Enhancing a Groundwater Remedy for TCE with ISCO - 9046

Steven L. Thompson and Del R. Baird
CDM
P.O. Box 789, Piketon, OH 45661

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). The U.S. Department of Energy is responsible for the cleanup of environmental media at the Portsmouth Gaseous Diffusion Plant (PORTS) in southern Ohio. During construction of the PORTS facility in the early 1950s, an electrical substation was constructed in the area of the X-740 Solid Waste Management Unit. The switchyard was removed upon completion of the X-530A Switchyard located directly north of the area. Adjacent to the area, the X-740 Waste Oil Handling Facility was constructed in 1982 and was in operation until 1992. Groundwater contamination at the X-740 area was first discovered during the Quadrant III RCRA Facility Investigation (RFI) Phase I field investigation conducted in 1992. The size of the TCE plume has remained relatively unchanged since 1999. The maximum detection of TCE concentration in a single monitoring well is 7600 ug/L.

The RFI process began in 1992 and was completed in 1997. The Cleanup Alternatives Study/Corrective Measures Study (CAS/CMS) report was approved on July 1998. The selected remedy for the X-740 groundwater plume, phytoremediation, was presented in the *Decision Document for Quadrant III*, approved in May of 1999. The major components of the selected remedy include phytoremediation by planting one-year-old hybrid poplar trees in the area of groundwater contamination; groundwater monitoring to confirm that the containment and treatment of contaminants sufficiently protect human health and the environment; and site deed restrictions that include retaining the existing security fencing to restrict access to prevent exposure to contaminated media, and to limit disturbance of the area, ensuring the integrity of the remedial action.

The X-740 Phytoremediation System was constructed and implemented in 1999. Based on the monitoring results, the 2007 evaluation determined that the X-740 Phytoremediation System has not performed as predicted by the Quadrant III CAS/CMS groundwater model. In a letter, Ohio EPA stated the current remedy is not achieving the goals outlined and required DOE to evaluate other remedial alternatives in conjunction with the current remedy.

To enhance the remediation of groundwater at the X-740 SWMU, a new remediation approach is being implemented for the unit. The new approach involves the injection of Modified Fenton's Reagent, using temporary direct push injection points, directly into the portion of the groundwater plume that currently contains TCE concentrations of 50 parts per billion (ppb) or higher. This new approach overcomes limitations imposed by heterogeneities in the subsurface by injecting relatively small quantities of reagent into a large number of temporary injection points over the area. These injections are then repeated as necessary on a grid pattern until performance goals are achieved.

Baseline and post-injection groundwater data from three complete Phase injection events are expected to be available in time for the conference. These data will be compared against the remediation end point as defined in the work plan to determine the progress of the remedy.

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 (0 to 1 ft) in the X-740 area. The average hydraulic conductivity values for the Gallia and Minford are approximately 2 ft/day and 0.56 ft/day, respectively. The Sunbury Shale is the uppermost bedrock unit but is absent at the X-740 area. The Berea Sandstone underlies the Sunbury Shale and is encountered at depths between 35 ft to 40 ft below ground surface (bgs). The primary source of water for the hydrogeologic flow system is natural recharge through precipitation. Natural groundwater flow beneath the X-40 area is directed to the west. The flow direction is the same for both the Gallia and Berea units.

The X-740 groundwater plume consists of volatile organic compounds, primarily trichloroethene (TCE). Dissolved TCE concentrations up to 7,600 micrograms per liter (ug/L) have been measured in the high-concentration area of the plume.

During construction of the PORTS facility in the early 1950s, an electrical substation was constructed in the area of the X-740 Solid Waste Management Unit. The switchyard was removed upon completion of the X-530A Switchyard to the north. Adjacent to the area, the X-109A building was constructed in 1955 and originally used as a waste oil reclamation facility. Adjacent to the X-109A building, the X-740 Waste Oil Handling Facility was constructed (Figure 1). The former X-740 Waste Oil Handling Facility, approximately 50 ft wide by 120 ft long, consisted of a diked concrete pad with a roof and sheet metal walls on the north, south, and west sides. The east side of the facility was open-sided, with plastic sheeting windbreaks to protect the interior from weather. During its period of operation from 1982 to 1992, the facility was used as a drum-staging area for approximately 8,000 gal/year of non-radionuclide-contaminated waste oils and 500 gal/year of non-radionuclide-contaminated waste solvents generated by various plant site activities. The drums were staged at the facility pending analysis of their contents before their final disposition. Empty drums that resulted from combining partially full drums were crushed in a hydraulic drum crusher in the northwest corner of the facility and disposed of at the X-735 Landfill. Effluent from the drum crusher was discharged to a sump pit that was installed in early 1986 and was located beneath the drum crusher pad.

The RCRA Facility Investigation (RFI) process began in 1992 and was completed in 1997. The Cleanup Alternatives Study/Corrective Measures Study (CAS/CMS) report was approved on July 1998.

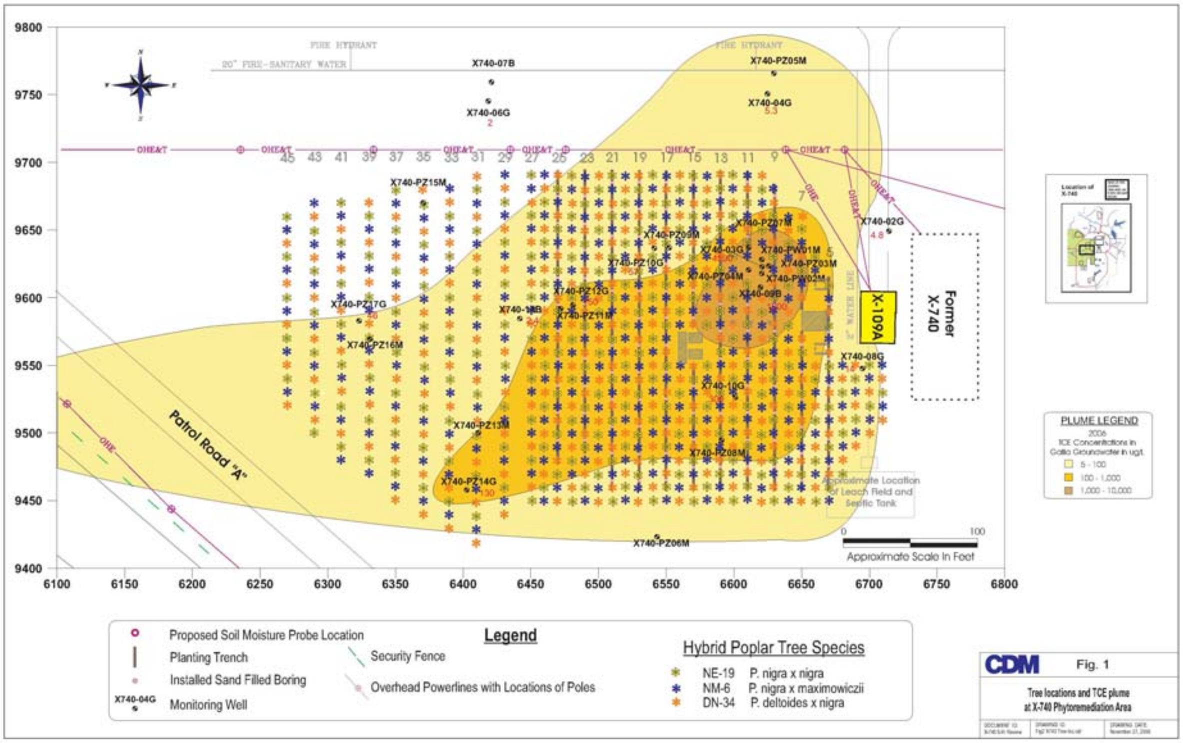

Figure 1. X-740 Area

DECISION DOCUMENT SELECTED REMEDY

The selected remedy for the X-740 groundwater plume, phytoremediation, was presented in the *Decision Document for Quadrant III*, approved in May of 1999. The major components of the selected remedy include: phytoremediation by planting one-year-old hybrid poplar trees in the area of groundwater contamination; groundwater monitoring to confirm that the containment and treatment of contaminants sufficiently protects human health and the environment; and site deed restrictions that include retaining the existing security fencing to restrict access, avoid exposure to contaminated media, and limited disturbance of the area to ensure the integrity of the remedial action[1].

The X-740 Phytoremediation Corrective Action was implemented at the X-740 area in 1999. A total of 766 one-year-old hybrid poplar trees were planted 10 ft apart in rows 10 ft to 20 ft apart, over an area of 2.6 acres (Figure 1). Two planting methods were used: some trees were planted in 2-ft wide x 10-ft deep trenches that were backfilled with soils amended with sand, peat moss, lime, and fertilizer prior to planting; others were planted in a 2-ft diameter x 10-ft deep boring that was also filled with amended soils. Sand-filled borings (sand stacks) were installed (20 ft apart) from the bottom of the trenches to bedrock with the purpose of enhancing the movement of contaminated groundwater into the trenches. The sand stacks consisted of 8-in. diameter borings to bedrock (approximately 30 ft deep) back-filled with coarse sand. The system was designed to allow contaminated groundwater to flow up through the sand stacks (due to the potentiometric head observed in the semi-confined Gallia groundwater) into the trenches for access by the tree roots. The trees planted in the borings were designed to consume more of the surface moisture, encouraging deeper root growth in the trenches due to competition [2].

The hybrid poplar trees were expected to develop a mature root system within two to three years after they were planted. It was estimated in the CAS/CMS that cleanup objectives of the corrective action would be achieved ten years after the trees matured. A December 2003 report, however, cited additional modeling and updated parameters from the 2003 growing season to reassess the validity of previous remediation time estimates [3]. The five-year review addendum model shows groundwater contamination above the Maximum Contaminant Level of 5 micrograms/liter (μg/L) for at least 20 years after the development of a mature root system.

Based on the monitoring results, the 2007 evaluation determined that the X-740 Phytoremediation System has not performed as predicted by the Quadrant III CAS/CMS groundwater model. Although the trees remove large amounts of water from the soil during the growing season, most of the transpired water appears to be from shallow surface infiltration moisture and not from the contaminated Gallia groundwater. In a letter dated March 26, 2007, Ohio EPA stated that the current remedy is not achieving the goals outlined in the approved CAS/CMS report. The state is requiring DOE to evaluate other remedial alternatives to be implemented in conjunction with the current remedy [4].

ISCO REMEDIATION APPROACH

To enhance the remediation of groundwater at the X-740 SWMU, a new remediation approach is being implemented for the unit. The new approach involves the injection of Modified Fenton's Reagent, using temporary direct push injection points, directly into the portion of the groundwater plume that currently contains TCE concentrations of 50 parts per billion (ppb) or higher. This new approach overcomes limitations imposed by heterogeneities in the subsurface by injecting relatively small quantities of reagent into a large number of temporary injection points over the area. These injections are then repeated as necessary on a grid pattern until performance goals are achieved.

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. 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 (CO_2). 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 CO_2. The pathway leading to mineralization is a function of pH [5].

ISOTEC's Modified Fenton's Reagent process was chosen for remediation of the X-740 SWMU 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. Also, 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 [6].

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 O_2 and CO_2 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.

ISCO REMEDIATION APPLICATION

Initiated during May 2008, injections are currently being conducted in a 66,900-square ft area (Figure 2). To date, three series of injections have been completed encompassing 262 injection locations. The average spacing during the 3 events was approximately 30 ft between injection locations. The injections targeted the Gallia formation.

Baseline groundwater samples were collected from 8 monitoring locations and 6 temporary monitoring locations. The groundwater samples were analyzed for TCE only. The monitoring locations were spread throughout the area to monitor the effectiveness of ISOTEC's Modified Fenton's Reagent. Groundwater samples were collected after each injection event.

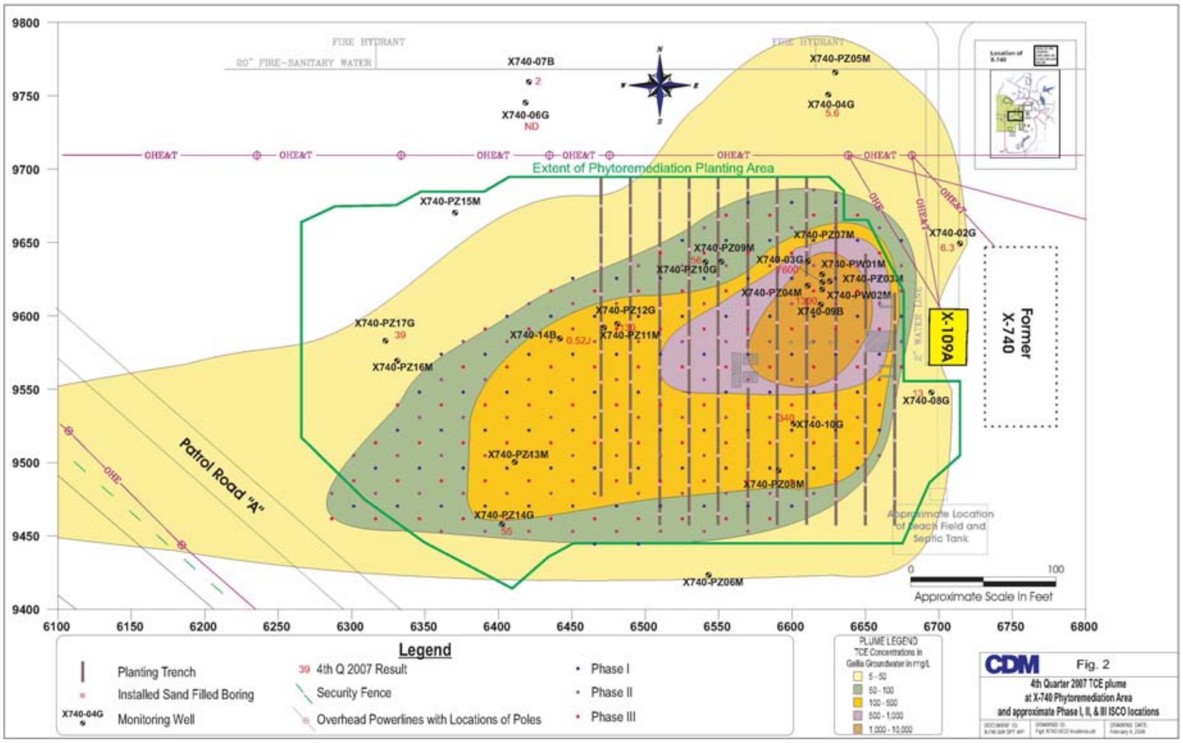

Figure 2. X-740 ISCO Locations

The groundwater contaminant concentrations varied by injection event and monitoring well. Table 1 summarizes the maximum groundwater results to date.

Table 1. Average TCE Concentrations in Soils

GW Location	Units	Baseline	Phase I	Phase II	Phase III
X740-03G	ug/L	3700	2700	400	7700
X740-09B	ug/L	1200	1700	940	1200
X740-10G	ug/L	170	130	260	440
X740-14B	ug/L	33	17	2.9	1.6 J
X740-PZ10G	ug/L	44	28	28	30
X740-PZ12G	ug/L	120	120	94	130
X740-PZ14G	ug/L	140	180	160	92
X740-PZ17G	ug/L	30	32	36	41
X740-TMP01G	ug/L	9.8	0.51 J	0.23 J	0.47 J
X740-TMP02G	ug/L	37	21	10	53
X740-TMP03G	ug/L	94	79	36	88
X740-TMP04G	ug/L	17	60	32	93
X740-TMP05G	ug/L	160	0.49 J	13	29
X740-TMP06G	ug/L	8.3	1.5	1.6	6.9

Max	ug/L	3700	2700	940	7700
Mean	ug/L	412	362	144	707
Min	ug/L	8.3	0.49 J	0.23 J	0.47 J

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 is a concern at the X-740 area due to the phytoremediation system in which 8-inch sand-filled borings (sand stacks) were installed (20 ft apart) from the bottom of the trenches to bedrock. Surfacing has been observed during the injections, but ISOTEC has adjusted in the field to minimize surfacing.

CURRENT STATUS

The Work Plan for the unit was approved by Ohio EPA in April 2008 and 3 sets of injections have been completed as of October 2008. A data review summarizing all three injection events has been completed with Ohio EPA. Additional monitoring will occur throughout 1^{st} and 2^{nd} quarter 2009 to monitor the effectiveness of the remedy. Based on the monitoring data, a path forward will be discussed with Ohio EPA.

CONCLUSIONS

Modified Fenton's Reagent can be effectively delivered to the X-740 SWMU and injections will continue throughout the area until at least one of the following criteria is met:

- Groundwater samples from X-740 area monitoring wells are at or below 50 ug/L for TCE.
- The remedy is no longer effective in removing additional TCE mass from the target area.

Currently, two more injection events are scheduled for 2009. Surfacing has not been a major issue and has not prevented successful delivery of ISOTEC's Modified Fenton's Reagent to the subsurface.

REFERENCES

1. Ohio EPA (Ohio Environmental Protection Agency) 1999. *Decision Document for Quadrant III of the Portsmouth Gaseous Diffusion Plant, Piketon Ohio,* March.
2. U.S Department of Energy 2007. *Supplemental Evaluation to the 2003 Five-Year Evaluation Report for the X-740 Phytoremediation System at the Portsmouth Gaseous Diffusion Plant, Piketon, Ohio*, DOE/PPPO/03-0038&D1, LATA/Parallax Portsmouth, LLC, Piketon, Ohio.
3. U.S Department of Energy 2003. *Addendum to the Five-Year Evaluation Report for the X-740 Phytoremediation Project at the Portsmouth Gaseous Diffusion Plant, Piketon, Ohio*, DOE/OR/11-3135&D1/A1, Bechtel Jacobs Company, LLC, Piketon, Ohio.
4. Galanti, M. March 26, 2007. Ohio Environmental Protection Agency, Southeast District Office, Logan, OH, letter to W. E. Murphie, U.S. Department of Energy, Portsmouth/Paducah Project Office, Lexington, KY.
5. 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).
6. U.S Department of Energy 2008. *Work Plan for the X-740 Groundwater Plume Optimization at the Portsmouth Gaseous Diffusion Plant, Piketon, Ohio*, DOE/PPPO/03-0061&D2, LATA/Parallax Portsmouth, LLC, Piketon, Ohio.