Environmental Bio-Systems, Inc.

TECH MEMO #109: IN-SITU REMEDIATION WITH CHEMICAL OXIDIZERS: OZONE, PEROXIDE AND PERMANGANATE

By Jim Jacobs, CHG, (415) 381-5195

THE PROBLEM: Volatile organic compounds (VOCs), include petroleum hydrocarbons and chlorinated solvents. Petroleum hydrocarbons, commonly associated with refueling and maintenance facilities, include chemicals such as gasoline, diesel, jet fuel, motor oil, and benzene, toluene, ethylbenzene and toluene (BTEX). Chlorinated solvents, commonly associated with electrical manufacturing and degreasing operations, include chemicals such as tetrachlorethylene (PCE), trichloroethylene (TCE) and dichloroethylene (DCE).

THE SOLUTION TO VOC DESTRUCTION: VOCs can be destroyed using chemical oxidizers such as ozone, hydrogen peroxide and potassium permanganate. The complete oxidation of VOCs produces carbon dioxide and water.

SPECIES	**VOLTS**	**IN-SITU APPLICATIONS**	**NOTES**
Fluorine	3.0	NO	
Hydroxyl Radical	2.8	YES	Assoc. with Fenton's Reagent; reaction: seconds
Ozone	2.1	YES	Generated on-site as a gas
Hydrogen Peroxide	1.8	YES	Commonly used liquid; reaction: sec to min; up to hours
Potassium Permanganate	1.7	YES	Long lasting, purple staining; reaction: min to hrs; up to days
Hydrochlorous Acid	1.5	NO	
Chlorine Dioxide	1.5	NO	
Chlorine	1.4	NO	
Oxygen	1.2	NO	

In-situ oxidation uses contact chemistry of the oxidizing agent to react with VOCs, munitions, certain pesticides and wood preservatives. The most common oxidizers used in soil and groundwater remediation are hydrogen peroxide (and the hydroxyl radical) and potassium permanganate, and ozone, which are non-selective oxidizers. Other oxidants are available, but are used less due to cost, time or potential toxic by-products.

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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 be usually provided by iron oxides within the soil or fill, or added separately 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 (Barb et al., 1950; Stanton et al., 1996). The chemistry is well documented (Watts, et al, 1991, 1992 and 1994) to destroy petroleum hydrocarbons and other volatile organic compounds. Hydrogen peroxide arrives in the field as a liquid stored in poly drums. When chemical oxidant hydrogen peroxide (H_2O_2) is injected into the subsurface, it decomposes readily into reactive hydroxyl radicals ($OH^{\bullet}$), hydroxyl ions (OH^-) and water (H_2O). The oxidation of a contaminant by hydrogen peroxide involves complex reactions influenced by a number of variables, including pH, reaction time, temperature, catalysts, and hydrogen peroxide dosage. In subsurface environments having pH of 8.0 or greater, strong or weak acids can be used to lower pH and optimize the oxidation process, as determined by a laboratory bench test. Hydrogen peroxide works best in acidic environments with low alkalinity. Chemical oxidant delivery systems have been described (Jacobs, 2000a, 2000b and 2001).

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 reaction scheme. Although handling hydrogen peroxide and other oxidants requires significant safety training and planning, the oxidant is effective at remediation and relatively inexpensive. 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), rootlets, heavier-end hydrocarbons, prior to oxidizing the lighter hydrocarbons.

Potassium permanganate ($2KMnO_4$) lasts longer and can react in an environment with much higher pH than hydrogen peroxide. For field use, potassium permanganate is shipped as a powder and is mixed with water creating a deep purple liquid. The solubility of potassium permanganate is strongly influenced by temperature and at 30 ^oC, the solution has slightly over an 8% concentration of potassium permanganate. The pH range is critical in being able to determine whether the oxidation reaction will be fast or slow. If trivalent chromium Cr (III) is present in the soil, adding potassium permanganate will oxidize the Cr (III) to Cr (VI). Field conditions indicate that once the oxidant is consumed, the Cr (VI) will revert back to Cr (III).

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Ozone (O_3) is a powerful gas phase oxidizer that can be used to treat VOCs. It must be generated on-site and the gas cannot be stored; therefore all the ozone gas that is generated must be injected into the subsurface or destroyed using an ozone destruction unit on the ozone generator. The ozone gas can be bubbled into closely spaced injection ports that release the bubbles into the aquifer for remediation. The smaller the bubbles, the more surface area and the faster they can travel through small pore spaces. Pushing the ozone gas through a diffusion pipes can produce micro-bubbles.

For all types of in-situ chemical oxidation methods, chemical compatibility of the injection equipment, personal protective equipment and safety procedures become critical with the injection of potentially dangerous chemicals including oxidizers, acids, bases, and other chemicals.

BIOREMEDIATION: Chemical oxidants 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. Potassium and sodium permanganate do not kill microbes. Hydrogen peroxide and ozone at higher concentrations will kill microbes, however, the oxygen rich treatment area will be attractive to indigenous populations in adjacent zones.

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.

SUMMARY: Chemical oxidants hydrogen peroxide, potassium permanganate and ozone can be injected into soil and groundwater impacted by VOCs. The remediation injection process 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.

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