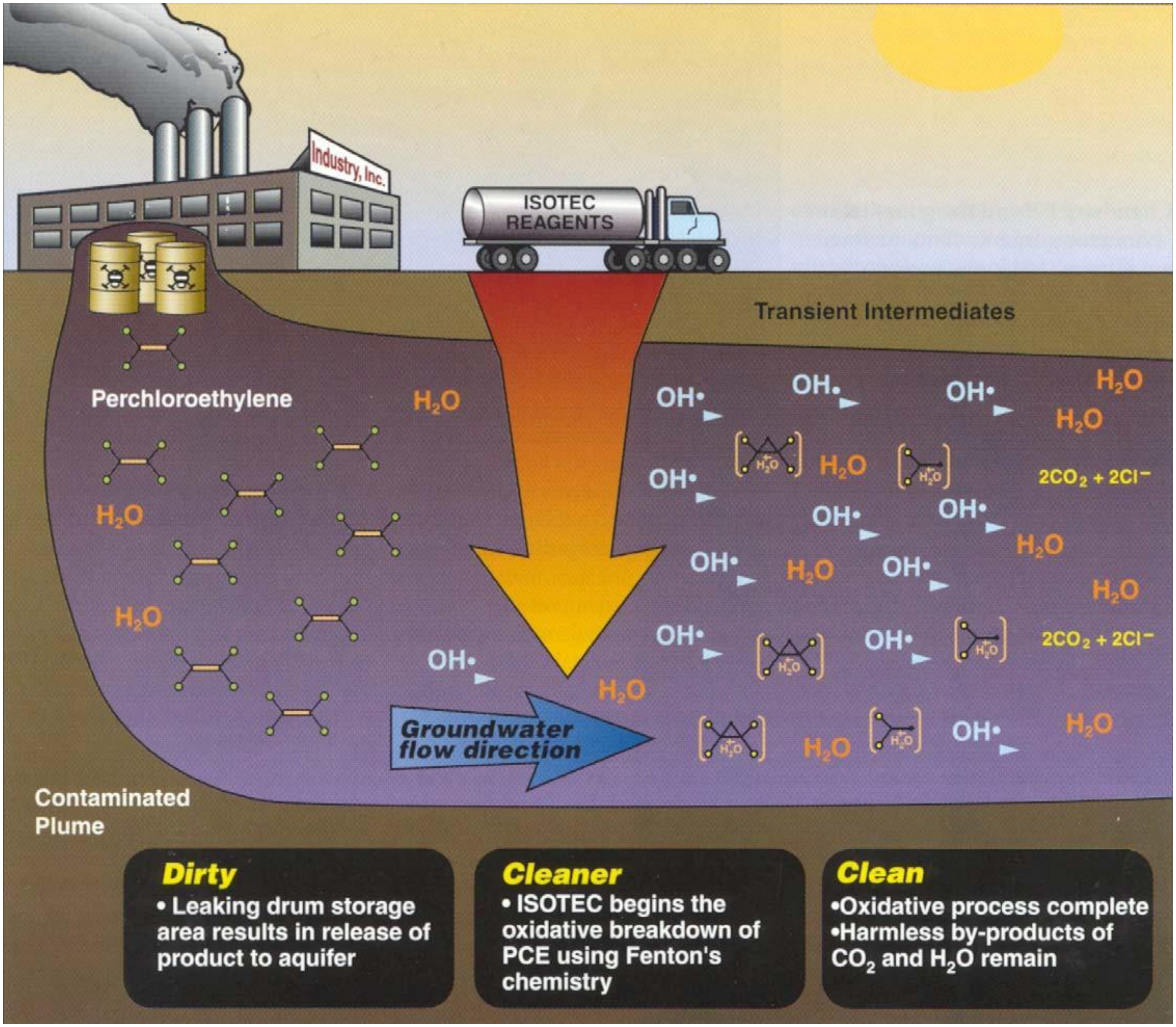

Oxidizing agent can finish cleanup where other systems taper off

Process remediates contaminated sites to no further action point

By Thomas Andrews, P.E., David Zervas, and Richard S. Greenberg, Ph.D

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A newly developed in situ remediation technology called the ISOTEC™ process has shown promise as an effective cleanup tool. The process uses chemistry known as Fenton's Reaction and focuses on the in situ creation of a powerful oxidizing agent to destroy complex organic contaminants. Complete oxidation of the organic compounds yields innocuous by-products commonly found in nature, primarily carbon dioxide and water.

Chemistry behind the remediation

Numerous organic contaminants are mineralized in the presence of hydroxyl radicals (OH). This mineralization or destruction occurs via oxidation. Studies have shown that when contaminated soil is treated with a catalyzed hydrogen peroxide application, contaminant desorption and oxidation can result. Complete mineralization or transformation of complex contaminants into simple, less toxic, compounds can occur via the oxidative process.

On a molecular level, the destruction occurs by cleavage of carbon-carbon bonds, creating fragments of the parent compound. Subsequent oxidative reactions break down the fragmented compounds completely to carbon dioxide and water. Past research has shown contaminant mineralization occurs by an addition/electron transfer followed by side chain cleavage in most aromatics; hydrogen abstraction in alkanes; and addition to the C=C or C≡C bonds in most unsaturated aliphatic compounds.

For chlorinated contaminants such as PCE and TCE, dechlorination precedes decarboxylation . However, in most contaminants, the initial reaction leads to the formation of intermediate radicals which undergo oxidation, reduction or dimerization based on the treatment conditions and existing contaminants.

Enhancing the chemical process

Scientists with In-Situ Oxidative Technologies Inc., Lawrenceville, N.J. , have conducted experiments focusing on optimizing the generation of hydroxyl radicals and maximizing the oxidizing agent's life to seek applications in remediation. Typically, hydrogen peroxide is unstable in natural conditions and rapidly degrades in the environment due to existing inorganic and organic catalysts.

Naturally occurring catalysts include iron oxyhydroxides and enzymes such as catalse and perosidasc. The instability of hydrogen peroxide serves to potentially limit an effective application to affected media.

	Pre-sample	Post-sample[1]	Post-sample[2]
Date VO Compound	12/25/1995 (ppb)	4/2/1996 (ppb)	10/28/1996 (ppb)
Benzene	3,870	6.85	ND
Toluene	8,690	40.4	ND
Ethylbenzene	1,520	15.5	5.11
Xylenes	11,100	115	19.6
Methyl t-butyl ether	6,150	ND	ND

Notes:
ppb=parts per billion or micrograms per liter (mg/l)
ND=indicates that the parameter was analyzed but not detected
1 = one month after second treatment
2 = four months after third and final treatment

Figure One

ISOTEC research has developed methods to control the rate of decomposition and extend the life of the oxidizing agent. This longevity increases the potential for hydroxyl radical formation, while allowing the oxidant to travel throughout the affected area, thereby covering a larger area of the targeted contamination.

The ISOTEC process in action

Bench scale, field pilot and full-scale treatment programs have been completed using in situ oxidative remediation of contaminated soil and groundwater. Factors relevant to the application of the process include hydrogeological conditions, soil chemistry and contaminant characteristics. A review of site information is necessary to determine that oxidative treatment is a viable remedial alternative. Implementation of the ISOTEC process is performed in three phases:

- Laboratory bench scale study
- On-site field pilot program
- Full-scale treatment

Laboratory bench scale phase

Samples of affected soil and groundwater are collected from the site and shipped to ISOTEC's laboratory. The samples are evaluated to determine whether oxidative remediation can treat the site specific contaminants and if so, the optimum treatment quantities. The samples are analyzed for known contaminants and their breakdown products to determine the actual effects of the treatment process.

The lab examines specific amounts of contaminant destruction when compared directly to the amount of reagent —catalyst and oxidant—applied. Differing amounts of reagent are added to series of experiments each containing site specific media to determine the optimum treatment conditions. Two control samples determine initial contaminant levels and examine volatilization losses during sample handling.

On-site pilot program

Upon completion of a successful laboratory study, hat is >70 percent conversion to CO_2+H_2O, a pilot program is performed as the second step to evaluate the oxidative treatment of site contaminants. The pilot program is typically performed on a portion of the actual contaminant plume from the previously identified source of contamination such as an underground storage tank or spill area.

Each pilot program treatment consists of introducing oxidizers and catalysts into the subsurface. The volume of discharge varies based on the level of contamination, volume of area to be treated, and subsurface characteristics. A specific stoichiometry determined during the lab study is used during the pilot program. The oxidant and catalyst are injected per point through a site-

	Pre-sample	Post-sample[1]
Date	7/31/1995	8/31/1995
VO Compound	(ppb)	(ppb)
Vinyl Chloride	3,390	ND
Trichloroethane	59.2	ND
Ethylbenzene	2,000	ND
Xylenes, total	3,400	ND
cis-1,2-Dichloroethene	270,000	ND

Notes:
ppb=parts per billion or micrograms per liter (mg/l)
ND=indicates that the parameter was analyzed but not detected
1 = one month after initial treatment

Figure two

engineered injection apparatus used to control flow of treatment chemicals into the subsurface.

Specific site monitoring is performed during the pilot program to obtain information related to the treatment process and subsurface characteristics. Media samples are collected from on-site points before and at various time intervals during and following treatment injections. Samples are analyzed for targeted contaminant parameters, as well as field parameters used to evaluate reaction efficiency and environmental response. Qualitative tests for hydrogen peroxide concentrations and hydroxyl radical activity are performed. A proprietary field screening method to detect hydroxyl radical concentrations directly has been developed.

Full scale treatment

The full scale treatment programs will generally consist of similar procedures as those developed during the pilot program. Based on the contaminant destruction, flow rates and radial effects noted during the pilot program, an injection program is designed which assures adequate distribution of the treatment chemicals into the entire plume or affected area. The specific stoichiometry is again used.

Case studies

Organic contaminants which have been successfully oxidized in the field include: total petroleum hydrocarbons; TCE; PCE; 1,1,1-Trichloroethane; 1,1-Dichloroethene; Vinyl Chloride, sis and trans-1,2-Dichloroethene; 1,2 Dichloroethane; Benzene, Toluene, Ethylbenzene and Xylenes (BTEX); t-Butyl Alcohol (TBA); Methyl-t-Butyl Ether (MTBE); and Polychlorinated Biphenyls.

The ISOTEC process was used at an industrial warehouse site in Northern New Jersey. Underground storage tanks holding gasoline had contaminated the groundwater with benzene, toluene, ethylbenzene and total xylene. The site geology consisted of soft red shales with interbedded, harder sandstone and minor amounts of conglomerate. Soils at the site were unsorted and unstratified material consisting of pebbles, cobbles, and boulders in a mixture of sand, silt and clay.

The laboratory study revealed an oxidizer and catalyst mixture which produced 100 percent destruction. In situ applications were performed under regulatory approval as part of a pilot program. A multiport delivery system was designed to introduce the treatment chemicals to the subsurface. Flow rates, hydroxyl radical production and radial influences were recorded and monitored during the pilot program.

Three treatments were performed over six months, ending in June 1996. See figure l. The pilot program was initially designed to treat a specific volume within the source area to be tested and to determine the extent of treatment of subsurface organic contaminants at the warehouse facility.

Based on pre-treatment vs. post-treatment analytical data, more than a 99 percent reduction in organic contamination was noted throughout the delineated plume area, with no contaminants detected above applicable state enforced groundwater quality standards.

The extent of treatment during the pilot program was estimated to be about 6 meters, based on the presence of radicals within hydraulically connected areas. Hydroxyl radical samples were collected during and after injection activities to examine the radial effects of the ISOTEC process, with positive results present at all injection points.

Three rounds of confirmatory groundwater sampling and analyses were performed, and the results were submitted to the regulatory agency. Following regulatory review, the agency approved the remedial effort and issued a No Further Action determination for the site. Another manufacturing and warehousing facility in Northern New Jersey was a site where historic spills of hazardous substances occurred over 15 years.

Areas of environmental concern consisted of a former drum storage area and a former underground storage tank. Groundwater was found to be contaminated with high concentrations of chlorinated solvents and gasoline constituents, including vinyl chloride, trichloroethene, cis-1,2-dichloroethene, ethylbenzene and total xylenes.

Field pilot program results indicated the ISOTEC process achieved more than a 99 percent decrease in total VOC concentrations in the groundwater contaminant plume after four weeks. Treatment during the field pilot program resulted in decreasing total VOC groundwater concentrations from 278,849 ppb to 178 ppb. See Figure 2

ISOTEC in conjunction with other technologies as the hydroxyl radical is a powerful oxidant that oxidizes contaminants at near diffusion controlled rates, treatment times can be greatly reduced with effects verifiable in days. Adjustments can be made to stochiometric ratios of the injectate and delivery system to rapidly maximize treatment efficiency.

The ISOTEC process chemically changes the composition of the contaminants in situ, resulting in final breakdown of carbon dioxide and water. The chemical injection systems are designed to be mobile and are reusable at multiple sites.

The process can be used in conjunction with existing treatment systems. Many pump and treat and soil vapor extraction systems reach a point where contaminant levels have stabilized. These systems also may not effectively treat remaining low level compounds with concentrations that may still exceed regulatory criteria. Employing the ISOTEC process with these systems can destroy and break down persistent compounds which could not be effectively liberated by pump and treat or SVE.

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