walls of marine brown algae (commonly known as giant brown seaweed or giant kelp). Sodium alginate is used in ice cream, to give it texture and to prevent the growth of ice crystals, and as a suspension agent in soft drinks.

   2. Microorganisms: BIOBEADS can encapsulate different types of bacteria that are isolated from soil and groundwater at contaminated industrial sites. Those that were isolated during BIOBEAD research included *Pseudomonas putida* and *Pseudomonas aeruginosa*. Mixed cultures have also been obtained. Even though the bacteria are encapsulated in a bead, they are still able to produce the enzymes that are necessary to degrade contaminants.

e. Air-uplift bioreactor: The air-uplift bioreactor is essentially a fluidized-bed reactor, an equipment item used in the chemical process industry. Regardless of whether the fluidized-

bed is bench-scale or full-scale, the concept is the same. A simple BIOBEAD fluidized-bed reactor can be visualized as vessel partially filled with BIOBEADS and contaminated groundwater. The vessel has an inlet at the bottom, and an outlet at the top. When air is forced into the bottom of the vessel it causes the beads and the water to "fluff up" as it rises to the outlet. The purpose of the air is two-fold in the case of BIOBEAD: it serves to "fluff up" and intimately contact the BIOBEADS and groundwater; and it serves as a source of oxygen for biodegradation. Like any other fluidized-bed reactor, the flow rate of the air must be optimized; too little airflow will not fluidize and suspend the bed, and too much air will blow the contents out the top.

In looking ahead to full-scale applications of BIOBEAD, the Department believes it may be feasible to construct BIOBEAD reactors that operate in a flow-through manner, rather than batch mode. Reactors of different sizes could be produced. The smallest may be miniature flow-through units that can be inserted into groundwater wells. The largest may be set up above ground, and a treatment system configured such that the flow-through reactor is part of a recirculating/re-injection-type system that includes the subsurface as part of the loop. In this way, bioremediation may be able to take place above and below ground at the same time, thereby shortening the time required for cleanup.

The above are just a few ideas that the Department would like to present for the sake of stimulating thought. No mention of how the Chapatwala Consultancy plans to implement BIOBEAD was made in the information that was submitted to the Department for evaluation as an Innovative Technology, and those plans may differ from the ideas presented here. There is little doubt, though, on the part of the Department that the BIOBEAD bench test arrangement can be transformed to a full-scale remediation system.

f. Effect of air rate: During tests, the rate of degradation increased as the amount of air was increased.

g. Operating conditions: The Department will not attempt to describe operating conditions of a BIOBEAD reactor in terms of a full-scale system, nor will it attempt to describe what may be optimum operating conditions. It will, however, in Figure 1, present a compilation of the bench-scale parameters that were discussed in the BIOBEAD research papers. The scale-up and optimization is more appropriately left to others.

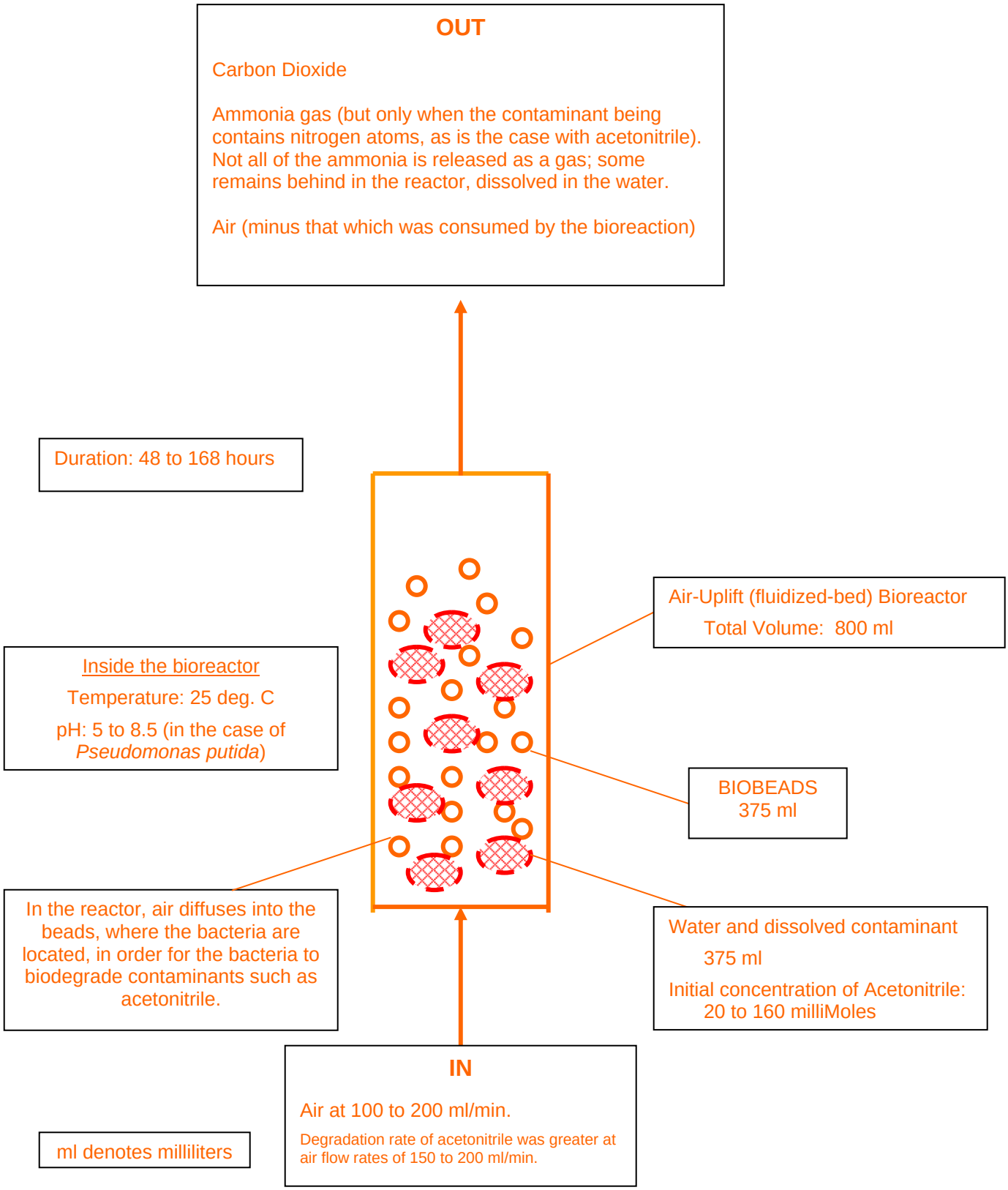

Figure 1. Compilation of operating conditions for the bench-scale tests.

Florida Department of

Memorandum **Environmental Protection**

TO: Richard Deuerling, Mail Station 3530
Division of Water Facilities
Underground Injection Control Section
Florida Department of Environmental Protection
2600 Blair Stone Road, Tallahassee, FL 32399-2400

FROM: _____
_____
_____

DATE: _____

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

Pursuant to Rule 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.

Site name: _____
Site address: _____
City/County: _____
Latitude/Longitude: _____
FDEP Facility Number: _____

Site owner's name: _____
Site owner's address: _____
_____
_____
_____

Well contractor's name: _____ (Note 1.)
Well contractor's address: _____
_____
_____
_____

Brief description of the in situ injection-type aquifer remediation project:

_____
_____

Summary of major design considerations and features of the project:

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

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

Site name: _____
FDEP facility no.: _____

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

The following is a summary description of the affected aquifer:

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

The injection well(s) features are summarized below, and/or a schematic of the injection well(s) is attached.

Direct-push or Conventional *(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 surface
Grouted interval: _____ to _____ feet below surface
Casing diameter, if applicable (inches): _____
Cased depth, if applic.: _____ to _____ feet below surface
Casing material, if applic.: _____

The in situ injection-type aquifer remediation plan for this contaminated site is intended to meet the groundwater cleanup criteria set forth in Chapter 62-777, 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 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 Chapter 62-520, 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.

Note 1. 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 2. Complete chemical analysis of injected fluid is required by Chapter 62-528, Florida Administrative Code. Proprietary formulations shall make confidential disclosure. Injected fluids must meet drinking water standards of Chapter 62-550, F.A.C., unless an injection zone of discharge has been permitted by Rule 62-522.300(2)(c), F.A.C., or by variance.