

June 2010

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Recommended Citation

Kiker, Jackson H.; Connolly, James B.; Murray, Willard A.; Pearson, Stuart C. Pearson; Reed, Stanley E. Reed; and Tess, Robert J. (2010) "Ex-Situ Wellhead Treatment of 1,4-Dioxane Using Fenton's Reagent," *Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy*: Vol. 15 , Article 18.

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Chapter 17

EX-SITU WELLHEAD TREATMENT OF 1,4-DIOXANE USING FENTON'S REAGENT

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ABSTRACT

At the U.S. Army Natick Soldier System Center (NSSC) in Natick, Massachusetts, groundwater is being pumped and treated to provide containment of a historical trichloroethene (TCE) plume. Upon discovering 1,4-dioxane (an emerging contaminant not previously monitored) at one of the monitoring wells above the Massachusetts Department of Environmental Protection drinking water goal of 3 µg/L, the existing on-site groundwater treatment system required augmentation to continue maintaining plume containment and meeting allowable discharge limits. Existing treatment consists of air-stripping and granular activated carbon, which both have a low efficiency for treating 1,4-dioxane. The concentration of 1,4-dioxane in the TCE plume requiring treatment is less than 100 micrograms per liter (µg/L) and approximately 10 to 20 µg/L in the 4 to 6 gallon per minute (gpm) combined discharge stream from three new extraction wells. Because 1,4-dioxane was only identified in a isolated portion of the TCE plume and not in the 75 to 90 gpm flow to the existing treatment system from this TCE plume and others, a goal was to provide in-situ or wellhead treatment for the 1,4-dioxane and not to treat the 75 to 90 gpm flow.

An engineering study was conducted to evaluate 1,4-dioxane and TCE treatment options, with key considerations being that 1,4-dioxane was detected at a low concentration, the extracted water was high in total suspended solids (TSS) and iron oxides, flow-rates needed for containment were small (< 6 gpm), 1,4-dioxane was highly localized, and the size of the physical plant had to be small. Viable options that were considered included the following Advanced Oxidation

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Processes (AOPs): Fenton's Reagent, hydrogen peroxide with ultraviolet (UV) light, hydrogen peroxide with ozone, and catalyzed persulfate.

Based on the engineering study, ex-situ application of Fenton's Reagent was selected as a practical cost-effective solution. Bench-scale jar testing demonstrated that naturally occurring iron found in the water was sufficient to provide the metal catalyst needed for the Fenton's reaction, and that stoichiometrically over-dosing hydrogen peroxide would decrease treatment residence-time necessary for achieving remediation goals and compensate for hydrogen peroxide dissipating side-competition reactions.

Keywords: advanced oxidation process (AOP), groundwater, 1,4-dioxane, trichloroethene (TCE), Fenton's reagent, hydrogen peroxide, and wellhead.

1. INTRODUCTION

Granulated activated carbon (GAC) and air-stripping (AS) treatment of groundwater extracted to provide containment of trichloroethene (TCE) and tetrachloroethene (PCE) plumes has been part of the on-going environmental restoration of the aquifer at the US Army Natick Soldier Systems Center (NSSC) in Natick, MA, since 1977. In 2005, with the concern over emerging contaminant 1,4-dioxane being discovered in chlorinated solvent plumes across the nation, a select group of NSSC long term monitoring program (LTMP) wells were sampled for 1,4-dioxane. The 1,4-dioxane sampling showed that 1,4-dioxane, an EPA group B2 probable human carcinogen, was present consistently in one monitoring well (MW-124B) and detected sporadically at other monitoring wells, and the 1,4-dioxane was co-mingled with TCE in the groundwater of Area of Concern (AOC) Buildings (Bldg) 63, 2, & 45.

Because NSSC is in a groundwater protection Zone 2 (that area of an aquifer which contributes water to a drinking water well under the most severe pumping and recharge conditions that can be realistically anticipated) with the underlying aquifer being considered GW-1 (i.e. drinking water aquifer), the chosen remedial action operation at this AOC was containment of the groundwater plume, which now included as a new requirement the containment of the 1,4-dioxane contaminated groundwater. Groundwater containment at the AOC was to be achieved by connecting the AOC extraction wells to the existing groundwater extraction and treatment system (GWETS), which treats influent from extraction wells that contain two other TCE/PCE groundwater plumes. The GWETS treatment train technology consists of GAC and AS both of which are known to have low efficiencies for removing 1,4-dioxane, because 1,4-dioxane has a low

octanol/water partition coefficient (0.537) and a low Henry's Law constant (4.88×10^{-6} atm m³/mol) (Howard 1990).

Therefore neither of these technologies individually or in combination could achieve 1,4-dioxane removal from the extracted groundwater sufficiently to meet the GWETS 1,4-dioxane discharge limit (3 µg/L). The extent of 1,4-dioxane groundwater contamination is limited to the distal end of the previously characterized AOC 63, 2, & 45 TCE plume and is only detected in one extraction well, so wellhead treatment of 1,4-dioxane was to be performed instead of reconfiguring the GWETS treatment train, which treats influent water (90 gallons per minute [gpm]) from the other plumes, which have no 1,4-dioxane contamination.

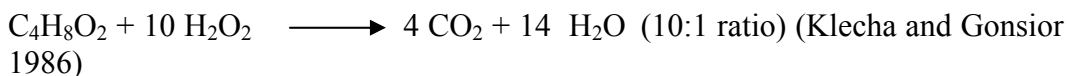
An engineering feasibility and cost analysis study was performed to determine the optimum well-head treatment method. The key criteria for the basis of selection were the ability to treat by destruction co-mingled TCE and 1,4-dioxane found in the AOC 63, 2 & 45 plume with 1,4-dioxane levels ranging from 150 µg/L, the maximum historical detection, to 6 µg/L, the historical minimum detected in the groundwater. The 1,4-dioxane detections have shown a steady decrease since 2005, so there does not appear to be a steady source, which also factored into the need for a small and portable well-head treatment unit that could be moved or readily demobilized. 1,4-dioxane is a known solvent stabilizer in 1,1,1 trichloroethane (TCA); however, TCA has not been detected in groundwater at levels sufficient to be the cause for 1,4-dioxane detection. To achieve the remedial action objective of groundwater containment, an extraction flow-rate of less than 6 gpm was required. The typical groundwater extracted from this plume was high in turbidity and typically a translucent beige color from iron oxides.

Advanced oxidation processes (AOP), involving the generation of a free radical, were evaluated. The suspended solids and iron content made the ultraviolet (UV)/hydrogen peroxide AOP treatment impractical due to attenuation of the incident UV radiation and the need to constantly clean the UV lamps. Hydrogen peroxide with ozone was considered but this AOP uses proprietary reaction chambers, which are more cost effective for higher flow rate conditions and a permanent setting. Catalyzed persulfate treatment might have added sulfur compounds to the GWETS effluent, and some of the effluent is used for non-potable water purposes. Fenton's reagent was selected as the wellhead treatment technology based upon the demonstrated ability to destroy 1,4-dioxane and TCE under controlled reaction conditions with sufficient residence time and because of its relatively low-cost. Fenton's reagent is not a proprietary mixture and can be formulated from commercially available bulk reagents, which can be administered without a complex reaction chamber. Further, the main ingredient in Fenton's reagent hydrogen peroxide (H₂O₂) is consumed or breaks down to yield water.

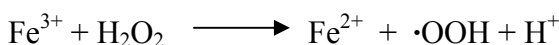
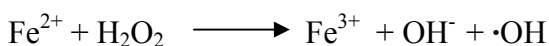
1.1 Fenton's Reagent

Fenton's Reagent; Hydrogen peroxide in the presence of an iron catalyst yields strong oxidizing agents capable of 1,4-dioxane mineralization.

1.1.1 1,4-Dioxane Mineralization (Theoretical)



Fenton's reagent catalytic reaction sequence involving iron that forms hydroxyl radical ($\cdot\text{OH}$), which is one of the strongest oxidizing agents;



1.1.2 Prerequisite Conditions for Fenton's Reagent:

- Iron: Ferrous or ferric iron (US Peroxide 2009).
- pH range (3-5 Standard Units [SU]): This serves to dissolve iron making it available in solution as a catalyst that is not consumed in the reaction, but creates hydroxyl radicals from the hydrogen peroxide.
- Residence Time: Fenton's reagent as a function of concentration and reaction conditions will require a minimum contact time with 1,4-dioxane for removal.

Other AOPs utilize ozone or UV-light to create the hydroxyl radical, and these types of AOPs have been used successfully for ex-situ treatment of groundwater at several locations. According to an United States Environmental Protection Agency (USEPA 2006) literature survey, there were no sites where Fenton's reagent was used for ex-situ 1,4-dioxane treatment. The purpose of this paper is to describe how bench scale jar testing using Fenton's reagent led to a full-scale implementation of Fenton's reagent to successfully treat ex-situ TCE and 1,4-dioxane contaminated groundwater at the wellhead.

2. MATERIALS AND METHODS

2.1 Materials

Thirty-five percent hydrogen peroxide (H_2O_2), ferrous sulfate ($\text{FeSO}_4\cdot\text{H}_2\text{OX}$), ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3\cdot\text{H}_2\text{OX}$), and sodium sulfite (Na_2SO_3) were obtained from Afla Aesar and were reagent grade. Concentrated hydrochloric acid was technical

grade. Various hydrogen peroxide solutions were prepared by dilution of 35% hydrogen peroxide by de-ionized (DI) water. Iron catalyst solutions were prepared using ferrous sulfate or ferric chloride solutions prepared by dissolving 7.9 grams of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ or 2.9 grams of $(\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O})$ solids respectively into 1-liter of DI water. Sodium sulfite, Fenton's reagent quenching reagent, was prepared by dissolving 75.6 grams of Na_2SO_3 solid into 1-L of DI water. 1,4-dioxane solutions were collected from NSSC groundwater monitoring (MW-124B) or extractions well (EW-3) by using low-flow sampling techniques (USEPA 1996) to obtain representative groundwater samples for the jar-testing. 1,4-dioxane concentrations in groundwater were determined by off-site laboratory analysis. Site groundwater solutions typically contain TCE and PCE as determined by 16 years of groundwater monitoring in addition to levels of 1,4-dioxane ranging from 6 $\mu\text{g/L}$ to 150 $\mu\text{g/L}$ collected from MW-124B and EW-3.

2.2 Analytical Methods

Aqueous 1,4-dioxane jar-testing sample aliquots were analyzed by Accutest Laboratory in Marlborough, Massachusetts, a Department of Defense Quality System Manual certified laboratory using EPA Region I 1,4-dioxane analysis method EIASOP-VOADIOXI (USEPA 2003), as modified to use selective ion monitoring (SIM), at $m/z = 88$ (parent ion) and $m/z = 58$ (secondary ion), to increase quantitative sensitivity. This method uses a heated purge block (EPA Method 5035) to increase the quantitative extraction efficiency, which yields a typical calibration response factor of 0.020. The method detection limit (MDL) was 0.18 $\mu\text{g/L}$ with a calibration range from 1.0 $\mu\text{g/L}$ to 100 $\mu\text{g/L}$.

EM Quant peroxide test strip papers used to check the hydrogen peroxide levels during testing had a range of 0 to 25 mg/L and were obtained from EMD Chemicals Inc. (stock no. 10011-1).

YSI Inc. pH probe was calibrated using standard stock calibration solutions of pH 4 SU, pH 7 SU, and pH 10 SU.

2.3 Experimental Apparatus

Open topped 500-ml Kimax beakers were used as reaction vessels in the bench scale jar-testing and filled to a volume of 250 ml with the NSSC groundwater and dosed with amendments for the various trials. Intermittent mechanical stirring with was provided by using a glass rod.

2.4 Experimental Procedure

1,4-dioxane contaminated groundwater representative of the site condition to be treated was obtained from MW-124B or EW-3 at NSSC, as MW-124B represents a worse case scenario and EW-3 represents typical wellhead treatment plant (WTP) influent. Collected groundwater was stored with headspace in a 5-gallon carboy pending treatment trials. Groundwater used for all trials was acidified by the addition of 35% HCl until the pH was in the optimum acidity range for Fenton's reagent (3.0 to 5.0 SU) to be tested, as determined by a YSI pH probe monitoring the pH adjustment. The pH adjusted water was then divided into equal aliquots of 250-ml and placed into 500 ml open top beakers at atmospheric pressure and room temperature (ca. 25 °C). Either ferrous iron or ferric iron was spiked at the experimental trial levels and then hydrogen peroxide at concentrations ranging from 2.0 mg/L to 12,000 mg/L was added. Once hydrogen peroxide was added all of the conditions necessary for Fenton's reagent chemistry to yield hydroxyl radicals were present (low pH, dissolved ferric or ferrous ion, and hydrogen peroxide). Intermittent stirring was provided for all trials. Beakers were left open-topped and not temperature controlled. Initial reaction temperature was typically <20 °C, which is slightly above ambient groundwater temperature, as determined during the acidification step by the YSI probe. Residence time of the reaction was measured from the time hydrogen peroxide was added to the reaction beaker and ended upon collection of a sample aliquot. Reaction conditions were slowed for select sample aliquots by refrigeration (<6°C). For other sample aliquots the Fenton's reagent conditions were quenched by the addition of a sodium sulfite solution. Sample aliquots were collected by pouring the reaction vessel contents into an unpreserved (i.e no HCl) 40-ml volatile organic compound (VOC) sample vial with Teflon septum and leaving no headspace. Collected sample aliquots were stored at <6 °C pending analysis at the contract laboratory.

3. RESULTS AND DISCUSSION

Several experimental trials (A–D) were conducted to determine the applicability of using Fenton's reagent for remediation of 1,4-dioxane, and the optimal dosing levels of iron catalyst, acid, and hydrogen peroxide for remediation of 1,4-dioxane contaminated groundwater at NSSC.

3.1 Trial A Applicability of Fenton's Reagent to 1,4-Dioxane Remediation

Trial A: Objective was to establish the applicability of Fenton's reagent for removal of 1,4-dioxane from NSSC groundwater by dosing hydrogen peroxide at

concentrations ranging from 2 mg/L to 12,000 mg/L, which correspond approximately to 250% to 1,500,000% of the 10:1 stoichiometric ratio of hydrogen peroxide to 1,4-dioxane, see Figure 1 and Figure 2. An additional objective was to determine if longer residence times would remove 1,4-dioxane using lower hydrogen peroxide dosing levels, from 2 mg/L to 8 mg/L, which correspond to approximately 250% to 1,000% of the 10:1 stoichiometric ratio of hydrogen peroxide/1,4-dioxane, see Figure 3. Trial A conditions are provided in Table 1.

Table 1. Trial A Fenton's Reagent Experimental Conditions

Iron Species	Iron Catalyst Level (mg/L)	Residence Time (hours)	pH Levels	Initial 1,4-dioxane Level (µg/L)
Fe(II)	60	5, 24	3.1, 4.35, 6.07	30.1

Untreated groundwater from MW-124B had a slight translucent beige color typical of the ambient groundwater. Upon addition of Fenton's reagent at all pH values, the acidified solution color changed from clear to a characteristic ferric oxide red-orange color with the tint proportional to the hydrogen peroxide level dosed, and the 1,200 mg/L and 12,000 mg/L hydrogen peroxide dosed beakers yielded the most intense color change, which indicated that the Fenton's reaction was producing ferric iron species. After 1.5 hours of the 5-hour residence time elapsed, the hydrogen peroxide levels were determined using hydrogen peroxide test strips. All beakers dosed with less than 10 mg/L hydrogen peroxide were non-detect for hydrogen peroxide, and beakers dosed with 1,200 mg/L and 12,000 mg/L hydrogen peroxide had residual hydrogen peroxide in excess of 25 ppm (test strip maximum detection limit). Dosing hydrogen peroxide at levels <10 ppm did not yield sufficient 1,4-dioxane removal at 5 hours, and 1,4-dioxane removal measured after 24 hours, with similar hydrogen peroxide dosing levels, did not yield significant differences compared to 5-hours, see Figures 1 and 2. This suggests that 1,4-dioxane removal using Fenton's reagent occurs in a much shorter time-span for this media, and a longer residence time does not increase removal efficiency, most likely because the relatively lower levels of dosed hydrogen peroxide has been consumed. hydrogen peroxide dosed at 12,000 mg/L (1.2%) at pH 4.35 SU and at 1,200 mg/L (0.12%) at pH 3.2 SU resulted in complete 1,4-dioxane removal, and hydrogen peroxide doses at 12,000 mg/L at pH 3.2 had produced a 97% 1,4-dioxane reduction, see Figure 3, which demonstrated the applicability of Fenton's reagent to remove 1,4-dioxane from NSSC groundwater.

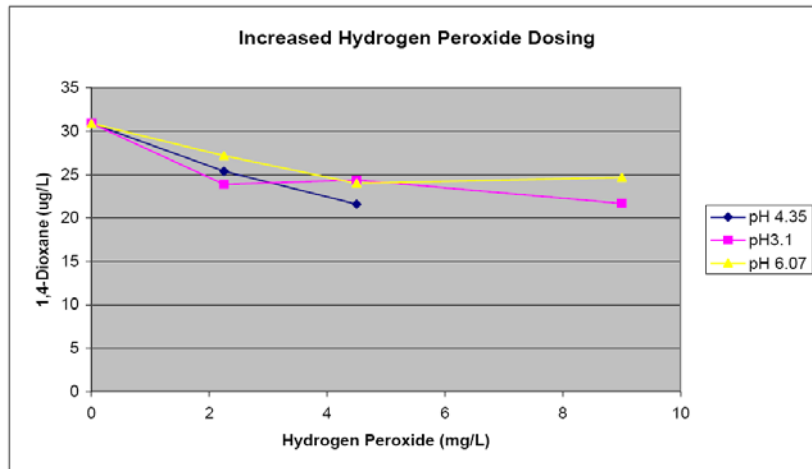


Figure 1. Removal of 1,4-dioxane from MW-124B groundwater treated ex-situ with Fenton's reagent at various pH levels (3.1, 4.35, and 6.07 SU) and hydrogen peroxide dosed at 2 mg/L, 4 mg/L, and 8 mg/L with dissolved ferrous iron (60 mg/L) and a 5-hour residence time.

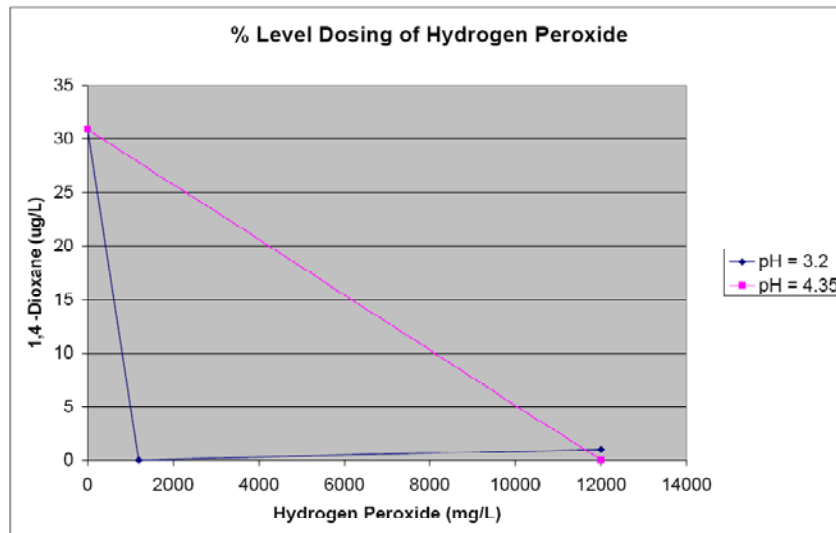


Figure 2. Removal of 1,4-dioxane from MW-124B groundwater treated ex-situ with Fenton's reagent at various pH levels (3.1 and 4.35 SU) and hydrogen peroxide dosed at 1,200 mg/L and 12,000 mg/L with dissolved ferrous iron (60 mg/L) and a 5-hour residence time.

3.2 Trial B Optimize Hydrogen Peroxide Dosing Level and Minimize Residence Time for 1,4-Dioxane Remediation

Trial B: Objective was to minimize hydrogen peroxide dosing levels and residence time needed for removal of 1,4-dioxane from NSSC MW-124B groundwater by dosing hydrogen peroxide at concentrations of 90 mg/L, 45 mg/L, 22.5 mg/L, 11.25 mg/L, 5.6 mg/L, and 2.8 mg/L, which correspond to

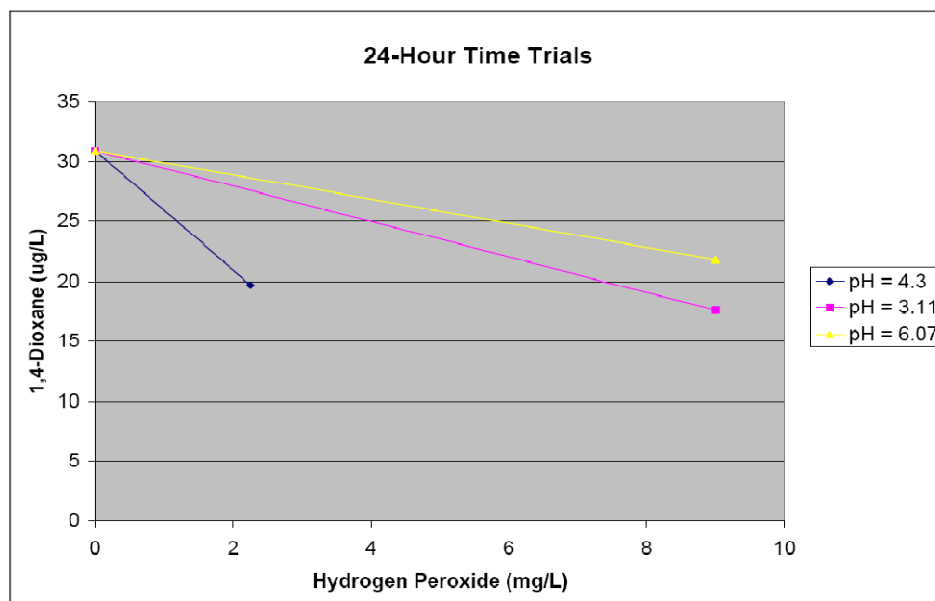


Figure 3. Removal of 1,4-dioxane from MW-124B groundwater treated ex-situ with Fenton's reagent at various pH levels (3.1, 4.35, and 6.07 SU) and hydrogen peroxide dosed at 2 mg/L and 8 mg/L with dissolved ferrous iron (60 mg/L) and a 24-hour residence time.

approximately 11,250% to 350% of the 10:1 stoichiometric ratio of hydrogen peroxide to 1,4-dioxane. Hydrogen peroxide removal as a function of residence time was conducted by dosing hydrogen peroxide concentrations of 90 mg/L, 45 mg/L, and 22.5 mg/L and taking sample aliquots every hour over a 5-hour duration, see Figure 4. The functional dependence of 1,4-dioxane removal at a 3-hour residence time for varying concentrations (90 mg/L to 2.8 mg/L) of dosed hydrogen peroxide is shown in Figure 5. Trial B conditions are provided in Table 2. For these trials the hydrogen peroxide was determined as a function of time using hydrogen peroxide test strips, see Table 3.

Table 2. Trial B Fenton’s Reagent Experimental Conditions

Iron Species	Iron Catalyst Level (mg/L)	Residence Time (hours)	pH Levels	Initial 1,4-dioxane Level (µg/L)
Fe(II)	60	1, 2, 3, 4, 5	ca. 3.2	35

Table 3. H₂O₂ levels as a Function of Initial Hydrogen Peroxide Dosing and Elapsed Residence Time

Initial H ₂ O ₂ Dose (mg/L)	Elapsed Residence Time		
	H ₂ O ₂ levels at <1 Hour	H ₂ O ₂ levels at 1.5 Hours	H ₂ O ₂ levels at 2.5 Hours
90	>25 mg/L	>25 mg/L	>25 mg/L
45	> 10 mg/L	>10 mg/L	>5 mg/L
22.5	>2 mg/L	>2 mg/L	2 mg/L
11.25	0 mg/L	0 mg/L	0 mg/L
5.6	0 mg/L	0 mg/L	0 mg/L
2.8	0 mg/L	0 mg/L	0 mg/L

As in Trial A, untreated groundwater from MW-124B for Trial B had a slight translucent beige color typical of the ambient groundwater. Dosing hydrogen peroxide at 90 µg/L resulted in a relatively darker red-orange solution than lesser dosing levels as a function of hydrogen peroxide dosing, and as a function of time the solutions became less opaque to translucent, especially for relatively low-level hydrogen peroxide doses (2.8 mg/L). This change in color intensity with hydrogen peroxide dose and time corresponds to the hydrogen peroxide levels measured in the various reaction beakers, as the hydrogen peroxide levels decreased the color intensity decreased markedly for the reaction beaker dosed with 2.8 mg/L hydrogen peroxide. As shown in Figure 4 for hydrogen peroxide dosed between 22.5 mg/L to 90 mg/L, 1,4-dioxane removal is complete in 1-hour with residual unreacted hydrogen peroxide in excess of 2 to 25 mg/L respectively, which suggest that a 1-hour resident time is adequate for 1,4-dioxane removal under these conditions. The concentration dependence of 1,4-dioxane removal at a 3-hour residence time shows that 11.25 mg/L hydrogen peroxide, see Figure 5, is approaching the threshold of minimum hydrogen peroxide dosing needed for complete 1,4-dioxane removal. At <1 hour the hydrogen peroxide levels in the reaction beaker dosed with 11.25 mg/L hydrogen peroxide is 0 mg/L and 1,4-dioxane was completely removed, which demonstrates that hydrogen peroxide

was not rate limiting at this dosing level and the Fenton’s reagent had adequate residence time for reaction completion.

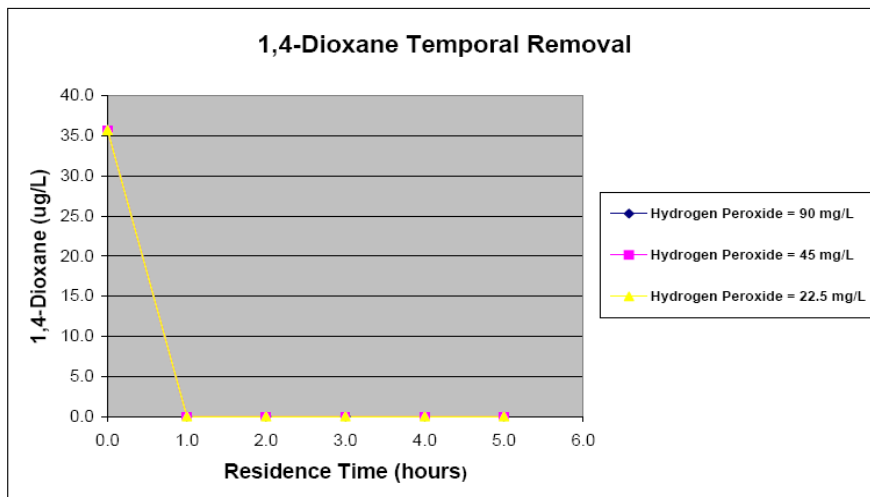


Figure 4. Removal of 1,4-dioxane as a function of time from MW-124B groundwater treated ex-situ with Fenton’s reagent at pH 3.2 and hydrogen peroxide dosed at 22.5 mg/L, 45 mg/L, and 90 mg/L with dissolved ferrous iron (60 mg/L) and sample aliquots collected every hour for a 5-hour elapsed residence time.

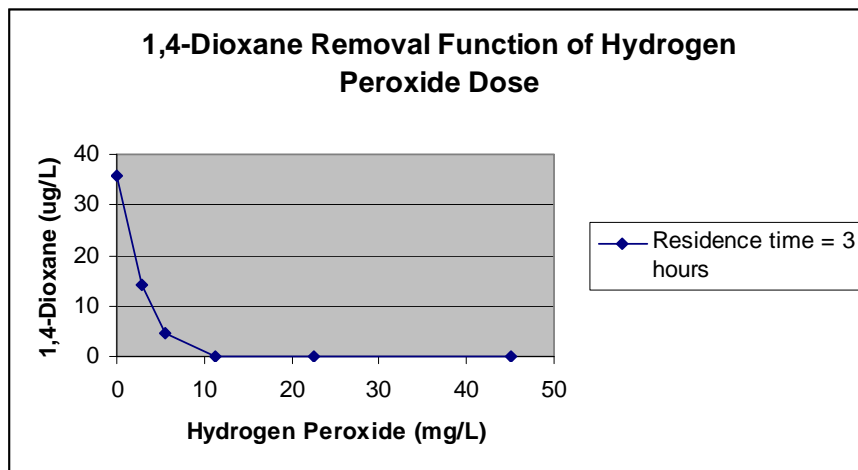


Figure 5. Removal of 1,4-dioxane from MW-124B groundwater treated ex-situ with Fenton’s reagent at pH 3.2, and dissolved ferrous iron (60 mg/L) at a 3-hour residence time as a function of initial hydrogen peroxide dose.

3.3 Trial C Acidification Requirements and Acid Neutralization Evaluation

Trial C: Objective was to determine quantitatively the amount of acid required to lower the ambient NSSC Groundwater from EW-3 to pH 3.1, which is suitable for Fenton’s reagent chemistry to remove 1,4-dioxane and determine the amount of base needed to restore the pH after treatment. Wellhead influent water from EW-3 was obtained and titrated with HCl to determine a typical dosing rate, which was determined to be approximately 3.17 gallons/day (gpd). Base titrations of EW-3 groundwater treated by Fenton’s reagent (pH 3.1, hydrogen peroxide dose 45 mg/L, and 60 mg/L ferrous iron) showed that raising the pH by addition of 0.01 N sodium hydroxide would not be cost-effective.

The effluent from the WTP is transported to the GWETs in a pipeline shared by 4 other extraction wells and then combined in a header with groundwater from 3 additional extraction wells. The natural acid buffering capacity of all of this water was tested to determine if it was adequate to raise the WTP effluent pH, see Table 4.

Table 4. Demonstrated Groundwater Buffering Capacity to Raise Post Fenton’s Reagent Wellhead Treatment Plant Effluent

NSSC EW-3 Groundwater	Fenton’s Reagent pH Adjustment	Fenton’s Reagent Effluent pH	Buffering by 4 Additional Extraction Wells	Buffering by All Extraction Wells
6.67 SU	3.1 SU	2.91 SU	4.8 SU	5.7 SU

By combining the WTP effluent with the all other extracted NSSC groundwater en-route to the GWETS for treatment and discharge, the natural buffering capacity of additional extracted groundwater is utilized resulting in raising the post Fenton’s reagent pH to an acceptable level.

3.4 Trial D Optimize Iron Catalyst Dosing Levels for 1,4-Dioxane Remediation

Trial D: Objective was to determine the optimum ferrous or ferric iron dosing level required to provide the catalyst needed by Fenton’s reagent to remove 1,4-dioxane from EW-3 groundwater. Iron dosing trials were conducted at pH 3.1 SU with a 22.5 mg/L hydrogen peroxide dose and a 1-hour residence time, see Table 5.

Table 5. Trial D Dependence of 1,4-Dioxane Removal on Iron Dosing Concentration and Iron Species

Iron Species Dosed	Added Iron Catalyst Level (mg/L)	Post Treatment 1,4-dioxane Level (µg/L)
Fe(II)	30	0
Fe(II)	15	0
Fe(II)	10	0
Fe(II)	2.5	0
Fe(III)	30	0
Fe(III)	15	0
Fe(III)	10	0
Fe(III)	2.5	0
No Iron Dosed	0	0

All iron dosing trials had complete removal of 1,4-dioxane, but most significantly the trial without any iron dosing also had complete 1,4-dioxane removal. The groundwater in the vicinity of MW-124B and EW-3 contains sufficient iron, most likely ferric iron due to the beige color of the groundwater and high oxidation reduction potential, to provide sufficient iron catalyst for Fenton's reagent without the need for additional dosing. The source of this iron is attributed to the aquifer geology of silty sands.

3.5 1,4-Dioxane Wellhead Treatment Plant

The 1,4-dioxane WTP consists of the following components, as illustrated on Figure 6:

1. WTP Spill Containment Features
2. pH Adjustment Tank
3. Hydrochloric acid feed line to pH adjustment tank
4. Fenton's Reagent Reaction Tank
5. Hydrogen peroxide and iron sulfate feed lines to Fenton's Reagent Reaction Tank
6. Discharge pump to convey water from the WTP to the GWETS

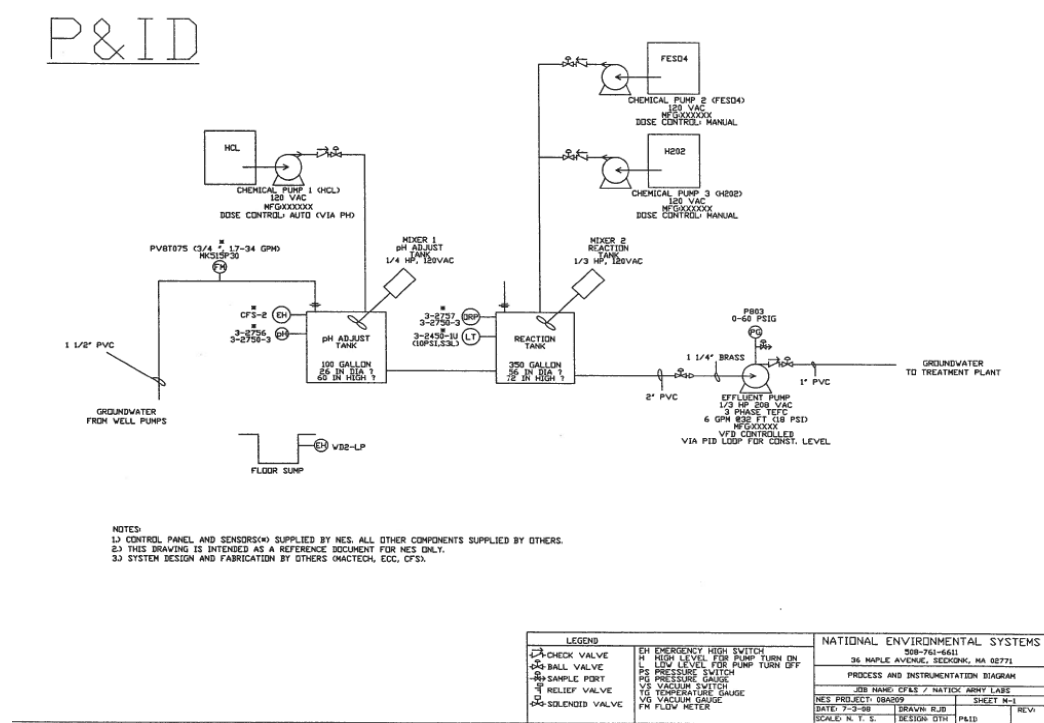


Figure 6. Wellhead Treatment Plant System Components.

3.5.1 1,4-Dioxane Wellhead Treatment Plant Spill Containment Features

The 1,4-dioxane WTP building was constructed to provide secondary spill containment in the event of a plumbing or component leakage and for weather protection. The WTP is housed in a wooden shed equipped with two heaters and a corrosion-resistant exhaust fan. Drums of chemicals are stored on polyethylene spill pallets. The pH Adjustment Tank and Fenton’s Reagent Reaction Tank are placed within a polyethylene spill containment system, and the floor of the shed is lined with rubber matting. There is a floor sump, within the spill containment system for the pH Adjustment Tank and Fenton’s Reagent Reaction Tank, equipped with a high water level indicator. If the high water level indicator is activated, the WTP will shut down and the system’s telemetry module telephones the on-call WTP operator for notification.

3.5.2 pH Adjustment Tank

Combined groundwater pumped from extraction wells EW-2, EW-3, and EW-4 enters the WTP and is directed to a 100-gallon polyethylene pH Adjustment Tank, where HCl is dosed into the tank via a chemical metering pump. Flow entering the pH Adjustment Tank is monitored by a paddle-wheel flow sensor. When flow

is less than 1-gpm, a low-flow alarm is triggered and the WTP is shut down. A pH probe mounted in the pH Adjustment Tank controls the amount of HCl added by the metering pump in order to maintain a pH of approximately 3.5. Contents of the tank are mixed with a clamp mount mixer. The pH Adjustment Tank has approximately a 20-minute retention time, and it ensures a consistent flow rate and water quality to the Fenton's Reagent Reaction Tank. Water flows via a gravity overflow to the Fenton's Reagent Reaction Tank.

3.5.3 Hydrochloric Acid Feed Line to pH Adjustment Tank

A chemical metering pump feeds HCl from a 55-gallon drum to the pH Adjustment Tank. The speed of the pump is controlled by a pH sensor in the pH Adjustment Tank. HCl is transferred and discharged through low-density polyethylene (LDPE) tubing, which is suspended above the pH Adjustment Tank liquid level.

3.5.3 Fenton's Reagent Reaction Tank

Water in the 350-gallon Fenton's Reagent Reaction Tank is mixed via clamp mount mixer with hydrogen peroxide and, if necessary, iron sulfate can be dosed into this tank. Hydrogen peroxide is metered into the Fenton's Reagent Reaction Tank at a constant rate of 0.55 gpd via a variable speed chemical pump. An oxidation reduction potential (ORP) sensor continuously records tank ORP levels. High-water level and low-water level sensors will trigger alarms and WTP shut-down if the water level within the tank reaches a high water level. The 350-gallon Fenton's Reagent Reaction Tank provides a design retention time of approximately 60 minutes.

3.5.4 Hydrogen Peroxide and Iron Sulfate Feed Lines to the Fenton's Reagent Reaction Tank

Since start up of the WTP, only hydrogen peroxide has been dosed to the Fenton's Reagent Reaction Tank, via a variable speed chemical pump directly from the H₂O₂ chemical drum through LDPE tubing. Dose control is manual, and the pump is set at the lowest possible setting, which achieves a dosing rate of approximately 0.55 gpd. The discharge from the tubing is suspended above the liquid level in the Fenton's Reagent Reaction Tank.

3.5.5 Wellhead Treatment Plant Discharge

After treatment, water is pumped from the Fenton's Reagent Reaction Tank via a 3-phase effluent pump to a pipeline leading from the Buildings 63, 2, and 45 AOC

to the GWETS. The WTP effluent is controlled by the water level sensor in the Fenton's Reagent Reaction Tank.

The WTP effluent en-route to the GWETS is combined with groundwater from other extraction wells (not treated for or containing 1,4-dioxane), and the combined flow passes through an AS and GAC prior to discharge to the NSSC stormwater sewer.

3.6 1,4-Dioxane Wellhead Treatment Plant Operational Performance

The results of treatment of 1,4-dioxane by the WTP using Fenton's reagent are shown in Figure 7. The 1,4-dioxane influent concentrations to the WTP have decreased from 7.2 $\mu\text{g/L}$ on September 9, 2008, to less than 1 $\mu\text{g/L}$ on September 2, 2009. The WTP effluent has been consistently less than the Massachusetts Department of Environmental Protection drinking water goal of 3 $\mu\text{g/L}$ and typically non-detect (<0.18 $\mu\text{g/L}$ method detection limit). The typical operational parameters are shown Table 6.

Table 6. Wellhead Treatment Plant Design Operational Parameters

H₂O₂ Dose Rate	Average H₂O₂ Level	Iron Dose Rate	Acid Dose Rate	pH	Retention Time	Base Dose Rate	WTP H₂O₂ Effluent (mg/L)	GWETS H₂O₂ Effluent (mg/L)
0.55 gpd	19.1 mg/L	0 gpd	3.17 gpd	3.5	30 min	0 gpd	1.0	0.0

4. CONCLUSION

Ex-situ well-head treatment using Fenton's reagent been successfully removing 1,4-dioxane and TCE from contaminated groundwater during the last 1.5 years of operation. 1,4-dioxane influent levels of up to 8 $\mu\text{g/L}$ have been reduced to levels below the MCP criteria (3 $\mu\text{g/L}$) and usually to non-detect (<0.18 $\mu\text{g/L}$) levels. The well-head treatment plant has the demonstrated capacity to treat influent 1,4-dioxane levels of 35 $\mu\text{g/L}$, and this unit with minimal changing of hydrogen peroxide dosing rates could treat influent with higher 1,4-dioxane levels and higher flow rates.

Iron and suspended materials, which may be detrimental to other treatment processes, are used here to great advantage, as ambient iron present in the site groundwater is used as the iron catalyst needed for Fenton's reagent. The low pH of the Wellhead Treatment Plant effluent is raised by the buffering capacity of the

untreated GWETs influent water combined with it en-route to the existing GWETs. Both of these adaptations of Fenton's reagent to NSSC conditions have resulted in significant economy in plant operations.

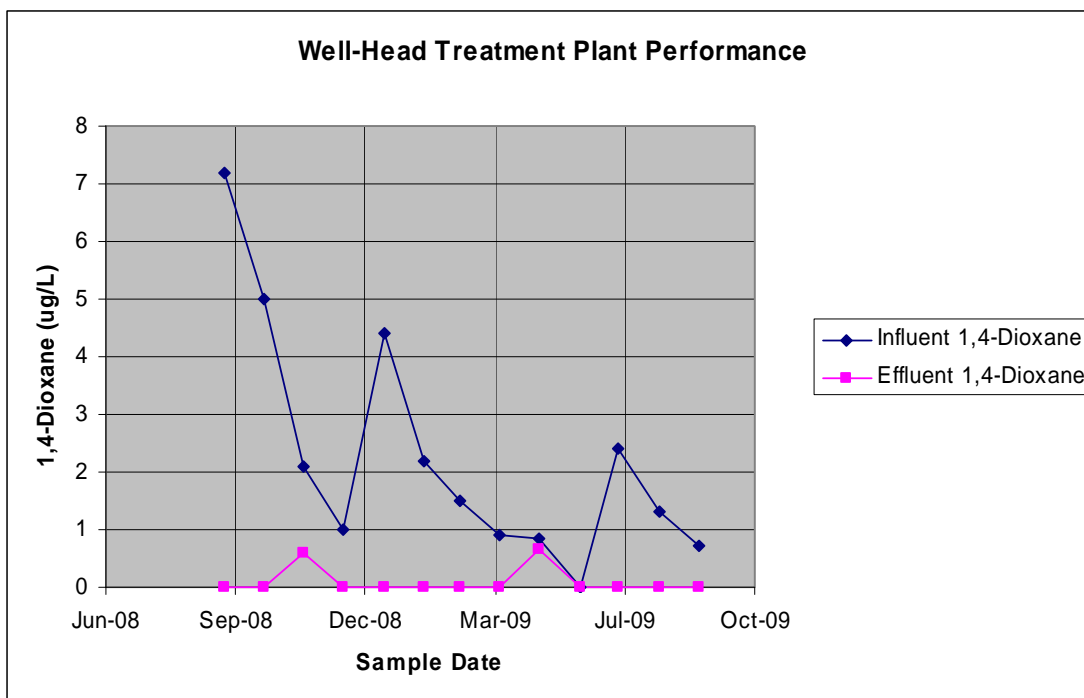


Figure 7. Wellhead Treatment Plant influent and effluent 1,4-dioxane levels since the plant start up.

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