

**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**

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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 (H₂O₂) 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 reducing the mass of 1,4-dioxane in 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 can be applied as a mass reduction remedial technology for Unit E and possibly 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 aquifer around the injection site (the general area surrounding the zone of H₂O₂ injection).
2. Geochemical changes in the aquifer around the injection site.

TECHNOLOGY BACKGROUND

ISCO is a remediation technology that involves the subsurface injection of oxidants for the in-place treatment of organic contaminants. While there are numerous examples highlighting the application of this technology (EPA, 1998 and ESTCP, 1999), ISCO is still an emerging technology. ISCO has been most successful when applied for mass reduction in contaminant source areas. This technology is usually not applied as a plume containment strategy.

The four oxidants most frequently used in ISCO include hydrogen peroxide (including 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.

Hydrogen peroxide, one of the most powerful oxidizers known (oxidation potential = 1.8 V) is often combined with iron to form Fenton's reagent. Through catalysis, hydrogen peroxide can be converted into hydroxyl radicals (oxidation potential = 2.8 V) with a reactivity second only to fluorine (oxidation potential = 3.0 V). If insufficient iron is available either as an additive or naturally in the subsurface, hydroxyl radical production may be limited. 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). A low pH range of 2 to 4 is preferred to facilitate the generation of hydroxyl radicals, although this reaction is feasible up to neutral pH (Siegrist, 1998).

For the purpose of this test, it is anticipated that there will be sufficient chemically-available iron in the injection zone. pH adjustments for this test are not considered to be practical for a variety of reasons, including safety (i.e., management of acids) and undesirable effects to the subsurface environment such as mobilization of metals. As such, no pH adjustments will be made for this test.

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).

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.

WORK PLAN

Site Selection

Pall has selected the area of MW-85 for this test. Shown on Figure 1, the MW-85 area was selected because it is located centrally along the transverse axis of the Unit E plume in a relatively thick portion of the aquifer and is fairly accessible for work activities. A generalized geological cross section of the site is provided as Figure 2. A well log for the MW-85 is provided in Appendix 1.

Test Site Configuration

Pall will install a network of wells at the chosen site. The network of wells will include: one injection well, constructed of one, four-inch diameter steel casing equipped with a 10-foot stainless steel screen, and 23, one-inch diameter PVC observation wells, each equipped with a five-foot stainless steel or PVC screens. The observation wells will

consist of six nested well sets with each nest consisting of four, one-inch PVC observation wells. The exception will be at the MW-85 nest, which will consist of three, one-inch PVC wells equipped with five-foot screens and MW-85.

The injection well will be drilled with 6¼-inch diameter hollow stem augers. The nested observation wells will be drilled with 4¼-inch diameter hollow stem augers. Each observation well boring (with the exception of one boring at MW-85) will contain two, one-inch wells (two soil borings will need to be drilled, as only two, one-inch wells will fit inside a 4¼-inch auger). The observation wells will be used to collect groundwater samples during the testing. Pall proposes to install the observation wells in a downgradient direction relative to the horizontal groundwater flow direction (see Figure 3 for the locations and depths of the injection and observation wells). 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 (sand, gravel, cobbles/boulders) with no distinct fine-grained layers identified during the subsurface soil sampling at this site. Field data collected in the area of MW-85 indicate the horizontal groundwater flow direction is generally east and the approximate groundwater velocity is 2 feet per day.

Injection Procedures and Frequency

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, based on the high hydraulic conductivity of the materials in the injection site area, 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.

Pall proposes to inject hydrogen peroxide in daily batches rather than on a continuous basis due to concerns over the ability to maintain site security and safety under continual-injection operations. Each daily injection will occur on a continuous basis if possible. If necessary, Pall may break the daily batch injection events into successive injection events as site conditions warrant.

Heat production, due to ISCO using hydrogen peroxide, can sometimes be problematic. Initially, Pall plans to inject a 10% solution (by weight) of hydrogen peroxide. The 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 and concentrations as low as 11% can cause groundwater to boil (Vance, 2002). Consequently, Pall will periodically monitor injection zone temperature during the daily batch injections. If heat production cannot be controlled, the concentration of hydrogen peroxide injected may 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 safely managed.

Estimated Impact of the Injection

Natural soil oxidant demand has been reported to range from 1 to 10 grams per kilogram (gm/kg) (Mumford and Allen-King, 2003) or 1 to 20 gm/kg (Clayton, personal communication). If a cubic foot of saturated soil weighs 55 kilograms (121 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/ft³ 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 1/100th to 1/1,000th 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 (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 (wide) x 80 feet (long) x 40 feet (high). The actual shape of the treatment zone will depend on site conditions.

Note that the demand for hydrogen peroxide will decrease as the natural aquifer 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.

In-situ hydraulic conductivity testing will be performed using the injection well before and after injection of hydrogen peroxide into 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 changes as a result of the injection of hydrogen peroxide during the 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. Changes in water quality data will be plotted against both time and hydrogen peroxide dose, in pounds, each on separate graphs for all observation wells. The graphs will document changes in contaminant concentrations and assist in judging the effect of the hydrogen peroxide injection.

Approximately 9,000 gallons of fluid (water and hydrogen peroxide) will be injected during this test. This mass of injected solution will displace some contaminated groundwater around the injection well, making it difficult to determine whether 1,4-dioxane changes in the groundwater are the result of dilution or oxidation. In this regard, levels of dissolved oxygen, nitrate, nitrite, iron, manganese, sulfur, and sulfite in the groundwater samples will be measured in addition to other parameters. The absolute concentrations of these analytes and the temporal changes in each will be used to determine the oxidation-reduction potential in the aquifer. Comparison of the rate of change in these compounds, particularly oxygen, to the rate of change in the contaminant concentration will help the assessment of whether 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	5-7 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 12 to 14 Weeks

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