

**WORK PLAN FOR THE  
TESTING OF IN-SITU OXIDATION  
USING HYDROGEN PEROXIDE FOR THE TREATMENT OF  
1,4-DIOXANE AT THE PALL LIFE SCIENCES FACILITY**

December 22, 2003



## **Table of Contents**

INTRODUCTION

OBJECTIVES OF THE TESTING

TECHNOLOGY BACKGROUND

WORK PLAN

Site Selection

Test Site Configuration

Injection Procedures and Frequency

Estimated Impact of the Injection

Groundwater Sampling and Hydraulic Conductivity Testing

Health and Safety During Testing

PROPOSED METHODS FOR DATA ANALYSIS

PROJECT SCHEDULE

REFERENCES

## **Tables, Figures and Appendices**

Table 1 – Proposed Analytes and Sampling Frequencies

Figure 1 - Site Location Map

Figure 2 - Geologic Cross Section MW-85 Test Site Area

Figure 3 – Geologic Cross Section MW-64 Test Site Area

Figure 4 - MW-85 Test Site Configuration

Figure 5 - MW-85 Cross Section

Appendix 1 - Well Logs

Appendix 2 - Groundwater Sampling Standard Operating Procedures (SOPs)

## **Appendix 3 – Sample Handling, Preservation SOPs**

### **INTRODUCTION**

This work plan describes the field activities intended to develop data regarding the feasibility of in-situ chemical oxidation (ISCO) for treatment of 1,4-dioxane associated with the Pall Life Sciences facility located at 600 South Wagner Road in Ann Arbor, Michigan.

The test will examine the application of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) for the treatment of 1,4-dioxane-contaminated groundwater. The results of this test will assist in determination of the feasibility of using ISCO for treatment of the 1,4-dioxane plume within the Unit E aquifer and possibly other aquifers.

### **OBJECTIVES OF THE TESTING**

This test is intended to provide sufficient information to determine if ISCO using hydrogen peroxide, or hydrogen peroxide with an iron catalyst (Fenton's reagent), can be applied as a remedial technology for Unit E and other aquifers. This will primarily be judged by the successful reduction in 1,4-dioxane concentrations and the ability to maintain acceptable geochemical conditions in the treated aquifer.

The primary objectives of the in-situ test are to examine the following:

1. 1,4-Dioxane Reductions in the Injection Zone.
2. Geochemical Changes in the Injection Zone.

### **TECHNOLOGY BACKGROUND**

ISCO is a remediation technology that involves subsurface injection of oxidants that are capable of treating organic contaminants in place. There are numerous examples of the application of this technology (EPA, 1998 and ESTCP, 1999). ISCO is still an emerging technology. This technology is usually not applied as a plume containment strategy. Rather, ISCO has been most successful when applied at highly contaminated sites or to contaminant source areas, to reduce contaminant concentrations and thereby the dissolved plume dimensions and severity.

The four oxidants most frequently used in ISCO include hydrogen peroxide (Fenton's reagent), potassium and sodium permanganate, and ozone. Hydrogen peroxide and potassium permanganate may be the most commonly used oxidants (Brown). Complete mineralization to carbon dioxide and water is the desired endpoint of an ISCO process.

For hydrogen peroxide, Fenton's reagent is typically produced on site by adding an iron catalyst to a hydrogen peroxide solution. If insufficient iron is available, hydroxyl radical production may be limited. A pH adjustment may be needed, since ferrous iron is more soluble at acidic pH. When soils contain chemically available iron, supplemental iron, in the form of dissolved ferrous sulfate heptahydrate or other iron salts may not be required (Teel et al, 2001). For the purpose of this test, it is expected that there will be sufficient chemically-available iron in the injection zone, and supplemental iron salts will not be required with the hydrogen peroxide injection solution.

Problems may occur when too many iron minerals are present in the soil. If the iron is in a mineralized form not readily available for dissolution, the natural catalytic activity of the mineralized iron decomposes the hydrogen peroxide to oxygen and water and does not create the hydroxyl radical. This would limit treatment success.

The effectiveness of ISCO is sensitive to variations in the geological conditions in the treatment zone (such as hydraulic conductivity distribution and mineral types), as well as to the distribution of contaminant mass. Chemical oxidants react with, and can be consumed by, other constituents in the groundwater and aquifer matrix, not just the target chemical. In many instances, overcoming these reactions adversely impacts the cost of application to the point of being impractical (Vance, 2002).

## **WORK PLAN**

### **Site Selection**

Pall is considering two locations for the ISCO testing: the area of MW-85 and the area of MW-64. These areas are shown on Figure 1. Pall prefers to do the testing at the MW-85 site, but access to this site for the testing is uncertain at this time. As such, Pall is proposing the MW-64 site as an alternative. Geological cross sections of the two sites are provided as Figures 2 and 3. Well logs for the wells are provided in Appendix 1.

### **Test Site Configuration**

Pall will install a network of wells at the chosen site. The new wells will include an injection well constructed of 4-inch stainless steel casing equipped with a 10-foot stainless steel screen, and 1- to 2- inch PVC observation wells equipped with 5-foot PVC well screens. Existing wells at the sites will be also used as observation wells. The observation wells will be used to collect groundwater samples during the testing. Pall proposes to install the observation wells in a downgradient and side gradient direction relative to the horizontal groundwater flow direction. Aquifer thickness, aquifer composition, groundwater flow, and the mass of hydrogen peroxide to be injected were the primary considerations in determining the proposed observation well spacing.

At the MW-85 location, the aquifer is approximately 50-feet-thick and comprised of coarse-grained materials with no distinct fine-grained layers identified during the subsurface soil sampling at this site. The horizontal groundwater flow direction is generally east. Pall will establish four nested observation well sets, each consisting of three wells, including the use of MW-85 at one of the locations. The proposed well configuration in the MW-85 test area is shown on Figure 4 and in cross section on Figure 5. The wells will be constructed of one-inch-diameter PVC. The three wells in each nest will be installed in a single borehole.

At the MW-64 location, the aquifer is approximately 13-feet-thick and is comprised of coarse-grained materials with no distinct fine-grained layers identified during the subsurface soil sampling at the site. The horizontal groundwater flow direction in the MW-64 area is interpreted to be to the east. Pall will install 3 observation well sites in addition to the existing observation well (OW-3). The proposed well configuration in the MW-64 test area is shown on Figure 6 and in cross section on Figure 7. The wells will be constructed of 2-inch-diameter PVC and equipped with a 5-foot PVC well screen. Because the aquifer at this location is relatively thin, nested wells are not warranted.

### **Injection Procedures and Frequency**

Pall proposes to inject hydrogen peroxide in batches rather than on a continuous basis, due to concerns over the ability to maintain site security and safety under continual operation/injection. The injections will take place three times per day. Pall initially plans to inject a 10% solution (by weight) of hydrogen peroxide. A 10% solution, as compared to more concentrated solutions, will minimize the temperature rise in the groundwater due to disassociation of the reagent and its reaction with contaminants and natural inorganic and organic reduced species. A pound of hydrogen peroxide can release 1,200 BTUs of heat energy and up to six cubic feet of oxygen gas. Concentrations as low as 11% can cause groundwater to boil (Vance, 2002). If heat or gas production cannot be controlled, the concentration of hydrogen peroxide injected may need to be reduced, or the injection event time interval increased. Conversely, Pall may elect to increase the concentration of hydrogen peroxide (up to 25%) if heat buildup can be managed.

The injection will take place over a period of 15 working days. During this period, a total of approximately 9,000 gallons of 10% hydrogen peroxide, or an equivalent mass of hydrogen peroxide, will be injected.

Peroxide will be introduced into the well casing and is expected to flow into the formation under an increased hydraulic head created by the injection. If necessary, compressed air will be used to pressurize the injection well after introduction of the hydrogen peroxide. Pall may need to adjust the injection frequencies based on field conditions.

## Estimated Impact of the Injection

Natural soil oxidant demand has been reported to range from 1 to 10 grams per kilogram (Mumford and Allen-King, 2003) or 1 to 20 gm/kg (Clayton, personal communication). If a cubic foot of saturated soil weighs 55 kilograms (110 pounds) and the average oxidant demand was 10 gm/kg, the total oxidant demand would be 550 grams per cubic foot. If the average demand were much less (as would be expected for a sand), for example, 1 gm/kg, the demand would be 55 grams. If the pore space in a cubic foot of aquifer was 30% of its volume and the weight of 10% hydrogen peroxide was 8.75 pounds per gallon, the hydrogen peroxide mass in a cubic foot would be 1.96 pounds (7.48 gallons/ft<sup>3</sup> x 0.3 x 8.75 pounds/gallon / 10). If the excess oxygen of all hydrogen peroxide (~47% by weight) in the pore space of a cubic foot of aquifer were converted to oxidant, the mass would be 0.92 pounds (roughly 1/100<sup>th</sup> to 1/1,000<sup>th</sup> of the natural soil oxidant demand).

If 600 gallons of 10% hydrogen peroxide were injected for 15 days (9,000 gallons), the maximum oxidant supply would be approximately 3,700 pounds or 1,778,320 grams (9,000 gallons x 8.75 pounds/gallon x 0.1 x 0.47). If the natural oxidant demand is 55 grams per cubic foot (1 gm/kg), the amount of hydrogen peroxide could impact 32,338 cubic feet of aquifer (1,778,320 grams/55 grams per cubic foot).

The shape of the reaction zone is expected to be somewhat ellipsoidal, with the longest axis parallel to groundwater flow. The volume of an ellipsoid is calculated as follows:



Volume of an ellipsoid =  $(4/3) \pi r_1 r_2 r_3$

For reference, a volume of 32,338 cubic feet equates to a treatment zone of approximately 20 feet x 20 feet x 40 feet. The actual shape of the treatment zone will depend on site conditions.

Note that the demand for hydrogen peroxide will decrease as the natural demand is satisfied. Therefore, the radius of the aquifer volume impacted by the oxidant will increase over time, i.e., if there were to be repetitive injections at a given location.

## Groundwater Sampling and Hydraulic Conductivity Testing

Groundwater samples will be collected from all associated observation wells. The samples will be collected in accordance to the schedule provided in Table 1. The groundwater samples will be collected using low-flow sampling procedures. Detailed procedures for anticipated sampling and field measurement techniques to be used for this work are provided in Appendix 2, Standard Operating Procedures (SOPs).

Groundwater samples will be collected in appropriate containers and preserved, as required by the analytical methods and SOPs provided in Appendix 3.

After injection of hydrogen peroxide into the injection well, in-situ hydraulic conductivity testing will be performed on the injection well. The primary purpose of the testing is to determine whether the hydraulic conductivity of materials in the screen zone of the well change as a result of the injection of hydrogen peroxide during the pilot testing.

## **PROPOSED METHODS FOR DATA ANALYSIS**

The concentration of dissolved 1,4-dioxane and other dissolved constituents in the injection zone will be determined by analysis of groundwater samples collected from the observation wells. Water quality data will be plotted against time and hydrogen peroxide dose, in pounds, on separate graphs for each observation well. The graphs would document changes in contaminant concentrations and assist in judging the effect of the hydrogen peroxide injection.

As discussed above, hydrogen peroxide may need to be injected at a concentration of 10% (or less) to avoid localized heating of the groundwater due to disassociation of the reagent. Approximately 9,000 gallons of fluid (water and hydrogen peroxide) will be injected to deliver sufficient hydrogen peroxide to overcome natural oxidant demand and produce an observable effect. This mass of injected water will displace some contaminated groundwater around the injection well. As a result, it is necessary to develop analytical methods to assist in determining whether the observable effects of ISCO are attributable to reaction rather than to dilution.

In this regard, levels of dissolved oxygen, nitrate, nitrite, iron, manganese, sulfur, and sulfite in the groundwater samples would also be measured in addition to other parameters. The absolute concentrations of these analytes and changes in each will be used to determine the oxidation-reduction potential of the aquifer. Comparison of the rate of change in these compounds, particularly oxygen, to the rate of change in contaminant concentration would help decide if the observed changes are similar in magnitude and rate and, therefore, whether they reflect reaction or dilution.

## PROJECT SCHEDULE

Pall proposes to complete the test within 8 to 10 weeks upon receiving site access.

Test Phase	Time to Complete (approximate)
Well Installation	2-3 Weeks
Test Site Setup	3 Days
Pre-injection Sampling/Testing	1 Day
Hydrogen Peroxide Injection	3 Weeks
Post-injection Sampling Testing	1 Day
Data Analysis/Reporting	3 Weeks
Total Project Length =	Approximately 8 to 10 weeks

## REFERENCES

Brown, R.A., In-Situ Chemical Oxidation: Performance, Practice and Pitfalls; an Environmental Resources, Inc., document:  
[http://www.afcee.brooks.af.mil/ER/techworkshop/postworkshop/tuesday/pm/sourcezoneremediation/brown\\_abst.pdf](http://www.afcee.brooks.af.mil/ER/techworkshop/postworkshop/tuesday/pm/sourcezoneremediation/brown_abst.pdf)

EPA, 1998. Field Application of In Situ Remediation Technologies: Chemical Oxidation, EPA 542-R-98-008, 31 pp., September 1998,  
<http://www.epa.gov/swertio1/download/remed/chemox.pdf>

ESTCP, 1999. Technology Status Review In Situ Oxidation, November 1999, 42 pp.,  
[http://www.estcp.org/documents/techdocs/ISO\\_Report.pdf](http://www.estcp.org/documents/techdocs/ISO_Report.pdf)

K.G. Mumford, K.G., Thomson, N.R. and Allen-King, R.M., Investigating the Kinetic Nature of Natural Oxidant Demand During ISCO. Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 2002

Teel, Amy L., Wargberg, Christopher R., Atkinson, David A., and Watts, Richard J., 2001. Comparison of Mineral and Soluble Iron Fenton's Catalysts for the Treatment of Trichloroethylene, Water Resources, Vol. 35, No. 4, pp. 977-984, 2001.

Vance, D.B., 2002. A Review of Chemical Oxidation Technology,  
<http://2the4.net/html/chemoxwp.htm>