

## **In-Situ Chemical Oxidation with Klozur™ Activated Persulfate: Co-Mingled Plume Of Chlorinated Solvents and 1,4 Dioxane**

Remediation Contractor: Redox Tech - Morrisville, NC  
Chemical Supplier: FMC Corporation - Philadelphia, PA

### 1) Site Description

The site is located within the Piedmont (physiographic province) of North Carolina. The property contains a divided warehouse and active manufacturing building that is equipped with loading docks and a small office. The property is bordered by an active railroad track. A release of solvents or cleaning agents from an industrial process occurred primarily in the vicinity of the loading docks. The major contaminants were 1,1,1-trichloroethane (1,1,1-TCA), 1,1-dichloroethene (1,1-DCE), and 1,4-dioxane. The site sits in a mixed zone of an industrial and residential area within a fairly large city. The impacted area is 1.5 acres or roughly 68,000 square feet. One-half of the treatment area was underneath an existing building (concrete/slab floor) and the other half was outside of the building. Based on initial sampling, there were very high concentrations of contaminants; some analytical results indicated the potential presence of Dense Non-aqueous Phase Liquid (DNAPL) in the vadose zone and in the saturated zone. Even though there were no known active drinking water wells near the site, there was potential receptor impact through vapor intrusion. The goal of the remediation was to reach realistic clean-up levels to allow the property to be resold.

### 2) Site Characterization

Contamination ranged from the surface down to 100 feet below ground surface. The subsurface materials in the target area consisted of Piedmont soils, including a heterogeneous mix of sand, silt and clay. In the lower treatment depths of 50-100 feet, there was some Saprolite, which is composed of layers of clayey silt and silty clay. Based on prior characterization performed at the site, there was a vertical gradient downward as well as some complicated geologic features, such as suspected clastic dykes, which produced significant flow path contrasts.

Activated persulfate was selected as the oxidant of choice because of its known ability to degrade the target contaminants. FMC Corporation's remediation grade persulfate, Klozur™, was used in conjunction with various activation methods. Target injection volumes of activated persulfate were selected based on the sum of the prior characterization data, which included multiple level groundwater data. Vertical intervals were determined based on layered isoconcentration contour maps. The bulk of the activated persulfate was injected in the area that was used to unload 1,1,1-TCA from rail shipments, however discrete contaminant volumes were addressed that were some distance away from the shallow source area, at around 100 feet deep. Both the vadose and saturated zones were treated at this site.

Vadose zone treatment consisted of cluster wells in a small area, with a higher density of injection points to insure comprehensive lateral distribution, and better contact. Two years prior to activated persulfate treatment, Fenton's chemistry was used to treat a portion of the source area in a pilot study. This activity created many surface flow paths, which made

it difficult to laterally distribute the activated persulfate without daylighting. To overcome this, cluster wells were installed, and numerous re-injections at smaller volumes were performed to decrease the chance for surfacing of the oxidant. Because of high concentrations of contaminant were known to exist in the vadose zone, fairly high concentrations of persulfate were injected (15-25 wt% persulfate).

Saturated zone injections exhibited significant channeling, probably as a result of clastic dykes and other formation heterogeneity. Because of this, the injectate moved in significantly different flow paths, depending on whether they were inside or outside the dyke.

### 3) Treatment Selection/Design

The treatment selection and design consisted of combinations of multiple catalysts, such as hydrated lime, sodium hydroxide (for base-catalyzed remedies), FeEDTA (ferric), and steam activation used in conjunction with persulfate.

For both the vadose and saturated zone under the building, hydrated lime and steam activation, in combination with persulfate, were primarily used. These combinations have proven to be very economical. It should be noted that as a by-product of the reaction between the contaminant and activated persulfate sulfate will be formed. There is a secondary drinking water standard of 250 mg/L for sulfate (taste issue). In addition to catalyzing the persulfate, hydrated lime will combine with the sulfate in solution to form gypsum, thereby reducing the concentration of sulfate in ground water.

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. Instead, sodium hydroxide was used to catalyze the persulfate.

Well design and installation for the shallow source area included direct injection (Geoprobe™) and auger holes with a high density of application points. The need for a large number of points was due to daylighting to the surface as a result of prior remediation activities (Fenton's chemistry).

Well design and installation for the deep source area included direct injection (Geoprobe™ to a maximum depth of approximately 80 feet) and deep (100 feet) injection points installed using a mud rotary drill rig. A higher density of injection points was also used in the deep source area.

#### 3-a) Energy and Oxidant - Target Temperature

A threshold number of calories (amount of heat) is needed to catalyze a persulfate molecule. The selected average target temperature for this site was 45 degrees C for 1,1,1 -TCA (primary contaminant) based on FMC literature. The oxidant concentration was based on Total Oxidant Demand (TOD) Test (ref: Haselow et. el, *Estimating the Total Oxidant Demand for In Situ Chemical Oxidation Design*, Remediation Autumn 2003). Temperatures achieved in the subsurface ranged from 25-60 degrees C on average. Higher temperatures (up to

100 degrees 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.

### 3-b) Injection/Transfer of Heat in the Subsurface

Steam injection was used to heat up the subsurface. Steam was injected into the subsurface through injection wells. The same injection points that were used for the steam activation were also used for the injection of persulfate. Steam was injected under pressure, ranging from 20-150 psi. Convection and conduction were the delivery mechanisms relied upon for heat distribution in the treatment zone.

### 3-c) Injection of Persulfate in the Subsurface

Due to the variable permeability encountered at the site, pressure injections were used. Pressure injections for persulfate ranged from 20-200 psi depending on the geology encountered within the injection interval. The control of lateral spreading is generally accomplished by injection from the down gradient plume toward the source. The vertical injection interval ranged from 20-100 feet. For all but the deep injection wells, single point injection wells with approximately 1-2 feet injection intervals were used.

### 3-d) Limits of Free Product

With separate phase product and chemical oxidation (in this case, persulfate oxidation) there generally has to be a mass transfer of the contaminant to the aqueous phase. Then, the (required stoichiometric amount of) oxidant has to come in contact with the contaminant of concern in order for the oxidation to occur. Source reduction is always advised when the source is accessible and removal is economically feasible. Source reduction can be achieved by direct removal, soil vapor extraction (SVE), air sparging or other methods.

## 4) Remedy Implementation/Performance Monitoring

### 4-a) Remedial Action Objectives/Cleanup Goals

The Remedial Action Objectives were to reduce the contaminant concentrations to set target concentrations:

#### Starting Concentrations:

1,1,1 - TCA - 203 mg/L  
1,1 -DCE - 82 mg/L  
1,4 Dioxane exceeding 50 mg/L,

Reduction of the contaminants, to the following concentrations, had to be met in order for the property to be sold:

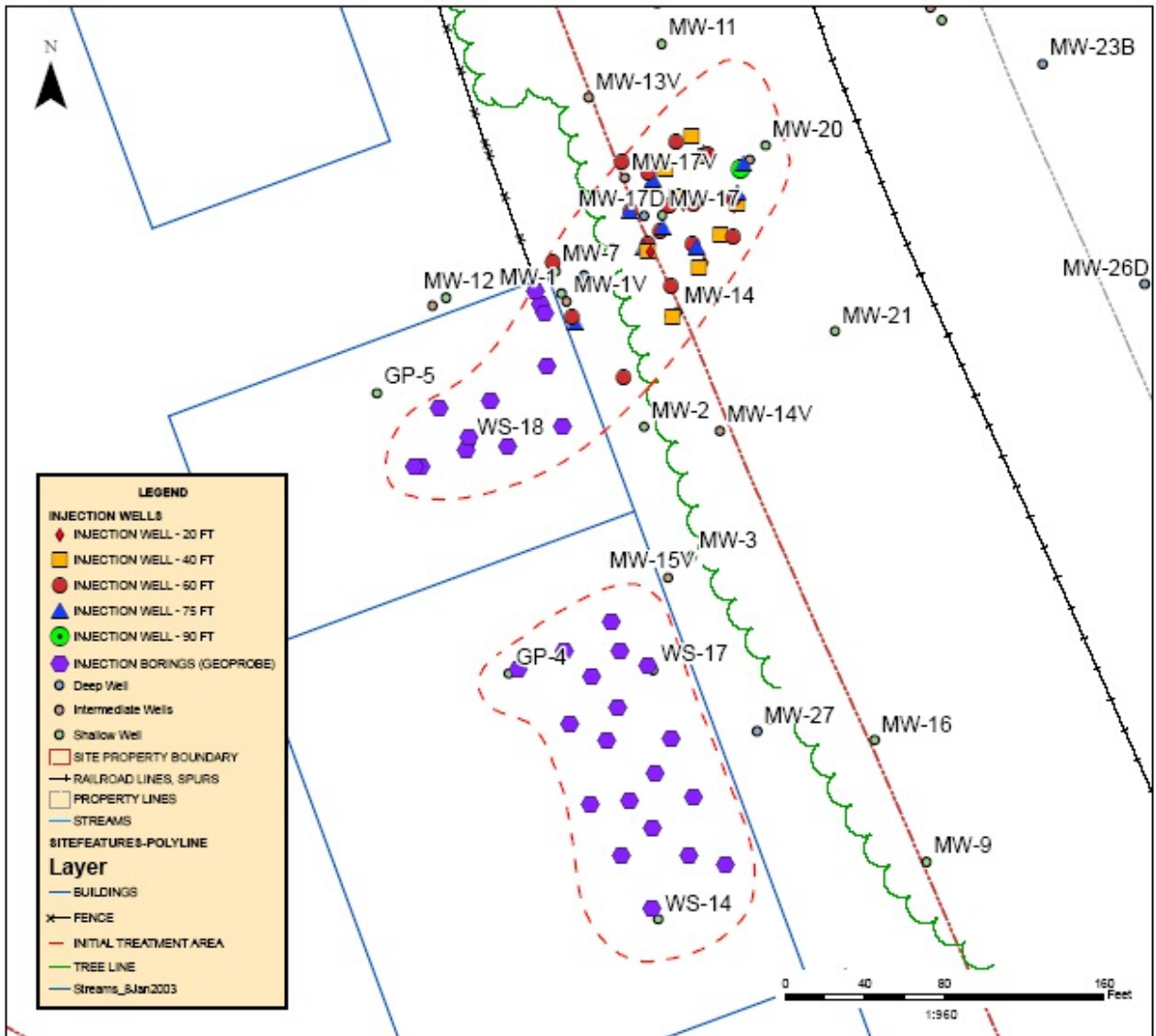
1,1,1 -TCA & 1,1 -DCE combined < 16 mg/L  
1,4 Dioxane < 5 µg/L

### 4-b) Vapor Release

A SVE system was used during injection at locations inside the building. No contaminant vapor exceedences were measured through the duration of the project.

4-c) Number of Injection Points (picture/diagram)

There were a total of 30 injections points installed inside the building, which encompassed one-half the treatment plume. Outside the building, approximately 60 injection points were installed.



Injections occurred periodically from September 2004 through June 2005. Approximately 100,000 lbs of Klozur™ persulfate was used. To catalyze the persulfate, multiple activators were used. Their quantities are as follows:

Activators

- \* 2,500 lbs of calcium hydroxide
- \* > 500 million BTU's steam
- \* 17,700 lbs of sodium hydroxide (25 wt%)

Oxidant

\* 100,000 lbs Klozur™ persulfate

Per injection point (total of 90 points, 30 inside the building and 60 outside the building), on average;

- \* 5 million BTU's of steam
- \* 25 lbs of calcium hydroxide
- \* 200 lbs of sodium hydroxide
- \* 1,200 lbs of Klozur™ persulfate

Again, the quantities above were averaged; however more mass and energy were put in to some points versus others, depending on the contaminant mass and amenability of the subsurface.

4-d) Hot Sampling

Temperatures were typically not high enough in the monitoring wells to warrant special sampling procedures. So, no hot sampling was required.

4-e) Timing Between Injections

The timing between activator (steam, NaOH, Ca(OH)<sub>2</sub>) injection and oxidant injection occurred from hours to days depending on injection location specific conditions (e.g. daylighting concerns).

4-f) Issues with Drilling into DNAPL Zones ("drag down")

There were no issues with drilling into NAPL or DNAPL zones. No "drag down" was observed based on well concentration data.

4-g) Groundwater Rebound Data

BASELINE GROUNDWATER ANALYTICAL RESULTS						POST-REMEDIATION GROUNDWATER ANALYTICAL RESULTS							
AQUIFER ZONE	WELL ID	8/27/2004 COMPOUND CONCENTRATION, PPB				7/11/2005 COMPOUND CONCENTRATION, PPB				3/13/2006 COMPOUND CONCENTRATION, PPB			
		1,1-DCE	1,1,1-TCA	Combined	1,4 Dioxane	1,1-DCE	1,1,1-TCA	Combined	1,4 Dioxane	1,1-DCE	1,1,1-TCA	Combined	1,4 Dioxane
S	GP-4	14200	313	14513	NT	<1	7.36	<8.36	NT	<1	<1	<2	NT
S	MW-1	27800	96000	123800	29000	<2	909	<911	<5	<1	3740	<3741	NT
T	MW-1v	89000	99800	188800	24.1	<32	31.9	<63.9	<5	<16	360	<376	NT
T, B	MW-1d	4950	4390	9340	<5	71.2	11700	11771.2	<5	<7	4220	<4227	NT
S	MW-2	94.1	52.3	146.4	NT	23.6	20.7	44.3	NT	NT	NT	NT	NT
S	MW-3	24.3	5.93	30.23	NT	19.6	8.14	27.74	NT	NT	NT	NT	NT
S	MW-7	5670	57700	63370	199	170	7560	7730	<5	<8	7240	<7248	NT
S	MW-9	0.418	0.47	0.888	NT	<1	<1	<2	NT	NT	NT	NT	NT
S	MW-11	711	1410	2121	<5	841	1470	2311	<5	770	1050	1820	NT

S	MW-12	32.7	23.8	56.5	NT
T	MW-13v	<1	<1	<2	NT
S	MW-14	12000	9950	21950	3440
T	MW-14v	58.9	76.2	135.1	NT
T	MW-15v	4.22	<1	<5.22	NT
S	MW-16	3.11	0.96	4.07	NT
S	MW-17	33700	73000	106700	3400
T	MW-17v	18.9	23.7	42.6	NT
B	MW-17d	48.1	1.73	49.83	<5
S	MW-20	71400	63700	135100	<5
T	MW-20d	55300	12400 0	179300	<5
S	MW-21	<1	<1	<2	NT
B	MW-26d	<1	<1	<2	NT
S	WS-14	81700	5180	86880	NT
S	WS-17	44400	23600	68000	NT
S	WS-18	32500	1060	33560	NT

136	43.3	179.3	NT
<1	<1	<2	NT
<1	23.9	<24.9	<5
1490	1120	2610	NT
7.84	<1	<8.84	NT
3.31	0.5	3.81	NT
<1	262	<263	<5
<1	1910	<1911	NT
127	<1	<128	<5
46.1	3270	3316.1	<5
<5	4740	<4745	<5
<1	<1	<2	NT
<1	<1	<2	NT
<2	1090	<1092	NT
<10	11800	<11810	NT
<2	664	<666	NT

NT	NT	NT	NT
NT	NT	NT	NT
<1	13.8	<14.8	NT
NT	NT	NT	NT
NT	NT	NT	NT
NT	NT	NT	NT
<1	217	<218	NT
<2	491	<493	NT
NT	NT	NT	NT
<4	3020	<3024	NT
<4	7510	<7514	NT
NT	NT	NT	NT
NT	NT	NT	NT
<1	928	<929	NT
<4	7270	<7274	NT
NT	NT	NT	NT

Aquifer Zones (Note: Zones are interconnected with one another, distinction is for reporting purposes only)

S = Saprolite Zone

T = Transition Zone

B = Bedrock Zone


<1 = Result less than laboratory practical quantitation limit (shown in PPB).

1,1-DCE = 1,1-Dichloroethene

1,1,1-TCA = 1,1,1-Trichloroethane

NT= Not Tested For This Compound

PPB - Parts per Billion or micrograms per liter (ug/L)

 indicates source area

Keeping the pH of the aquifer as close to neutral as possible to decrease metals solubilization/mobilization.

#### 4-h) In-Situ Process Control

Monitoring nearby wells for water level changes, presence of persulfate, concentrations of sulfate (by-product of the reaction), ORP, pH and temperature depending on the activator) can all be used to evaluate the progress and success of oxidant application. An increase in electrical conductivity is an important way to understand the zone of influence of the injection. Other process controls include logging of volumes injected and depths, chemical probing with depth information and surface geophysics, such as ground penetrating radar where appropriate.

Process control changes were implemented due to daylighting issues in the source area (utilized higher density injection points and sodium hydroxide). Interim field screening was used because some contaminants had more mass in

specific areas than previously identified. Within these areas, the amount of persulfate was increased to account for the higher contaminant mass. The use of process control optimization allowed the site to be remediated.

#### 4-i) Intermediates Monitored

Concentrations of 1,1,1 - TCA and 1,1 - DCE were monitored after injection events using an SRI portable GC. 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 periodically monitored due to the need for lab testing versus field testing.

#### 5) Cost Information

This was a guaranteed fixed price contract for < \$1 million. The consultant who performed the work for this site met the guaranteed fixed price financial requirement. Concentrations have remained below target levels for a year after completion of remediation costs.

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.

#### 6) MNA or ENA Component

Monitored natural attenuation (MNA) was a component of the remedy used at this site. MNA was used to negotiate treatment levels above MCLs

A by-product of the persulfate reaction is sulfate. Sulfate could potentially hinder full reduction of the contaminants with the addition of sulfate to the system but this is very site specific. Dissolved sulfate ions are highly soluble and generally move rapidly through the aquifer, so ambient sulfate conditions usually return in a few months. Sulfate concentrations at the site have remained below 250 ppm, which is the secondary drinking water standard.