



JENNIFER M. GRANHOLM  
GOVERNOR

STATE OF MICHIGAN  
DEPARTMENT OF ENVIRONMENTAL QUALITY  
LANSING



STEVEN E. CHESTER  
DIRECTOR

October 27, 2004

Mr. Farsad Fotouhi, Vice President  
Corporate Environmental Engineering  
Pall Corporation  
600 South Wagner Road  
Ann Arbor, Michigan 48103

Dear Mr. Fotouhi:

SUBJECT: Proposed Ozone/Hydrogen Peroxide Technology

Although the application you submitted in March 2004 for reissuance of National Pollutant Discharge Elimination System (NPDES) Permit No. MI0048453 is administratively complete with respect to the treated groundwater discharge from Outfall 001, I will need additional information with respect to your proposal for utilizing the "new" ozone/hydrogen peroxide ( $O_3/H_2O_2$ ) technology in order to fully complete the application.

In the cover letter accompanying the application for reissuance of NPDES Permit No. MI0048453, you indicate your intent to convert the "core" (i.e., Wagner Road) treatment system to processes utilizing  $O_3/H_2O_2$  technology. With your application submittal, you have submitted data generated from the 30-day continuous-operation, field "pilot" test of Pall Life Sciences' 200 gpm mobile treatment unit, which I am currently in the process of reviewing. In order to facilitate this review, I am also utilizing the information contained in your submittal dated October 7, 2002, since only sampling data was included with the NPDES application.

The application's cover letter states that a "report regarding the testing will be submitted in the near future." It should be noted that I did not receive any supplemental information subsequent to the time of the application's submittal in March 2004.

My review of the application information and the associated data has generated several questions/comments as follows.

**Comment/Question #1 – Application Amendment (Request for Additional Information)**

It is my assumption that the 30-day continuous-operation, field "pilot" test utilized the "Pall Advanced **200 gpm**  $O_3/H_2O_2$  Test Unit" described in the October 2002 report submittal. NPDES Permit No. MI0048453, which authorizes the discharge of treated groundwater from the "core" treatment system to the unnamed tributary of Honey Creek, authorizes flow rates up to and including 1.872 MGD. A review of the Discharge Monitoring Report data for your facility indicates that effluent flows from the core treatment system can approach the permitted authorized flow on a daily basis based upon your needs to expedite your remediation activities and the associated needs for purging/extracting "large" quantities of groundwater. These facts generate the question of whether Pall Corporation has designed an overall system of  $O_3/H_2O_2$  units to accommodate flows through the treatment system that approach the 1.872 MGD level.

As you know, although the NPDES application contained detailed information on the existing UV/H<sub>2</sub>O<sub>2</sub>-based treatment system, the application with respect to the proposed technology contained only sampling data from the field study. Therefore, we request that you amend the application in writing to include a more detailed description of the proposed treatment system based upon your intent to convert the treatment system to the new technology. For example, do you plan to utilize several reactor units similar in size to the 200 gpm test unit, or will you design larger reactor units that provide a greater flow-through treatment capability?

The application amendment should, at a minimum, include a water flow diagram of influent flow from the "Red Pond" through the proposed treatment system into the "Green Pond." This water flow diagram must indicate the size (i.e., treatment capacity), configuration (i.e., series or parallel), and number of reactor units that will be utilized at the core treatment system. The water flow diagram should also indicate the proposed location of chemical feed points for the hydrogen peroxide feeds, pH adjustment, etc. In addition, I request that you provide a narrative description to accompany the water flow diagram that provides any pertinent information, such as chemical application rates, etc.

#### **Comment/Question #2 – Effluent Characteristics**

Section III, B., of the NPDES application, "Outfall Information," requires information on effluent characteristics, which you have provided based upon the effluent characteristics achieved from the existing treatment system. In addition, you have provided sampling data from the 30-day continuous pilot testing, which appeared to yield an average 1,4-dioxane of approximately 2 µg/L. However, it is noted that the pilot operation was a smaller scale application as compared to the system that will be utilized for long-term operation in the core treatment system.

Please provide expected maximum daily concentrations, expected maximum monthly average concentrations, and expected long-term average concentrations for effluent 1,4-dioxane concentrations which you expect to see in the effluent using the proposed O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> technology. These expected concentrations should be indicative of the effluent concentrations you expect to see at influent/effluent flow rates approaching the daily maximum authorized flow rate of 1.872 MGD. I do understand that you cannot be certain of what concentrations you will actually see in the effluent. However, we ask that you certify in writing as to the proposed effluent 1,4-dioxane concentrations based upon your field tests and other information. Please submit this information as part of the application amendment described in the previous comment.

#### **Comment/Question #3 – Treatment System Redundancy**

Although we assume the proposed technology is intended to provide some advantages over the existing UV/H<sub>2</sub>O<sub>2</sub>-based treatment system (see subsequent comments), it is my understanding, based upon a review of the October 2002 report, that the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> technology is less equipped to mineralize higher influent 1,4-dioxane concentrations. You confirmed this fact in our telephone conversation of October 19, 2004. (I believe you stated that higher influent 1,4-dioxane concentrations necessitated use of the greater mineralization energy provided by the UV lamps.)

During our telephone conversation, I believe you further stated that the existing technology processes would remain "in place" at the Wagner Road "core" treatment system. Based upon this, do you plan to create redundancy in the system such that, if higher 1,4-dioxane

concentrations are transmitted to the Red Pond from the extraction wells, the Red Pump House could direct influent flow to the existing UV/H<sub>2</sub>O<sub>2</sub>-based treatment system. Although it may not be absolutely necessary to incorporate this redundancy into the system based upon recent "influent" concentrations in the Red Pond, it will obviously provide an additional level of assurance if the existing technology is available for use.

Please confirm in writing that you do plan to incorporate this redundancy into the overall treatment scheme. In addition, if you do plan to accomplish this redundancy, please indicate how you plan to engineer this flexibility (valving in the pump house?).

#### **Comment/Question #4 – Intermediate Breakdowns Compounds**

Regarding effluent characteristics, in addition to 1,4-dioxane, there has been some question, primarily from the citizen's group, as to whether the presence of intermediate breakdown compounds from the incomplete mineralization of 1,4-dioxane in the effluent may have adverse water quality impacts. For some of these intermediate breakdown compounds, such as oxalic acid and methoxyacetic acid, the Department of Environmental Quality (DEQ) has derived aquatic toxicity values (i.e., final acute values and final chronic values). If these values are exceeded, adverse impacts to aquatic biota can occur.

Regarding intermediate breakdown compounds, the October 2002 report indicates that, during the June 2002 field tests, analyses for these compounds were conducted and "none of these analytes were detected." The results of a single sample for each of the four compounds were provided as an attachment. Regarding these analyses, these respective reported detection limits (RDLs) may be the best available for analysis of these compounds. However, as stated in my November 22, 2002, memorandum to Ms. Sybil Kolon, Remediation and Redevelopment Division, Jackson District Office, these RDLs are relatively insensitive with respect to concentrations in parts per billion (with the exception of the RDL utilized for analysis of the presence of oxalic acid), or when compared to the detection limit for 1,4-dioxane (i.e., 1 ppb). Therefore, these analytical results do not necessarily indicate the concentrations at which these compounds may exist in the effluent. Further, as in the case of methoxyacetic acid, the RDL does not allow for a direct determination of whether this compound is discharged at levels exceeding Water Quality Standards (i.e., the water quality value is below the RDL).

The October 2002 report states that "During operation of the mobile unit, more breakdown analyses will be performed." Were any additional samplings and analyses performed for the presence of the intermediate breakdown compounds during the 30-day continuous pilot study in February/March of 2004? Similar to the information requested for 1,4-dioxane, I request that, with the requested application amendment, you submit maximum daily concentrations and expected maximum monthly average concentrations for the four intermediate breakdown compounds. These concentrations should be indicative of those which you expect to see in the effluent at higher flows (i.e., greater than 1.5 MGD) using the proposed O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> technology.

I do recognize that, since the RDLs are likely higher than the discharge concentrations, it is likely that you will not be able to directly determine the concentrations of these compounds in the effluent and that determining these concentrations make be a difficult endeavor. However, I request that you make a determination using your knowledge of the mineralization reaction or any other applicable rationale. If necessary, estimated concentrations may be acceptable.

**Comment/Question #5 – Hydrogen Peroxide Feed Rates**

The October 2002 report describes the reactions whereby the 1,4-dioxane is degraded/mineralized. Although the ozone itself can degrade, via direct and indirect mechanisms, 1,4-dioxane in the wastestream, you state that through the addition of hydrogen peroxide “the oxidation efficiency is increased by conversion of ozone molecules to hydroxyl radicals; and ozone transfer from gas phase to the liquid is improved due to an increase in ozone reaction rates.”

It is my understanding, based upon our telephone conversation, that one of the advantages the proposed treatment technology provides over the existing technology is lower chemical application/usage. This results in the question of whether a lower amount of hydrogen peroxide and the associated dehalogenation agent, sodium bisulfite, will be applied via chemical feed to the treatment stream while utilizing the proposed  $O_3/H_2O_2$  technology.

As you know, on one or two occasions, your effluent exceeded the acceptable level for whole effluent (chronic) toxicity. Although it has not been confirmed, we suspect that excess sodium bisulfite (i.e., sodium bisulfite not utilized in the reaction to reduce effluent hydrogen peroxide) contributed to these results. Obviously, a lower necessary hydrogen peroxide application/feed rate will allow for a lower sodium bisulfite application/feed rate.

The October 2002 report states on page 13, regarding field tests for the Pall Advanced 200 gpm  $O_3/H_2O_2$  Test Unit, that the “best result was with a natural pH of 7.2, low peroxide treatment (**10-15 ppm**), and a one-minute contact time.” This comment precedes Table 4, and I assume refers to the 10 ppb 1,4-dioxane concentration (yielded in Sample ID oz-200-0-7.2-91-1M), which was the best result achieved in any of the various field tests. However, Table 4 indicates that this result was achieved with a **100 ppm** hydrogen peroxide dosage rate (**not 10-15 ppm**). I do note that a field test represented in Table 2 (i.e., Sample I.D. oz-200-10-7.2-91-1M) indicated that a low dosage rate of 10 ppm could yield a relatively good resultant 1,4-dioxane concentration (12 ppb). The October 2002 report further states that “It is expected that peroxide at too high of a concentration will act as free radical scavenger” and “The reduction in cleaning at higher concentrations of peroxide showed this scavenging of the hydroxyl radical.”

Regarding the February/March 2004 30-day continuous pilot testing, no information on hydrogen peroxide dosage rates was provided.

Please indicate in writing whether use of the proposed technology will result in a lower hydrogen peroxide feed rate, and a lower associated sodium bisulfite feed rate, when compared with the existing technology. In addition, please indicate the hydrogen peroxide dosage rate that you will be utilizing in conjunction with the proposed  $O_3/H_2O_2$  technology and how this was selected as the optimal dosage rate.

**Comment/Question #6 – Ozone/Hydrogen Peroxide Technology Advantages**

Regarding advantages provided by the  $O_3/H_2O_2$  technology, it is assumed that the new technology will result in lower electrical utility usage/consumption. The previous item discusses the likelihood of whether the new technology will result in lower hydrogen peroxide and sodium bisulfite feed rates.

Regarding use of other chemicals, the existing treatment process utilizes two pH adjustments: a lowering of pH in the influent through a sulfuric acid feed and the raising of pH through addition of sulfuric acid prior to discharge to the Green Pond. It is my understanding that, for the existing technology, it is necessary to lower the alkalinity of the influent groundwater to reduce scaling on the UV lamps and, in addition, a pH of approximately 6 S.U. is the optimal range for the mineralization reaction to occur. The pH is then raised prior to discharge to assure compliance with the NPDES permit's effluent limitations.

Regarding the  $O_3/H_2O_2$  technology, the October 2002 report seemed to indicate that the optimal pH for the mineralization reactions to occur was a relatively neutral pH (around 7.2 S.U.). This, of course, raises the question regarding the degree of pH adjustment that will be necessary for the  $O_3/H_2O_2$  technology.

In general, there is little information contained in the documents which I have in my possession to clearly identify the reasons that Pall Life Sciences is intending to implement this conversion of the core treatment system to the  $O_3/H_2O_2$  technology. Please describe in writing the advantages or improvements that the proposed technology provides, including advantages reflected in treatment cost savings, improvements with respect to treatment efficiencies, and any associated environmental benefits.

**Comment/Question #7 – Sampling Data from the 30-Day Continuous Test**

Regarding the sampling data generated by the 30-day continuous pilot test, the NPDES application contained three data tables (one each for 1,4-dioxane, bromide, and bromate). For each of these data tables, there are five columns of data corresponding to five sampling locations, including a column for influent (i.e., Red Pond) and a column for effluent from the unit (i.e., "Outfall"). The other three columns are indicated as Sampling Locations B, G, and H, but nowhere in the application materials is there an indication of the associated physical locations. Are Sampling Locations B, G, and H associated with extraction wells or are these intermediate sampling locations in the treatment stream? Please indicate in writing the physical locations corresponding to Sampling Locations B, G, and H.

**Comment/Question #8 – Contact Time/Retention Times**

Regarding contact times, the October 2002 report states (on page 13), with respect to the field studies for the "Pall Advanced 200 gpm  $O_3/H_2O_2$  Test Unit," that the "best result was with a natural pH of 7.2, low peroxide treatment (10-15 ppm), and a **one-minute contact time.**" This particular field test (see Table 4, Sample ID oz-200-0-7.2-91-1M) yielded a relatively good resultant effluent 1,4-dioxane concentration of 10 ppb, which was the best result from the various field tests with the 200 gpm unit. However, the Table 3 results indicate that, with the pH and hydrogen peroxide dosage rate held constant, the increased contact time (i.e., **15 minutes vs. 1 minute**) provided a higher level of treatment. The report also states that when "comparing contact times, a longer wait was shown to be more effective."

For the 30-day continuous pilot testing, no information on contact times (or any other parameters) has been provided for inclusion in my review.

For my information, please indicate in writing the contact times that you plan to utilize in the proposed  $O_3/H_2O_2$  technology that will be installed in the core treatment system. In addition, please indicate how you arrived at this optimal contact time. The submittal of contact times is

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not required information, but will allow me to better understand the parameters associated with the proposed technology.

Please submit the requested information in writing as soon as possible. If you have any questions, please contact me at the telephone number below.

Sincerely,

Alec Malvetis  
Lakes Erie and Huron Permits Unit  
Permits Section  
Water Bureau  
517-335-4124

am/sea

cc: Mr. Robert Reichel, DAG  
Mr. Mitchell Adelman, Jackson District Office, RRD, DEQ  
Ms. Sybil Kolon, Jackson District Office, RRD, DEQ  
Ms. Debora Snell, SWQAS, Jackson District Office, Water Bureau, DEQ  
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