

TOSC Review of “Work Plan Testing of In-situ Oxidation for the Treatment of 1,4-Dioxane at the Pall Life Sciences Facility”

By: Susan Masten, Ph.D.
Professor
Department of Civil and Environmental Engineering
Michigan State University
East Lansing, MI 48824

For: Technical Outreach Services for Communities (TOSC) Program
Michigan State University

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Inquiries should be directed to:

Kirk Riley, Program Manager
B-100A Research-Complex-Engineering
Michigan State University
East Lansing, MI 48824
(517) 355-7493
rileyki@egr.msu.edu



Review of
“Work Plan Testing of In-situ Oxidation
for the Treatment of 1,4-Dioxane at the Pall Life Sciences Facility”
(Dated October 17, 2003 by Pall Life Sciences, Inc.)

Introduction

At the request of Scio Residents for Safe Water, Ann Arbor, Michigan, officials, and other parties, the Technical Outreach Services Communities (TOSC) Program has conducted a review of a work plan submitted to the Michigan Department of Environmental Quality by Pall Life Sciences. The work plan is titled, “Work Plan Testing of In-situ Oxidation for the Treatment of 1,4-Dioxane at the Pall Life Sciences Facility.” See http://www.egr.msu.edu/tosc/gelman/PLS_In-Situ_Work_Plan_Oct_20031.pdf. Dr. Susan Masten, Professor of Environmental Engineering at Michigan State University, conducted the review for TOSC.

This Pall Life Sciences Work Plan outlines testing that will be accomplished to determine the efficacy of using ozone, hydrogen peroxide, and the combination of ozone/hydrogen peroxide (Peroxone) for the destruction of 1,4-dioxane. Pall Corporation plans to inject ozone or hydrogen peroxide or a combination of the two into confined aquifers contaminated with 1,4-dioxane. Ozone will be injected either as a gas or as an aqueous solution. Hydrogen peroxide will be injected as an aqueous solution.

Technology Background

Pall Corp. claims “the technology has the potential advantages of achieving rapid and complete treatment” (p. 1). However, they provide no basis for this statement nor do they provide any published data to support this claim. Although the Peroxone process has been used for the ex situ oxidation of 1,4-dioxane it has not, to my knowledge, ever been used in an in situ application for this purpose.

Pall Corp. claims that “ozone is a gas that is highly soluble in water” (p. 2). The solubility of ozone is approximately 3 times that of oxygen and is therefore considered to be moderately soluble in water. Although Pall Corp. claims that in situ ozonation could be achieved by injecting water containing ozone into the aquifer this technique is very likely to be highly ineffective due to the reactivity of ozone. The pH of the groundwater in the aquifer underlying Ann Arbor ranges from 6.5 to 7.6. The half-life of ozone in water having a pH of 7-8 is on the order of seconds. In order to stabilize ozone, one would need to dissolve ozone into water having a low pH (<3), which presents its own problems in terms of safety and acid handling. The resulting change in the pH of the groundwater may cause the solubilization of metals from aquifer materials.

What is TOSC?

The Technical Outreach Services for Communities (TOSC) program promotes community involvement in environmental decision-making through educational and technical assistance services, and is funded under a grant from the U.S. Environmental Protection Agency. TOSC is housed in the Midwest Hazardous Substance Research Center. Participating universities include Purdue University, Michigan State University, Kansas State University, and the Virginia Polytechnic Institute and State University.

TOSC program services seek to build community understanding of site contamination problems and empower citizens and local government to participate more effectively in the decision making process. TOSC faculty, working collaboratively with citizens, design educational workshops that address key questions and concerns. Additionally, TOSC reviews documents and provides professional guidance on site cleanup work.

The authors state that ozone would oxidize 1,4-dioxane to carbon dioxide, water and oxygen. The authors fail to provide any documentation to substantiate this statement, and it is known that ozone has a low reactivity with 1,4-dioxane¹. In addition, Pall claims that ozone breaks “hydrocarbon rings and chains... into smaller molecules that are highly susceptible to further oxidation by ozone”. Again, no references are provided to support this misleading and incorrect statement. Ozone is highly selective and will only react appreciably with chemicals that have double bonds or are aromatic in nature. The substitution of moieties onto the aromatic or double bond will greatly affect reactivity. For example, electron-donating groups, such as chlorine, result in a decrease in reactivity (chlorobenzene is less reactive with ozone than is benzene) where as the presence of an electron-withdrawing group such as a methyl group increases reactivity (toluene is more reactive with ozone than is benzene). The oxidation of hydrocarbons by ozone is rarely complete as documented by incomplete reduction in the COD of the water or wastewater². Work by Masten’s group (and numerous other research groups) has shown that the oxidation of some aromatic compounds can result in the accumulation of smaller molecular weight compounds. On page 2, Pall claims that the radical species (I presume they mean hydroxyl radicals) are more powerful oxidants than ozone. While this is true for hydroxyl radicals, hydroxyl radicals are less selective than ozone, and will react with many species, including soil organic matter, metals, carbonate and bicarbonate.

Stage A – H₂O₂

Pall Corp. states that “hydrogen peroxide is easily converted to hydroxyl free radicals which break down a variety of organic compounds”. Hydroxyl radicals ($\cdot\text{OH}$) often react with hydrocarbons via a hydrogen abstraction reaction. This reaction does not result in complete mineralization of the parent hydrocarbon. The statement that chemical oxidation using hydrogen peroxide essentially “steals” electrons from another compound is misleading because hydrogen peroxide can act as an oxidant and as a reductant. Chemical oxidation results in the reduction of the oxidant, it gains electrons and in the oxidation of the target compound, which loses electrons. However, while this explanation makes sense with metallic species, it is less useful with organic compounds since the traditional redox approach is less useful.

Pall Corp. (page 2) states that “because there is typically no oxidant in the deep soil pores and low permeability soil layers, there is a strong driving force concentration gradient) (*sic*) for the oxidant to diffuse into these locations where contaminants are sequestered and oxidize the contaminant”. This statement implies that Pall expects to rely on the diffusion of hydrogen peroxide through the aquifer to the contaminated area (assumably because the low hydraulic conductivity of the aquifer material precludes rapid advective transport). If this were the case, with an aqueous diffusivity³ of 0.0000102 cm²/sec, the injected hydrogen peroxide would likely be decomposed long before it ever diffused to the contaminant.

Pall Corp. (page 3) suggests that they will inject “less concentrations of hydrogen peroxide”. It is unclear to what they are comparing the hydrogen peroxide concentration. A concentration of 12% by weight is sufficiently high to achieve exothermic reactions should there be sufficient reactive material at the injection point. Hydrogen peroxide is to be injected in 1-gallon doses. No justification for this dose is given. In addition, Pall states that “it may be necessary to lower the natural pH of the groundwater to 6.5. No mention of how much sulfuric acid would be necessary to accomplish this (which could have been estimated based on the alkalinity of the groundwater). The safety issues related to the transport, storage, and handling of sulfuric acid are not discussed. It is unclear whether five days of testing will be sufficient to determine process efficacy.

¹ K Kosaka*, H Yamada**, S Matsui*** and K Shishida, The effects of the co-existing compounds on the decomposition of micropollutants using the ozone/hydrogen peroxide process, Water Science & Technology 42(7-8):353–361

² For example, see C.D. Adams, P.A. Scanlan, N.D. Secrist, Oxidation and biodegradability enhancement of 1,4-dioxane using hydrogen peroxide and ozone, Environ. Sci. Technol., 28(11):1812-1818.

³ http://risk.lsd.ornl.gov/cgi-bin/tox/TOX_9801

Pall states that compressed air will be used to pressurize the well after injection of hydrogen peroxide. The effect of the pressurization on hydraulic control is not discussed.

Groundwater Sampling

Pall states that they will monitor for hydraulic conductivity, oxidation reduction potential (ORP), dissolved oxygen (DO), temperature and specific conductance. Pall Corp. does not state if it will test for 1,4-dioxane. If not, how will the efficacy of treatment be assessed? Given the failed Chronic Toxicity Test (in effluent samples collected) in Fall 2002, it seems prudent to perform toxicity testing on all samples collected. A QA/QC plan is necessary and should have been submitted.

Stage B – O₃

The first paragraph in this section essentially repeats much of what was stated before. As such, the same concerns mentioned above carry over to this paragraph.

Ozone is to be applied into PVC piping. Unless the ozone-resistant piping is used, ozone is likely to react with the piping, resulting in, at a minimum, leaks in the piping and, possibly, the release of organic coatings on the PVC into the groundwater. As such, ozone-resistant materials need to be utilized. Again, in this study, compressed air is to be used. No mention is made as to what impact the compressed air will have on contaminant migration or hydraulic control or if saturation of ozone in water can be achieved using this treatment method.

Specific control measures to prevent the accidental release of ozone are not provided. A health and safety plan, documenting detailed safety procedures to ensure that ozone levels do not exceed OSHA PELs and STELs along with MDEQ requirements for air emissions of ozone is necessary.

It is unclear whether five days of testing will be sufficient to determine process efficacy.

Pall Corp. (page 10) provides limited results, suggesting the efficacy of ozone injection and the problems related to bromate formation. Bromate concentrations presented in Table 1 appear to be quite high, but since no concentration units are given, it is unclear if this assumption is correct.

Groundwater Sampling

Pall states that they will monitor for hydraulic conductivity, oxidation reduction potential (ORP), dissolved oxygen (DO), temperature and specific conductance. Pall Corp. does not state if it will test for 1,4-dioxane. Bromate concentrations should be measured. If 1,4-dioxane and bromate are not monitored, how will the efficacy of treatment be assessed? Given the failed Chronic Toxicity Test (in effluent samples collected) in Fall 2002, it seems prudent to perform toxicity testing on all samples collected. A QA/QC plan is necessary.

Stage C – O₃/H₂O₂

The first paragraph in this section essentially repeats much of what was stated before. As such, the same concerns mentioned above carry over to this paragraph.

Pall states that “hydroxyl radicals react very rapidly to oxidize organic contaminants to non-hazardous compounds carbon dioxide and water” (*sic*). While the first part of this statement is generally true, there is no indication that complete mineralization occurs, nor can the generalization that non-hazardous compounds be made. In fact, several studies by Masten’s group have shown that ozonation by-products of some aromatic compounds are more inhibitory to gap junction intercellular communication than the parent compound.

Pall states in this section that bromate will be measured during Stage B (no mention of bromate sampling is made during Stage B discussions). The mixing of hydrogen peroxide and ozone will be difficult to control during Stage C experiments, bromate should be measured during this stage as well as during Stage B.

It is unclear whether five days of testing will be sufficient to determine process efficacy.

Groundwater Sampling

Pall states that they will monitor for hydraulic conductivity, oxidation reduction potential (ORP), dissolved oxygen (DO), temperature and specific conductance. Pall Corp. does not state if it will test for 1,4-dioxane. Bromate concentrations should be measured. If 1,4-dioxane and bromate are not monitored, how will the efficacy of treatment be assessed? Given the failed Chronic Toxicity Test (in effluent samples collected) in Fall 2002, it seems prudent to perform toxicity testing on all samples collected. A QA/QC plan is necessary.