

## **Controlled Vadose Zone Saturation and Remediation (CVSR) Using Chemical Oxidation**

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### **Abstract**

Controlled Vadose Zone Saturation and Remediation (CVSR) is essentially a long overdue advancement of standard in-situ treatment methods that have been traditionally used in the saturated zone. Unsaturated zone treatment technologies are not new, but they normally revolve around mechanical operations such as soil vapor extraction (SVE). While the cost of CVSR is comparable to SVE, it can generally be performed within a much shorter timeframe (6 months). To our knowledge, this is only the second published report combining CVSR with in-situ chemical oxidation (ISCO).

CVSR technology was successfully applied to an active industrial site in Illinois. Alkaline activated sodium persulfate using sodium hydroxide was used to treat the shallow soils to a depth of 15 feet. The vadose zone soils were contaminated with a variety of VOC constituents including PCE, TCE, methylene chloride, ethylbenzene, toluene, and total xylenes. Prior to the field injections, a soil buffering test was performed in the laboratory in order to determine the amount of sodium hydroxide needed to raise the pH of the soil to above 10.5 units and maintain it for five days.

Because chemical oxidation relies on diffusion of oxidants in an aqueous medium, the vadose zone soils were saturated using a combination of vertical injection wells, an infiltration gallery, and horizontal injection wells installed beneath two small buildings. The infiltration gallery and the horizontal wells were initially used to percolate water into the vadose zone to achieve saturation. The vertical and horizontal wells were then used to inject the hydroxide and oxidant. A total of 12 vertical injection wells were installed in two treatment areas along with the infiltration gallery. Due to the presence of low permeability silts and clays, each vertical injection well had an estimated radius of influence of 10 feet. Approximately 4,700 gallons of sodium hydroxide (25% concentration) and 11,500 pounds of sodium persulfate were injected over a 27 day period in November and December of 2008. A second injection of activated persulfate was performed in Area 1 in August 2009.

The concentrations of the compounds of concern, PCE, TCE, methylene chloride, ethylbenzene, toluene, and total xylenes, all decreased from 88% to 99% within 180 days after treatment. The ISCO injections attained the site-specific soil cleanup criteria, in conjunction with an engineered barrier, established by the State of Illinois EPA.

### **Project Site Description**

The project site is located in a suburb located just north of Chicago, Illinois. The site was impacted by various volatile organic constituents, including toluene, ethylbenzene, total

xylenes, acetone, methylene chloride, PCE, and TCE. Two areas of concern exist at the site; the Filling Room (Area 1) and the Fill Pipe area (Area 2). The Filling Room Area measured approximately 3,850 ft<sup>2</sup> and the Fill Pipe Area measured 1,200 ft<sup>2</sup>. Depth to groundwater beneath the site is approximately 5 feet below ground surface (bgs) beneath the Filling Room Area and 15-16 feet bgs in the Fill Pipe Area. Soils were predominantly silty clays and clayey silts with some sandy stringers. No visual LNAPL or DNAPL was present in the monitoring wells prior to the ISCO treatment, although the high concentrations in the soil and groundwater (over 1% saturation level) indicate that LNAPL or DNAPL could be present at the site.

The vadose zone soils in the two areas of concern were the primary target for remediation. At the Filling Room Area (Area 1), the target treatment zone was from 2 feet to 8 feet bgs. At the Fill Pipe Area (Area 2), the target treatment zone was from 2 feet to 15 feet bgs

### **Project Objectives**

The objective of the ISCO injection was to reduce the soil concentrations of VOCs at the Site to concentrations below site-specific Tier 2 Soil Remediation Objectives established by the State of Illinois EPA. To accomplish the ISCO treatment, the vadose zone soils were initially saturated with water using an infiltration gallery and horizontal injection wells in order to create an aqueous media and allow for dispersion of oxidants.

### **Infiltration Gallery and Injection Well Construction**

JAG Consulting Group designed and installed an infiltration gallery in Areas 1 and 2 to saturate the vadose zone and to provide an aqueous medium for dispersion and diffusion of the persulfate radicals and to provide oxidant contact with all the soil particles and VOCs within the vadose zone. In addition, eight horizontal wells were drilled under the two small buildings located in Area 1 in order to treat VOC contamination under the buildings (see Figure 1). The horizontal borings were drilled with a horizontal boring machine, as shown in Figure 2.

ENVIRON installed eleven new vertical injection wells, designated IW-1 to IW-11, within the two treatment areas on November 5 to 7, 2008 (see Figure 1). Eight of the new injection wells in Area 1 were screened from approximately 3 feet to 8 feet bgs, while the remaining three injection wells in Area 2 were screened from 3 feet to 15 feet bgs. The injection wells were constructed of 2-inch schedule 40 PVC casing and screen. At ground surface, each injection well was completed with a concrete pad and a flush-mounted steel well box. Based on the low permeability silts and clays, each injection well had an estimated radius of influence of 10 feet. Following installation, the injection wells were developed by ENVIRON by surging the sand pack and removal of water until clear water was produced.

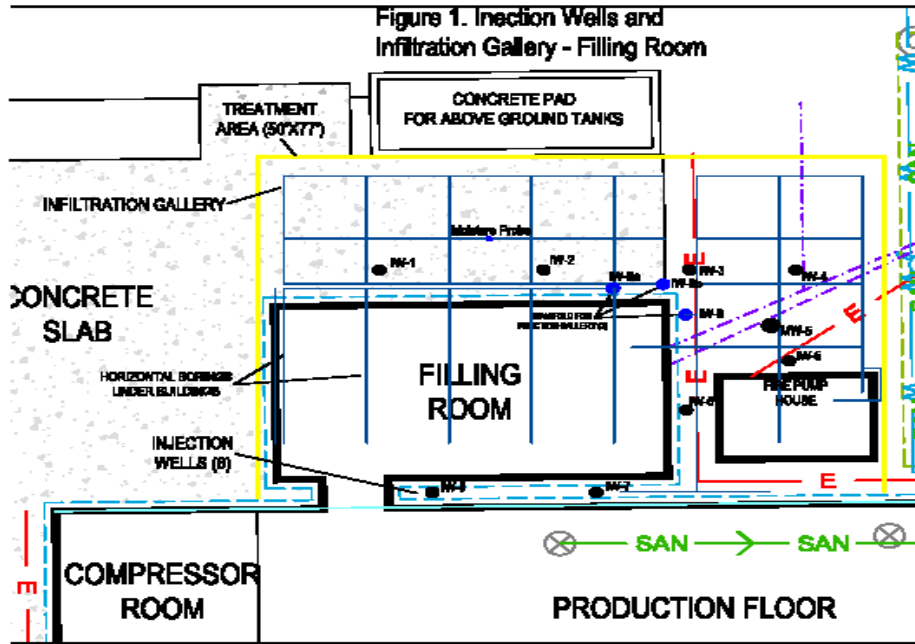


Figure 2. Drilling of Horizontal Wells (Area 1)



### **Bench Scale Testing**

A soil buffering test in the laboratory was performed and confirmed that the soils beneath the site are highly buffered. The buffering test was performed by determining the amount of sodium hydroxide required to raise and maintain the pH of the soil above 10.5 units for a period of five days. This provided a scale-up quantity of sodium hydroxide that would be required in the field.

A laboratory bench scale soil oxidant demand (SOD) test was also performed. The results indicate SOD values (3.0 to 4.5 g/kg) to be in the normal to slightly elevated range. Contributors to SOD include naturally occurring organics in the soil, the presence of reduced metals, and high alkalinity and total dissolved solid (TDS) levels which can cause scavenging of oxidants. The SOD results were interpreted to mean that some slight amount of interference with oxidation may occur and additional injection events of persulfate may be required to attain the low cleanup objectives for the soil.

### **Injection Events**

The first injection event occurred from November 18 to December 15, 2008 (27 day period). Approximately 4,700 gallons of sodium hydroxide (25%) and 11,500 pounds of sodium persulfate (5,320 gallons at 24%) were injected into the wells over this period. Freezing temperatures and snowfall caused many delays in early December 2008 which extended the injection period. For safety reasons, no excess pressure (less than 20 psi) was applied during the injections (only gravity feed pressures were used).

During the ISCO injections, ground surfacing of chemicals (daylighting) was observed often and was immediately controlled by turning off the flow valve leading to the nearest injection well. Neutralization of the caustic sodium hydroxide that bubbled to the surface was accomplished by use of a mild muriatic acid (HCl) solution, while the persulfate was neutralized using a mild solution of sodium bisulfite (reducing agent). Field personnel inspected the injection areas and observed no visible signs of subsurface degradation, subsidence, or bulging of pavement.

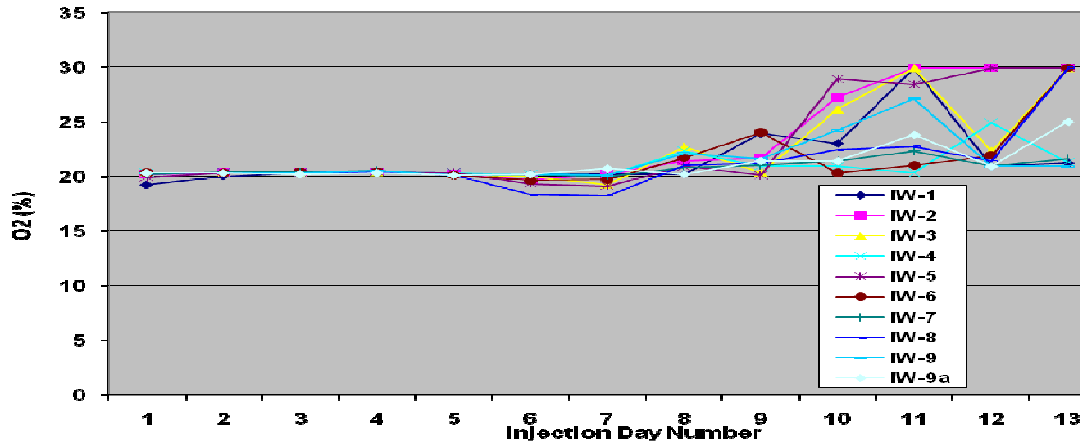
The second injection event was only performed in Area 1 and occurred from August 4 to August 16, 2009 (12 day period). A total of 2,600 gallons of sodium hydroxide was injected into Area 1 and 2,475 gallons of sodium persulfate (at 24% solution) was injected during this injection event.

### **Air Quality Monitoring Data**

To protect the health and safety of field personnel, facility employees, and the public during field activities, and to monitor for the potential migration of subsurface gas vapors, JAG Consulting Group implemented an air monitoring program. The emissions from each injection well and various points in and around the work area were monitored periodically throughout each workday with a four gas air quality meter that monitored for oxygen, carbon dioxide, carbon monoxide, and lower explosive limit.

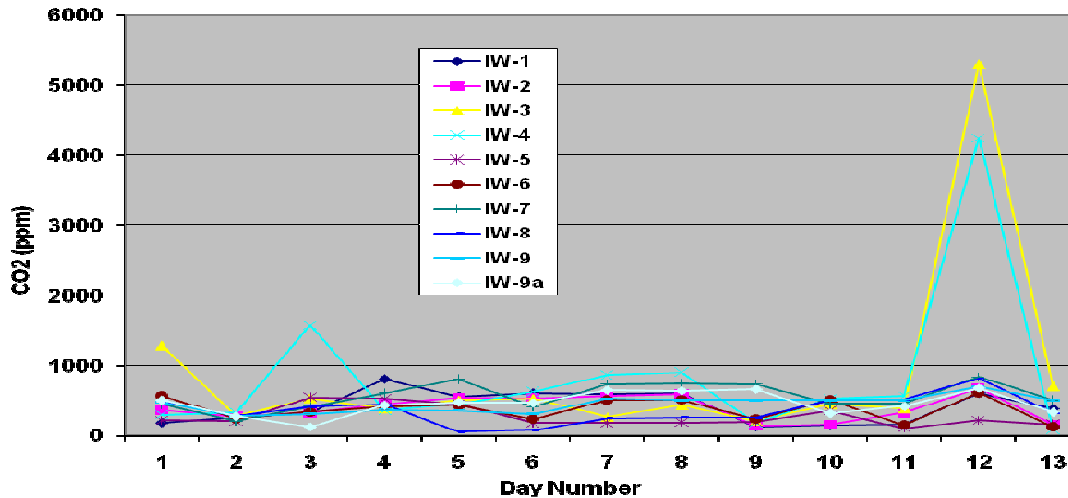
During the sodium hydroxide injections, (Days 1 through 6) only minor fluctuations in oxygen levels were detected (see Figure 3.). However, during the persulfate injections starting on Day 9 and 10, an immediate increase in oxygen level up to 23% to 29% was detected in the injection wells and generally stayed elevated throughout the ISCO injection. This observation was expected, as persulfate is known to release small quantities of oxygen gas as it degrades VOCs.

**Figure 3. Oxygen Levels During ISCO Injections**



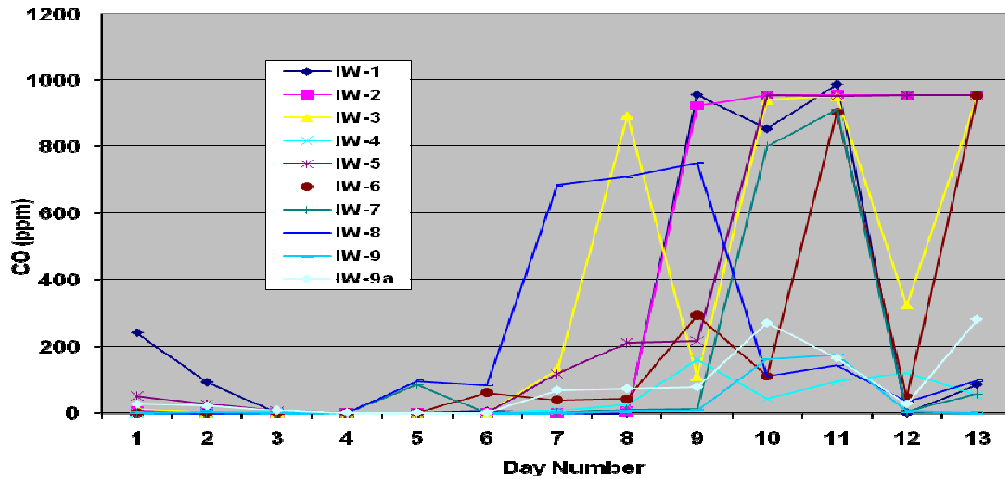
Carbon dioxide (CO<sub>2</sub>) levels were observed to generally remain at moderate levels (200 ppm to 500 ppm) for the first 11 days of injections. Starting on Day 12, the carbon dioxide levels increased dramatically to levels above 4,000 ppm in injection wells IW-3 and IW-4 (see Figure 4). Carbon dioxide gas is formed as a breakdown product as hydrocarbon bonds are destroyed by the persulfate.

**Figure 4. Carbon Dioxide Levels During ISCO Injections**



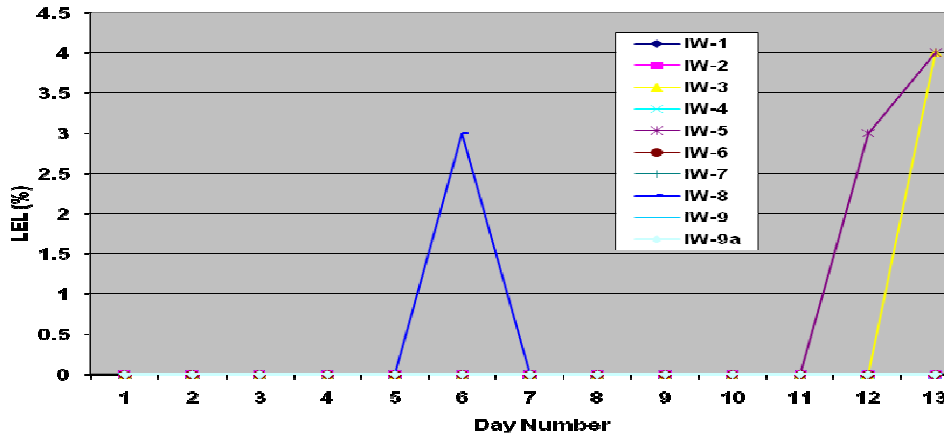
Carbon monoxide (CO) levels generally remained at low levels (less than 200 ppm) for the first 6 to 8 days. Starting on Day 8 and 9, the carbon monoxide levels increased to levels above 800 ppm in the injection wells (see Figure 5). Carbon monoxide gas is also formed as a breakdown product as hydrocarbon bonds are destroyed.

**Figure 5. Carbon Monoxide Levels During ISCO Injections**



The lower explosive limit (LEL) levels were generally non-detectable during most days of ISCO injections. The only detected readings were 4% LEL on Day 13 in injection well IW3, 4% LEL on Days 12 and 13 in injection well IW-5, and 3% LEL in injection well IW-8 on Day 6 (see Figure 6). The LEL readings are most likely caused by the displacement of VOC gases inside the well casing.

**Figure 6. LEL Levels During ISCO Injections**



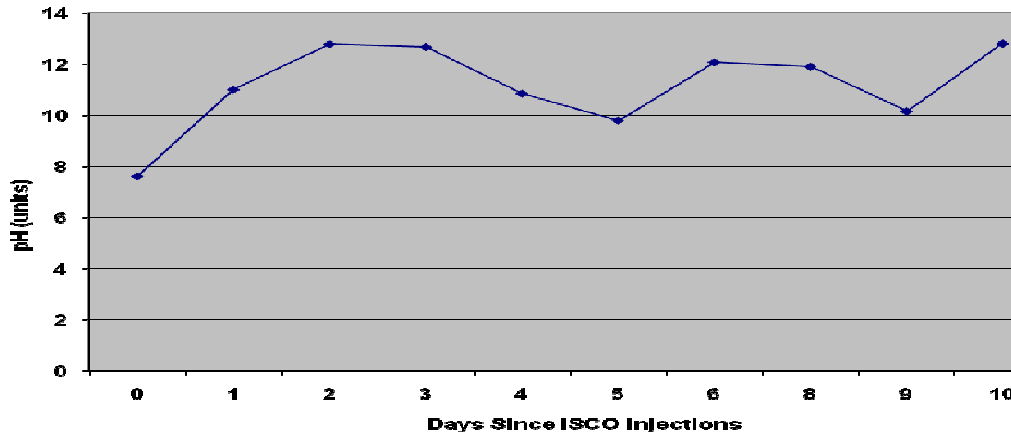
**Water Quality Monitoring Data**

Water quality monitoring data was also collected on a daily basis during the injections from monitoring wells MW-5 and MW-6. The water quality parameters collected from these wells were used to verify that the persulfate and hydroxide were fully dispersing into the treatment zone and were also used to verify the radius of influence.

In monitoring well MW-6, the pH immediately increased to over pH 11 during the hydroxide injections and stayed in that range during the entire period (see Figure 7). pH levels above 10.5 are required to activate the sodium persulfate. However, in monitoring well MW-5, no significant change in the pH occurred during the injection period. Note that monitoring well MW-6 was located approximately 4 feet from the nearest injection well, while monitoring well MW-5 was located approximately 15 feet from the nearest injection well. It is suspected that a pH increase was not monitored in well MW-5,

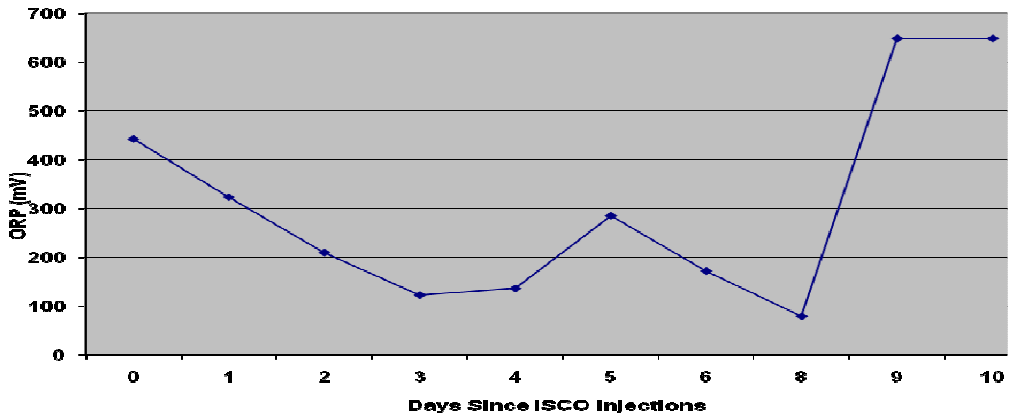
because the ROI was much less than 15 feet and the surface percolation of oxidants was not reaching the screened area of the monitoring well (below 5 feet depth).

**Figure 7. pH In Monitoring Well MW-6**



In monitoring well MW-6, the oxidation reduction potential (ORP) level decreased slightly during the hydroxide injections, but then rose to over 600 mV during the persulfate injections (starting at Day 9, see Figure 8). In general, elevated ORP levels above 300 mV indicate that oxidative conditions were prevalent and confirm that the persulfate was activated.

**Figure 8. ORP In Monitoring Well MW-6**



**Contaminant Reductions**

All of the soil VOCs showed a significant reduction in concentration as a result of the ISCO injections. With only a few exceptions, most all of the VOC concentrations in Area 1 and Area 2 were decreased from 88% to 99%. The VOC concentration reductions are summarized in Tables 1 and 2 below.

**Table 1. Reduction of VOCs in Area 1**

Baseline Boring No.	Corresponding Confirmation Boring No.	Constituent	Initial Concentration (ug/kg)	After ISCO Concentration (ug/kg)	Percent Reduction
SB-7	SB-48	PCE	8,800	2,800	68.2%
		TCE	1,200	10	99.2%
		Methylene Chloride	2,200	10	99.5%
		Ethylbenzene	240,000	97,000	59.6%

Baseline Boring No.	Corresponding Confirmation Boring No.	Constituent	Initial Concentration (ug/kg)	After ISCO Concentration (ug/kg)	Percent Reduction
		Xylenes (Total)	1,400,000	470,000	66.4%
		Toluene	370,000	150,000	59.5%
<b>SB-12</b>	<b>SB-38</b>	PCE	48,000	2,300	95.2%
		TCE	2,400	100	95.8%
		Methylene Chloride	9,300	350	96.2%
		Ethylbenzene	260,000	9,400	96.4%
		Xylenes (Total)	1,300,000	47,000	96.4%
		Toluene	1,100,000	38,000	96.5%
<b>SB-14</b>	<b>SB-58</b>	PCE	45,000	14,000	68.9%
		TCE	1,700	10	99.4%
		Methylene Chloride	620	440	29.0%
		Ethylbenzene	72,000	27,000	62.5%
		Xylenes (Total)	430,000	160,000	62.8%
		Toluene	87,000	120,000	-37.9%
<b>SB-15</b>	<b>SB-40</b>	PCE	52	470	-803.8%
		TCE	23	5	78.3%
		Methylene Chloride	640	5	99.2%
		Ethylbenzene	12,000	4.8	100.0%
		Xylenes (Total)	39,000	10	100.0%
		Toluene	45	4.8	89.3%

Table 2. Reduction of VOCs in Area 2

Baseline Boring No.	Corresponding Confirmation Boring No.	Constituent	Initial Concentration (ug/kg)	After ISCO Concentration (ug/kg)	Percent Reduction
<b>SB-17</b>	<b>SB-33</b>	PCE	160,000	180	99.9%
		TCE	5,900	10	99.8%
		Methylene Chloride	360	1	99.7%
		Ethylbenzene	880	12	98.6%
		Xylenes (Total)	1,200	82	93.2%
		Toluene	52,000	1,400	97.3%
<b>SB-20</b>	<b>SB-35</b>	PCE	220,000	1,900	99.1%
		TCE	4,500	280	93.8%
		Methylene Chloride	620	10	98.4%
		Ethylbenzene	250	19	92.4%
		Xylenes (Total)	1,900	10	99.5%
		Toluene	1,900	10	99.5%
<b>SB-8</b>	<b>SB-34</b>	PCE	1,700,000	190,000	88.8%
		TCE	16,000	4,200	73.8%
		Methylene Chloride	5,900	10	99.8%
		Ethylbenzene	2,900	850	70.7%
		Xylenes (Total)	220,000	7,000	96.8%
		Toluene	200,000	22,000	89.0%

In Area 2, the ISCO injections, in conjunction with the use of an engineered barrier attained the site-specific soil cleanup criteria established by the State of Illinois EPA after the first injection. A second injection of persulfate was performed in treatment Area 1 in August 2009 and this area has also attained the State of Illinois soil cleanup levels.