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TECH MEMO #101: CONCEPTS OF CHEMICAL OXIDATION IN SOIL & WATER USING FENTON'S REAGENT

By Jim Jacobs, CHG, 415-381-5195

THE PROBLEM: Petroleum hydrocarbons such as gasoline, diesel, jet fuel, motor oil, and benzene, toluene, ethylbenzene and toluene (BTEX) are commonly found at current and former fuel service stations and vehicle maintenance centers. Chlorinated solvents including tetrachlorethylene (PCE), trichloroethylene (TCE) and dichloroethylene (DCE) are commonly found at former industrial facilities and other locations. Taken collectively, these compounds are called volatile organic compounds (VOCs).

REDEVELOPMENT POTENTIAL: VOCs occurring at industrial facilities, military bases and other areas offer special challenges in locations where there is a high demand for the redevelopment of the former industrial area. In cases such as this, a rapid and cost effective method of VOC destruction is needed that can be used without the commitment to years of costly operations and maintenance typically associated with soil vapor extraction or pump and treat systems currently employed for VOC remediation of soil and groundwater, respectively.



Injecting hydrogen peroxide through the drill rod of a direct push rig.

NEW REMEDIATION APPROACH:

Hydrogen peroxide can chemically oxidize VOCs forming carbon dioxide and water as end products.

ENVIRONMENTAL BIO-SYSTEMS uses both a direct push method as well as a specialized lance system for the rapid delivery of treatment chemicals (Jacobs, 2000a, 2000b, 2001). In-situ chemical oxidizers have the potential for rapidly treating soils contaminated with toxic and persistent organic wastes (Ho, et. al., 1995). In-situ oxidation uses contact chemistry of the oxidizing agent to react with volatile organic compounds. The most common oxidizer used in soil and groundwater remediation is hydrogen peroxide (and the hydroxyl radical).

FENTON'S REAGENT

Hydrogen peroxide when in contact with a metal catalyst such as iron (II), which is commonly known as Fenton's reagent, forms the more powerful oxidizer, the hydroxyl radical. The metal catalyst can

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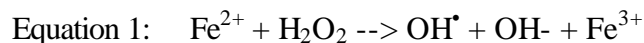
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be usually provided by iron oxide within the soil or fill, or added separately as an iron salt, such as iron sulfate. Fenton's reagent has been well documented for over 100 years and has been in use in water treatment plants for well over 50 years. The chemistry of Fenton's reagent to destroy petroleum hydrocarbons and other volatile organic compounds is well documented (Watts, et al, 1990, 1991, 1992 and 1994).

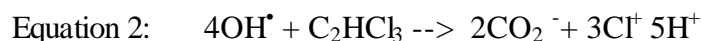
Hydrogen peroxide arrives in the field as a liquid stored in poly drums or larger containers. When chemical oxidant hydrogen peroxide (H₂O₂) is injected into the subsurface, it decomposes readily into reactive hydroxyl radicals (OH[•]), hydroxyl ions (OH⁻) and water (H₂O). The oxidation of a contaminant by hydrogen peroxide involves complex reactions influenced by a number of variables, including pH, reaction time, temperature, catalysts, contaminant concentration, and hydrogen peroxide dosage. In subsurface environments having pH of 8.0 or greater, strong or weak acids have been used to lower and optimize the oxidation process, as determined by a laboratory bench test. Hydrogen peroxide works best in acidic environments of pH of 2 to 4 with low alkalinity.

HYDROXYL RADICAL

The hydroxyl radical (OH[•]) in the subsurface can be used to rapidly mineralize hydrocarbon, solvent and other contaminants to water and carbon dioxide. This reaction is enhanced in the presence of iron. Iron is naturally occurring in soil and groundwater or can be added during the injection process, if needed. The reaction is based on the principle of Fenton's Reagent where the iron and hydrogen peroxide initially react to form hydroxyl radicals and other by-products as shown in Equation 1. The subsequent complex reactions of Fenton's process have been well documented by Barb (1950) and Spencer et al. (1996) and are not included here.



TCE (C₂HCl₃) is an industrial degreaser commonly used in equipment maintenance. The oxidation reaction of trichloroethylene (TCE) is shown in Equation 2:



Any hydrogen peroxide not used in the oxidation process breaks-down to water and oxygen in a matter of hours. In addition to the reaction described in Equation 2, there are also a large number of competing reactions including the free radical scavengers, most importantly, carbonate and bicarbonate alkalinity, that will greatly affect the overall

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reaction scheme. Hydrogen peroxide can also serve as an oxygen source for microbes in the subsurface to enhance biodegradation of contaminants. Therefore, many in-situ chemical oxidation projects are designed to move into a second, longer-term bioremediation phase due to all the newly available oxygen in the subsurface.

REMEDICATION INJECTION PROCESS (RIP[®])

The RIP[®] system has been designed to handle high concentrations of hydrogen peroxide, a commonly available oxidant which is effective at remediation and relatively inexpensive. The RIP[®] field procedures require significant safety training and planning.

The reaction time for hydrogen peroxide in the subsurface is usually seconds to minutes, with occasional reactions being completed within minutes to hours. Therefore, close spacing of the injection ports is generally required due to the short reaction period of hydrogen peroxide. During injections, the temperature of the reaction liquids is monitored to evaluate the success of the reactions. Based on field observations, temperatures of the reaction liquids less than approximately 35 to 41 °C indicate that the hydrogen peroxide is reacting properly. Excessive temperatures (approaching 80 °C to 90 °C) indicate that the exothermic reaction is consuming peroxide at a very rapid and uncontrolled rate. Forensic chemical analysis from various sites have shown that the hydrogen peroxide reaction tends to work first on the longer chain carbon sources, including total organic carbon (TOC), woody fragments, and heavier-end hydrocarbons, prior to oxidizing the lighter hydrocarbons. Trace chlorine from chlorinated compounds will likely combine with sodium or calcium ions to form salts or with hydrogen to form weak acids. Careful evaluation of the chemistry of the soil and water are required prior to the start of any injection process.

RECOMMENDED PLAN: ENVIRONMENTAL BIO-SYSTEMS recommends a review of the existing physical and chemical data, including pH, permeability, lithology, and water depth, concentrations of VOCs, alkalinity, and other data. A simple laboratory bench test (5 to 10 working days) is recommended to optimize the pH, and dosage of the hydrogen peroxide, as well as evaluate the addition of iron or acids. A pilot-scale in-situ remediation project can occur within a few days after the bench test results are available. After a pilot-scale project is performed, a large-scale full remediation program can be developed. In some cases, the pilot-scale size project may be enough to treat a lingering hot spot. For hydrocarbon impacted sites, the hydrogen peroxide reaction will liberate large amount of free oxygen, allowing for a second treatment phase using aerobic bioremediation of the contaminants.

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SUMMARY: Hydrogen peroxide injection using the RIP[®] system to treat soil and groundwater impacted by VOCs is rapid, precise, less disruptive and generally lower cost than most of the alternative remediation methods.

COMPANY BACKGROUND: Since 1990, ENVIRONMENTAL BIO-SYSTEMS has been a leader in in-situ remediation. The company has developed proprietary injection remediation technologies, allowing for successful remediations of metals, hydrocarbons, and chlorinated solvents.

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