In situ Remediation of 1,4-Dioxane using Electrical Resistance Heating

Daniel Oberle, P.E.
Emily Crownover, Ph.D.

INTRODUCTION

An increasing number of states are establishing enforceable 1,4-dioxane cleanup goals due to recent improvements in analytical detection methods and existing carcinogenic risk information for 1,4-dioxane. Historically, 1,4-dioxane was used as a stabilizer for chlorinated solvents, primarily 1,1,1-trichloroethane. In addition, 1,4-dioxane has been used in a broad range of products including but not limited to paint, antifreeze, shampoos, cosmetics, aircraft deicing fluid, and fumigants. If released, 1,4-dioxane presents significant remediation challenges as it is highly mobile. Due to its high solubility, 1,4-dioxane will readily dissolve in groundwater. The low octanol-water partition coefficient causes the transport of any 1,4-dioxane in groundwater to be minimally slowed by sorption to soil particles or suspended sediments. In addition, a low Henry's Law constant suggests that transfer of 1,4-dioxane from water to air is negligible under ambient conditions. Furthermore, 1,4-dioxane is resistant to biodegradation by indigenous soil microorganisms. (Mohr, 2010)

The treatment of 1,4-dioxane has been reported with limited success. 1,4-dioxane has been shown to be resistant to treatment by conventional technologies including sparging, soil and vapor extraction, bioremediation, and select oxidation processes. Effective remedial treatment has been largely limited to expensive, predominantly *ex situ* treatment by advanced chemical oxidation using processes that produce hydroxyl radicals. (EPA, 2006) (DiGuiseppi W, 2007)

Electrical Resistance Heating (ERH) was conducted to treat tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), trichlorobenzene, xylenes, and Freon 113 at a site where 1,4-dioxane was also present. While not part of the treatment goals, 1,4-dioxane was detected prior to ERH treatment with a maximum concentration of 140 µg/L. In the course of successfully reducing concentrations of the contaminants of concern at this site, the concentration of 1,4-dioxane was also substantially reduced to 1.4 µg/L resulting in a 99.0% removal, as shown in Table 1. Furthermore, pre-ERH 1,4-dioxane concentrations were reduced in another monitoring well from 44 µg/L to non-detect. The minimum detection limit was 0.5 µg/L therefore greater than 98.9% reduction of 1,4-dioxane was achieved. *In situ* remediation of 1,4-dioxane to this degree had not been reported before, therefore further research and development efforts were conducted to further understand the substantial concentration reductions.

Table 1. Field Reductions of 1,4-Dioxane Concentrations by Monitoring Well

Monitoring Well	Sampling Depth (ft bgs)	Pre-ERH 1,4-Dioxane Concentration (µg/L)	Post-ERH 1,4-Dioxane Concentration (µg/L)	Percent Reduction
MW-1S	95	140	1.4	99.0%
MW-1D	117-122	44	Non-detect	>98.9%

PHASE I: WATER TESTING

Due in part to the relatively high boiling point of 1,4-dioxane and low Henry's Law constant under ambient conditions, 1,4-dioxane has been reported to be an inefficiently strippable compound. In the presence of water, the boiling point of 1,4-dioxane is depressed below its sea level boiling point of 101 °C. A positive azeotrope occurs at 82% mass 1,4-dioxane in water resulting in a maximum boiling point depression to 87.7 °C. At low part per million concentrations typical for a remediation site with 1,4-dioxane, the boiling point is depressed below the boiling point of water which is in a temperature range that can be treated by ERH. Henry's Law constant for 1,4-dioxane at 25 °C has been reported to be 0.0002 in dimensionless units. (Vainberg S, 2006) Prior testing has indicated that at the boiling point of water, 1,4-dioxane has a Henry's law constant of 0.01 in dimensionless units resulting in a 50 fold increase. (Stantec Corporation - Treatability Testing Services) During boiling, the mass fraction of 1,4-dioxane in the steam will be approximately 11 times greater than the mass fraction of 1,4-dioxane in the water from which it was boiled. (Scheider CH, 1943) As steaming continues, this will drive the concentrations of 1,4-dioxane into solution exponentially towards zero. This allows for effective remediation of 1,4-dioxane using the ERH technology.

Existing vapor-liquid equilibrium data for 1,4-dioxane in water have previously been reported for concentrations significantly higher than low part per million concentrations commonly observed at 1,4-dioxane remediation sites. A laboratory study was conducted to observe vapor-liquid equilibrium behavior of 1,4-dioxane in water at concentrations more relevant to the environmental remediation industry. A 1-L solution of 26 mg/L 1,4-dioxane solution was boiled on a hot plate in a sealed 2-L Erlenmeyer flask connected with 1/2-inch Teflon tubing to a sealed 1-L Erlenmeyer flask for condensate collection. During boiling, the resultant volatiles in this closed system were condensed by surrounding the Teflon tubing with ice. At four different time points, the liquid and condensate were sampled using the EPA Method 8260 with selective ion monitoring (SIM). Concentration results from this study are shown in Table 2.

Table 2. 1,4-Dioxane/Water System Vapor Liquid Equilibrium Data

Percent Water Boiled	Liquid 1,4-Dioxane Concentration (mg/L)	Percent Concentration Reduction	Condensate 1,4-Dioxane Concentration (mg/L)
0%	26.0	0%	230
13.2%	8.00	69.2%	36
39.5%	0.260	98.9%	3.4
65.8%	0.0160	99.94%	0.55
98.7%	0.00630	99.98%	0.62

A mass balance assessment was conducted that indicated sufficient precision between the total mass of 1,4-dioxane boiled in comparison to the total mass of 1,4-dioxane recovered in the condensate (relative percent difference in mass distribution analysis = 23.0%).

PHASE II: SOIL TESTING

Six 500-gram subset samples of soil containing 21.9% moisture were used to conduct the study. Based on this moisture content, each subset sample contained 390.5 grams of soil and 109.5 grams of water. One subset sample was immediately transferred into a 4-ounce sample jar to represent the starting 1,4-dioxane concentrations prior to any testing. Another subset was transferred to a 4-ounce sample jar for a loss on ignition (LOI) procedure to determine total organic carbon which was found to be 0.07%. Three subsets were heated in a covered petri dish with small holes in the cover to allow steam removal from the subsample. Upon confirmation of percent water boiled for each subset (20%, 45%, and 80%), the samples were transferred to 4-ounce sample jars and cooled. A fourth subset served as a control sample to evaluate any potential losses of 1,4-dioxane attributable to sample handling. The control subset was transferred to a petri dish using the same procedure as the heated subset samples. Rather than heating, the control was placed at room temperature for 10 minutes, the longest subset sample heating session. Analyses of 1,4-dioxane in the subset soil samples were conducted using the US EPA Method 8260B SIM. A summary of the results is shown in Table 3.

Table 3. Soil 1,4-Dioxane/Water Removal Data

Percent Water Boiled	1,4-Dioxane Concentration (mg/kg)	Percent Concentration Reduction
0%	5.4	0%
20%	0.67	87.6%
45%	<0.58	>89.3%
80%	<0.51	>90.6%

After 20% of the moisture was boiled from the soil, 1,4-dioxane concentrations were reduced by 87.6%. After 45% of the moisture was boiled from the soil, the 1,4-dioxane concentrations were below the minimum detection limit for the sampling procedure. Therefore, significantly higher reductions were likely achieved in the soil samples with 45% and 80% water boiled.

ENERGY DENSITY CALCULATIONS

Phase I and II test results were used to develop a percent removal curve for 1,4-dioxane as a function of energy density.

Phase I Water Testing Energy Density Calculations: The term “energy density” refers to the amount of energy required on a per volume basis to achieve a specific cleanup objective. To express the energy density value in terms of energy density per cubic yard of saturated soil, it was assumed that each cubic yard of saturated soil contains 150 gallons of water, thus requiring 370 kWh/yd^3 of latent heat energy to boil all of the water from the saturated soil. The Phase I test data used to tabulate energy density are shown below in Table 4. This does not include any retardation factors that may exist from organics in the soil and it does not account for the specific heat required to bring the system to boiling temperature, nor does it account for heat losses.

Table 4. Energy Density Calculation Data

1,4-Dioxane (mg/L)	Percent Concentration Reduction	Percent of Water Boiled	Pounds of Water Boiled	BTUs in Water Boiled	kWh in Water Boiled	Latent Energy Density (kWh/yd^3)
26	0%	0%	0	0	0	0
8	69.23%	13.2%	0.29	282	0.08	49
0.285	98.9%	39.5%	0.87	843	0.25	146
0.016	99.94%	65.8%	1.45	1404	0.41	243
0.0063	99.98%	98.7%	2.17	2106	0.62	364

Phase II Soil Testing Energy Density Calculations: A fully-saturated fine sand would typically have a density of approximately 119 lb/ft^3. Assuming 100% saturation, a cubic yard of fine sand contains approximately 1,900 pounds of soil and 1,300 pounds of water. To achieve 87.6% removal of 1,4-dioxane indicated by the soil subset data from 20% removal of soil moisture would equate to boiling 260 lbs of water from a cubic yard of saturated sand. The latent heat energy for each pound of water boiled from a sample is 0.28 kilowatt hours (kWh) per pound of water boiled. Therefore the energy density required to boil 20% of the moisture from a saturated sample would be 75 kWh (260 lbs x 0.28 kWh/lb).

For samples boiled more aggressively, 1,4-dioxane was removed to below minimum detection limits. Therefore, the starting data point and the sample with 87.6% removal of 1,4-dioxane were used to generate the energy density plot below in Figure 1 which is overlapped onto the energy density plot from the Phase I water study.

The data from both phases of the test indicate that a latent heat energy density of 75 kWh/yd^3 will provide a 90% removal efficiency for 1,4-dioxane and 150 kWh/yd^3 of latent heat energy is required to achieve a 99% removal of 1,4-dioxane. Assuming that 60 kWh/yd^3 of energy density are required to bring the system up to temperature (specific heat), the total required energy to achieve 99 percent removal (without heat loss) is estimated at 210 kWh/yd^3. Assuming that 35% of the energy input is transferred as heat to the surroundings by conductive and convective heat loss, the total estimated energy density to achieve a 99% reduction in 1,4-dioxane concentrations is estimated at 325 kWh/yd^3.

This model estimates that the cost for treatment of 1,4-dioxane will be between $150 and $300 per cubic yard, depending on the size and shape of the site and the degree of cleanup required. For comparison, the cost to treat a common ERH site will typically range from $150 to $250 per cubic yard. The overall cost for ERH remediation will vary depending on factors including but not limited to the size and depth of the treatment area and the percent reduction required for different contaminants.

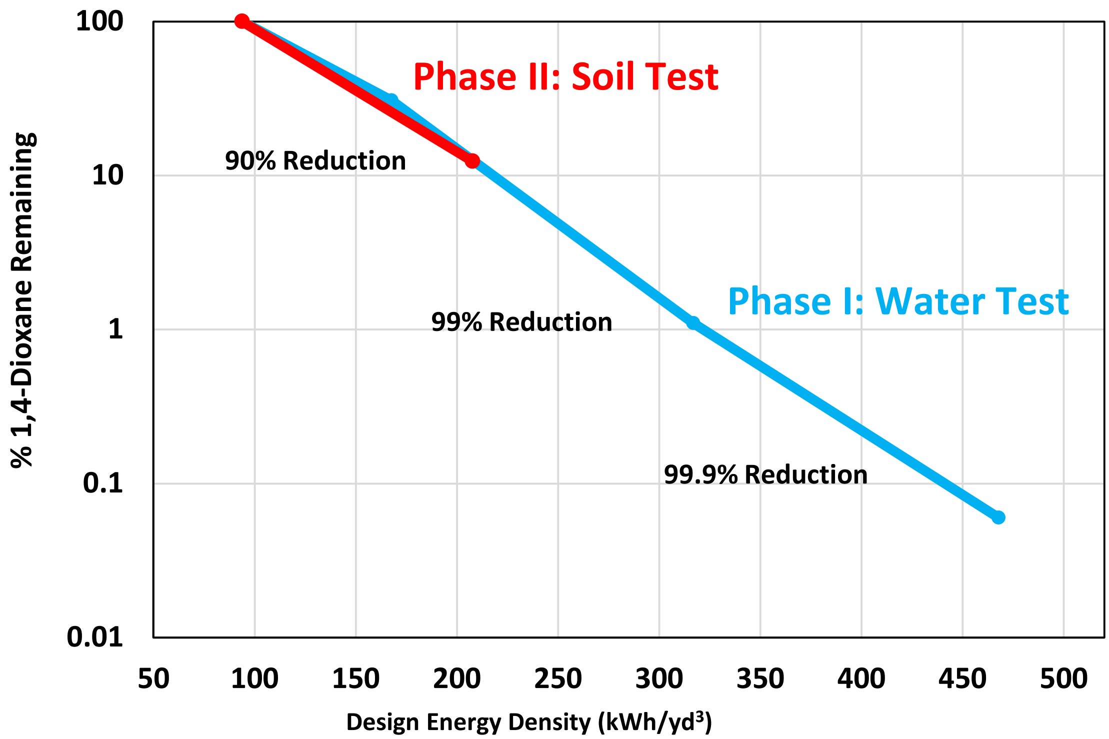

Figure 1. 1,4-Dioxane Energy Density Graph

ERH 1,4-DIOXANE TREATMENT

Recently, an ERH remediation was conducted at a site located on the west coast of the U.S. with a treatment depth of 30 ft bgs that contained TCE and TCA, as well as 1,4-dioxane. Prior to ERH, 1,4-dioxane concentrations ranged from 1,000 to 90,000 µg/L over all of the sampling locations with an average of 25,000 µg/L. Following 186 days of ERH operations, 1,4-dioxane concentrations at all sampling locations were reduced to less than 50 µg/L, resulting in a greater than 99.8% removal of 1,4-dioxane, as shown in Figure 2.

.

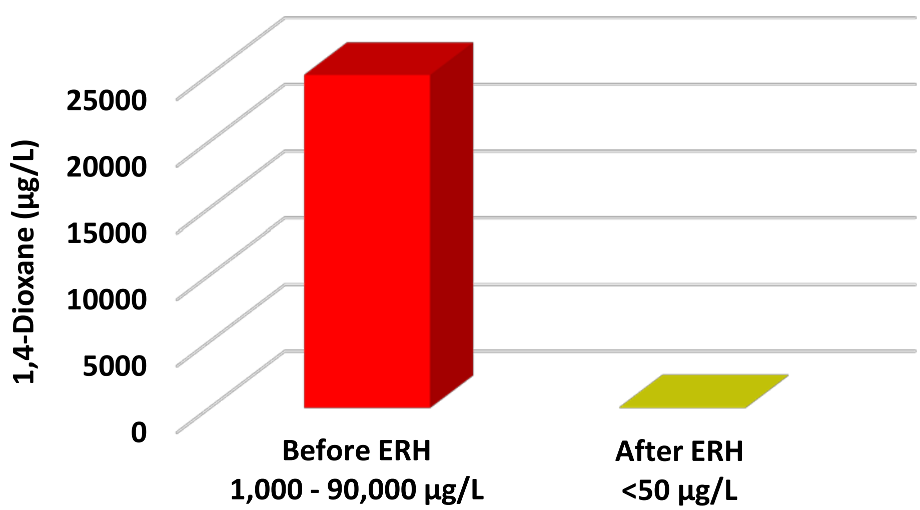

Figure 2. 1,4-Dioxane Concentrations Before and After ERH Remediation (99.8% removal)

An energy density of 175 kWh/yd^3 was applied to this site. Based on the field data at this site, the model shown in Figure 1 appears to overestimate the design energy density necessary to achieve a 99.9% reduction. The laboratory studies confirm that 1,4-dioxane is a strippable compound at elevated temperatures and low ppm concentrations, however, there may be another mechanism causing additional reduction of 1,4-dioxane concentrations in the field.

As heating occurred during the ERH remediation, the water vapor and volatilized contaminants were collected using a vapor recovery system with an extracted air flow rate and steam flow rate of 1500 scfm and 1000 scfm, respectively. The water vapor and volatilized contaminants entered the condenser where the water vapor was condensed and the volatilized contaminants were isolated for vapor treatment. The condenser outlet concentrations of 1,4-dioxane in both the condensed steam as well as the gas phase were measured and found to be 1600 ppb in the gas outlet and 94 µg/L in the condensate. This resulted in 0.12 lb/day in the gas phase and 0.006 lb/day in the condensed steam indicating that 95% of the dioxane remained in the vapor phase and only 5% in the condensate.

SUMMARY

Unprecedented *in situ* treatment of 1,4-dioxane using ERH has been observed in the field, resulting in a greater than 99.8% removal from the subsurface due to steam stripping. While 1,4-dioxane is resistant to conventional treatment methods, ERH is effective due to the substantial increase in Henry's Law constant at elevated temperatures and azeotropic behavior of 1,4-dioxane causing depression of its boiling point in the presence of water. Significant levels of 1,4-dioxane transition to the vapor phase at temperatures approaching the boiling point of water and as steaming occurs in an ERH remediation, concentrations of 1,4-dioxane in solution will be driven exponentially towards zero. The data from the Phase I water testing and Phase II soil testing both indicate that a latent heat energy density of 75 kWh/yd^3 will provide a 90% removal efficiency for 1,4-dioxane and 150 kWh/yd^3 of latent heat energy is required to achieve a 99% removal of 1,4-dioxane. The model developed with the data collected estimates that the cost for treatment of 1,4-dioxane will range from $150 to $300 per cubic yard.

REFERENCES

DiGuiseppi W, W. C. (2007). Treatment Options for Remediation of 1,4-Dioxane in Groundwater. *Environmental Engineer: Applied Research and Practice*, 1-7.

EPA. (2006). *Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications.* Washington D.C.: Office of Solid Waste and Emergency Response.

Mohr, T. K. (2010). *Environmental Investigation and Remedation 1,4-Dioxane and Other Solvent Stabilizers.* Boca Raton, FL: CRC Press.

Scheider CH, L. C. (1943). The Ternary System Dioxane-Ethanol-Water. *Journal of the American Chemical Society*, 1063-1066.

Stantec Corporation - Treatability Testing Services (2013). *Personal communications with Dr. Angus McGrath and David Schroder regarding in-house testing and research performed in 2007.*

Vainberg S, M. K. (2006). Biodegradation of Ether Pollutants by Pseudonocardia sp. Strain ENV478. *Applied and Environmental Microbiology*, 5218-5224.

Daniel Oberle, P.E. is Vice President of Engineering for TRS Group, Inc.
doberle@thermalrs.com

Emily Crownover is Research and Development Engineer for TRS Group, Inc.
ecrownover@thermalrs.com