

## IN SITU OXIDATION OF DNAPL USING PERMANGANATE: IDC CAPE CANAVERAL DEMONSTRATION

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**ABSTRACT:** DOE, DOD, USEPA and NASA, formed the Interagency DNAPL Consortium to jointly fund a large scale field demonstration of three chlorinated solvent remediation technologies, at NASA's Launch Complex 34, located at Cape Canaveral, Florida. *In situ* chemical oxidation using potassium permanganate was chosen as one of the demonstration projects and was successfully completed in May 2000. The site geology consists of several stratigraphic units containing layered, heterogeneous lithology with permeability contrasts of two orders of magnitude. TCE was present before treatment at up to 30,000 mg/kg in soil, and 1,500 mg/L in groundwater. Approximately 6,100 kg of TCE (including 5,039 kg of DNAPL) was estimated by Battelle and EPA to lie within the 50-foot by 75 foot by 45 foot deep demonstration plot. The permanganate injection strategy consisted of direct push pressure injection (lance permeation). Over 150,000 pounds of permanganate were injected at two-foot discrete intervals at numerous locations across the cell in a three-phase injection program. The total reduction in TCE mass was calculated through collection and analysis of over 192 discrete soil samples. The results show that the overall mass of TCE within the cell was reduced by 82% and that 84% of the DNAPL was eliminated.

**SYSTEM DESIGN:** The oxidation demonstration consisted of the design, installation, and operation an *in situ* chemical oxidation treatment technology using potassium permanganate (KMnO<sub>4</sub>) to destroy DNAPL and residual chlorinated ethenes in soil and groundwater. The KMnO<sub>4</sub> reacts with chlorinated ethenes, such as DCE, TCE, PCE and VC, to oxidize the compounds through cleavage of the double bonds. The balanced chemical reaction for the oxidation of TCE at a normal pH is:



As seen from the reaction, carbon dioxide, manganese dioxide, potassium ions, chloride ions and a hydrogen ion are produced from the reaction of TCE and KMnO<sub>4</sub>.

At this site, direct push pressure injection (lance permeation) was selected as the application method. A system was designed to deliver permanganate at precise dosages over 2-foot vertical intervals from the top of the contaminated zone to the base of the demonstration at 45 feet below grade. This design was chosen based on the fact that formation permeabilities and contaminant mass distribution varied both laterally and vertically. The permanganate dose and application rate and duration were adjusted at each point to provide the desired loading corresponding to the level of contaminant mass at that location and vertical interval. The cell was divided into three different lithologic units for treatment: an Upper Sand Unit (USU, Zone A), a Middle Fine Grained Unit (MFGU, Zone B) and Lower Sand Unit (LSU, Zone C). The MFGU zone and base of the LSU contained a high proportion of silt, clay, and shell lenses. A total of nineteen separate

injection rods and injection tips were driven to the desired depths by a direct push rig. The injection tip consisted of a customized Geoprobe<sup>®</sup> open interval, 360-degree-circumference, hole-perforated drive stem located between two wider diameter sections that functioned as packers. The perforated drive probe had 0.25-inch perforations and a 0.010 inch slot continuous wire-wound stainless-steel screen.

The permanganate delivery system consisted of an on-site continuous mix, automated feed system developed by the permanganate supplier, Carus Chemical Company (Carus). The early configuration used a 45,000-pound portable dry bulk hopper to provide both storage and dry solids feeding to the mix unit. The bulk hopper was replaced during Phase III in favor of the use of 1,500 kg (3,300 lb.) “Cycle Bin” steel, skidded containers of free-flowing grade permanganate. The permanganate solution was mixed to an injection concentration range of 0.2% to 3.0% by mixing the dry, free-flowing potassium permanganate solid with hydrant water. This system was able to produce an automated effluent at a programmable flowrate and permanganate concentration.

A high-pressure chemical feed pump was used to convey KMnO<sub>4</sub> from the mix tank to an injection well manifold via PVC pressure hoses with dry-disconnect quick-connect fittings. The piping manifold was used to meter flow to the individual injection drive-stems. Each of the nineteen manifold lines had a totalizing flowmeter, pressure gauge, throttle valve, check valve, and PVC hosing. The flow rates per point ranged from 0.1 to 6.1 gpm at wellhead pressures of 15-55 psig.

**TREATMENT OPERATIONS:** The permanganate treatment was conducted in phases so that the interim results obtained could be used to focus subsequent injections. An initial pilot tracer test was performed using a solution consisting of 2% sodium fluoride and 2% permanganate. This test was used to finalize the design parameters and illustrated the radial influence from the proposed injection points along with the consumption of permanganate as a function of distance and contaminant mass surrounding the injection point. Three permanganate injection phases were completed over a 61 period from September 1999 to April 2000. An injection sequence summary is listed below:

<b>Injection Sequence Summary</b>					
Phase	Start	End	Days of Injection (hours)	Mass Injected (lbs)	Zones Injected
Pilot	8/12/99	8/14/99	36	1,402	B1 to B5
I	9/8/1999	10/29/1999	32	62,676	All
II	11/17/1999	11/24/1999	8	13,825	A1 to A5, B1 to B2
III	3/20/2000	4/17/2000	21	72,750	A5, B2, B3, C1 to C5
<b>Total</b>			<b>61</b>	<b>150,653</b>	

**CLEANUP EFFECTIVENESS:** The cleanup effectiveness was determined through analysis of soil and groundwater pre- and post-treatment as part of the EPA SITE Program performance monitoring implemented by Battelle. Battelle and IT calculated the TCE reduction in

groundwater using nested monitor wells located within the cell. The groundwater cleanup effectiveness was determined to be 83% for the USU, 95% for the MFGU and 89% for the LSU. The soil cleanup effectiveness within the oxidation cell was determined by Battelle using 12 soil borings sampled before and 1 month after treatment. The results show that the overall mass of TCE within the cell was reduced by 82% and that 84% of the DNAPL was eliminated. Battelle defined DNAPL as any TCE soil concentration greater than 300 mg/kg. A summary of the mass reduction by zone is shown in the following table. The most significant change in TCE reduction was in the LSU Zone C5. TCE concentrations in C5 (samples taken at 44 feet bgs) with initial concentrations as high as 8,000 mg/kg were all less than 100 mg/kg, with six boring results below 7 mg/kg.

<b>TCE Mass Reduction Summary</b>						
Stratigraphic Unit	Total TCE Mass (kg)		DNAPL Mass (kg)		Total TCE	DNAPL
	Pre-Treatment	Post-Treatment	Pre-Treatment	Post-Treatment		
USU	846	23	601	10	-97%	-98%
MFGU	1,048	233	749	163	-78%	-78%
LSU	4,228	844	3,689	637	-80%	-83%
<b>Total</b>	<b>6,122</b>	<b>1,100</b>	<b>5,039</b>	<b>810</b>	<b>-82%</b>	<b>-84%</b>

The overall TCE decreases in each lithologic zone are skewed by the presence of discrete areas within each interval (as defined by the soil boring for that area) with a high post-treatment TCE concentration. Permanganate was still present in the soil and groundwater during the sampling event and additional treatment and TCE reduction have likely occurred since the one month post-treatment sampling

#### **CONCLUSIONS:**

- Full cell TCE reduction was calculated to be 82%. DNAPL concentrations were estimated to be reduced by as much as 84%.
- Significant chloride increases were noted in groundwater within the cell adding additional data to support the oxidation of TCE, rather than migration out of the cell.
- No evidence was observed of the formation of MnO<sub>2</sub> crust on the surface of DNAPL pockets from the oxidation reaction with TCE. The soil cores from areas of DNAPL showed an even distribution of KMnO<sub>4</sub> for a given soil characteristic. Also, the complete degradation of portions of the site that were presumed to have DNAPL is evidence that DNAPL was not effectively shielded from the KMnO<sub>4</sub>. The DNAPL observed on site was believed to be residual DNAPL saturation within pore matrices as opposed to “pools” of DNAPL. The pre- and post-treatment hydraulic conductivity testing performed by Battelle showed no significant difference from the permanganate injection. This result demonstrates that the formation was not plugged with MnO<sub>2</sub> solids.
- Potassium data, permanganate data and TCE concentrations in groundwater all indicated that some displacement of dissolved TCE and KMnO<sub>4</sub> did occur outside of the oxidation cell during treatment. For future site applications displacement can be minimized by treatment of the whole plume, by using an outward to inward injection pattern or including a groundwater extraction system for plume control.