

Initial Results of ISCO for a Large TCE DNAPL Source Area - 8065

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ABSTRACT

This paper will describe the results of an *in situ* chemical oxidation (ISCO) remedial action currently in progress to address subsurface contamination by trichloroethene (TCE) dense nonaqueous phase liquid (DNAPL). The U.S. Department of Energy is responsible for the cleanup of environmental media at the Portsmouth Gaseous Diffusion Plant (PORTS) in southern Ohio. The X-701B Solid Waste Management Unit is an unlined surface impoundment at PORTS which was operated from 1954 to 1988. A TCE plume in groundwater emanates from the unit and is approximately 2,200 feet in length. Metals, radioactive inorganics, and other organic chemicals are also present at lower concentrations in the groundwater. An ongoing 1.6-acre TCE DNAPL source area for the plume is believed to exist upgradient in the vicinity of the X-701B pond. The extent of the source area is inferred from actual recovery of DNAPL in production wells and from detection of TCE concentrations between 100 and 1,000 mg/L in monitoring wells.

Previous remedial activities at X-701B have included a Resource Conservation and Recovery Act (RCRA) closure and a technology demonstration that recirculated permanganate solutions between two horizontal wells. Results of sampling after these remedial activities showed that the permanganate effectively destroyed TCE in portions of the aquifer where adequate contact was achieved, but that uniform distribution by the recirculation system was problematic. As a result, the TCE concentration in the groundwater eventually rebounded after the treatment.

To overcome distribution issues and to more aggressively remediate the source, a new remediation approach is being implemented for the unit. The new approach involves the injection of Modified Fenton's Reagent directly into the source area using temporary direct push injection points. This new approach provides the ability to overcome limitations imposed by heterogeneities in the subsurface by injecting relatively small quantities of reagent into a large number of temporary injection points across the source area. These injections are then repeated, as necessary, on a grid pattern until performance goals are achieved.

The remediation is being implemented in four phases under a work plan approved by the Ohio Environmental Protection Agency. Phase I, the pilot test, was conducted over a small portion of the source area. Phase II currently involves full-scale treatment of the source area. In Phase III, the source area will be monitored for TCE rebound. Phase IV will involve limited treatment for the downgradient portion of the plume.

INTRODUCTION

The Portsmouth Gaseous Diffusion Plant (PORTS) is located in a rural area of Pike County, Ohio. The U.S. Department of Energy (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). 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 consists primarily of trichloroethene (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 dense nonaqueous phase liquid (DNAPL) has been pumped from one well within the unit. Several other organic chemicals, metals, and radioactive inorganics 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 near the pond. The groundwater plume (Figure 1), approximately 2,200 ft long, is elongated west to east and extends from a point just west of the X-701B pond downgradient to the Little Beaver Creek. 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 upgradient near the X-701B pond, and is identified in the X-701B Decision Document [1] as the focus for the remedy.

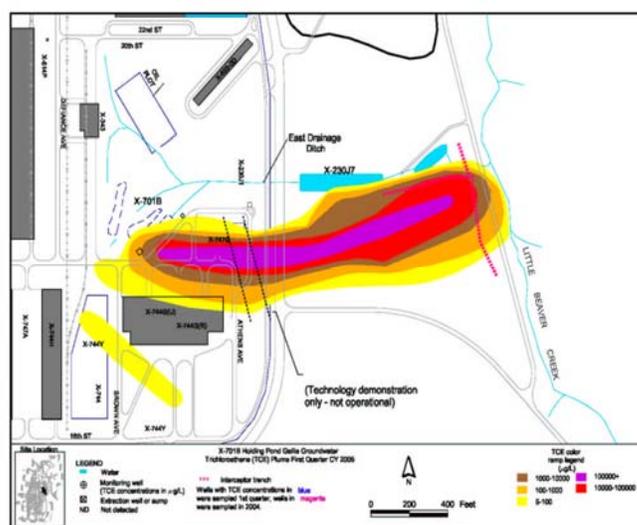


Fig. 1 X-701B Groundwater Plume

Previous remedial activities at X-701B include a Resource Conservation and Recovery Act (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.

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 Modified Fenton's Reagent directly into the source area using temporary direct push technology (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 *in situ* chemical oxidation (ISCO) 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 ISCO. 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 ISCO, the destruction of contaminants occurs in the aqueous phase. Yet some types of ISCO 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 effects, 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 carbon dioxide (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 pH [2].

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 within 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 [3].

In the ISOTEC process, an aqueous catalyst solution and an aqueous stabilized hydrogen peroxide solution are prepared immediately before 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 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 expected to provide 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.

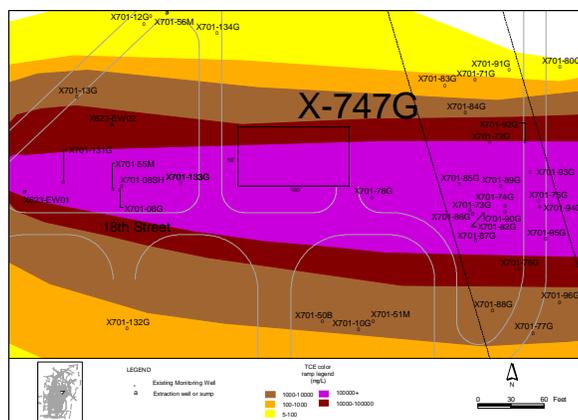
ISOTEC has noticed that, for their Modified Fenton's process, there is a difference between the subsurface radius that is "physically" affected by an injection event and the subsurface radius where remediation occurs at a significant rate. For this reason, the radius of "physical" effect is commonly 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[4]. 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 ft area (Figure 2). Modified Fenton's Reagent 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 downgradient well: X701-78G. All samples were analyzed for pre-selected volatile organic compounds (VOCs), metals, and radionuclides.



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 October 2006, Phase II is applying the Phase I technology to the entire source area for the plume. Phase II injections are currently being conducted in a 99,639-square ft area (Figure 3). Three series of injections have been completed thus far consisting of a total of 397 injection locations. The average spacing during the 3 events was approximately 30 ft between injection locations. The injections targeted the Gallia formation and the top of the Sunbury formation.

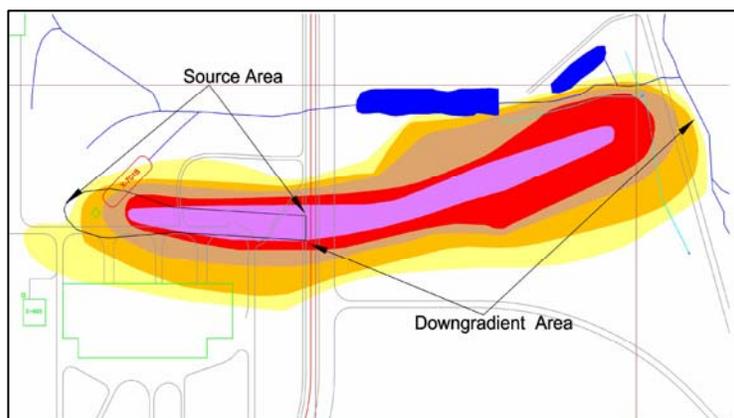


Figure 3. X-701B Identified Source Area

Baseline groundwater samples were collected from 16 monitoring locations and soil samples were collected from 17 monitoring locations. The groundwater samples were analyzed for TCE, metals, uranium and technetium-99. The soil samples were analyzed for only TCE. The monitoring locations were spread throughout the source area to monitor the effectiveness of ISOTEC's Modified Fenton's Reagent. Groundwater samples were collected after each injection event and the soil samples were collected after the second and third injection event.

The groundwater contaminant concentrations varied by injection event and monitoring well. So far, none of the monitoring results for TCE were below the preliminary remediation goal (PRG) of 5 ug/L. Also, the monitoring results for uranium, technetium-99 and hexavalent chromium have remained below the respective PRGs.

The soil TCE concentration also varied by monitoring location and by soil horizon. Three samples were collected from each soil sample location: one sample in the Minford/Gallia interface, one sample in the Gallia, and one sample in the Gallia/Sunbury interface. The results varied throughout the source area, but a positive downward trend in TCE concentration has been noted, such that 17 of the 51 latest soil samples are now below the TCE PRG of 48 micrograms per kilogram (ug/kg) (Table 1) [5].

As described during Phase I near-real time groundwater quality data were collected from various monitoring wells in the treatment area as well as downgradient. The downgradient wells are used to monitor any activity that may cause COCs to mobilize. All downgradient wells have shown no activity and routine sampling has shown no mobilization of any COCs. All data collected in the treatment area has shown what was expected per Phase I: short increases in pressure and no significant changes in pH, DO, ORP, temperature, or specific conductivity.

One of the concerns for ISOTEC's Modified Fenton's Reagent is the potential for surfacing. Surfacing occurs when gas produced by the chemical reaction accumulates in the subsurface and finds a pathway to migrate to the surface. The surfacing appears as an active seep on the ground surface. Surfacing was observed during Phase I and has also been observed during Phase II. All surfacing events during Phase I were collected and shipped offsite for disposal. The first four surfacing events during Phase II were sampled and analyzed for TCE. The four sample results were non-detect for TCE, so the remaining surfacing events are treated as non-hazardous per the work plan.

ISOTEC's Modified Fenton's Reagent is being effectively delivered to the X-701B source area. Phase II will be complete when groundwater remediation goals are achieved or when mass destruction between successive injections becomes negligible.

Table 1. Average TCE Concentrations in Soils

Soil Sampling Location	Height Above Sunbury(ft)	Units	Phase II Baseline	Phase IIb	Phase IIc	Most Recent Sample Less Than PRG?	General Trend
S-01	5'-10'	Ug/kg	360	9	61	No	Down
	1'-5'	Ug/kg	233	5	16	Yes	Down
	0'-1'	Ug/kg	5,100	11,000	21	Yes	Mixed
S-02	5'-10'	Ug/kg	71.0	0.29	4	Yes	Down
	1'-5'	Ug/kg	159	5	6	Yes	Down
	0'-1'	Ug/kg	1,400	5	9	Yes	Down
S-03	5'-10'	Ug/kg	2,242	790	2,150	No	Mixed
	1'-5'	Ug/kg	510	110	8	Yes	Down
	0'-1'	Ug/kg	38,500	910	62,500	No	Up
S-04	5'-10'	Ug/kg	5,651	100	180	No	Down
	1'-5'	Ug/kg	1,901,112	1	75	No	Down
	0'-1'	Ug/kg	14,540	58	190,000	No	Up
S-05	5'-10'	Ug/kg	87	2	33	Yes	Down
	1'-5'	Ug/kg	205	3	12	Yes	Down
	0'-1'	Ug/kg	145,000	150	21,000	No	Down
S-06	5'-10'	Ug/kg	63	2	1	Yes	Down
	1'-5'	Ug/kg	12,840	14	15	Yes	Down
	0'-1'	Ug/kg	45,500	64	630	No	Down
S-07	5'-10'	Ug/kg	1,050	10	240	No	Down
	1'-5'	Ug/kg	270	6	112	No	Down
	0'-1'	Ug/kg	62,000	32	705,000	No	Up
S-08	5'-10'	Ug/kg	22,000	920	7,100	No	Down
	1'-5'	Ug/kg	5,950	16	62	No	Down
	0'-1'	Ug/kg	83,500	53	4,200	No	Down
S-09	5'-10'	Ug/kg	715	1	4,200	No	Up
	1'-5'	Ug/kg	32,750	6	7,040	No	Down
	0'-1'	Ug/kg	50,000	310	315,000	No	Up
S-10	5'-10'	Ug/kg	10,700	260	1,400	No	Down
	1'-5'	Ug/kg	445	3	2,720	No	Up
	0'-1'	Ug/kg	57,000	130,000	215,000	No	Up
S-11	5'-10'	Ug/kg	14,300	2	38	Yes	Down
	1'-5'	Ug/kg	375	9	5	Yes	Down
	0'-1'	ug/kg	110,000	340,000	400	No	Mixed
S-12	5'-10'	ug/kg	1,600	26	1,500	No	Mixed
	1'-5'	ug/kg	175	59	56	No	Down
	0'-1'	ug/kg	16,000	500,000	148,200	No	Mixed
S-13	5'-10'	ug/kg	13,300	480	3,900	No	Up
	1'-5'	ug/kg	157	15	24	Yes	Down
	0'-1'	ug/kg	17,000	480	10,845	No	Mixed
S-14	5'-10'	ug/kg	3,900	2,400	9,100	No	Up
	1'-5'	ug/kg	11,733	228	18,338	No	Up
	0'-1'	ug/kg	285,000	220,000	24,500	No	Down
S-15	5'-10'	ug/kg	4,150	1	1,060	No	Down
	1'-5'	ug/kg	870	5	12	Yes	Down
	0'-1'	ug/kg	113,500	55,000	102,000	No	Mixed
S-16	5'-10'	ug/kg	75	1	23	Yes	Down
	1'-5'	ug/kg	61,750	13	2,431	No	Down
	0'-1'	ug/kg	235,000	1,000,000	2,800	No	Mixed
S-17	5'-10'	ug/kg	30,000	56	9,800	No	Down
	1'-5'	ug/kg	20,425	43	8	Yes	Down
	0'-1'	ug/kg	53,500	90,000	8,900	No	Mixed

Phase III - Phase III, planned to start during the Spring of 2009, 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 three sets of Phase II injections were completed as of August 2007. The Phase IIc report has been issued, summarizing the first three injection events for Phase II and specifying a path forward for the remaining Phase II injections.

CONCLUSIONS

The goals for Phase I of the remedy were successfully achieved. The data collected indicate that:

- Reagent delivery via DPT is feasible for the unit at less than 75 psig without significant surfacing of treated groundwater.
- On average, a single work crew can complete approximately 8 injection locations per work day.
- 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).
- Near-real time water quality data indicate 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.

Phase II is currently in progress and has shown that Modified Fenton's Reagent can be effectively delivered to the X-701B Source Area. Phase II injections will continue throughout the source area until at least one of the following criteria is met:

- Groundwater samples from source area monitoring wells are below the TCE groundwater PRG.
- The remedy is no longer effective in removing TCE mass from the source area.

Currently, two more injection events are scheduled for 2008. Surfacing has not been a major issue and has not prevented successful delivery of ISOTEC's Modified Fenton's Reagent to the subsurface.

REFERENCES

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