WORK PLAN

TESTING OF IN-SITU OXIDATION

FOR THE TREATMENT OF 1,4-DIOXANE

AT THE PALL LIFE SCIENCES FACILITY

October 17, 2003

Pall Corporation

Introduction

This work plan describes the field activities that are planned to develop site-specific 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 three oxidants for the destruction of 1,4-dioxane: ozone (O_3), Hydrogen Peroxide (H_2O_2), and O_3/H_2O_2. If favorable, the results will form a basis for the application of ISCO for treatment of the 1,4-Dioxane plume within the Unit E aquifer and possibly other aquifers.

Work Plan Purpose

This document describes the objectives, technology background, and the general procedures that will be used in field-testing.

Objectives

The objectives of the in-situ test are to further examine the following items regarding ISCO:

1. 1,4-Dioxane Reduction Rates
2. Hydraulic and Geochemical Changes in the Injection Zone
3. Reaction Byproducts

This test is intended to provide sufficient information to determine if ISCO can be applied as a remedial technology for the Unit E and other aquifers. This will primarily be judged by the successful reduction in 1,4-dioxane concentrations and an examination of reaction byproducts, and hydraulic and geochemical charges in the injection zone. Through this study, additional information will be obtained regarding such items as dosage rates, injection pressures, radius of influence and oxidant ratios. These later items will be further evaluated should this technology be considered feasible.

Technology Background

In-situ chemical oxidation is a remediation technology that involves subsurface injection of oxidants that are capable of destroying organic contaminants in-place. The technology has the potential advantages of achieving rapid and complete treatment. General feasibility and design challenges relate to ensuring that the oxidation reactions will achieve an adequate level of treatment and that the oxidant can be effectively injected and distributed into the subsurface so that target treatment intervals are contacted with oxidant.

One oxidant chemical used for in situ applications is ozone. Ozone is a gas that is highly soluble in water. In-situ ozone injection can potentially be carried out using either gaseous ozone or using water laden with dissolved ozone. Ozone oxidation destroys organic molecules such as 1,4-dioxane, producing primarily carbon dioxide, water, and oxygen. Ozone oxidation reactions proceed in a number of intermediate steps, where the hydrocarbon rings and chains are broken into smaller molecules that are highly susceptible to further oxidation by ozone or by microbial processes. Another treatment mechanism involves reaction of ozone gas with soil transition metals, such as iron and manganese, to form radical species. The radical species are more powerful oxidizers of organic compounds than ozone, and their treatment process is known as "advanced oxidation".

Testing Procedures

Three different in-situ tests will be conducted at three different locations within PLS's property. The stages of the testing will be as follows:

Stage	Oxidant	Injection Well	Observation Well
A	H_2O_2	MW-22	TW-10
B	O_3	A new 2" well installed ~10' upgradient of MW-11d	MW-11d

C	$O_3 + H_2O_2$	A new 2” well installed ~10’ upgradient of MW-64	MW-64

Stage A - H_2O_2:

Hydrogen peroxide is easily converted to hydroxyl free radicals (OH*) which breakdown a variety of organic compounds. The oxidation of organic compounds reduces the carbon chain into smaller and smaller pieces, ultimately to carbon dioxide, water and simple compounds. Chemical oxidation using hydrogen peroxide essentially “steals” electrons from another molecule. This process is called oxidation. All organic compounds can be oxidized. During this process, an oxidant (hydrogen peroxide) is injected at varying concentrations into the aquifer. Because there is typically no oxidant in the deep soil pores and low permeability soil layers, there is a strong driving force concentration gradient) for the oxidant to diffuse into these locations where contaminants are sequestered and oxidize the contamination.

To promote radical oxidation and to slow the decomposition of H_2O_2, less concentrations of H_2O_2 (e.g. 12% by weight) will be injected in MW-22. The H_2O_2 will be injected in 1-gallon doses. It may be necessary to lower the natural pH of groundwater to a pH of 6.5. If needed, sulfuric acid will be used to lower the pH at the time of injection. This will be determined if H_2O_2 is unable to lower 1,4-dioxane by itself.

Compressed air will be used to pressurize the well after introduction of the H2O2. This will force the water column into the aquifer. This pressurization will be repeated at 15 minutes intervals between doses to assist in dispersal of the H_2O_2. The TW-10 extraction well, located approximately 50 feet from MW-22, will be shut down during this testing and will be utilized as an observation well. This test is to be conducted during five business days.

Groundwater Sampling and Hydraulic Conductivity Testing

Groundwater samples will be collected from both MW-22 and TW-10. The samples will be collected in accordance to the schedule provided in Tables 1a and 1b. The groundwater samples will be collected using low-flow sampling procedures.

Prior to injection of H_2O_2 into MW-22, in-situ hydraulic conductivity testing will be performed. The hydraulic conductivity testing will be performed prior to, and after, the injection of H_2O_2 and after the testing has ended. 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 ozone during the pilot testing.

Field measurements for Oxidation Reduction Potential (ORP), pH, Dissolved Oxygen (DO), Temperature and Specific Conductance will be made using a dedicated water quality probe and recorder.

Stage B – O_3:

One oxidant chemical used for in-situ applications is ozone. Ozone is a gas that is highly soluble in water. In-situ ozone injection can potentially be carried out using either gaseous ozone or using water laden with dissolved ozone. Ozone oxidation destroys organic molecules such as 1,4-Dioxane, producing primarily carbon dioxide, water, and oxygen. Ozone oxidation reactions proceed in a number of intermediate steps, where the hydrocarbon rings and chains are broken into smaller molecules that are highly susceptible to further oxidation by ozone or by microbial processes. Another treatment mechanism involves reaction of ozone gas with soil transition metals, such as iron and manganese, to form radical species. The radical species are more powerful oxidizers of organic compounds than ozone, and their treatment process is known as “advanced oxidation”.

This single well O_3 injection testing will involve the injection of ozone into a single well, and monitoring of the downgardient observation well. Ozone will be introduced into the screen zone of a new 2” PVC injection well 10 to 20 feet upgradient from MW-11d. A pressure of approximately 24 PSI will be utilized to saturate the 50' water column with ozone. Compressed air will then be utilized to pressurize the water column into the aquifer. This pressurization will be repeated at various intervals (to be determined in the field) between doses to assist in dispersal of the ozone. This test is to be conducted during five business days.

Groundwater Sampling and Hydraulic Conductivity Testing

Groundwater samples will be collected from both the new well and MW-11d. The samples will be collected in accordance to the schedule provided in Table 2a and 2b. The groundwater samples will be collected using low-flow sampling procedures.

Prior to injection of O_3 into the new well, in-situ hydraulic conductivity testing will be performed. The hydraulic conductivity testing will be performed prior to, and after, the injection of O_3 and after the testing has ended. 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 ozone during the pilot testing.

Field measurements for ORP, pH, DO, Temperature and Specific Conductance will be made using a dedicated water quality probe and recorder.

Stage C - O_3/ H_2O_2

The process of mixing ozone and hydrogen peroxide is developed for the destruction of organic compounds. Ozone disassociates as well as reacts with hydrogen peroxide to produce an intermediate, hydroxyl radical (•OH). Hydroxyl radicals are the second most powerful oxidizing agent found in nature. These hydroxyl radicals react very rapidly to oxidize organic contaminants to non-hazardous compounds carbon dioxide and water. The oxidation chemistry using ozone and hydrogen peroxide to create hydroxyl radicals is well known. The overall balanced reaction for ozone and hydrogen peroxide to yield hydroxyl radical is:

$$2O_3 + H_2O_2 \rightarrow 2{\bullet}OH + 3O_2$$

At stage B test (injection of O_3 only), the concentrations of bromate will be monitored during this portion of the pilot study. The oxidation path is Bromide (Br) to Hypobromite (HOBr/OBr) to Bromate (BrO3). Hydrogen peroxide reduces hypobromite back to bromide. When ozone is minimized, less ozone is available to oxidize hypobromite to bromate before hydrogen peroxide reduces hypobromite back to bromide. The reduction of hypobromite by hydrogen peroxide is orders of magnitude faster than the oxidation of hypobromite to bromate by ozone. That’s why hydrogen peroxide is added in this portion of the pilot study.

A combination of ozone and hydrogen peroxide will be introduced into the screen zone of a newly installed injection well. A minimum pressure of approximately 65 PSI will be utilized to saturate the 150' water column with ozone and pressurize the water column into the aquifer. A simultaneous injection of 50% solution of hydrogen peroxide will be pumped into the screen zone at an initial mole ratio of approximately 2.2. This combination dosing will be repeated at various intervals (to be determined in the field) between doses to assist in dispersal of the ozone. The MW-64 temporary extraction well will be shut down during this testing and will be utilized as an observation well. This test is to be conducted during five business days.

Groundwater Sampling and Hydraulic Conductivity Testing

Groundwater samples will be collected from both the new well and MW-64. The samples will be collected in accordance to the schedule provided in Table 3a and 3b. The groundwater samples will be collected using low-flow sampling procedures.

Prior to injection of O_3/H_2O_2 into the new well, in-situ hydraulic conductivity testing will be performed. The hydraulic conductivity testing will be performed prior to, and after, the injection of O_3/H_2O_2 and after the testing has ended. 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 ozone during the pilot testing.

Field measurements for ORP, pH, DO, Temperature and Specific Conductance will be made using a dedicated water quality probe and recorder.

Health and Safety During Testing

Health and safety procedures to be employed during the testing are summarized in Appendix A.

Testing Schedule

The in-situ testing will be implemented beginning November 3, 2003 and will be continued until December 3, 2003. A report of the testing will be prepared and submitted to the Michigan Department of Environmental Quality (MDEQ) on December 15, 2003.

BACKGROUND

In June 2003, Pall Life Sciences (PLS) performed a short duration In-Situ Pilot Test where a small amount of O_3 was injected into MW-52s for less than 2 hours. The main objectives of the June 13, 2003 In-Situ Pilot Test were to evaluate issues related to the delivery of O_3 to a subsurface formation and changes in hydraulic conductivity of screen zone materials.

PLS also monitored water quality during the In-Situ Pilot Test to observe relative changes in specific water quality parameters.

Specific information regarding the June 2003 In-Situ Pilot Test is summarized as follows:

Test Date	Friday, June 13, 2003
Test Well	MW-52s
Injection Start Time	12:33
Injection End Time	14:28
Injection Rate	1 SCFM
Injection Pressure	15.5 PSI
Ozone Concentration by Weight	6.50%
Total Amount of Ozone Injected	1.3 Lbs.
Observation Wells	MW-10d, TW-13, TW-8, MW-50, MW-52i, MW-52d

GROUNDWATER SAMPLING

Groundwater sample were collected periodically from wells MW-10d, TW-13, TW-8, MW-50, MW-52i and MW-52i . The samples were collected and analyzed for a variety of water quality parameters including bromate, bromide, 1,4-dioxane, pH and ORP.

The water quality results from the groundwater sampling are summarized in Table 1.

Table 1.

	TimeBromateBromide1,4-dioxanepH
MW-52s	
6/12/2003	164179649196.95
6/13/2003	090765689027.72

6/13/2003 1444 184 63 331 6.28 6/14/2003 439 6.49 6/15/2003 461 6.59 6/16/2003 395 6.82 MW-10d 6/12/2003 1655 47 105 649 7.02 6/13/2003 0911 618 6.95 6/13/2003 1333 46 108 632 6/13/2003 1450 89 18 1195 6.74 6/14/2003 1059 652 6.68 6/15/2003 1054 662 6.73 6/16/2003 1341 667 7.04 TW-13 6/12/2003 1715 131 36 1324 7.00 6/13/2003 0916 1279 6.78 6/13/2003 1459 84 84 1252 6.82 6/14/2003 1104 1211 6.93 6/15/2003 1058 1226 6.96 6/16/2003 1346 1210 6.98 TW-8 6/12/2003 1722 23 127 1191 6.97 6/13/2003 0924 1134 7.01 6/13/2003 1508 18 139 1128 6.85 6/14/2003 1109 1212 6.78 6/15/2003 1130 1187 6.86 6/16/2003 1352 1143 7.03 MW-50 6/12/2003 1727 123 36 7.00 6/13/2003 0922 361 7.03 6/13/2003 1515 113 88 356 6.79 6/14/2003 6.69 6/15/2003 6.77 6/16/2003 7.05 MW-52i 6/13/2003 1311 nd 36 nd MW-52d 6/13/2003 1315 nd 25 nd

HYDRAULIC CONDUCTIVITY TESTING

In-Situ hydraulic conductivity testing in MW-52s was completed on June 13 and 18, 2003 as part of an in-situ ozone injection pilot study. The hydraulic conductivity testing, which consisted of pneumatic slug testing, was performed prior to, and after, the injection of ozone into monitoring well MW-52s. The primary purpose of the testing was to determine whether the hydraulic conductivity of materials in the screen zone of the well changed as a result of the injection of ozone during the pilot testing.

The pneumatic slug testing equipment used consisted of the following: A Solinst water level meter, a Honda Air with air regulator, a pneumatic slug test “T”, equipped with K-packers and pressure gauge, an In-Situ MiniTROLL® pressure transducer (MiniTROLL) with associated cables, and a laptop computer with applicable software. All equipment, which was placed in MW-52S, was washed with Liquinox and water and rinsed with de-ionized water prior to placement in the well.

The following procedures were used to conduct pneumatic slug testing of monitoring well MW-52S on June 13, 2003 (prior to) and June 18, 2003 (after) the ozone injection pilot study at MW-52S.

Monitoring well MW-52S was opened and allowed to equilibrate to atmospheric conditions and a manual static water level measurement was collected. A MiniTROLL was then inserted through the “T” and into the water column. The “T” was then set on the well casing. The “T” is equipped with two K-packers to prevent air from escaping through the top of the well. The top of assembly was sealed with a rubber stopper. To release the air, the valve on the “T” was opened, allowing the pressurized air to quickly release into the atmosphere. A photograph of the complete setup, including the “T” assembly, is shown below.

The first pneumatic slug test was conducted with 3 pounds per square inch (psi) in the well. This was accomplished by closing the “T” assembly, connecting the air compressor hose and regulator to the “T” and starting the air compressor. The pressure regulator was slowly increased until the gauge on the “T” assembly was at the desired pressure (for the first test, 3 psi). After this pressure was established, manual readings from the MiniTROLL were observed. The test began once the MiniTROLL readings approached background readings. To begin the test, the MiniTROLL was started and as quickly as possible the pressurized air in the well was released by opening the valve on the "T" assembly. Pressure measurements were collected and converted to feet of water logarithmically using the MiniTROLL transducer. The test was terminated after the water level recovered to pretest levels. The second and third tests were conducted similarly with 6 and 8.5 psi, respectively. Increasing the test pressure allowed for a greater radius of influence.

Data Analysis

The data was imported into Aquifer Win 32 for the analysis of hydraulic conductivity. The Hvorslev method (Hvorslev, 1951) was used for to calculate the hydraulic conductivity of materials intersected in by the screen zone. The following assumptions apply to the Hvorslev method:

- Aquifer is fully confined.
- The aquifer is homogeneous, isotropic, and of uniform thickness.
- Well loss is negligible.
- Storage effects are assumed to be negligible.
- Groundwater flow is unsteady.
- A volume of water or slug is injected into, or is discharged from, the well.
- Well is of finite diameter and may partially penetrate the aquifer.
- A lateral constant head boundaries exists at a finite distance from the test well for the full penetration case.
- The length of the well screen is significantly larger than the diameter of the well.

Copies of the resulting plots are provided in Appendix 1 and the results are tabulated in Table 1.

Table 1 – Summary of Hydraulic Conductivity Data

Test	Hyd. Conductivity Pre-Ozone Injection	Hyd. Conductivity Post-Ozone Injection	Percent Change
3.0 PSI	59	54	-8.5
6.0 PSI	44	35	-20.5
8.5 PSI	38	31	-18.4

Note – Hyd. Cond.
In gallons/day/sq. foot

SIGNIFICANT RESULTS OF THE IN-SITU PILOT TEST

PLS was able to successfully deliver O_3 to MW-52s. The initial analytical result indicated that concentrations of 1,4-dioxane in groundwater sampled from MW-52s were lowered from 919 ug/L to 395 ug/L. During testing, unusual levels of bromide and bromate were detected in groundwater sampled from MW-52s. It appeared that at some of the observation locations, bromate was converting back to bromide.

This slug testing suggests the hydraulic conductivity in the screen zone of MW-52s decreased after ozone injection. The reduction ranged between 8.5 and 20.5 percent. The most probable reason for this reduction is gas entrapment in the open pore spaces. It is unlikely that mineral precipitation, if any, would have resulted in such a change.

Summary of Potential Controls and Requirements for Ozone Field Pilot Test Activities		
Engineering Controls and Personal Protective Equipment	Inspection Requirements	Training Requirements
Engineering controls to include: ventilation, catalytic ozone destruction units PPE to include: Nonconductive hardhat, nitrile inner gloves, leather work gloves, safety glasses, work shoes and steel-toes boots.	Inspect electrical connections, ground continuity-resistance, polarity, line voltages, and test motor rotations prior to start-up. Pre- and post-operation visual inspection of mechanical equipment. Inspect ozone system for leaks on start-up. Ozone monitoring in work area breathing zone, sensitive receptor locations, and subsurface locations where ozone may collect such as crawl spaces and/or sewers.	Hazards communication regarding ozone, pressurized gases, site activities. Emergency response procedures. Ozone injection equipment-specific training. Hazardous waste site operations (HAZWOPER) Tailgate Safety Meeting Site specific orientation

Principal Work Activity	ES&H Hazards	Recommended Controls	Permits & Training
Mobilizing and demobilizing ozone injection equipment	Electrical equipment	Ascertain whether any part of a circuit is located such that a person, tool, or machine may come into contact with the circuit. No energized lines will be serviced. Verify grounding and overload protection prior to start-up and testing. Check ground resistance, ground continuity, polarity, and line voltages prior to system start-up. Identify shutdown locations. Verify disconnect locations and shielding. Verify lock out-tag out procedures, and equipment, prior to start-up. Use ground fault circuit interrupter (GFCI) receptacles, or portable GFCI device, for convenience power, instruments, etc. PPE – Non-conductive hardhat, safety glasses, leather gloves and work shoes.	Qualified personnel should inspect electrical connections and grounding prior to start-up and testing. Lock out-tag out procedures, and equipment Tailgate Safety Meeting Site specific orientation

	Pressurized gases (stored energy)	Over pressure relief valve set to 10% above maximum working pressure. Verify location on air receiver and between inlet stop valve and air compressor. Verify discharges from relief valves are located so that it is not a hazard to personnel. Verify pressure measurement locations and review depressurization procedures. Review piping and valve positions required to depressurize system prior to maintenance. Secure compressed gas cylinders in an upright position to prevent unintentional fall. Use protective valve shields when not in use. Do not move cylinders without valve shields in place. Smoking is prohibited wherever compressed cylinders are stored, handled, or used. Secure all quick make-up connections with lasing and hose clamps. Wire or pins in quick connect fittings are not acceptable for use as lashing. No repair work shall be done until the stop valve in the air line is closed and tagged “OUT OF SERVICE – DO NOT USE”. PPE – No conductive hard hat, safety glasses, leather gloves and steel-toed work boots.	
	Heavy lifting	Use proper lifting techniques (flex at the knees and use legs when lifting). Obey sensible lifting limits	
	Hot/Cold Stress	Train workers to recognize symptoms of hot and cold stress.	

Principal Work Activity	ES&H Hazards	Recommended Controls	Permits & Training

Injection of ozone into subsurface	Ozone exposure PEL: 0.1 ppm OSHA-15 min STEL: 0.3 ppm OSHA-8 hr TWA: 0.1 ppm	HAZWOPER site controls during operations. Check wind direction and select an assembly location. Measure background ozone concentration prior to start-up. Monitor ozone in work area breathing zone and any sensitive receptor locations. Cease operations if ozone levels reach STEL at anytime. PPE – Hardhat, safety glasses, work gloves, steel toed work shoes/boots. No respirators are certified for use with ozone, prevention and ventilation are primary engineering controls. Lock-out tag-out depressurization valves. Use ozone reducing catalyst beds when depressurizing or maintaining ozone system. Label tanks to identify the chemical contents, and the associated hazards.	Hazards communication regarding ozone, pressurized gases, site activities. Emergency response procedures. Ozone injection equipment-specific training. Hazardous waste site operations (HAZWOPER) Tailgate Safety Meeting Site specific orientation Lock-out tag-out procedures, and equipment.
	Fire/Explosion	Monitor oxygen concentration and LEL level in enclosed spaces where ozone/oxygen may collect such as crawl spaces and/or sewers. Maintenance of ozone system by trained operators only: do not use pipe dope, lubricants or otherwise contaminate the ozone production system. Open and close valves slowly. Fire extinguishers (A/B) shall be suitably placed, distinctly marked, readily accessible, and maintained in a fully charged and operable condition. No open flames are to be used at anytime.	
	Spills/Leaks	Establish evacuation route, assembly point, and emergency response prior to generating ozone. Use potassium iodide impregnated materials to verify the system is leak free during start-up of ozone production. System will be hydrostatic tested prior to mobilization to the site. Monitor ozone concentration in the work area-breathing zone. Evacuate if ozone levels reach STEL at anytime. Check wind direction and re-evaluate assembly point in the event of a release. Remotely shutdown ozone generation equipment. Use catalytic ozone destruction units on vent lines when depressurizing.	
	Mechanical hazards	Verify motor/belt guards are in place while operating.	

Principal Work Activity	ES&H Hazards	Recommended Controls	Permits & Training
monitoring ozone in the subsurface.	Ozone exposure PEL: 0.1 ppm OSHA-15 min STEL: 0.3 ppm OSHA-8 hr TWA: 0.1 ppm	Set-up gas monitoring instruments in a central area within the exclusion zone with good ventilation, add fans as needed. Connect sampling equipment prior to opening wellhead valves for sampling. Use ozone-reducing catalyst beds on instrument vent lines. Monitor ozone in work area breathing zone and any sensitive receptor locations. Cease operations if ozone levels reach STEL at anytime. PPE – Hardhat, safety glasses, work gloves, steel toed work shoes/boots. No respirators are certified for use with ozone, prevention and ventilation are primary engineering controls. Lock-out tag-out depressurization valves. Use ozone reducing catalyst beds when depressurizing or maintaining ozone system. Label tanks to identify the chemical contents, and the associated hazards.	Hazards communication regarding ozone, pressurized gases, site activities. Emergency response procedures. Ozone injection equipment-specific training. Hazardous waste site operations (HAZWOPER) Tailgate Safety Meeting Site specific orientation

	Fire/Explosion	Monitor oxygen level and LEL in enclosed spaces where ozone/oxygen may collect such as crawl spaces and/or sewers. No flame ionized detectors (FID) or open flames may be used. Fire extinguishers (A/B) shall be suitably placed, distinctly marked, readily accessible, and maintained in a fully charged and operable condition.	
	Spills/Leaks	Establish evacuation route, assembly point, and emergency response prior to generating ozone. Close wellhead valves after sampling. Monitor ozone concentration in the work area breathing zone. Evacuate if ozone levels reach STEL at anytime. Check wind direction and re-evaluate assembly point in the event of a release. Remotely shutdown ozone generation equipment.	
	Mechanical hazards	Verify wellhead connections are secure to prevent well cap/head from becoming a projectile.	