

# **In-situ Remediation of MTBE Using In Situ Chemical Oxidation (ISCO) Technology**

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## **WHAT IS MTBE?**

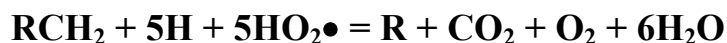
Methyl-tert-butyl ether (MTBE) has been used in California as a fuel additive to increase the oxygen content of gasoline since 1989, to meet State and Federal clean air regulations. This reformulated gasoline is required to contain no less than 2.7% oxygen, which is equal to 15% MTBE by volume. The Environmental Protection Agency (EPA) has tentatively classified MTBE as a possible human carcinogen, and in February of 1991, the California EPA office of Environmental Health Hazard Assessment (OEHHA) established an interim action level of 35 parts per billion (ppb) for MTBE.

Methyl-tert-butyl ether (MTBE) is a colorless, flammable liquid with a turpentine-like odor, is highly soluble and extremely volatile. MTBE is a dangerous groundwater contaminant because of its mobility and resistance to biodegradation in either aerobic or anaerobic conditions. MTBE will essentially move at the same rate as groundwater, due to its tendency not to adsorb onto the vadose zone material. Groundwater in equilibrium with gasoline containing 15% MTBE could contain as much as 9,600 parts per million (ppm) MTBE.

## **INTRODUCTION TO CHEMICAL REMEDIATION**

Today's environmental climate demands application of versatile remedial solutions to address a wide range of environmental challenges. In Situ Chemical Oxidation (ISCO) was developed as an aggressive technology to meet this challenge, providing an innovative solution to the issues of MTBE, BTEX, and chlorinated hydrocarbons in soil and groundwater. This process, known as ISCO involves the injection of an oxidizing agent into the subsurface to remediate a wide range of volatile and semi-volatile contaminants, and controlling the distribution using vacuum extraction technologies.

When injected into the subsurface in the proper concentrations, oxidizing agents react with naturally occurring iron ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) to produce the hydroxyl radical ( $\text{OH}^\cdot$ ), commonly known as Fenton's reagent. The hydroxyl radical is a very strong oxidizer and will break down hydrocarbons and organic compounds to carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ), usually within a few minutes of injection. Heat is formed as a result of the oxidation, and is an additional benefit of chemical treatment. The increased temperature raises the vapor pressure of existing Volatile Organic Compounds (VOCs), making them more susceptible to extraction using vapor extraction systems. A summary of the chemical reaction is shown below.



Where: RCH<sub>2</sub> is a hydrocarbon  
HO<sub>2</sub>• is the superoxide radical

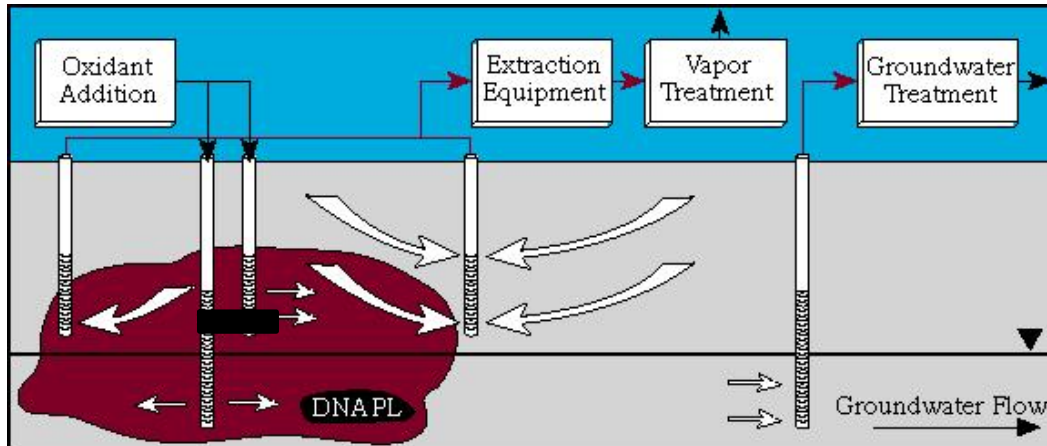
During the reaction, Fe<sup>2+</sup> and Fe<sup>3+</sup> are used as a catalyst for the reaction and are therefore not consumed during the process. This permits use of this technology under conditions of varying degrees of naturally occurring irons, with the only affect being on the rate of reaction. As the reaction occurs, ferric hydroxide is formed. When combined with water, the ferric hydroxide releases a hydroxyl radical, which causes the pH of the water to rise (become more basic). While the pH should be monitored throughout, Terra Vac has proven the process to be effective over a pH range from 6.2 to 8.5. Some studies have indicated that the preferred pH would be in the 2 to 3 range.

Previously, this process of chemical treatment was used to treat soils and wastewater in an above ground reaction chamber. Terra Vac has developed a means of providing this treatment in-situ. Native soil microbes typically are killed in the area exposed to high concentrations of oxidant, since the hydroxyl radical is not selective in it's consumption. However, the native microbes quickly repopulate the area after treatment. It appears that the residual oxygen and warmth left after oxidation is more beneficial to the overall soil microbe population than the localized effects of Fenton's Reagent. This residual oxygen also provides for enhanced natural biodegradation.

### **DUAL VACUUM EXTRACTION (DVE™)**

Introduction of the oxidant is accomplished utilizing gravity feed or pressurized delivery systems as determined by the subsurface conditions existing at the site, and may be combined with other technologies such as Vacuum Extraction (VE) or Dual Vacuum Extraction (DVE). Direct contaminant oxidation occurs within the immediate area of the point of injection, eliminating concerns in these zones. Additionally, the oxidizing agent may be pulled through the contaminated subsurface using the vacuum system, to increase remedial effectiveness.

The DVE technology is a highly effective method of remediation, removing both water and vapors through the same well. The combined removal of water and vapor allows for an efficient process of capillary fringe remediation. The capillary fringe is treated by lowering the water table, exposing the smear zone to air flow. The ISCO system utilizes the DVE system to create an artificial gradient in the center of the subject area while injecting oxidant into the surrounding edges of the impacted area. The oxidant is then pulled across the capillary fringe, oxidizing VOCs suspended in the smear zone. Figure 1 illustrates a typical ISCO system.



**Figure 1. ISCO Conceptual Illustration**

## **ISCO USED TO OBTAIN SITE CLOSURES**

ISCO has successfully been applied in numerous bench-scale studies, at a Superfund site in Pennsylvania, and at BTEX remediation sites in Utah and California. The ISCO process has been approved for use by the Los Angeles Regional Water quality control Board (RWQCB) and the Orange County Health Care Agency, as well as by the EPA and other state regulatory agencies. It has been used to provide a method of treating Dense Non-Aqueous Phase Liquids (DNAPL), without large groundwater recovery systems being necessary. It has also been used to obtain closure of two (2) BTEX-contaminated groundwater sites in the San Diego, California area.

At one of these sites, the process was used to reduce Total Petroleum Hydrocarbon (TPH) levels as gasoline from 27,000 ppb to non-detectable within four (4) months of commencing operations. Benzene concentrations were also reduced to below 1 ppb. Within one year from project commencement, the site was granted closure by the San Diego RWQCB. This site is believed to be the first full-scale use of this technology in the world. This technology was selected following unsuccessful cleanup attempts made by other environmental consultants.

## **PILOT TEST PERFORMED FOR REMEDIATION OF MTBE**

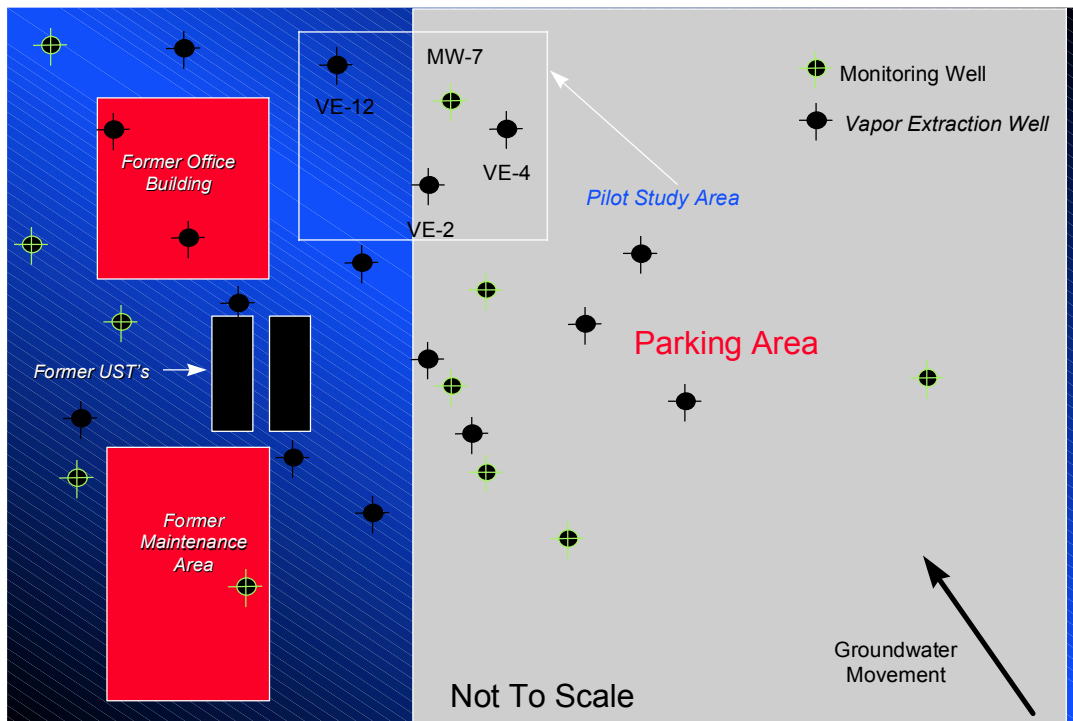
The second site was contaminated with BTEX, and in addition, with MTBE. In 1993, an in-situ Dual Vacuum Extraction (DVE™) system was installed.

A pilot test was conducted at this site in June 1996, to determine the feasibility of using the ISCO process for effective remediation of MTBE. The site was formerly used as a rental car facility which utilized underground storage tanks (USTs) for refueling their rental fleet. A leak in a transfer line was believed to have caused the release of approximately 16,000 gallons of petroleum hydrocarbons. By August, 1993, several

subsurface investigations had been conducted identifying residual hydrocarbons in subsurface soil and groundwater.

From the ground surface to approximately 10 feet below, the soils consisted of hydraulic fill material composed of fine to medium grain sands with shell material and clayey zones. Below this, the lithology was characterized by bay deposits consisting of fine grained sands interbedded with dense clay layers. Groundwater was encountered at approximately 10 feet below grade surface (bgs), with a hydraulic conductivity estimated to be between  $10^{-8}$  and  $10^{-10}$  centimeters per second (cm/s). A groundwater sample from one well was found to contain 5.8 mg/l iron(Fe).

A total of four wells (MW-7, VE-2, VE-4 and VE-12) were used to determine the effectiveness of the OxyVac™ system. The well locations are shown in Figure 2. These wells were chosen based on their relative locations and groundwater contaminant concentration levels. All wells were sampled prior to injection for benzene, toluene, ethylbenzene, total xylenes and MTBE. Each well was sampled for the same parameters following injection. In addition, probes were introduced into the wells below the water surface to monitor groundwater temperatures, pH and conductivity. Temperatures were monitored continuously throughout the test and for approximately 12 hours following injection. Groundwater levels were measured before and after performance of the test.



**Figure 2.**

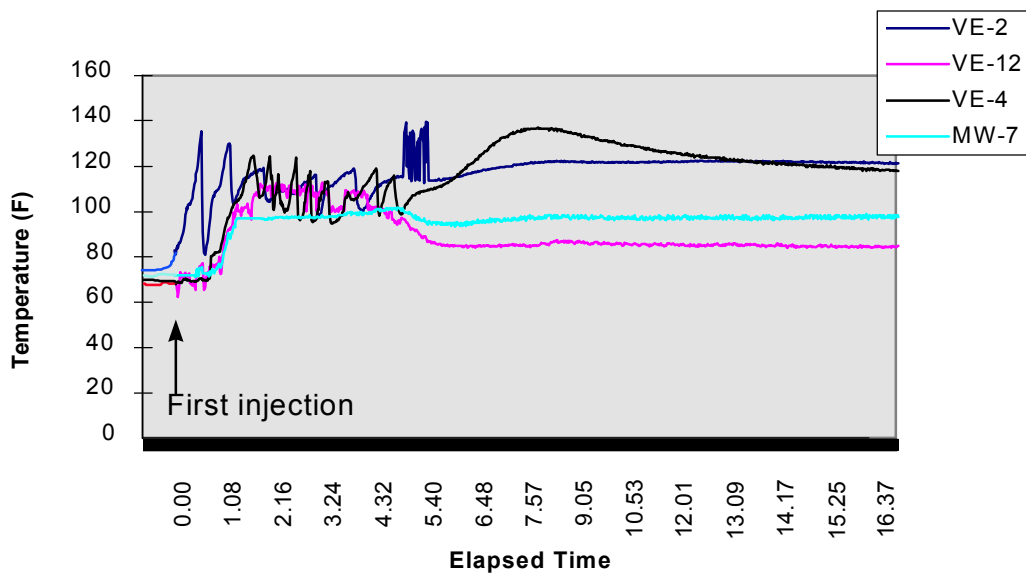
**Relative Locations of Test Wells**

Monitoring well MW-7 was converted to DVE and used to create the artificial gradient needed to pull the oxidant across the smear zone. Surrounding wells VE-2, VE-4, and VE-12 were tested to determine the radius of influence (ROI) being created by the vacuum applied at MW-7. Vacuum readings were greater than 11" H<sub>2</sub>O at each wellhead. The three VE wells were then utilized to inject a predetermined concentration of oxidant in preset quantities. Injection started with well VE-2, with injections into VE-4 and VE-12 commencing approximately 1 hour later.

## **PILOT TEST RESULTS**

Groundwater temperature was continuously monitored in all wells. Temperatures in the injection wells began increasing almost immediately following injection. The highest temperature rise (70°F) was recorded in VE-4 approximately 8 hours after injection. The DVE™ well, MW-7, experienced a temperature rise beginning approximately one hour after injection, and culminating in a 30 degree temperature rise almost 5 hours into the test.

A graphical representation of the temperature data is shown in Figure 3. The graph indicates that the temperature in MW-7 increased significantly approximately 1 hour after injection into VE-2 and was sustained for the duration of the monitoring. The temperature profile for well VE-4 shows a large increase in temperature long after injections were completed. This may be attributed to an area of high concentration groundwater being introduced to the oxidant due to the artificial gradient, although it's true cause is unknown. Dramatic fluctuations in the temperatures were the result of conducting the injections in batches, vice using continuous injection methods.



**Figure 4. Temperature Vs Time Following Injection**

Groundwater sampling activities were conducted following the test to monitor for water level, pH, and conductivity. The samples were sent to an independent laboratory for analysis using EPA Method 8015, modified for gasoline and EPA Method 624. Comparative physical properties of the groundwater are indicated in Table 1. The decrease in water levels was due to the artificial gradient created by the DVE™ process. The increased pH was attributed to the hydroxyl radicals which were released into the water from the ferric hydroxide. The reduced conductivity was due to the chemical reaction in the wells reducing the concentration of hydrocarbons and microbes in the groundwater.

Significant decreases can be seen in the BTEX components as well as the MTBE concentrations in each of the injection wells. Benzene levels in VE-2 decreased from 3,100 µg/l to 49 µg/l, VE-4 from 16 µg/l to 1.8 µg/l, and VE-12 from 1,800 µg/l to non-detectable. Slight increases were noted in these levels from the sample taken at MW-7. This was due to drawing constituents into this well, using the DVE™ process. This situation can be remedied by stopping the DVE™ system and performing injection into this well.

	MW-7		VE-2		VE-4		VE-12	
	Before	After	Before	After	Before	After	Before	After
H <sub>2</sub> O Level (ft)	16.95	13.20	15.40	12.40	15.90	13.00	15.10	12.70
pH	7.06	9.04	6.62	8.63	7.03	8.47	6.87	8.52
Conductivity (µmhos/cm)	11.37	7.33	8.57	2.06	16.28	3.80	8.97	1.34
MTBE (µg/l)	470	99	820	19	58	7.90	3,100	99
MTBE Reduction (%)		80		98		86		97

Table 1. Analytical Comparison

Figure 4 is a graphical representation of the MTBE levels for each well used in the pilot test. Of particular interest from these results is the reduction in MTBE in the groundwater. The average reduction of MTBE from the three injection wells was 94%, with only one application. (The results from MW-7 were removed to prevent the overall results from becoming skewed.) It should be noted that while initial reduction from this treatment is dramatic, some rebound has been noted in contaminant concentrations in most applications. This rebound has been typically shown to be approximately 10%, though this number varies based on site-specific conditions. The amount of rebound is contingent upon not performing any additional oxidant injections.

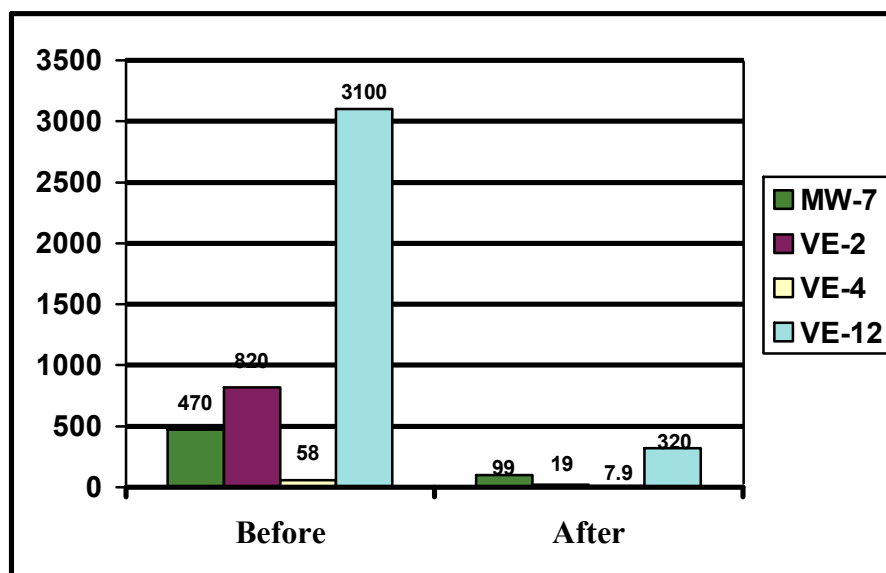


Figure 4. MTBE Analytical Results (PPB)

## CONCLUSIONS

As the test results indicate, MTBE can be effectively treated “in-situ”, without the expense of removing the soil to establish an “ex-situ” cell. This process may be used for large or small sites as a full scale remediation process, however, care must be taken when evaluating use of this technology. Designers should be aware of the requirement to perform multiple injections to ensure complete treatment of the site, since rebound of contamination levels will occur. During the performance of the test, vapor samples were collected and analyzed to determine whether boiling of the MTBE was occurring, which would indicate a secondary reason for the reduction in concentrations. No increase in vapor concentrations was noted. Since vapor extraction is not effective in remediation of saturated soil zones, this supports oxidation as the major cause of the reduction in MTBE concentrations.

Cost effectiveness was evaluated at a site which required cleanup of BTEX contaminants in saturated soils from 30 to 40 feet below grade surface over an area covering approximately 20 yd<sup>2</sup>. The cleanup goal of less than 1 ppb benzene was achieved at a cost of only \$350 per yd<sup>3</sup>. This was an in-situ cost, with no excavation taking place, no unsightly stockpiles, and no interruption of normal business.