

Case Study Catalyzed Hydrogen Peroxide Treatment of a TCE DNAPL Plume - 10073

Steven L. Thompson, Paul Cross and Del R. Baird
CDM, Piketon, Ohio 45661

ABSTRACT

The U.S. Department of Energy (DOE) is responsible for the cleanup of environmental media at the Portsmouth Gaseous Diffusion Plant which is located in southern Ohio. The X-701B Solid Waste Management Unit (SWMU) is an unlined surface impoundment at the facility which was operated from 1954 to 1988. A significant trichloroethene (TCE) groundwater plume emanates from the unit, and is approximately 2,200 ft in length. Metals, radionuclides, and other organic chemicals are also present in the groundwater, and complicate the remediation process. An ongoing 1.6 acre TCE DNAPL source area for the plume is believed to exist in the vicinity of the X-701B pond. The extent of the source area is inferred from actual recovery of DNAPL in production wells, as well as TCE concentrations between 100 and 1,000 mg/L in monitoring wells.

Previous remedial activities at X-701B have included a RCRA Closure of the pond, and several technology demonstrations for the cleanup of groundwater. The technology demonstrations have been unsuccessful in identifying an approach for cleaning up the unit, but have demonstrated the difficulty of conducting a remedy in these non-uniform, low permeability soils.

In order to overcome these issues and to more aggressively remediate the source, a new remediation approach has been implemented. The new approach uses direct injection of Catalyzed Hydrogen Peroxide into the source area using temporary direct push injection points. This new approach attempts to overcome limitations imposed by heterogeneities in the subsurface by injecting relatively small quantities of reagent into a large number of temporary injection points. These injections are then repeated, as necessary on a grid pattern, until the performance goals for the remedy are achieved. It is hoped that the close spacing of the grid pattern will compensate for the relatively short half-life of Catalyzed Hydrogen Peroxide in the subsurface.

The remediation is being implemented in four phases under an Ohio EPA approved Work Plan. The Phase I pilot test was conducted over a small portion of the source area during 2005-2006. Phase II is currently performing full scale treatment of the source area. Phase III will eventually monitor the source area for TCE rebound, and Phase IV will perform limited treatment for the down gradient portion of the plume.

Baseline and post-injection groundwater and soil data from six complete Phase II injection events will be presented. The data will show that significant reductions in contaminant mass have been achieved in the majority of soil horizons. However the data also indicates that, a thin, low permeability, high porosity clay layer on top of bedrock still contains a significant source of TCE for the plume.

INTRODUCTION AND SITE BACKGROUND

PORTS is located in a rural area of Pike County, Ohio. DOE activities at PORTS include environmental restoration, waste management, and operation of non-leased facilities. The principal groundwater flow system for PORTS is limited to four geologic and hydraulic units (Minford, Gallia, Sunbury Shale, and Berea Sandstone). The uppermost unconsolidated unit is the Minford, with an approximate thickness of 25 to 30 feet (ft). The Gallia and the silt of the lower Minford constitute the unconsolidated aquifer at PORTS. The Gallia unit underlies the Minford and is relatively thin (4 to 8 ft) in the area near the X-701B pond. The average hydraulic conductivity values for the Gallia and Minford are approximately 40 ft/day and 0.62 ft/day, respectively. The uppermost bedrock unit is the Sunbury Shale. This unit is typically encountered at a depth of approximately 30 ft below ground surface (bgs) and the Sunbury is considered to be an effective aquitard. The Berea Sandstone underlies the Sunbury Shale and is encountered at depths between 40 to 45 ft bgs.

The primary source of water for the hydrogeologic flow system is natural recharge through precipitation. Natural groundwater flow beneath the X-701B pond is directed to the east and northeast. The flow direction is the same for both the Gallia and Berea units.

The X-701B groundwater plume primarily consists of TCE and its degradation products. Dissolved TCE concentrations up to 1,200,000 micrograms per liter (ug/L) have been measured in the source area of the plume and DNAPL has been pumped from one well within the unit. Several metals, radioactive inorganics, and other organic chemicals have also been identified as contaminants of concern (COCs) and are components of the plume. The primary release mechanisms are surmised to have been migration of separate-phase and dissolved contaminants from the bottom and sides of the X-701B pond and leakage from several chemical process pipelines (currently inactive) that cross the plume area in proximity to the pond. The groundwater plume (Figure 1) is elongated west to east and extends from a point just west of the X-701B pond, downgradient to the Little Beaver Creek, and is approximately 2,200 ft in length. The plume is relatively narrow north to south, approximately 250 ft wide in the X-701B holding pond area, and expands to approximately 500 ft wide as it approaches Little Beaver Creek. A localized source area for the plume is believed to exist up gradient near the X-701B pond, and is identified in the X-701B Decision Document (Ohio EPA 2003) as the focus for the remedy.

Previous remedial activities at X-701B include a RCRA closure and a technology demonstration that recirculated permanganate solutions between two horizontal wells. Results showed that the permanganate effectively destroyed TCE in portions of the aquifer where adequate distribution was achieved, but that oxidant delivery using the recirculation approach was problematic. In addition, TCE concentration in the treatment area eventually rebounded to near the saturation point.

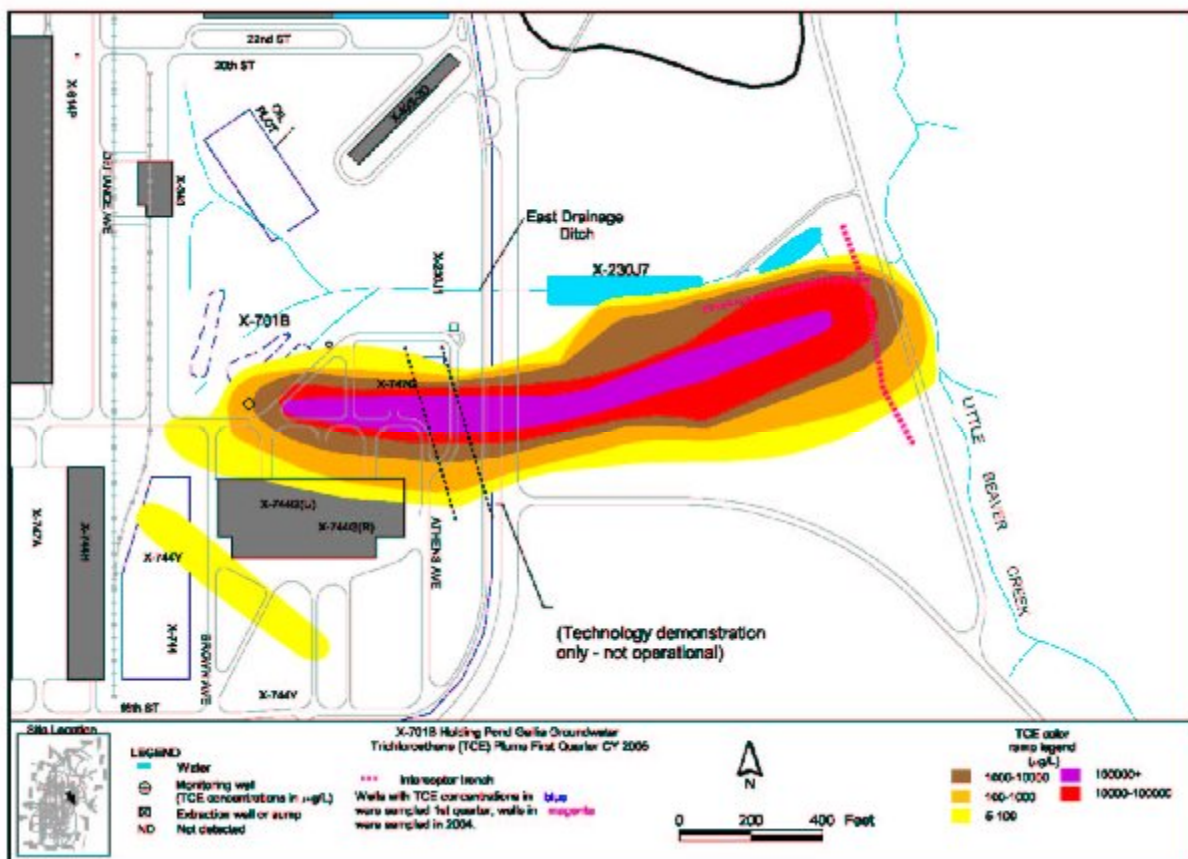


Figure 1. X-701B Groundwater Plume

In order to overcome oxidant delivery issues and to more aggressively remediate the source, a new remediation approach is being implemented. The new approach involves the injection of Catalyzed Hydrogen Peroxide directly into the source area using temporary DPT injection points. The primary advantage of this approach (as compared to injection wells) is that the oxidant can be targeted directly to multiple contamination zones at a reasonable cost.

This targeting reduces limitations imposed by heterogeneities in the subsurface and is achieved by injecting a relatively small volume of reagent into each of the injection points that are distributed over a large area.

REMEDICATION APPROACH

The remediation of groundwater contamination using Catalyzed Hydrogen Peroxide involves injecting oxidant(s) directly into the source and downgradient areas of the plume. The oxidant(s) react with contaminants to produce innocuous substances such as carbon dioxide, water, and, in the case of chlorinated compounds, inorganic chloride. It is important to consider the natural oxidant demand (the consumption of oxidant due to reactions unrelated to contaminant destruction) of an aquifer when designing and implementing Catalyzed Hydrogen Peroxide. Because oxidants are non-selective and will react with other constituents in the aquifer and the soil, sufficient oxidant must be added both to satisfy the natural oxidant demand and to destroy the target contaminant. Natural oxidant demand will normally remain relatively high during early injections, and will diminish for subsequent injection events in the same area.

During the injection of Catalyzed Hydrogen Peroxide, the destruction of contaminants occurs in the aqueous phase. Catalyzed Hydrogen Peroxide can stimulate much faster dissolution of contaminants from the DNAPL phase and desorption of contaminants from aquifer solids. In addition, contaminants bound to organic soil matter are liberated when oxidant reacts with organic matter. Because of these factors, oxidant injections may result in significant increases in contaminant concentrations within groundwater if the subsurface has significant DNAPL and/or sorbed phase contaminant mass. Such cases, however, are an indication of successful remediation because the overall mass of contaminant (dissolved, adsorbed, and DNAPL) in the aquifer system decreases. Subsequent injections of oxidant then address any temporary increases in groundwater concentrations. Five common oxidants used for soil and groundwater remediation of chlorinated organic solvents are permanganate, persulfate, Fenton's reagent, Modified Fenton's Reagent, and ozone. Several oxidant molecules are typically required for the complete mineralization of the solvent to CO₂. The oxidant first attacks the carbon double bonds of an alkene, and then subsequent oxidant molecules proceed to break down the solvent into esters, organic acids, and ultimately CO₂. The pathway leading to mineralization is a function of pH¹.

Because of the presence of a significant DNAPL mass in the subsurface at X-701B, ISOTEC's Modified Fenton's Reagent process was chosen for remediation of the source area. Fenton's chemistry is characterized by the combination of soluble iron with low concentrations of hydrogen peroxide to produce hydroxyl radicals (OH•). These hydroxyl radicals are very powerful, short-lived oxidizers, typically reacting within minutes or hours. Iron with a valence of +2 is used to catalyze the reaction; maintaining the iron ion in solution is important for the process to be successful. To eliminate the necessity of performing the reaction under low-pH conditions, as is the case with traditional Fenton's chemistry, ISOTEC's process utilizes complexed iron during the treatment process. In addition, a proprietary agent is added to stabilize the hydrogen peroxide and to reduce its reaction rate with the subsurface. This reduction in reaction rate can increase the radius of effect for the treatment. The degree of stabilization is adjustable and can be tailored to a specific site's geologic setting. Overall, ISOTEC's proprietary Modified Fenton's treatment process is very fast compared to persulfate and permanganate treatment systems. The oxidant is typically consumed within a few days. Hydrogen peroxide breaks down either into water and oxygen or into water and carbon dioxide if it reacts with an organic solvent. The iron catalyst is reduced and ultimately precipitates out of solution.

In the ISOTEC process, an aqueous catalyst solution and an aqueous stabilized hydrogen peroxide solution are prepared immediately prior to an injection event. The catalyst solution is prepared from two ISOTEC solid products. Catalyst A provides the source of iron and Catalyst B provides a chelating agent for the iron. The stabilized hydrogen peroxide solution is prepared by mixing water, industrial-grade hydrogen peroxide, and a proprietary ISOTEC stabilizing agent. The mixing of catalyst and oxidant solutions occurs in the subsurface.

Injections are typically conducted in one of two sequences. Under the preferred sequence, injections proceed in the following order: water, oxidant solution, water, catalyst solution, water. If the aquifer is pore space limited, or if there is an unusually large contaminant mass present, an alternative sequence can be utilized. Under the alternative

¹ F.W. Schwartz, H. Zhang, "Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zone Flooding Schemes", U.S. DOE Final Report for Project Number 54585, (2000).

sequence, injections proceed in the following order: water, catalyst solution, water, oxidant solution, water. Under both approaches, the quantity of reagent injected and the rate of injection for each component are adjusted in accordance with field conditions. The preferred sequence is thought to result in a greater radius of influence, but may also sometimes result in excessive production of O₂ and CO₂ near the injection point. These gases may fill the available pore space and stall the injection.

ISOTEC has noticed that, for their Modified Fenton's process, there is a difference between the subsurface radius that is "physically" affected by an injection event and the subsurface radius where remediation occurs at a significant rate. For this reason, the radius of "physical" effect is commonly referred to as "the radius of effect" (ROE) and the radius for effective remediation is referred to as "the radius of influence" (ROI). The ROE is typically much larger than the ROI; however, it is much easier and less expensive to measure the ROE for an injection event.

Groundwater remediation for X-701B is currently proceeding under four separate phases.

Phase I – Phase I was completed during the fall of 2005. The goals for Phase I were: (1) to initiate treatment of contaminated groundwater and soils in the smaller source area and (2) to develop system efficiency and remediation effectiveness data that could be used for the design of the remaining injections over the full treatment zone. System efficiency refers to the optimization of time, energy, and cost toward the achievement of remediation goals. Examples of efficiency parameters include achievable injection rates, subsurface pressures, reagent concentrations and volumes, ROE, and ROI.

Phase I injections were conducted in a 5,000-square foot area. Catalyzed Hydrogen Peroxide was injected into eight temporary direct-push injection points during each of three injection events (total of 24 injection points). The injection events were separated in time by approximately one month. The number and spacing of the injection points for each event were based upon an anticipated 15-ft ROI. The injections targeted the Gallia formation and the top of the Sunbury formation.

Prior to the start of Phase I, four new monitoring wells were installed in the Phase I treatment area: X701-145G, -146G, -147G, and -148G). Baseline soil and groundwater samples were obtained from the new monitoring wells and baseline groundwater samples were also collected from down gradient well X701-78G. All samples were analyzed for pre-selected volatile organic compounds (VOCs), metals, and radionuclides.

Before, during and after each Phase I injection event, near-real time groundwater quality data was collected from each of the four new monitoring wells in the treatment area. This data collection was accomplished by installing multi-parameter water quality instruments in the wells. The data from these instruments provided an indication of the ROE. The instruments measured and recorded pH, temperature, specific conductivity, oxidation/reduction potential (ORP), dissolved oxygen concentration (DO), and pressure. Internal data loggers within the instruments recorded each of the data channels at pre-determined time intervals as small as 1 minute. The instruments were installed using a sanitary seal at the top of each well to minimize the potential for surfacing of treated groundwater.

After each Phase I injection event, groundwater samples were collected from the four new monitoring wells and a downgradient well (X701-78G) and were analyzed for the same analyte list as the baseline samples.

After completion of all Phase I injection events, soil samples were collected at the same locations and for the same analytes as the baseline soil samples.

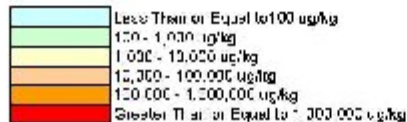
Phase II - Initiated during the Fall of 2006, Phase II is applying the Phase I technology to the entire source area for the plume. The Phase II area is approximately 99, 700 ft² with Catalyzed Hydrogen Peroxide being injected in 120-140 injection points per event. To date a total of six injection events have been completed. Based on the ROI monitored during Phase I, a grid pattern was established with each injection event being spaced laterally 30 ft apart. The first injection locations set a bench mark for the entire project and were used to establish each injection event's 30 ft grid. On average a total of 200 gallons of Catalyzed Hydrogen Peroxide was delivered through each injection location.

Prior to the start of Phase II, 16 monitoring wells throughout the injection area were sampled to provide a baseline. Also, baseline soil sample were collected from 17 locations throughout the injection area. All samples were

analyzed for pre-selected volatile organic compounds (VOCs), metals, and radionuclides. After each injection event groundwater samples were collected from the 16 monitoring wells to monitor the progress of each injection event. Also, after Phase II (b,c,d,e, and f) soil samples were collected from the 17 locations and compared to the previous soil samples collected. Each soil sampling location was collected at three separate horizons. Table I below summarizes the soil samples collected.

Table I. Soil Sampling Location Results

Soil Sampling Location	Height Above Surface (ft)	Units For Results	Phase II Baseline	Phase IIa	Phase IIb	Phase IIc	Phase IId	Phase IIe	Phase IIf	Most Recent Sample Less Than PRC?	Overall Percent Reduction	Overall Increase
S-01	5'-10'	ug/kg	360	8	61	<18	1'	2		Yes	98.5%	
	1-5'	ug/kg	233	5	16	5	3	1		Yes	98.7%	
	0-1'	ug/kg	5,000	11,000	21	370,000	8,940	16,000		No		3.7
S-02	5'-10'	ug/kg	770	0.781	4	5	1	1		Yes	98.3%	
	1-5'	ug/kg	169	5	8	4	2	9		Yes	94.1%	
	0-1'	ug/kg	1,400	5	9	40	23,363	70		No	94.4%	
S-03	5'-10'	ug/kg	2,242	790	2,160	800	1,045	920		No	65.4%	
	1-5'	ug/kg	510	110	0	30	120	120		No	76.5%	
	0-1'	ug/kg	98,500	810	62,500	2,318	51,750	24,000		No	37.7%	
S-04	5'-10'	ug/kg	5,651	100	180	4	7	270		No	95.2%	
	1-5'	ug/kg	1,281,112	1	75	2,915	3	157		No	100.0%	
	0-1'	ug/kg	74,540	38	190,000	12,000	240,000	80,000		No		3.1
S-05	5'-10'	ug/kg	67	2	35	62	2	1		Yes	99.0%	
	1-5'	ug/kg	200	3	12	48	12	18		Yes	91.4%	
	0-1'	ug/kg	45,000	150	21,000	257,000	882,000	253,950		No		1.8
S-06	5'-10'	ug/kg	0	2	1	1	2	1		Yes	99.1%	
	1-5'	ug/kg	12,840	14	16	10	140	5		Yes	100.0%	
	0-1'	ug/kg	45,500	34	330	26,000	60,000	770		No	90.3%	
S-07	5'-10'	ug/kg	1,060	10	240	28	74	26		Yes	97.8%	
	1-5'	ug/kg	570	9	172	6	4	18		Yes	93.4%	
	0-1'	ug/kg	62,000	32	705,000	2,190,000	118,500	42,000		No	32.3%	
S-08	5'-10'	ug/kg	22,000	820	7,100	10,000	180	500		No	87.7%	
	1-5'	ug/kg	5,950	16	60	10	150	100		No	96.7%	
	0-1'	ug/kg	80,500	50	4,200	430,000	430	44,000		No	47.3%	
S-09	5'-10'	ug/kg	715	1	4,700	4	37	5		Yes	98.3%	
	1-5'	ug/kg	32,750	9	7,040	40	295	570		No	99.2%	
	0-1'	ug/kg	60,000	310	516,000	213,000	8,000	1,800		No	96.4%	
S-10	5'-10'	ug/kg	10,700	290	1,400	4	150	870		No	95.7%	
	1-5'	ug/kg	445	3	2,720	4	35	15		Yes	96.7%	
	0-1'	ug/kg	57,000	180,000	215,000	1,100,000,000	270,000	290,000		No		<1.0
S-11	5'-10'	ug/kg	74,300	2	30	35	110	2,200		No	64.8%	
	1-5'	ug/kg	975	8	5	2	1	5		Yes	98.2%	
	0-1'	ug/kg	13,000	340,000	400	14,300,000	130,000	140,000		No		1.5
S-12	5'-10'	ug/kg	1,600	26	1,500	11	100	120		No	82.5%	
	1-5'	ug/kg	100	38	100	20	100	9		Yes	96.7%	
	0-1'	ug/kg	16,000	600,000	148,200	96,000	440,000	450		No	97.3%	
S-13	5'-10'	ug/kg	70,300	430	1,500	7,200	430	500		No	95.8%	
	1-5'	ug/kg	167	16	24	31	23	58		Yes	77.4%	
	0-1'	ug/kg	17,000	430	10,045	110,000	970	6,000		No	52.4%	
S-14	5'-10'	ug/kg	3,800	2,400	9,100	8,800	3,100	580		No	95.3%	
	1-5'	ug/kg	11,733	220	16,380	24	530	29		Yes	99.8%	
	0-1'	ug/kg	285,000	230,000	24,500	510,000	88,000	1,500		No	98.5%	
S-15	5'-10'	ug/kg	4,150	1	1,080	395	290	340		No	91.8%	
	1-5'	ug/kg	670	3	12	0	15	75		No	91.6%	
	0-1'	ug/kg	113,000	10,000	102,000	290,000	22,000	305,000		No		3.0
S-16	5'-10'	ug/kg	75	1	75	8,100	40	55		Yes	96.0%	
	1-5'	ug/kg	61,750	10	2,400	2,850	90	12		Yes	99.9%	
	0-1'	ug/kg	235,000	1,000,000	2,800	82,000	880,000	650,000		No		2.5
S-17	5'-10'	ug/kg	30,000	50	9,800	1,700	9,900	1,400		No	95.3%	
	1-5'	ug/kg	20,425	45	8	86	135	9		Yes	100.0%	
	0-1'	ug/kg	53,500	80,000	8,800	150,000	110,000	209,000		No		3.9
Overall	ug/kg	72,883	34,621	11,716	1,385,858	58,008	33,913					



Phase II will be complete when groundwater remediation goals are achieved or when mass destruction between successive injections becomes negligible.

Phase III - Phase III, planned to start during the Spring of 2011, will monitor TCE groundwater concentrations to ensure that significant rebound does not occur following Phase II.

Phase IV - Phase IV will provide limited treatment for the downgradient portion of the plume and will continue groundwater monitoring for the unit until remediation goals are achieved.

CURRENT STATUS

To date, all Phase I activities have been completed and the Phase I report has been issued.

The Final Remediation Work Plan for the unit was approved by Ohio EPA in October, 2006, and the initial set of Phase II injections was completed during the Fall of 2006. Two additional injection events were completed during the summer of 2007 and three additional injection events were completed during the summer and fall of 2008.

CONCLUSIONS

The goals for Phase I of the remedy were successfully achieved. The data collected thus far indicates:

1. Reagent delivery via DPT is feasible for the unit at less than 75 psig without significant surfacing of treated groundwater.
2. On average, a single work crew can complete approximately 8 injection locations per work day.
3. On average each injection location is capable of receiving approximately 75 gallons of stabilized hydrogen peroxide (12%_w), plus 75 gallons of catalyst solution (~3,000 mg Fe/L).
4. Near-real time water quality data indicates that the radius of influence for the injections is affected by heterogeneities within the formation. However, on average, a 15-foot radius of influence is achievable in the east-west direction.

During Phase II significant quantities of Catalyzed Hydrogen Peroxide have been delivered to the subsurface in the source area via direct push technology (DPT) which was developed during Phase I. Using DPT over 130,000 gallons of catalyzed hydrogen peroxide has been delivered thus far at 788 injection locations in the source area. Overall, based on the results shown in the table above a significant reduction in TCE soil concentration has been observed, but the results have not reach the end point goal of 48 ug/kg.

REFERENCES

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