Technology
Overview Report

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Ultraviolet/Oxidation Treatment

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FOREWORD

About GWRTAC

The Ground-Water Remediation Technologies Analysis Center (GWRTAC) is a national environmental technology transfer center that provides information on the use of innovative technologies to cleanup contaminated groundwater.

Established in 1995, GWRTAC is operated by the National Environmental Technology Applications Center (NETAC) in association with the University of Pittsburgh's Environmental Engineering Program through a Cooperative Agreement with the U.S. Environmental Protection Agency's (EPA) Technology Innovation Office (TIO). NETAC is an operating unit of the Center for Hazardous Materials Research and focuses on accelerating the development and commercial use of new environmental technologies.

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About "O" Series Reports

This report is one of the GWRTAC "O" Series of reports developed by GWRTAC to provide a general overview and introduction to a groundwater-related remediation technology. These overview reports are intended to provide a basic orientation to the technology. They contain information gathered from a range of currently available sources, including project documents, reports, periodicals, Internet searches, and personal communication with involved parties. No attempts are made to independently confirm or peer review the resources used.

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ABSTRACT

This technology summary report is an overview of information collected by GWRTAC on ultraviolet (UV)/oxidation treatment processes for the treatment of contaminated groundwater. Information provided includes an introduction to general principles and techniques associated with this technology, a general discussion of the applicability to groundwater remediation, limited data relating to results of its use, advantages and limitations of use of this technology. Also provided are a list of references cited, and related references compiled during preparation of this report.

UV/oxidation is a destruction process that oxidizes organic and explosive constituents in contaminated groundwater by the addition of strong oxidizers and irradiation with ultraviolet light. The oxidation reactions are achieved through the synergistic action of high intensity UV light alone, or in combination with patented treatment reactor design (in some cases), ozone (O_3) and/or hydrogen peroxide (H_2O_2). The UV/oxidation process generates highly reactive hydroxyl radicals (OH•) that react with and destroy most organic chemical compounds. If complete mineralization is achieved in the reaction, the final products of the process are carbon dioxide, water and salts

A wide variety of organic and explosive contaminants are susceptible to destruction by UV/oxidation, including petroleum hydrocarbons; halogenated solvents; phenol; pentachlorophenol; pesticides; dioxins; glycols; polychlorinated biphenyls; explosives such as TNT, RDX, and HMX; creosote; Freon 113; vinyl chloride; benzene, toluene, ethylbenzene, and xylenes (BTEX); methyl tertiary butyl ether; cyanide; mixed organic/radioactive waste and other organic compounds. According to the information reviewed, UV/Oxidation has most often been used for contaminant concentrations in groundwater below 500 mg/L. Organics such as benzene can be treated to nondetectable levels; others, such as, 1,1-dichloroethane, are typically reduced by 96 percent. Also, organisms such as *Salmonella* and *E. Coli* have reportedly been significantly reduced using UV/oxidation.

UV/oxidation processes can be configured in batch or continuous flow operations, depending on the flowrate under consideration. A key advantage cited for UV/oxidation treatment technology is that it is a destruction process (i.e. no toxic by-products are generated in the reaction), as opposed to air stripping or carbon adsorption, for which contaminants are extracted and concentrated in a separate phase.

This document was prepared for distribution by the Groundwater Remediation Technology Analysis Center (GWRTAC). GWRTAC is being operated by the National Environmental Technologies Application Center (NETAC), under a Cooperative Agreement with the EPA's Technology Innovation Office (TIO).

TABLE OF CONTENTS

1.0 INTRODUCTION

UV/oxidation processes combine the use of ultraviolet light (UV) and chemical oxidants such as ozone (O_3) and hydrogen peroxide (H_2O_2) to destroy organic contaminants in groundwater. In most UV/oxidation processes, high intensity UV radiation is combined with H_2O_2 to oxidize organic contaminants to carbon dioxide and water. Through direct photolysis, the UV light reacts with the H_2O_2 to generate hydroxyl radicals (OH•), which are highly reactive, and are second only to fluorine in relative oxidation potential. The hydroxyl radicals then attack the organic molecules resulting in the destruction of the parent organic compound. The reaction is aided by the direct photolysis of the organic molecule by the UV light which can break or activate certain atomic bonds making the molecule more susceptible to oxidation. With sufficient oxidation and exposure to UV energy, the reaction by-products are carbon dioxide, water, and the appropriate inorganic salt. Depending of the chemical structure of the organic molecules, the hydroxyl radical reaction pathway can be one of addition reactions, subtraction reactions of a combination of both, leading to the mineralized end products (3, 4, 5).

2.0 APPLICABILITY

In general, UV/oxidation is applicable at sites where groundwater is contaminated with ***volatile organic compounds (VOC's), semi-VOC's, aromatics, alcohols, ketones, aldehydes, phenols, ethers, phthalates, glycols, pesticides, ordnance compounds, dioxins, PCB's, PAH's, COD, BOD, TOC and most other forms of organic carbon.***

3.0 METHODOLOGY

Successful implementation of a UV/oxidation process depends on a number of factors. These factors include ***equipment design, contaminant type and concentration, water quality parameters, and oxidant type and dosage.*** Potential adverse effects from water quality parameters such as suspended solids, iron, alkalinity, and background COD levels, can be effectively managed with proper pretreatment and/or utilization of proprietary catalytic additives. Proper equipment design is of paramount importance in achieving optimum UV/oxidation treatment performance for any application (3).

In most cases, ***bench-scale*** or ***pilot testing*** is required to ***evaluate*** necessary design requirements and system sizing. Properly designed full-scale UV/oxidation equipment should at a minimum maintain the following engineering design features:

- meet all applicable manufacturing codes and OSHA safety requirements;
- include a properly designed UV reactor which maximizes the utilization of available UV light energy and provides sufficient turbulent mixing, even at low flow rates;
- an effective and low maintenance automatic quartz tube and reactor chamber wall cleaner;
- an oxidant dosing system which allows for multiple point dosing and continuous adjustment of the oxidant dosage;
- UV lamp/power turn-down capability while maintaining constant UV density;
- PC- or PLC- based automation features; and,
- a configuration for minimum space requirements while maintaining serviceability and ease of upgrade for future expansion.

Without the above design features, full-scale equipment can become operationally cumbersome and cost prohibitive (3).

4.0 TECHNOLOGY PERFORMANCE

Note: The following information is provided for informational purposes only.

GWRTAC (EPA TIO, NETAC, CHMR, and the University of Pittsburgh) neither endorses nor in any way recommends the companies discussed below. No effort has been made, nor will be made, to verify the accuracy of the information provided, or to assess the validity of any claims about the companies. GWRTAC makes no warranties, expressed or otherwise, without limitation or liability, for the completeness, accuracy, or usefulness on the information provided.

It has been reported that UV/oxidation has been in full-scale groundwater treatment application for more than 12 years. Currently, UV/oxidation processes are in operation in more than 150 full-scale remedial applications. A majority of these applications are for groundwater contaminated with petroleum products or with a variety of industrial solvent-related organics such as TCE, DCE, TCA, and vinyl chloride. Presented below are selected examples of UV/oxidation systems, their performance and cost information for sites utilizing UV/oxidation treatment technology (3).

4.1 CAVOX® (Magnum Water Technology)

The CAVOX® process uses a synergistic combination of hydrodynamic cavitation and ultraviolet (UV) radiation (and where necessary, the addition of hydrogen peroxide and metal catalysts) to oxidize contaminants in groundwater. The process is designed to remove organic contaminants from groundwater **without** releasing volatile organic compounds into the atmosphere. Neither the cavitation chamber nor the UV lamp or hydrogen peroxide reaction generates toxic by-products or air emissions. The CAVOX® process cannot handle free product or highly turbid waste streams, since these conditions tend to lower the UV reactors' efficiencies. UV lamp output can be varied from 360 watts to over 20,000 watts, depending on the waste stream (2, 6).

This technology was accepted into the SITE Demonstration Program in the summer of 1992, and was demonstrated for four weeks in March 1993 at Edwards Air Force Base Site 16 in California. Tests at a Superfund site treated leachate containing 15 different contaminants. Pentachlorophenol, one of the major contaminants, was reduced by 96 percent in one test series. In other tests, the process successfully treated cyanide contamination. The process has also remediated a former gasoline station site over a 2-year period. The CAVOX® process achieved removal efficiencies of greater then 99.9 percent for tricholorethene, benzene, toluene, ethylbenzene, and xylenes. No quartz tube scaling was observed (2, 6).

4.2 ULTROX (A Division of ZIMPRO Environmental, Inc.)

The ULTROX process uses hydrogen peroxide, ozone and UV radiation to destroy toxic organic compounds in groundwater. Off-gas from the treatment system passes through an ozone destruction Decompozon unit, which reduces ozone levels before air venting (8).

A field-scale demonstration was completed in March 1989 at the Lorentz Barrel and Drum Company site in San Jose, California. The technology is fully commercial, with over 30 systems installed.

Flow rates ranging from 5 gallons per minute to 1,050 gpm are in use at various industries and site remediations. Documented demonstration results are as follows:

Contaminated groundwater treated by the system met regulatory standards at the appropriate parameter levels. The Decompozon unit reduced ozone to less than 0.1 ppm, with efficiencies greater than 99.9 percent. VOC's present in the air within the treatment system were not detected after passing through the Decompozon unit. Total organic carbon removal was low, implying partial oxidation of organics without complete conversion to carbon dioxide and water (8).

4.3 PEROX PURE (Vulcan Peroxidation Systems, Inc.)

The PEROX PURE process uses UV radiation with hydrogen peroxide to destroy organic compounds in contaminated groundwater. The PEROX PURE technology treats groundwater contaminated with chlorinated solvents, pesticides, polychlorinated biphenyls, phenolics, fuel hydrocarbons, and other organic compounds at concentrations ranging from a few thousand milligrams per liter to one microgram per liter or lower. In some cases, the treatment system can combine with air stripping, steam stripping, or biological treatment to optimize treatment results (9).

The PEROX PURE technology was accepted into the SITE Demonstration Program in April 1991. A treatment system was demonstrated in September 1992 at the Lawrence Livermore National Laboratory (LLNL) Site 300 Superfund site in California. This technology has been successfully applied to over 80 sites throughout the United States, Canada, and Europe. The demonstration test results showed that in most cases, the PEROX PURE technology reduced trichloroethane, tetrachloroethane, chloroform, and dichloroethane to below analytical detection limits. For each organic contaminant, the PEROX PURE technology complied with California action levels and federal drinking water maximum contaminant levels at the 95 percent confidence level. The quartz tube wipers effectively cleaned the tubes and eliminated the interference caused by tube scaling (3, 9).

5.0 TECHNOLOGY ADVANTAGES

Advantages offered by UV/oxidation processes in the treatment of contaminated groundwater include the following:

- $UV/O_3/H_2O_2$ treatment processes do not add to the pollutant load to the groundwater treatment system. This is in contrast to many of the existing end-of-pipe pollution abatement systems presently in use which merely transfer the waste from one medium to another leaving, for example, combustion by-products or contaminated absorbent for further disposal (1).

- UV radiation enhanced ozone treatment with hydrogen peroxide additions have been used in the successful treatment of particularly refractive substances such as ferricyanides and other chemical compounds (1, 3,).

6.0 TECHNOLOGY LIMITATIONS

Limitations associated with UV/Oxidation processes involve the following:

- In UV/oxidation using H_2O_2, the process is only efficient at rather low wavelengths (below 200 nm).
- The aqueous stream being treated must provide for good transmission of UV light. High turbidity and high suspended solids concentration in the groundwater causes interferences.
- Free radical scavengers can inhibit contaminant destruction efficiency. Excessive dosages of chemical additives may also act as a scavenger.
- The aqueous stream to be treated by UV/oxidation should be relatively free of heavy metal ions (less than 10 mg/l) and insoluble oil or grease to minimize the potential for fouling of the UV quartz sleeves. High alkalinity and carbonates in the groundwater may also cause fouling of both the reactor vessels and the UV quartz sleeves.
- Pretreatment of the aqueous stream may be required to minimize ongoing cleaning and maintenance of UV reactor and quartz sleeves.
- Costs may be higher than competing technologies because of energy requirements at some installations.
- Handling and storage of oxidizers require special material handling and safety precautions.
- Possible air emission problems with ozone (O_3) as the oxidant have been encountered in some UV/oxidation systems (7, 8).

7.0 UV/OXIDATION GENERAL TREATMENT COST INFORMATION

UV/oxidation treatment costs are generally between $0.10 and $10.00 per 1,000 gallons treated (in 1994 dollars). Factors that influence the cost to implement UV/oxidation include:

- Degree of contaminant destruction required.
- Groundwater treatment system flowrate.
- Types and concentration of contaminants (as they effect oxidizer selection, oxidizer dosage, UV light intensity, and treatment time).
- Requirements for pretreatment and/or posttreatment (7).

Magnum Water Technology estimates the cost of using the CAVOX® process to be half the cost of other advanced UV/oxidation systems, and substantially less expensive than carbon adsorption. Because the process equipment has only one moving part, maintenance costs are minimal. The CAVOX® process does not exhibit the quartz scaling common with other UV equipment. Langelier's Index of Scaling is shifted negative by the CAVOX® process (6).

Direct operating and maintenance costs of the ULTROX Process are reported by the manufacturer for a number of applications. The costs range from $0.40 to $5.00 per 1,000 gallons. In general, it was found that this process was much less costly than alternatives, such as activated carbon. In one application, a comparison of various treatment strategies for groundwater contamination with TCE and other trace VOC's (total VOC concentration = 7.0 mg/L) found that the capital costs of air stripping with vapor phase granular activated carbon were less than the Ultrox Process, but the operation and maintenance costs of the Ultrox system were one-third to one-half of the alternatives (8).

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