

Catalyzed Persulfate Remediation of Chlorinated and Recalcitrant Compounds in Soil

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ABSTRACT: ERM and Redox Tech remediated soil impacted by a diverse suite of chlorinated compounds (alkanes and alkenes) and recalcitrant compounds (carbon tetrachloride and methylene chloride) at an Environmental Protection Agency (EPA) Region IV Superfund Site (Site) to below risk-based goals in seven months using catalyzed sodium persulfate. The persulfate was catalyzed with two activators, iron-EDTA and hydrogen peroxide, and thermally via steam injection. This field application was performed from October 2003 to April 2004 and covered an area of approximately 3,000 ft² (280 m²). Contaminants addressed in this report are those that exceeded Remedial Goals accepted by the US EPA during the Remedial Investigation, which included 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2-dichloroethane, carbon tetrachloride, methylene chloride, tetrachloroethene, trichloroethene, and 1,1-dichloroethene.

INTRODUCTION

Remedial Investigation. Approximately 50 soil borings were collected from 11,000 ft² (1020 m²) of area suspected to contain volatile organic compounds. Samples were collected from depths ranging from the ground surface to the water table, which was approximately 23 feet (7 m) below ground surface (bgs). Sample locations are identified in Figure 1. Most of this remedial investigation data was collected during 1996, along with supplemental data collected in 1998. Risk-based soil Remediation Goals (RGs) for the protection of ground water were derived based on hydraulic and solute transport models constructed to represent site conditions. Localized soil borings that exceed the RGs were grouped into three areas requiring treatment: AAA, BBB, and CCC as shown on Figure 1. The area requiring treatment was 3,000 square feet (280 square meters). Treatment depths ranged from 5 ft bgs to 25 ft bgs, as dictated by the RI data for each of three boring locations.

Additionally, three boring locations were advanced in October 2003 to collect soil data for comparison to the previous RI data collected in 1996. A soil sample was collected from one discrete depth from each

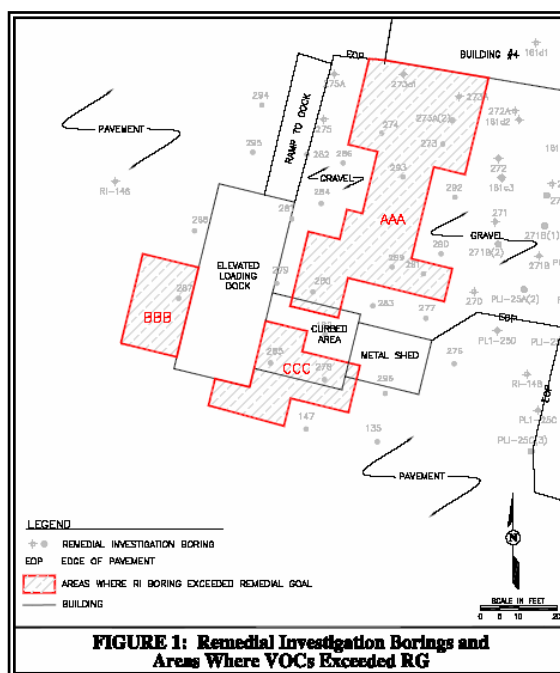


FIGURE 1: Remedial Investigation Borings and Areas Where VOCs Exceeded RG

boring location. These samples were collected prior to chemical oxidation treatment to set a more recent benchmark. The three discrete depths sampled were 3, 10, and 20 feet below ground surface (ft bgs). The 3 ft (1 m) bgs sample was near soil boring RI-287, the 10 ft (3 m) bgs sample was near RI-278, and the 20 ft (6 m) bgs sample was near RI-285.

Averages for the RI soil samples will be compared to the 2003 benchmark samples and the post-treatment data later in this report.

Oxidation Chemistry. Persulfate is a strong oxidant that has been widely used for initiating emulsion polymerization reactions, clarifying swimming pools, hair bleaching, micro-etching of copper printed circuit boards, and TOC analysis. The sodium form is the most commonly used for environmental applications. Sodium persulfate has the potential to destroy chlorinated and non-chlorinated organic compounds commonly encountered in contaminated soil and ground water. Sodium persulfate is very soluble, having a solubility of 56g/100 mL of water (56%), so it can be applied in concentrated form. Sodium persulfate oxidizes many of the same compounds as does permanganate but will also treat chloroalkanes. Persulfate also has reactivity similar to peroxide but is much more stable.

The persulfate anion is one of the strongest oxidants used in remediation. The standard oxidation reduction potential for the reaction



is 2.1 V, as compared to 1.8 V for hydrogen peroxide (H₂O₂). This potential is higher than the redox potential for the permanganate anion (MnO₄⁻) at 1.7 V, but slightly lower than that of ozone at 2.2 V.

Another persulfate oxidation mechanism is through free radicals. With the presence of certain catalysts, like heat, persulfate can be induced to form sulfate radicals (Block et al., 2004).



The sulfate radical has a similar reaction mechanism to the hydroxyl radical generated by the Fenton's chemistry. The sulfate radical is one of the strongest oxidizing species with a redox potential estimated to be 2.6 V, similar to that of the hydroxyl radical, 2.7 V.

Persulfate and sulfate radical oxidation has several advantages over other oxidant systems. In addition to its fast reaction kinetics, the sulfate radical is more stable than the hydroxyl radical and therefore able to transport to greater distances in the subsurface. Compared to permanganate, persulfate has less affinity for natural soil organics and is thus more efficient in high organic soils (Brown 2003). These attributes make persulfate a viable option for the chemical oxidation of a broad range of contaminants.

Although the persulfate anion by itself is a strong oxidizer, the reaction kinetics are slow for the more recalcitrant contaminants. However, generation of sulfate radicals can significantly enhance the kinetics of persulfate oxidation. Some catalysts, such as heat, transition metals, hydrogen peroxide, and UV radiation have been found to be able to initiate sulfate radical generation (Block et al., 2004).

Synergistic effects between hydrogen peroxide and sodium persulfate are believed possible, since hydroxyl radicals stimulate production of sulfate radicals and vice versa; this cycle of radical production has the potential to yield large-scale contaminant reduction (Block et al., 2004). It is also hypothesized that the hydrogen peroxide will quickly react with significant portion of the more reactive compounds, leaving the sulfate radicals to destroy the more recalcitrant compounds (e.g. carbon tetrachloride and methylene chloride).

Activation of persulfate yields a very potent tool for the remediation of a wide variety of contaminants, including chlorinated solvents (ethenes, ethanes and methanes), BTEX, MTBE, 1,4-dioxane, PCBs and polyaromatic hydrocarbons.

MATERIALS AND METHODS

This section describes the concentrations, volumes, and timing of the oxidant injections performed, as well as the verification samples collected to monitor the success of this in situ chemical oxidation.

Performing the In Situ Chemical Oxidation Injections. The soil was treated by injecting catalyzed oxidant solutions to chemically oxidize organic chemicals retained on the soil. Four injection events were used to treat the soil. 33 injection wells were installed in the 3,000 sq ft (278 sq m) area of soil to be treated. Injection wells were constructed of 1-inch (2.54 cm) diameter PVC to depths of 5 to 20 ft (1.5 to 6 m) below land surface with the bottom five feet (1.5 m) constructed of 0.010" slot well screen. Injection well locations are shown in Figure 2. Injection pressures were between 10 and 40 psi (approximately 500 to 2000 mmHg). During steam injection, soil temperatures up to 45C were observed. A summary of the chemical concentrations and volumes used during this soil remediation is given in Table 1.

TABLE 1. Injection Schedule (Volume, Conc., and Timing of Injections).

Injection Event #	Number of Injection Locations	Sodium Persulfate (L)	Iron-EDTA (L)	Hydrogen Peroxide (L)	Steam (MMBTU)	Potassium Permanganate (L)
		10.5 %wt	0.7%wt	8.4 %wt	per location	6 %wt
1	33	29500	13750	0	0	0
2	16	13250	0	7250	0	0
3	5	3750	0	0	5	2500
4	2	2000	0	0	4	0

The injections were performed in the order described below:

Injection 1. 13,750 liters of 0.7 weight percent iron-EDTA solution were injected into the soil via all 33 injection wells, and 29,500 liters of 10.6 weight percent sodium persulfate solution was then injected into the same wells.

Injection 2. 13,250 liters of 10.6-weight percent sodium persulfate were injected into 16 of the original 33 injection wells. Thereafter, 7,250 liters of 8.4 weight percent of hydrogen peroxide solution were injected into those same 16 wells.

Injection 3. The area of the third injection was determined based on analysis results of soil samples collected 1 month after the second treatment was completed. This third injection event was targeted to 10% of this initial treatment area. 2,500 liters of 6% potassium permanganate were injected into two temporary locations via direct push rods (in areas where sample results showed ethenes were persistent). Permanganate was used to reduce ethene concentrations, thus reducing the overall oxidant demand to be treated by the more-expensive persulfate. Next 3,750 liters of 10.4% sodium persulfate were injected into 5 temporary locations via direct push rods. 5 million BTUs of steam followed in each of those five temporary injection locations.

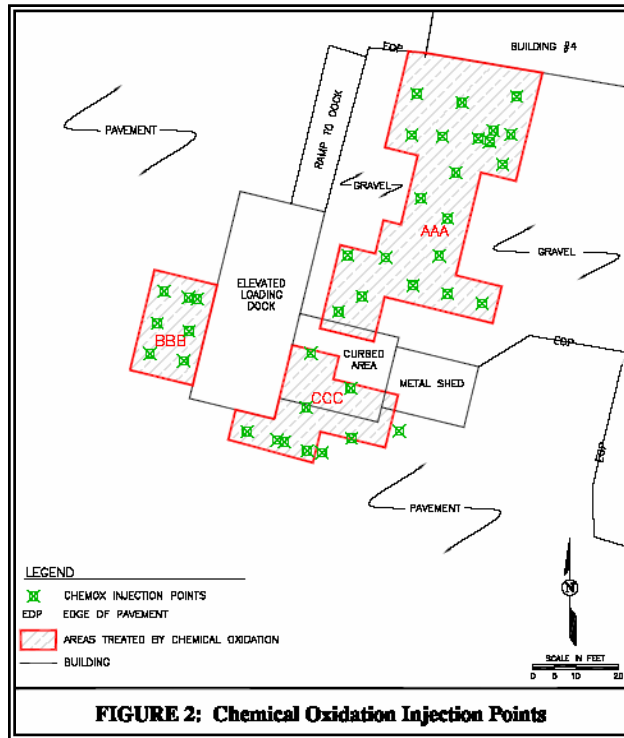


FIGURE 2: Chemical Oxidation Injection Points

Injection 4. The area of the fourth injection was determined based on analysis results of soil samples collected from the treatment area 1 month after the third treatment was completed. This injection event was targeted to 5% of this initial treatment area. Approximately 2,000 liters of sodium persulfate solution were injected into two temporary locations using direct push rods. 4 million BTUs of steam also were added into each boring location.

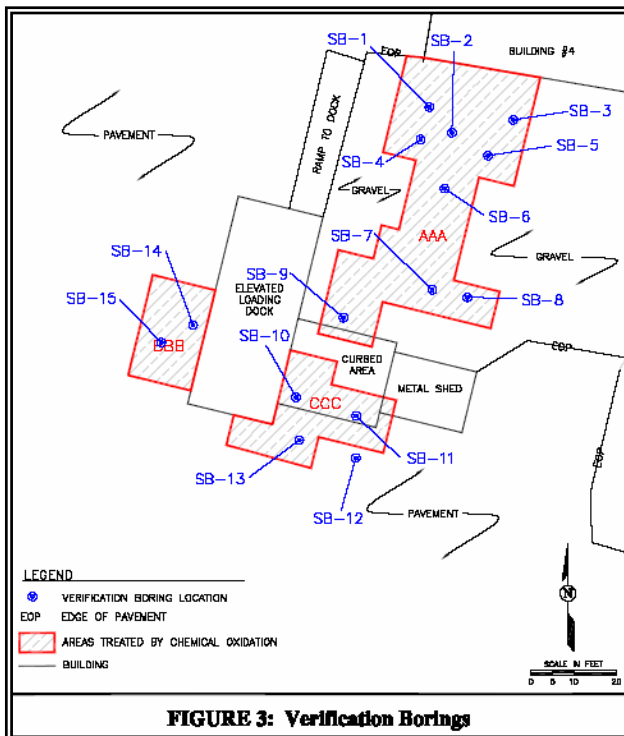


FIGURE 3: Verification Borings

Verification Sampling. EPA Region IV and the North Carolina Department of Environment and Natural Resources approved a plan where post-injection confirmation results from a particular 5-foot depth of each boring location were averaged for comparison to the risk-based goal, since the goals themselves were based on an area-averaging technique. The locations of the fifteen verification borings (SB-1 through SB-15) are shown in Figure 3. Risk-based soil RGs for the protection of ground water were

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derived based on hydraulic and solute transport models constructed to represent site conditions.

Direct push technology was used to collect soil samples in the areas where soil was treated by chemical oxidation. One performance verification boring was installed for each 200-ft² of treated surface area. The verification samples were collected from the same depth intervals in which VOC concentrations exceeded the remedial goals in historic samples. Because the constituents of concern are VOCs, each discrete sample was analyzed individually. The samples were not composited. For each soil boring location, the concentration of each VOC over a 5 ft (1.5 m) depth interval average was compared to the established performance standard for that VOC. The locations and dates of the performance verification samples are shown in Table 2. If the concentrations of one or more VOCs were greater than the applicable performance standards, additional chemical oxidation treatment was conducted at the location and depth represented by soil samples that exceeded the performance standards.

TABLE 2: Locations and Timing of Verification Sampling.

<i>Boring Location ID</i>		<i>Jan-04 Sampling Depths (m bgs)</i>		<i>Mar-04 Sampling Depths (m bgs)</i>		<i>Apr-04 Sampling Depths (m bgs)</i>
B-1	<i>Injections of iron-EDTA, sodium persulfate, and hydrogen peroxide (EVENTS 1 and 2)</i>	4 - 7	<i>Injections of sodium persulfate, potassium permanganate, and steam (EVENT 3)</i>	--	<i>Injections of sodium persulfate and steam (EVENT 4)</i>	--
B-2		4 - 7		4 - 7		--
B-3		2.5 - 7		5.5 - 7		5.5 - 7
B-4		4 - 7		4 - 7		--
B-5		2.5 - 7		2.5 - 7		2.5 - 7
B-6		4 - 5.5		--		--
B-7		2.5 - 4		--		--
B-8		4 - 5.5		--		--
B-9		1 - 2.5		--		--
B-10		5.5 - 7		--		--
B-11		2.5 - 7		--		--
B-12		2.5 - 6		2.5 - 6		2.5 - 6
B-13		5.5 - 7		--		--
B-14		0 - 1.5		--		--
B-15		0 - 1.5		--		--

After additional chemical oxidation treatment was conducted, additional performance standard verification samples were collected and analyzed from the areas and depths that previously exceeded the established performance standards (e.g. March and April 2004 samples shown in Table 2). This iterative process was followed until acceptable results were achieved. No further action was required for a location and 5-ft (1.5 m) depth interval once the concentrations of the individual VOCs were less than the applicable remedial goals.

RESULTS AND DISCUSSION

Data collected as part of the verification sampling in areas remediated for VOCs were evaluated by comparing the averaged sample results to the applicable performance standards. The first round of verification samples, which included 15 boring locations, indicated that approximately 90% of the area had been remediated to levels below the RGs. Averages were performed over each 5 ft (1.5 m) depth interval and then compared to the RGs. The first round of sampling indicated that approximately 90% of the area had been treated to below risk-based standards. This suggests that most of the VOC

contaminants were amenable to remediation using persulfate catalyzed by iron-EDTA and hydrogen peroxide. The next injection event used steam catalyzed persulfate to address the most recalcitrant compounds that remained. Samples were collected one month later which indicated that one small area remained for treatment (about 5% of the original area). A final highly targeted injection in that area brought the entire suite of chlorinated and petroleum compounds below regulatory standards.

The VOC results are summarized in Table 3 using the summary statistics of minimum value, maximum value, average, and average percent reduction in each compound.

Table 3: Comparison of PRE and POST Treatment VOC Concentration Statistics.

		1,1,1-Trichloroethane	1,1,2-Trichloroethane	1,2-Dichloroethane	Carbon Tetrachloride	Methylene Chloride	Tetrachloroethene	Trichloroethene	1,1-Dichloroethene
		Ethenes			Recalcitrant		Ethenes		
Remedial Goals		40,500	490	20	150	290	280	480	900
Average PRE-treatment Concentration		5,205	217	529	3,274	520	5,581	1,408	292
Average POST-treatment Concentration		365	28	5	9	7	41	96	40
Average % Reduction		93%	87%	99%	99.7%	99%	99%	93%	86%
Range of PRE-treatment results	MIN	4	4	8	580	7	3	2	3
	MAX	91,000	850	1,100	15,000	2,100	83,000	15,000	2,400
Range of POST-treatment results	MIN	1	1	1	1	2	1	4	1
	MAX	1,661	245	13	13	271	388	330	170

NOTE: All values are in ug/kg

The table is organized with the ethanes grouped together, followed by historically recalcitrant compounds, and then the more easily oxidized ethenes. The percent reductions noted after the catalyzed-persulfate remediation was complete ranged from 86-99% for ethanes and ethenes and was 99% for recalcitrant compounds, as shown in Table 3.

Final averages of soil left in place at the site are compared to pre-treatment average concentrations in Figure 4. This figure is arranged with ethanes on the left, recalcitrant compounds grouped in the middle, and ethenes grouped on the right. Reductions in each compound's average concentration are evident, including the

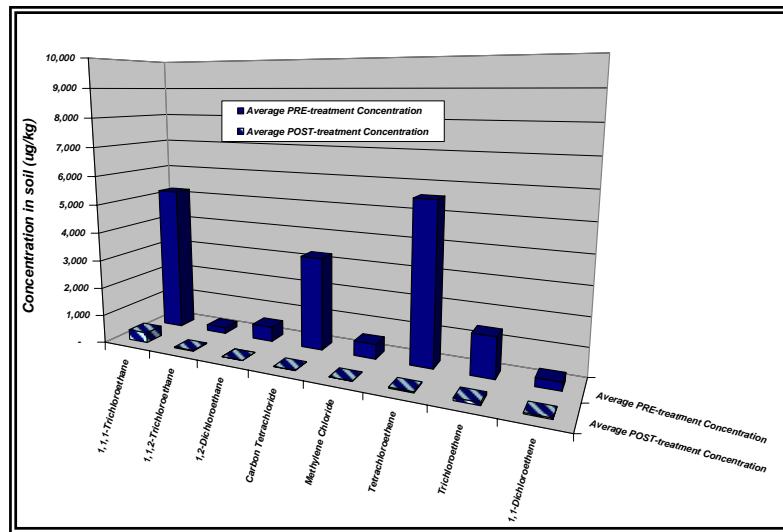


Figure 4: PRE-treatment and POST-treatment Average.

more recalcitrant compounds.

All volatile organic compounds that exceeded RGs prior to the chemical oxidation were below RGs after the remediation effort was completed. Ethanes were reduced, on average, by one order of magnitude while ethenes were typically reduced by two orders of magnitude. Carbon tetrachloride and methylene chloride were on average reduced by 2.5 orders of magnitude.

Three discrete locations are available for VOC concentration comparison in 1996, 2003 and 2004. A soil sample was collected from the same discrete depth/boring location each year. The 1996 and 2003 samples were collected prior to chemical oxidation treatment, and the 2003 samples were collected to serve as recent benchmarks of natural changes in the soil environment and advances in soil sampling technology between 1996 and 2003. The three discrete depths sampled were 3, 10, and 20 feet (1, 3, and 6 m) below ground surface.

Results are presented in Figure 5. The 2003 benchmark samples generally

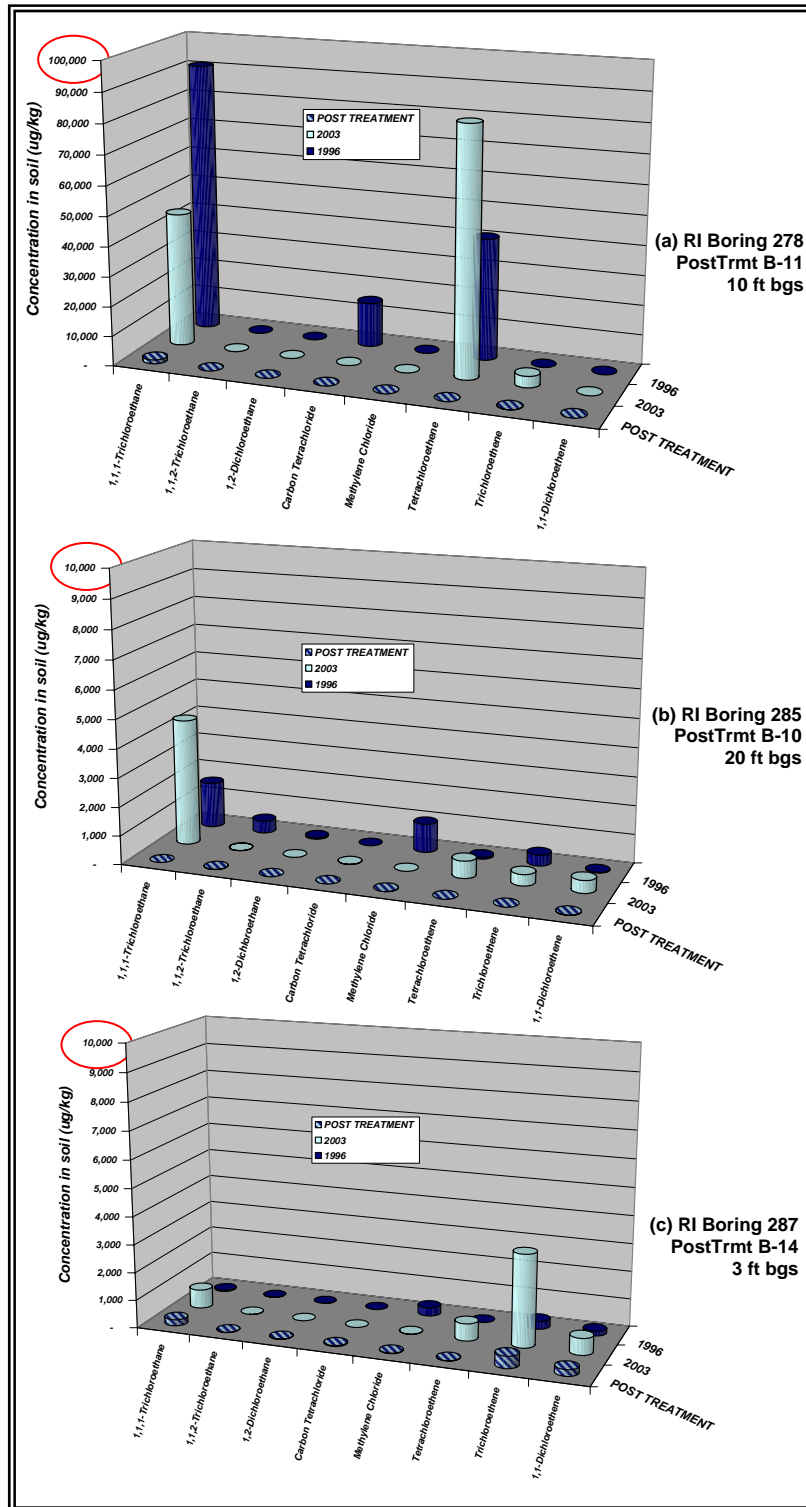


Figure 5: VOCs at Three Discrete Locations ('96, '03, '04).

showed higher concentrations than during the 1996 RI process for PCE, TCE, 1,1-DCE, and 1,1,1-TCA; however, methylene chloride and carbon tetrachloride were present lower concentrations in 2003 than in 1996. Although the concentration of ethenes/ethanes are indicated to be higher in 2003 than during the remedial investigation and planning process, Figure 5 shows the ethenes/ethanes were reduced by at least one order of magnitude during the chemical oxidation treatment, and by up to three orders of magnitude at some locations.

CONCLUSIONS

Contaminants that were treated to below Remedial Goals using catalyzed sodium persulfate injections include 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2-dichloroethane, carbon tetrachloride, methylene chloride, tetrachloroethene, trichloroethene, and 1,1-dichloroethene. This in-situ chemical oxidation proved that ethanes, ethenes, and some recalcitrant compounds can be oxidized by sodium persulfate catalyzed by iron-EDTA, hydrogen peroxide, and heat.

The remediation was completed at a substantial savings to “dig-and-haul” because existing infrastructure did not have to be removed. The ISCO remediation was completed for \$65 per ton. Excavation and disposal of the listed hazardous soil would have been approximately 3 to 4 times that amount.

REFERENCES

- Block, P.A., R.A. Brown, and D. Robinson. 2004. “Novel Activation Technologies for Sodium Persulfate In Situ Chemical Oxidation.” *Proceedings of the Fourth International Conference on the Remediation of Chlorinated and Recalcitrant Compounds*. Monterey, California.
- Brown, R.A., D. Robinson, and G. Skladany. 2003. “Response to Naturally Occurring Organic Material: Permanganate versus Persulfate.” *ConSoil 2003*. Ghent Belgium.