Department of
Environmental Protection

Jeb Bush
Governor

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

David B. Struhs
Secretary

July 22, 2002

Mr. Larry Presley
Clearwater Industries
7028 Pelican Island Drive
Tampa, Florida 33634

Re: *R 2000* Solar Photocatalytic Oxidation System

Dear Mr. Presley:

The Bureau of Petroleum Storage Systems hereby accepts the *R 2000* Solar Photocatalytic Oxidation System as an innovative technology for the treatment of recovered groundwater from petroleum contaminated sites. Although the concerns of this bureau are chiefly associated with petroleum remediation, we note your indication that the system also destroys other environmental contaminants such as herbicides, pesticides, chemical fertilizer runoff, and leachate from municipal and industrial landfills. This letter supersedes the original July 23, 1998 acceptance letter issued for the *R 2000* system, the only change being that of the inside address, which is now Clearwater Industries and no longer Resolution Financial Corporation.

R 2000 is an aboveground batch treatment process. The first step in that process is to pump a specific volume of groundwater (500 gallons for example) into a tank, where it is mixed with powdered titanium dioxide (a catalyst) to form a slurry of approximately 0.1 percent titanium dioxide by weight. In the second step, a pump recirculates the slurry between the tank and a bank of solar photoreactor panels (configured in parallel) for a predetermined period of treatment time. The treated slurry batch is then transferred to a settling tank, where gravity causes the titanium dioxide catalyst to settle, before the supernate is removed and discharged as clean effluent. The process then repeats itself.

The bureau has no objections to the use of *R 2000* for the remdiation of petroleum contaminated sites pursuant to Chapter 62-770, Florida Administrative Code, provided: (a) the considerations of this letter are taken into account; (b) a site specific Remedial Action Plan is approved by the Department; and

(c) the site specific plan includes a cost analysis that shows *R 2000* is the most cost-effective cleanup method in comparison to other viable alternatives, taking into account the sum of all construction, operating, maintenance and sampling costs over the expected project life (site cleanup time) for each alternative.

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. 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.

Preparers of 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 of Environmental Protection to inquire about the environmental acceptability of *R 2000*. To aid those reviewers, the Bureau of Petroleum Storage Systems provides supplemental information as enclosure 1.

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 its performance 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. You may contact me at 850/487-3299 if there are any questions.

Sincerely,

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

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Tom Conrardy - FDEP/Tallahassee

History:

inn_019.doc
7/23/1998

inn_019a.doc
7/22/2002

ENCLOSURE 1

SUPPLEMENTAL INFORMATION REGARDING THE *R 2000* SYSTEM

The information below may be helpful to reviewers of Remedial Action Plans prescribing the *R 2000* system, but should not be construed as the only considerations to be taken into account when reviewing an *R 2000* remediation plan.

1. Titanium dioxide (TiO_2): Titanium dioxide is a solid white powder that is insoluble in water. It is used commercially in toothpaste, as a food additive, and as the white pigment in exterior paints. The literature indicates that in dry form, it can sometimes be a mild skin irritant to humans. Tests performed on rats, by injecting doses that were 260 and 360 milligrams per kilogram of body weight, intermittently for a period as long as 2 years, could not conclude if it causes tumors.

   Given the commercial uses of titanium dioxide, the results of animal tests, its insolubility, its confinement to the equipment items of the treatment system, and that it will be separated from the treated slurry prior to effluent disposal, the Bureau of Petroleum Storage Systems believes that the public health risk posed by an *R 2000* system is low.

2. Chemical reactions: A mixture of contaminated groundwater and titanium dioxide catalyst recirculates as a 0.1 % slurry through an *R 2000* solar panel loop. Ultraviolet radiation striking the panel excites the catalyst, thereby creating hydroxyl radicals from some of the water molecules. These hydroxyl radicals are reactive, and they in turn oxidize contaminants, such as petroleum, to carbon dioxide and water. The titanium dioxide catalyst is unaffected by the reaction. If the contaminant is a chlorinated organic compound, then the reaction products will include chlorides.

3. Free product: Although chemical oxidation reactions are capable of destroying free petroleum product, it may be desirable to consider the amount of free product that is present on a site by site basis, to determine whether or not recovered groundwater should be passed through an oil/water separator before it enters the recirculating solar treatment loop.

4. Maximum influent concentration: *R 2000* information presented to the bureau did not indicate if there is a maximum

contaminant concentration that can be handled by the system. At a petroleum remediation test site, however, the influent contained approximately 2,600 parts per billion BTEX.

5. Catalyst life: It is suggested that Remedial Action Plans prescribing the *R 2000* process include an estimate of the useful life of the titanium dioxide catalyst, and provide for periodic inspection of its condition, and replacement if necessary to avoid effluent quality violations. It is the understanding of the bureau that, while the catalyst is unaffected by reactions which occur, its effectiveness can be reduced over time, possibly from coating of its surface.

6. Catalyst containment: "Washout" of approximately 10 percent of the catalyst has occurred at a Tyndall Air Force Base testing of the *R 2000* system. Therefore, Remedial Action Plans prescribing this system should provide for better containment of catalyst during the effluent disposal step if such a solids loading will clog a recharge gallery over time. A filter at the effluent pipe may help to prevent this loss of catalyst to a gallery.

7. Catalyst disposal: It will usually be the case that spent catalyst from the *R 2000* process does not require disposal as a hazardous waste. In the event that catalyst does become contaminated to the point that it is a hazardous waste, then it should be properly disposed.

8. Design and operating parameters: Remedial Action Plans prescribing solar photocatalytic oxidation should indicate the pertinent design and operating parameters, such as: illumination intensity, pH, the concentration of inorganic ions, and the concentration of organic reactants. The illumination intensity cited for a test system (for a cloudy day) was 31 watts per square meter. Additionally, plans should indicate the <u>overall average</u> flow rate at which groundwater will be processed; the instantaneous flow rate of slurry through the recirculating solar treatment loop; batch size; and the estimated treatment time per batch.

   The bureau believes that batch treatment time may have to be based on a worst case situation (the lowest expected radiation intensity) to ensure an adequate degree of treatment, in order to avoid effluent quality violations. For information purposes, the recirculation time at a petroleum remediation test site was 2 to 3 hours for an influent batch containing approximately 2,600 parts per billion BTEX.

9. Design and construction details: As in the preparation of any Remedial Action Plan, the bureau expects all plans prescribing the *R 2000* system to include all the pertinent details described in the Remedial Action Plan Checklist for a pump-and-treat system, such as layout, piping, valves, instrumentation, etc.

10. Solar panel orientation: The manufacturer of the *R 2000* solar photoreactors indicates that the panels will be effective if they are installed at an angle that is approximately 15 degrees from the horizontal and facing south.

11. Optimization: Unless there is a beneficial effect on site cleanup time by the stop-and-go recovery and treatment of groundwater on a batch basis, it may be worthwhile and cost-effective -- and perhaps even necessary -- for designers to optimize an *R 2000* setup, to ensure that contaminants are continuously removed from the subsurface. One way to create a continuous recovery of groundwater would be to use multiple tanks, piped and operated in such a way that while the first tank is filling, the second is treating, the third is settling catalyst, and a fourth is discharging effluent. Also, if a “once-through” system can be developed in the future to replace the batch system, then there would no longer be a need to worry about minimizing “dead time” in the recovery of groundwater.

12. Operating factor: The bureau assumes *R 2000* systems, operating unattended in batch mode at remediation sites for periods up to one month, must be fully and reliably automated. To ensure a high operating factor (minimization of downtime) this may require closer attention during the design of a control scheme, since level switches, timers, control valves, solenoid valves, interlocks, and instrumented shutdowns will play a more important role in this type of system, in comparison to their role in a more conventional treatment process. Designers may want to consider a degree of redundancy (or in-line spares, high-high level switches, low-low levels switches, etc.) for controls and instruments items whose failures will halt or severely disrupt the operation. It may also be prudent to include telemetry (with remote control capability) for user intervention.

13. Effluent sampling: The Bureau of Petroleum Storage Systems believes there may be unique effluent sampling considerations for *R 2000* systems, for which some degree of catalyst washout occurs with each batch of effluent disposed, and where the catalyst can become coated over time and loose some of its effectiveness. For such a situation, and especially since

R 2000 must operate automatically and unattended for at least a month at a time, it may be important to know that a decrease in system performance, due to washout and/or loss of catalyst, has not negatively impacted the quality of the effluent. The onus shall be on preparers of remediation plans prescribing an *R 2000* system to propose an effluent sampling plan that addresses this concern.