

# IN SITU CHEMICAL OXIDATION PILOT TEST: DESIGN CRITERIA AND RESULTS FOR OZONE AND HYDROGEN PEROXIDE INJECTION

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## Abstract

Petroleum hydrocarbons had been released to the subsurface at a former service station in southern California. Groundwater within a substantial plume was impacted by total petroleum hydrocarbons as gasoline (TPHg); benzene, toluene, ethylbenzene, and xylenes (BTEX); methyl tert-butyl ether (MTBE); and tert-butyl alcohol (TBA).

Previous full-scale remedial technologies, including dual-phase extraction and in situ bioremediation, had been implemented with limited success. In a new approach, an in situ chemical oxidation pilot test was designed and implemented to evaluate the potential effectiveness of combined ozone and hydrogen peroxide injection.

The pilot test focused on the source area, which still had elevated TPHg, BTEX, and MTBE concentrations in groundwater. TPHg, BTEX, and MTBE were also sorbed to soil throughout a smear zone above the current water table from seasonal and historical water level fluctuations. The depth to water was approximately 25 feet, and the low-yielding saturated zone consisted of interbedded silty sand, sandy silt, and clay.

Two nested injection wells were installed and spaced 20 feet apart in anticipation of a 10-foot radius of influence. Each well included a deep screened interval for ozone sparging and a shallow screened interval for hydrogen peroxide injection. Downgradient of the second injection well, a new observation well supplemented the existing configuration of nearby observation points. Seven observation points were monitored regularly during the pilot test.

A PulseOx 100 manufactured by Applied Process Technology, Inc., generated 2 pounds per day of ozone and injected ozone, hydrogen peroxide, and compressed air. Ozone, compressed air, and hydrogen peroxide were delivered to the two injection points in pre-programmed combinations, dosages, and sequences.

The pilot test ran as initially planned for 8 weeks; it was continued for an additional 4 weeks because TPHg, BTEX, and MTBE concentrations were reduced significantly. Groundwater samples were collected 2, 4, 8, and 12 weeks after the pilot test started and analyzed for TPHg, BTEX, and oxygenates. Dissolved oxygen (DO), oxidation reduction potential (ORP), temperature, conductivity, pH, and water levels were monitored frequently during the pilot test. DO and ORP data served as field indicators for monitoring the injection system radius of influence. By the end of the pilot test, DO was at a high reading of 20 milligrams per liter (mg/L) within a large 15-foot radius of the injection points. TPHg and benzene concentrations were reduced by 2 to 3 orders of magnitude. MTBE concentrations were reduced by 1 to 2 orders of magnitude.

The pilot test results provided design criteria for future tests of this technology. Conclusions reached from this pilot test include: (1) data to design a full-scale system can be gathered within 2 to 4 weeks of operation, (2) two to three injection points should be installed to account for subsurface variation at the site, and (3) radius of influence can be measured using relatively inexpensive downhole probes monitoring for DO and ORP.

## Introduction

### Site Description and History

The site, formerly occupied by an automobile service station, is in a mixed commercial and residential area of southern California. Three 10,000-gallon underground storage tanks (USTs) were removed in March 1999. Site assessment activities dating from 1987 through the present indicated the presence of gasoline-related petroleum hydrocarbons in soil and groundwater, both on and off site.

Previous remediation activities included excavation of soil from the source area, implementation of dual-phase extraction from 2000 through 2003, weekly groundwater extraction (overpurging) from 2002 through the present, and oxygen release compound injection.

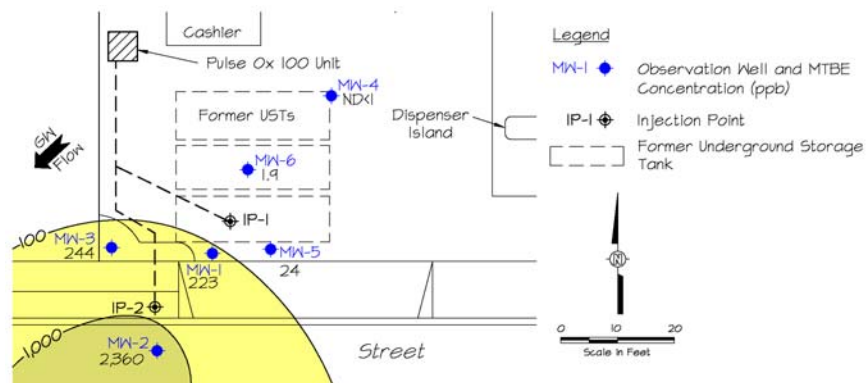
Despite the previous remediation efforts, a substantial plume of benzene, MTBE, and TBA was present in groundwater downgradient of the site, and elevated hydrocarbon concentrations were also present in groundwater near the former USTs at the southern portion of the site.

### Pilot Test Objectives and Scope of Work

In situ chemical oxidation (ISCO) was selected as the new remedial approach, and a pilot test was designed and implemented. The objectives of the pilot test were to (1) evaluate the effectiveness of ozone and hydrogen peroxide to remediate elevated TPHg, BTEX, MTBE, and TBA in groundwater; and (2) collect data to design a full-scale ISCO system for the site.

The pilot test included two nested injection points spaced 20 feet apart (IP-1 and IP-2) and seven observation wells (MW-1 through MW-7). Ozone and hydrogen peroxide were injected over a 12-week period and the observation wells were monitored and sampled periodically to track the effects of ISCO on groundwater. Groundwater samples were also collected 3 months after the pilot test ended to monitor for potential rebound in groundwater conditions. Figure 1 shows the pilot test area including injection and observation well locations.

**Figure 1 – Pilot Test Layout**



Hydrogeologic Setting

The regional lithology consists of Quaternary-aged alluvium and colluvium. The site lies within the Irvine subbasin of the Coastal Plain of the Orange County Groundwater Basin, in the central portion of Orange County. The basin underlies the lower Santa Ana River watershed, and water-bearing strata consist of thick deposits of interbedded marine and continental sand, silt, and clay. Two major water-bearing zones have been delineated within the subbasin: a shallow perched zone and a deep zone. The shallow perched zone is found within recent alluvium and stream deposits and is characterized by low-yielding sediments and poor water quality.

The ground surface has been graded and is relatively flat. Soils encountered during field activities and previous site assessments include sand to approximately 25 feet below grade and interbedded sand and silt to approximately 40 feet below grade, which was the maximum depth investigated in previous site assessments.

The depth to groundwater ranged from approximately 25 to 29 feet below grade during the year preceding the pilot test, with a groundwater gradient sloping slightly toward the south-southwest. Seasonal and historical water level fluctuations have created a smear zone in the sandy soil above the water table between 23 to 25 feet below grade.

**ISCO Pilot Test Activities**

Baseline Water Chemistry

Groundwater samples were collected from 11 monitoring wells before beginning the pilot test to establish the baseline groundwater quality for the chemical constituents listed in Table 1.

**Table 1 – Baseline Water Quality Testing Program**

<b>Chemical Group</b>	<b>Analytical Constituent</b>
Petroleum Hydrocarbons	TPHg, BTEX, MTBE, TBA, and other oxygenates
Inorganic Constituents	Manganese, ferric iron, total and hexavalent chromium, and carbonates
Water Quality Indicators	Chemical oxygen demand, pH, conductivity, DO, ORP, temperature

TPHg, BTEX, MTBE, and TBA were detected frequently. The highest TPHg concentration of 302,000 ug/L was detected in MW-1, along the southern site boundary adjacent to the source area. MW-1 also contained elevated concentrations of benzene and MTBE detected at 1,860 and 223 ug/L. The highest MTBE concentration of 2,360 ug/L was detected downgradient of the source area in well MW-2.

Iron and manganese were detected at low concentrations (less than 7.0 and 2.5 mg/L, respectively). Total chromium, hexavalent chromium, and carbonate concentrations were not detected or negligible. Chemical oxygen demand ranged from 6 to 174 mg/L, with the highest concentration found in MW-1.

DO concentrations were less than 0.75 mg/L in 9 of 11 wells. Wells MW-3 and MW-6 had 1.26 and 1.72 mg/L of DO, respectively. ORP measurements for all wells were below -100 millivolts (mV), indicating that baseline conditions were anaerobic and reducing. Figure 2 shows the baseline DO concentrations in the pilot test area.

Injection Point Design and Installation

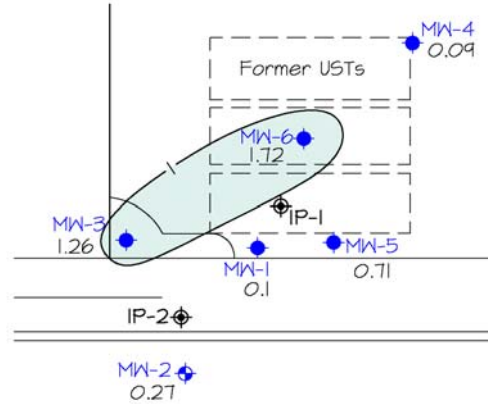
Two nested injection points were installed for the pilot test (IP-1 and IP-2). They were installed about 20 feet apart within and downgradient of the source UST area in the southern portion of the site (Figure 1). Each injection point included a deep ozone sparge point and a shallow peroxide injection point.

The sparge points were constructed using 1-inch-diameter Schedule 40 PVC well casing. Ozone was injected through an 18-inch-long porous HDPE sparge point at approximately 32 feet, and peroxide was injected through a 1-foot-long 0.01-inch slotted PVC screen at approximately 24 feet. Ozone sparge points are typically constructed using stainless steel casing because of material incompatibility with PVC. However, PVC was used because the pilot test was a short duration project and the material costs were low.

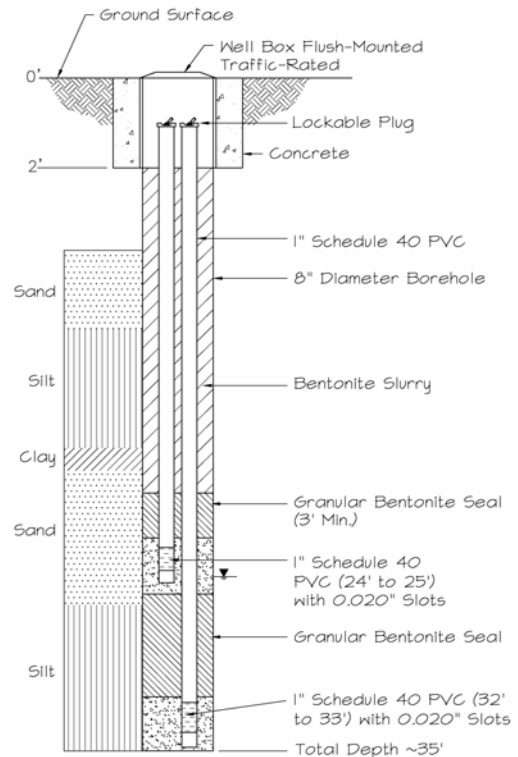
The ozone sparge depth was selected to inject into the groundwater near the base of the petroleum-impacted, saturated soils, so that ozone would migrate outward and upward and react with the peroxide and petroleum constituents. The hydrogen peroxide injection sparge depth was selected to inject at the top of the saturated zone and smear zone, so that peroxide would migrate outward and downward and react with ozone and petroleum constituents.

System Design and Specifications

A PulseOx 100 ISCO unit (ozone and hydrogen peroxide injection system) manufactured by Applied Process Technology, Inc., (APT) of Pleasant Hill, California, was used for the pilot test. The system injects air, oxygen, ozone, hydrogen peroxide, or a combination of ozone and hydrogen peroxide into the subsurface. The system can produce up to 2 pounds of ozone per day generated from oxygen created by a pressure swing adsorption system. Ozone can be injected into the subsurface at pressures up to approximately 20 to 25 pounds per square inch. An ambient ozone sensor connected to the PulseOx monitors for ozone in the event of leakage from the system.



**Figure 2 – Baseline DO Concentrations**



**Figure 3 – Injection Point Design**

The system can produce up to 2 pounds of ozone per day generated from oxygen created by a pressure swing adsorption system. Ozone can be injected into the subsurface at pressures up to approximately 20 to 25 pounds per square inch. An ambient ozone sensor connected to the PulseOx monitors for ozone in the event of leakage from the system.

The injection system was connected to the injection points via tubing placed inside plastic secondary containment pipe over the ground surface (the site was unoccupied and secured). Ozone was conveyed through Teflon tubing, and hydrogen peroxide was conveyed through polypropylene tubing.

The ozone and peroxide injection system delivered ozone to the subsurface in pulsed intervals. A typical pulsed delivery cycle included the injection of ozone for a 10-minute period followed by the injection of compressed air for a 10-minute period. The compressed air was used to force the ozone into the saturated zone and to flush the conveyance line and well casing to minimize the potential for degradation of the well casing and inline joints. The injection cycle was programmed to occur for 1 hour in each injection point followed by 1 hour without injection.

A 10-percent hydrogen peroxide solution was delivered to the subsurface by a feed pump. Peroxide injection began approximately 2 weeks after the ozone injection commenced, and the initial peroxide injection rate was approximately 0.25 gallon per day. Peroxide was injected at a low flow rate to minimize the potential for an uncontrolled exothermic reaction between the peroxide and the hydrocarbon mass present at the beginning of the pilot test. The peroxide injection rate was increased after 2 weeks to approximately 0.25 gallon per day per injection point, and then increased again after 2 weeks to approximately 3 gallons per day per injection point.

#### System Operation and Monitoring

After start-up, the injection system was inspected daily for the first 3 days and then at least weekly thereafter. Each system inspection included observing injection pressure, ozone injection flow, peroxide injection flow, and ambient air ozone concentrations in the vicinity of the injection system and the injection points.

Groundwater quality indicators were monitored at least weekly in seven wells (MW-1 through MW-7) near the injection points to assess the effects of ISCO on impacted groundwater. Depth to water was measured using an electric water-level sounder, and conductivity, DO, pH, ORP, and water temperature were monitored using a YSI downhole probe, model 556 MPS-20.

Groundwater samples were collected from the seven observation wells approximately 2, 5, 8, and 12 weeks after the pilot test started. The samples were analyzed for TPHg, BTEX, MTBE, TBA, and other fuel oxygenates. Rebound monitoring was also conducted 3 months after the pilot test ended at selected wells tested for TPHg, BTEX, and MTBE.

Selected wells were also tested for manganese, ferric iron, total and hexavalent chromium, carbonates, and chemical oxygen demand to evaluate potential changes from baseline conditions.

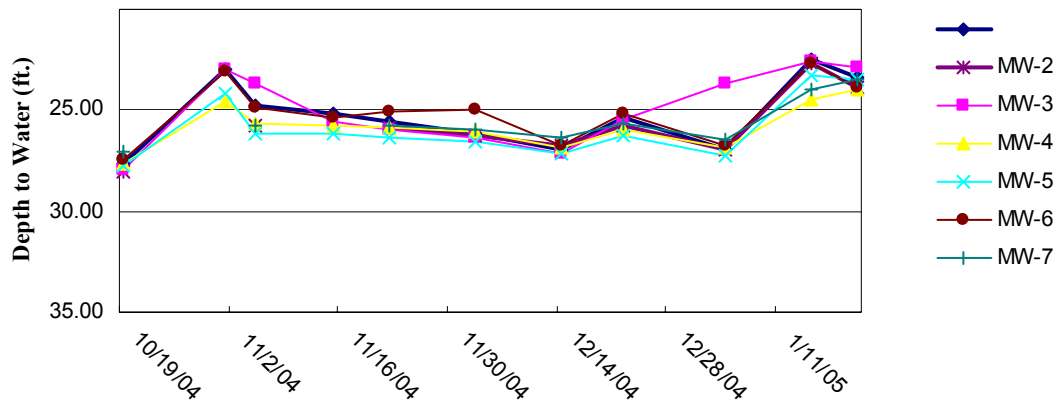
### **Pilot Test Results and Discussion**

#### Water Levels

Groundwater levels initially spiked upward after ozone injection began, particularly in the observation wells nearest the injection points. The water levels returned to near baseline levels

within approximately 1 week. Regional groundwater levels rose between October 2004 (baseline monitoring) and the end of January 2005 (end of pilot test). Much of the increase was observed from the end of December through January, reflecting heavy winter precipitation. Well MW-7 was approximately 36 feet downgradient of IP-2 and reflected the regional increase in water levels. Figure 4 shows water levels during the pilot test.

**Figure 4 – Water Levels in Observation Wells during the Pilot Test**



Hydrocarbon Concentrations

The following table summarizes changes in TPHg, benzene, MTBE, and TBA from the baseline sampling event (7 October 2004) to the end of the pilot test (28 January 2005). The rebound sampling results in May 2005, 3 months after end of the pilot test, are also included.

**Table 2 – Groundwater Analytical Results (Organics)**

Well ID	Sample Date	TPHg (ug/L)	Benzene (ug/L)	MTBE (ug/L)	TBA (ug/L)
MW-1 (6' from IP-1)	Oct 7 (baseline)	302,000	1,860	223	ND<1,000
	Nov 23	31,500	206	107	117
	Dec 14	16,400	75	71	ND<100
	Jan 4	3,200	3.5	31	ND<10
	Jan 28	1,000	2.5	7	--
	May 6 (rebound)	2,000	100	15	--
MW-2 (8' from IP-2)	Oct 7 (baseline)	8,930	348	2,360	386
	Nov 23	18,200	143	509	365
	Dec 14	1,840	6.3	312	245
	Jan 4	1,010	14	369	266
	Jan 28	4,000	175	40	--
	May 6 (rebound)	2,000	180	25	--
MW-3 (12' from IP-2)	Oct 7 (baseline)	480	11	244	110
	Nov 23	252	ND<1	301	93
	Dec 14	1,060	61	147	65
	Jan 4	ND<50	ND<1	ND<1	ND<10
	Jan 28	ND<50	ND<1	ND<1	--
	May 6 (rebound)	ND<50	ND<1	ND<1	--
MW-4 background well (28' upgradient from IP-1)	Oct 7 (baseline)	1,680	3.2	ND<1	ND<10
	Nov 23	5,990	62	ND<10	ND<100
	Dec 14	6,070	14	1.1	15
	Jan 4	2,780	12	1.4	20
	Jan 28	--	--	--	--
	May 6 (rebound)	--	--	--	--

The baseline samples indicated elevated concentrations of TPHg, benzene, MTBE, and TBA, especially in the vicinity of wells MW-1 and MW-2. Hydrocarbon concentrations increased initially after the pilot test began. This increase was likely caused by desorption from soil below the water table and within the smear zone.

The final groundwater sampling event results showed significant reduction in TPHg, benzene, and MTBE concentrations in observation wells within 20 feet of injection points IP-1 and IP-2. TPHg concentrations generally decreased for all observation wells except for wells MW-4 and MW-7, which were 28 and 36 feet from the injection points, respectively. Increased hydrocarbon concentrations were observed in other wells away from the pilot test and were likely caused by an increase in the water table and desorption of hydrocarbons from the smear zone.

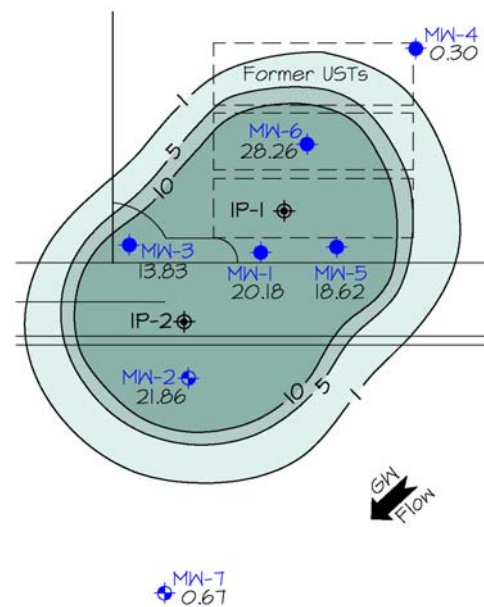
At well MW-1, benzene concentrations decreased from 1,860 to 2.5 ug/L after 12 weeks of ISCO. Benzene rebounded to 100 ug/L 3 months after the pilot test. At well MW-2, MTBE decreased from 2,360 to 40 ug/L with concentrations remaining low at 25 ug/L during the 3-month rebound sampling. TBA concentrations generally remained the same during the pilot test.

#### Indicator Parameters

DO, ORP, conductivity, water temperature, and pH were monitored at least weekly using a downhole probe in the observation wells during the pilot test. Water temperature and pH did not vary beyond normal fluctuations during the pilot test, while conductivity gradually increased.

ORP measurements were on the order of  $-200$  mV for baseline and remained at those levels for the duration of the pilot test in observation wells MW-4 and MW-7, the farthest wells from the injection points. ORP increased in observation wells near the injection points (MW-1, -2, -3, -5, and -6) from approximately  $-200$  mV to approximately  $+100$  to  $150$  mV.

DO measurements were generally below  $1$  mg/L during baseline monitoring and remained below  $1$  mg/L for the duration of the pilot test in the observation wells MW-4 and MW-7. DO increased in observation wells near the injection points. At the end of the pilot test, DO concentrations of approximately  $20$  mg/L were measured in the observation wells within  $10$  to  $15$  feet of the injection points. Figure 5 shows the DO concentrations after 12 weeks of pilot test operation.



**Figure 5 – DO Concentrations after 12 Weeks of Operation**

## Conclusions

The area affected by the ISCO pilot test covered approximately 45 by 65 feet, based on the estimated dissolved oxygen concentrations greater than 1 mg/l (Figure 5). BTEX appeared to be preferentially degraded based on a comparison of the reduction of BTEX, MTBE, and TBA in observation wells MW-1, MW-2, MW-3, MW-5, and MW-6. MTBE was also degraded while TBA was not significantly degraded during the 12-week test based on the decrease in concentrations observed in wells MW-3, MW-5, and MW-6, and to a lesser extent, MW-2. The trend indicates that additional ozone and peroxide injection will continue to reduce BTEX, MTBE, and TBA concentrations.

The results of this pilot test results provided design criteria for full-scale implementation of this technology. Injection points should be constructed following the pilot test design, except that ozone wells should be constructed using stainless steel casing. The wells can be placed using a 15-foot radius of influence.

The ISCO pilot test demonstrated the following:

1. Injection of ozone and hydrogen peroxide can rapidly reduce TPHg, BTEX, and MTBE concentrations within 12 weeks, even within a source area containing over 100,000 ug/L of TPHg and over 1,000 ug/L of benzene and MTBE.
2. Depending on the site lithology, a pilot test can generate the data necessary to design a full-scale ozone and peroxide injection system within 2 to 4 weeks of operation. Two to three injection points should be installed to account for site-specific subsurface variation.
3. Injection of ozone and peroxide may reduce TBA concentrations, although the rate of reduction within a source area is slower than for TPHg, BTEX, and MTBE.
4. The lateral impact of ISCO can be easily monitored using a downhole DO and ORP probe in nearby observation wells.
5. An increase in TPHg and BTEX concentrations may occur soon after injection begins and after injection ends (rebound). This increase is likely caused by desorption of petroleum constituents sorbed to soil particles.
6. If a pronounced smear zone is present at a site, the remediation effectiveness can be increased by (1) injecting peroxide into the capillary fringe, (2) operating the injection system to provide controlled fluctuations of the water table, or (3) operating the system during periods of seasonally high water levels.