

Warehouse Manufacturing Facility

Soil Vapor Extraction—Steam—In Situ Chemical Oxidation—Monitored Natural Attenuation

Site Name: Confidential Warehouse Manufacturing Facility

Site Location: Piedmont Area, North Carolina

Technology Used:

- In Situ Chemical Oxidation (ISCO)
(Sodium Persulfate)
- Thermal (Steam)
- Soil Vapor Extraction (SVE)
- Monitored Nature Attenuation (MNA)

Regulatory Program: North Carolina Voluntary Cleanup Program

Remediation Scale: Full

Project Duration: September 2004 to July 2005

Site Information: The site contains a warehouse and manufacturing facility located in an urban area in the Piedmont physiographic province of North Carolina. Zoning in the area allows a mixture of industrial and residential land uses.

Contaminants: Releases of solvents and cleaning agents have occurred at the site. The principal contaminants of concern are 1,1,1-trichloroethane (TCA), 1,1-dichloroethene (DCE), and 1,4-dioxane. The areal extent of the contamination is about 1.5 acres; contamination extends to about 100 ft below ground surface (bgs). The maximum detected concentrations found in the groundwater were 124 mg/L TCA, 89 mg/L DCE, and 29 mg/L 1,4-dioxane. These concentrations are sufficiently high to suggest that the TCA and DCE are present as dense non-aqueous phase liquids (DNAPL).

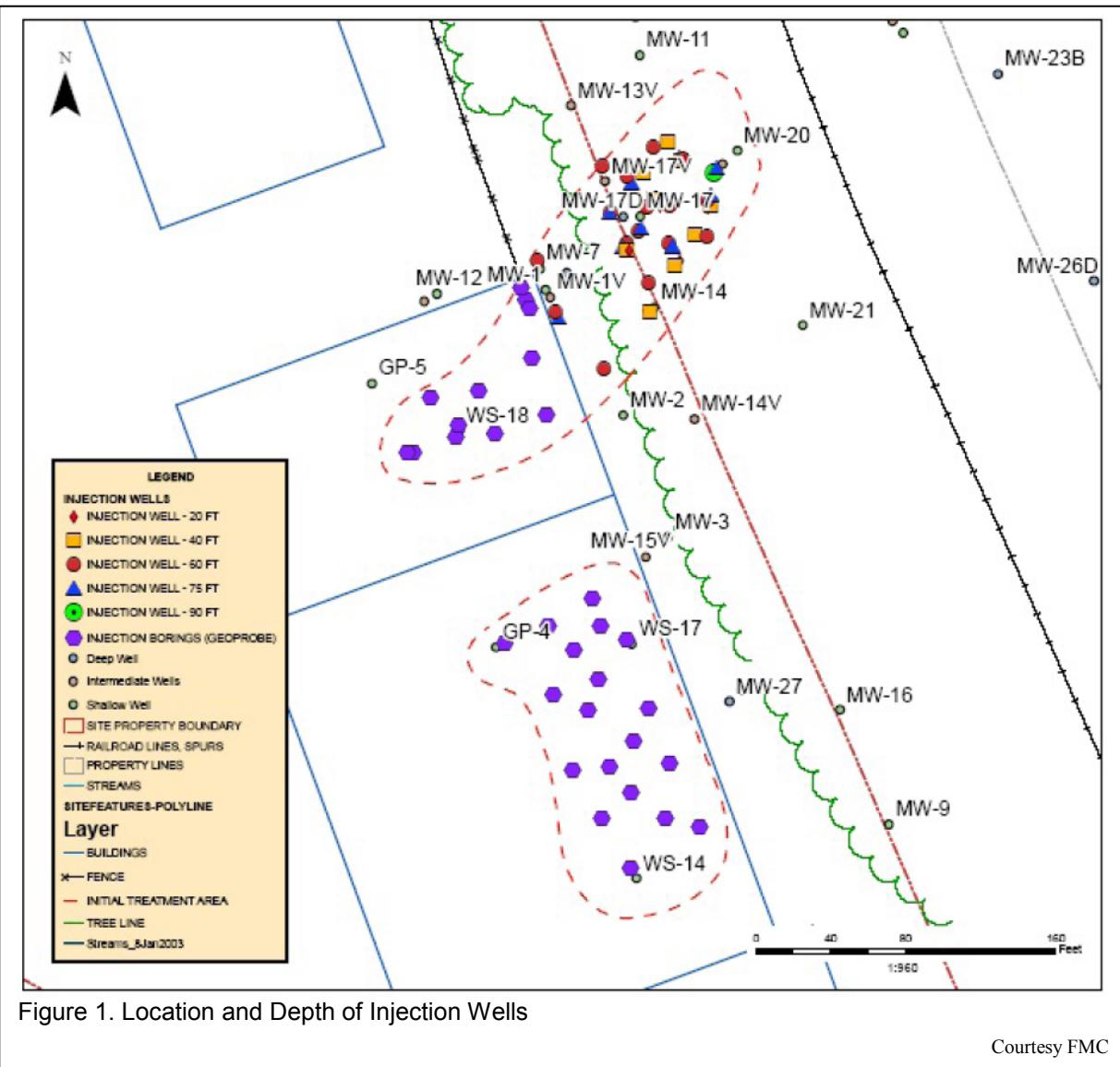
Hydrogeology: The site subsurface consists of interbedded mixtures of sand, silt, and clay. Some clayey-silt and silty-clay layers of saprolite appear below 50 ft bgs. Drilling logs suggest the presence of clastic dykes that may provide preferential flow paths.

Project Goals: The combined groundwater cleanup levels for TCA and DCA that were set through negotiations with the state for an industrial site had to be less than 16 mg/L. Concentrations of 1,4-dioxane had to be less than 5 µg/L. Groundwater in the immediate area of the site is not used for drinking water.

Cleanup Approach: ISCO using sodium persulfate was chosen for the remedial technology, though during a pilot study two years earlier, the vigorous reactivity of Fenton's Reagent on a portion of the source area had created preferential pathways to the surface and presented challenges for that portion of the source zone cleanup. Combinations of multiple catalysts, such as hydrated lime, sodium hydroxide (for base-catalyzed remedies), and steam activation were all used in conjunction with persulfate.

Thirty injection points were installed inside the building, which encompassed one-half of the area over the treatment plume. About 60 injection points were installed outside the building. Vertical profiling of contaminant concentrations in the soil and groundwater by direct push technologies was used to select injection depths. Figure 1 shows locations and depths of injection wells.

Due to the variable permeability encountered at the site, pressure injections were used. Pressure injections of persulfate ranged from 20-200 pounds per square inch (psi), depending on the geology encountered within the injection interval. The control of lateral spreading was accomplished by injection from the downgradient plume toward the source. The vertical injection interval ranged from 20-100 ft. For all but the deep injection wells, single point injection wells with approximately 1-2 ft injection intervals were used.



Hydrated lime and steam activation in combination with persulfate were used primarily for both the vadose and saturated zones under the building. This combination has proved very economical. In addition to catalyzing the persulfate, hydrated lime combines with the sulfate in solution to form gypsum, thereby reducing the concentration of sulfate in groundwater. However, sulfate is a byproduct of the reaction between the contaminant and activated persulfate. The secondary drinking water standard for sulfate (taste issue) is 250 mg/L. Because of the toxicity of the contaminants, a SVE system was used during injection at locations inside the building

to ensure no vapor exceedances occurred throughout the duration of the project.

Within the main source area, which included the railroad tracks and loading dock next to the building, hydrated lime and steam activation with persulfate were used initially. Due to difficulties with daylighting, which is a surface pathway not associated with the well bore, it was difficult to effectively transfer the heat using steam. Thus, sodium hydroxide was used instead to catalyze the persulfate.

When steam is used as the activation mechanism, a threshold number of calories (amount of heat) is required to catalyze a persulfate molecule. The selected average target temperature for this site was 45°C for 1,1,1-TCA (primary contaminant). The oxidant concentration was based on a Total Oxidant Demand Test (Haselow et. al 2003). Steam was injected under pressure at a range of 20-150 psi. Heat distribution in the treatment zone relied on convection and conduction. Temperatures achieved in the subsurface ranged from 25-60 °C on average. Higher temperatures (up to 100 °C) occasionally occurred at monitoring points due to preferential flow of steam. Subsurface temperatures were monitored in existing monitoring wells at multiple depths using thermocouples.

Well design and installation for the shallow source area included direct injection (Geoprobe®) and auger holes with a high density of application points. Well design and installation for the deep source area included direct injection (Geoprobe®) to a maximum depth of approximately 80 ft. Deep (100 ft) injection points were installed using a mud rotary drill rig. A higher density of injection points was also used in the deep source area.

Injections occurred periodically from September 2004 through June 2005. About 100,000 pounds of Klorozur™ persulfate were used, and various quantities of multiple activators were added to catalyze the persulfate:

- 2,500 pounds of calcium hydroxide
- > 500 million BTUs of steam
- 17,700 pounds of sodium hydroxide (25% by weight)

On average the amount of reactant each injection point received was:

- 5 million BTUs of steam
- 25 pounds of calcium hydroxide
- 200 pounds of sodium hydroxide
- 1,200 pounds of Klorozur™ persulfate

Higher than average quantities of mass and energy were put into some points, depending on

the contaminant mass and amenability of the subsurface. In some areas, only calcium hydroxide was used, and in other areas where daylighting was a problem, steam was not used and the persulfate was catalyzed using sodium hydroxide alone.

Monitoring nearby wells for water level changes, the presence of persulfate, concentrations of sulfate (byproduct of the reaction), oxygen reduction potential, pH, and temperature (depending on the activator) was used to evaluate remedial progress. Other process measurements used to evaluate success of oxidant application include measuring changes in electrical conductivity to estimate the zone of influence of the injection; logging injection volumes and their depths; chemical probing with depth information (direct push tools); and surface geophysics, such as ground penetrating radar, where subsurface conditions are appropriate.

Concentrations of TCA and DCE were monitored after injection events using a portable gas chromatograph (GC) made by SRI Instruments. Short-lived and relatively low concentrations of oxidation intermediates were occasionally observed and included less chlorinated ethanes and methanes (e.g., chloromethane, chloroethane). 1,4-dioxane was monitored less than GC measurable parameters because of the need for offsite laboratory analysis. Monitoring results were used to identify the areas that required additional treatment.

Project Results: The remedy took place under a guaranteed fixed-price contract for under \$1 million. The consultant who performed the work met the guaranteed fixed-price financial requirement. Concentrations have remained below target levels for a year after completion of remediation (Table 1). Overall cleanup costs were approximately \$5/ton of saturated soil. The chemical cost for treatment was roughly \$2/ton of soil. The remaining cost was steam and injection costs. The site is now in a MNA mode.

Sources:

FMC. Undated. In-Situ Chemical Oxidation with Klozur™ Activated Persulfate: Co-Mingled Plume of Chlorinated Solvents and 1,4-dioxane, 7 pp.

<http://www.envsolutions.fmc.com/Portals/fao/Content/Docs/TCA%20and%201,4%20Dioxane%20Case%20Study.pdf>

Haselow et. al. 2003. Estimating the total oxidant demand for in situ chemical oxidation design. Remediation Journal, Volume 13, Issue 4, p. 5-16.

<http://redox-tech.com/ISCOTODPaper.pdf>

U.S. EPA. 2006. Engineering Forum Issue Paper: In Situ Treatment Technologies for Contaminated Soil, EPA 542/F-06/013, 35 pp.
<http://www.epa.gov/tio/tsp/download/542f06013.pdf>

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Table 1. Contaminant Concentrations Over Time (µg/L)

Well No.	Baseline 8/27/04			Post Remediation 7/11/05			Post Remediation 3/13/06		
	DCE	TCA	Dioxane	DCE	TCA	Dioxane	DCE	TCA	Dioxane
GP-4(s)	14,200	313	NT	<1	7.36	NT	<1	<1	NT
MW-1(s)	27,800	96,000	29,000	<2	909	<5	<1	3,740	NT
MW-1v(t)	89,000	99,800	24.1	<32	31.9	<5	<16	360	NT
MW-1d(t,b)	4,950	4,390	<5	71.2	11,700	<5	<7	4,220	NT
MW-2(s)	94.1	52.3	NT	23.6	20.7	NT	NT	NT	NT
MW-3(s)	24.3	5.93	NT	19.6	8.14	NT	NT	NT	NT
MW-7(s)	5,670	57,700	199	170	7,560	<5	<8	7,240	NT
MW-9(s)	0.418	0.47	NT	<1	<1	NT	NT	NT	NT
MW-11(s)	711	1410	<5	841	1,470	<5	770	1,040	NT
MW-12(s)	32.7	23.8	NT	136	43.3	NT	NT	NT	NT
MW-13v(t)	<1	<1	NT	<1	<1	NT	NT	NT	NT
MW-14(s)	12,000	9,950	3,440	<1	23.9	<5	<1	13.8	NT
MW-14v(t)	58.9	76.2	NT	1,490	1,120	NT	NT	NT	NT
MW-15v(t)	4.22	<1	NT	7.84	<1	NT	NT	NT	NT
MW-16(s)	3.11	0.96	NT	3.31	0.5	NT	NT	NT	NT
MW-17(s)	33,700	73,000	3,400	<1	262	<5	<1	217	NT
MW-17v(t)	18.9	23.7	NT	<1	1,910	NT	<2	491	NT
MW-17d(b)	48.1	1.73	<5	127	<1	<5	NT	NT	NT
MW-20(s)	71,400	63,700	<5	46.1	3,270	<5	<4	3,020	NT
MW-20d(t)	55,300	124,000	<5	<5	4,740	<5	<4	7,510	NT
MW-21(s)	<1	<1	NT	<1	<1	NT	NT	NT	NT
MW-26d(b)	<1	<1	NT	<1	<1	NT	NT	NT	NT
WS-14(s)	81,700	5,180	NT	<2	1,090	NT	<1	928	NT
WS-17(s)	44,400	23,600	NT	<10	11,800	NT	<4	7,270	NT
WS-18(s)	32,500	1,060	NT	<2	664	NT	NT	NT	NT

NT=Not tested; (s) Shallow; (t)=Transition zone; (b)=Bedrock