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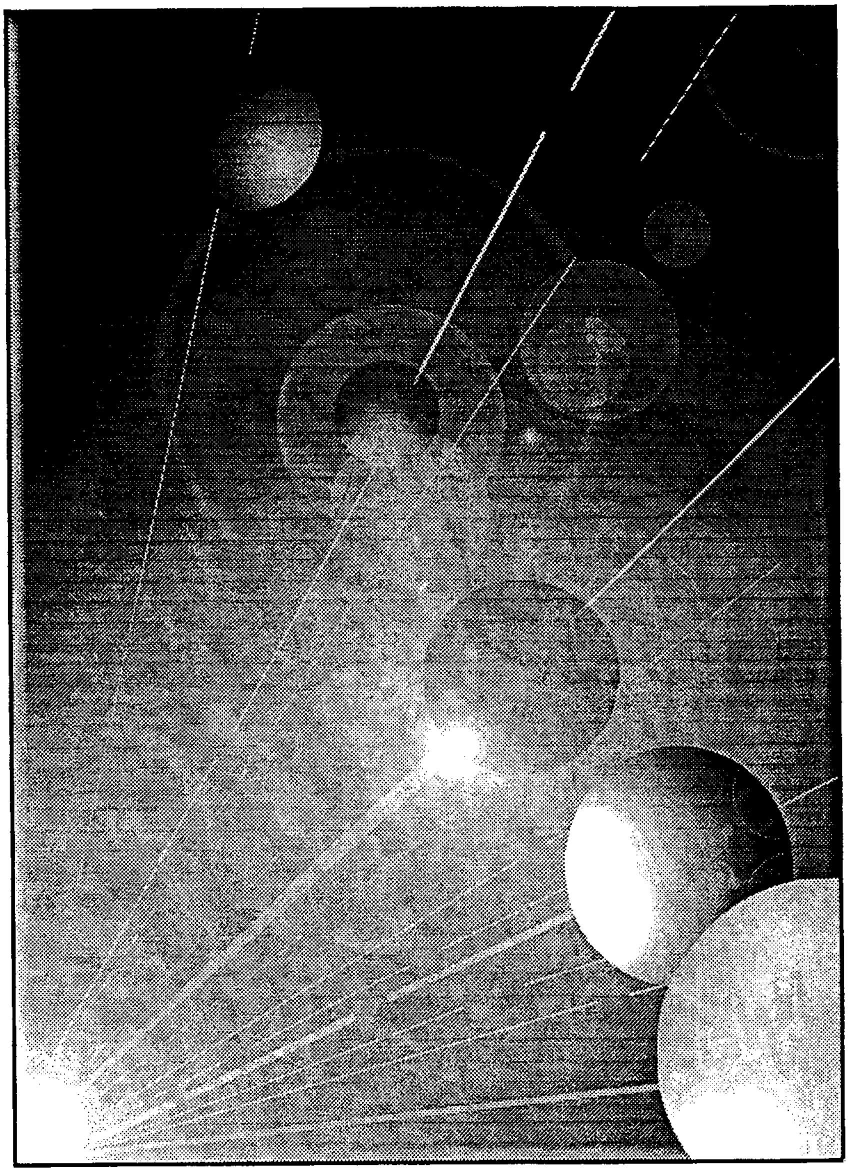
Handbook

Advanced Photochemical Oxidation Processes



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HANDBOOK ON ADVANCED PHOTOCHEMICAL OXIDATION PROCESSES

Center for Environmental Research Information
National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Notice

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Foreword

The U.S. Environmental Protection Agency (U.S. EPA) is charged by Congress with protecting the Nation's land, air, and water resources, Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and groundwater; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies and to develop scientific and engineering information needed by U.S. EPA to support regulatory and policy implementation of environmental regulations and strategies.

A key aspect of the Laboratory's success is an effective program for technical information dissemination and technology transfer. The Center for Environmental Research Information (CERI) is the focal point for these types of outreach activities in NRMRL.

This summary document, *Handbook* on *Advanced Photochemical Oxidation Processes,* produced by CERI, is a technical resource guidance document for environmental engineering practitioners.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

Abstract

This handbook summarizes commercial-scale system performance and cost data for advanced photochemical oxidation (APO) treatment of contaminated water, air, and solids. Similar information from pilot- and bench-scale evaluations of APO processes is also included to supplement the commercial-scale data. Performance and cost data is summarized for various APO processes, including vacuum ultraviolet (VUV) photolysis, ultraviolet (UV)/oxidation, photo-Fenton, and dye- or semiconductor-sensitized APO processes. This handbook is intended to assist engineering practitioners in evaluating the applicability of APO processes and in selecting one or more such processes for site-specific evaluation.

APO has been shown to be effective in treating contaminated water and air. Regarding contaminated water treatment, UV/oxidation has been evaluated for the most contaminants, while VUV photolysis has been evaluated for the fewest. Regarding contaminated air treatment, the sensitized APO processes have been evaluated for the most contaminants, while VUV photolysis has been evaluated for the fewest.

APO processes for treating contaminated solids generally involve treatment of contaminated slurry or leachate generated using an extraction process such as soil washing. APO has been shown to be effective in treating contaminated solids, primarily at the bench-scale level.

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Acronyms, Abbreviations, and Symbols

>	Greater than
<	Less than
$\mu g/cm^2$-min	Microgram per square centimeter-minute
μg/L	Microgram per liter
μmol/L	Micromole per liter
Ag	Silver
AIR	Adsorption-integrated-reaction
AOX	Adsorbable organic halide
APO	Advanced photochemical oxidation
BOD	Biochemical oxygen demand
BTEX	Benzene, toluene, ethylbenzene, and xylene
Calgon	Calgon Carbon Corporation
CB	Chlorobenzene
CFC-113	Trichlorofluoroethane
cfu/mL	Colony forming unit per milliliter
CHQ	Chlorohydroquinone
cm	Centimeter
co	Carbon monoxide
COD	Chemical oxygen demand
CP	Chlorophenol
cu	Concentration unit
2,4-D	2,4-Dichlorophenoxyacetic acid
DBCP	1,2-Dibromo-3-chloropropane
DCA	Dichloroethane
DCAC	Dichloroacetylchloride
DCB	Dichlorobenzene
DCE	Dichloroethene
DCP	Dichlorophenol
DNG	Dinitroglycerin
e^-_{CB}	Electron in the conduction band
EE/O	Electrical energy consumption per order-of-magnitude contaminant removal
eV	Electron volt
Fe(II)	Ferrous iron
Fe(III)	Ferric iron
Fe(III)(OH)$^{2+}$	Ferrihydroxalate
Fe_2O_3	Ferric oxide
g	Gram
GAC	Granular activated carbon
hv	Light energy
h^+_{VB}	Hole in the valence band
H_2O	Water molecule
H_2O_2	Hydrogen peroxide
HCI	Hydrochloric acid
HHQ	Hydroxyhydroquinone
HMPA	Hexamethylphosphoramide
H•	Hydrogen radical

Acronyms, Abbreviations, and Symbols (Continued)

IEA	Irreversible electron acceptor
kg	Kilogram
KSE	KSE, Inc.
kW	Kilowatt
kWh/m^3	Kilowatt-hour per cubic meter
L	Liter
L/min	Liter per minute
m	Meter
$M^{-1}cm^{-1}$	Liter per mole-centimeter
$M^{-1}s^{-1}$	Liter per mole-second
m^3	Cubic meter
m^3/h	Cubic meter per hour
Magnum	Magnum Water Technology, Inc.
Matrix	Matrix Photocatalytic, Inc.
MCL	Maximum contaminant level
mg/L	Milligram per liter
min	Minute
MNG	Mononitroglycerin
MTBE	Methyl-*tert*-butyl ether
mW/L	Milliwatt per liter
mW/cm^2-sec	Milliwatt per square centimeter-second
4-NA	4-Nitroaniline
N_2O	Nitrous oxide
NDMA	N-nitrosodimethylamine
NG	Nitroglycerin
nm	Nanometer
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxides
4-NP	4-Nitrophenol
NQ	Nitroguanidine
NREL	National Renewable Energy Laboratory
$O(^1D)$	Singlet oxygen
O&M	Operation and maintenance
O_2	Oxygen
$O_2^{\bullet -}$	Superoxide ion
O_3	Ozone
OH^-	Hydroxide ion
*OH	Hydroxyl radical
PAH	Polynuclear aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
PCE	Tetrachloroethene
PCP	Pentachlorophenol

Acronyms, Abbreviations, and Symbols (Continued)

PDU	Photolytic Destruction Unit
pfu/mL	Plaque-forming unit per milliliter
ppbv	Part per billion by volume
ppmv	Part per million by volume
psia	Pound per square inch absolute
PTI	Process Technologies, Inc.
RDX	Cyclonite
scmm	Standard cubic meter per minute
SITE	Superfund Innovative Technology Evaluation
SnO_2	Tin oxide
SVE	Soil vapor extraction
SVOC	Semivolatile organic compound
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
TCA	Trichloroethane
TCE	Trichloroethene
2,3,5-TCP	2,3,5-Trichlorophenol
TiO_2	Titanium dioxide
1,3,5-TNB	1,3,5-Trinitrobenzene
TNT	2,4,6-Trinitrotoluene
TOC	Total organic carbon
TOX	Total organic halides
TPH	Total petroleum hydrocarbons
UDMH	Unsymmetrical dimethylhydrazine
U.S. Filter	U.S. Filter/Zimpro, Inc.
U.S. EPA	U.S. Environmental Protection Agency
UV	Ultraviolet
VC	Vinyl chloride
VOC	Volatile organic compound
VUV	Vacuum ultraviolet
W	Watt
WEDECO	WEDECO UV-Verfahrenstechnik
Zentox	Zentox Corporation
ZnO	Zinc oxide

Glossary

Anatase. The brown, dark-blue, or black, tetragonal crystalline form of titanium dioxide

Band gap. The energy difference between two electron energy bands in a metal

Batch reactor. A container in which a reaction is performed without any inflow or outflow of material during the reaction

Bioassay test. A test for quantitatively determining the concentration of a substance that has a specific effect on a suitable animal, plant, or microorganism under controlled conditions

Biochemical oxygen demand (BOD). The amount of dissolved oxygen consumed by microorganisms during biochemical decomposition of oxidizable organic matter under aerobic conditions. The BOD test is widely used to measure the pollution associated with biodegradable organic matter present in wastewaters.

Black light. Ultraviolet (UV) radiation having a relatively long wavelength (in the approximate range of 315 to 400 nanometers). It is also called UV-A, near-UV, or long-wave radiation.

Brookite. A brown, reddish, or black, orthorhombic crystalline form of titanium dioxide

Catalyst. A substance that alters the rate of a chemical reaction and that may be recovered essentially unaltered in form and amount at the end of the reaction

Chemical oxygen demand (COD). A measure of the oxygen equivalent of organic matter that is susceptible to oxidation by a strong chemical oxidant under acidic conditions. The COD test is widely used to measure the pollution associated with both biodegradable and nonbiodegradable organic matter present in wastewaters.

Complex. A compound formed by the union of a metal ion with a nonmetallic ion or molecule called a ligand or complexing agent

Conduction band. An energy band in a metal in which electrons can move freely, producing a net transport of charge

Congener. A chemical substance that is related to another substance, such as a derivative of a compound or an element belonging to the same family as another element in the periodic table. For example, the 209 polychlorinated biphenyls are congeners of one another.

Doping. Introduction of a trace impurity into ultrapure crystals to obtain desired physical properties. Transistors and other semiconductor devices are created by carefully controlled doping.

Electrical conductivity. A measure of the ability of a solution to carry an electrical current. It varies with both the number and type of ions present in a solution.

Electromagnetic radiation. A form of energy that appears to be both waves and particles (called photons). It includes visible light, UV radiation, radio waves, X-rays, and other forms differentiated by their wavelengths and equivalent energies.

Excimer laser. A laser containing a noble gas such as argon or krypton and another gas such as fluorine. It functions based on the creation of a metastable bond between the two gas atoms that readily return to the ground state and is a useful source of UV radiation.

First-order reaction. A chemical reaction in which the decrease in concentration of component "A" with time is proportional to the residual concentration of "A'

Glossary (Continued)

Half-life. The time required for a given material to decrease to one-half of its initial amount during a chemical reaction

Hydraulic retention time. The time spent by a unit volume of water in a reactor expressed as the ratio of the reactor volume to the influent flow rate

Implicit price deflator. The ratio of gross national product (GNP) measured at current prices to GNP measured at prices in some base year

Long-wave radiation. UV radiation having a relatively long wavelength (in the approximate range of 315 to 400 nanometers). It is also called UV-A radiation, near-UV radiation, or black light.

Maximum contaminant level (MCL). A value set by the US. Environmental Protection Agency (U.S. EPA) representing the maximum permissible level of a contaminant in water that is delivered to any user of a public water system. MCLs are derived from health risks that are modified based on practical considerations.

Molar absorption coefficient. The reduction in light intensity while light passes through a solution of unit concentration and unit path length

Near-ultraviolet radiation. UV radiation having a relatively long wavelength (in the approximate range of 315 to 400 nanometers). It is also called UV-A radiation, long-wave radiation, or black light.

Oxidant. A chemical that decreases the electron content of other chemicals

Oxidation potential. The difference in electrical potential between an atom or ion and the state in which an electron has been removed to an infinite distance from this atom or ion

Photochemical oxidation. A chemical reaction influenced or initiated by light that removes electrons from a compound or part of a compound

Photochemical reaction. A chemical reaction induced or catalyzed by light or other electromagnetic radiation

Photoconductivity. The increase in electrical conductivity displayed by many nonmetallic solids when they absorb electromagnetic radiation

Photodecarboxylation. Removal of a carboxyl radical through a photochemical reaction

Photo-Fenton process. Generation of hydroxyl radicals through decomposition of hydrogen peroxide using ferrous or ferric iron under near-UV radiation or visible light

Photolysis. Use of radiant energy (electromagnetic radiation) to produce a chemical change

Pseudo-first-order reaction. A chemical reaction that appears to follow first-order reaction kinetics for a specific reactant when all other reactants are present at levels in excess of stoichiometry

Quantum yield. For a photochemical reaction, the number of moles of a reactant consumed or the number of moles of a product formed per Einstein of light (per mole of photons) absorbed at a given wavelength

Radical. An uncharged species containing one or more unpaired electrons

Rutile. A reddish-brown, tetragonai crystalline form of titanium dioxide

Glossary (Continued)

Saturated organic compound. An organic compound in which all the available valence bonds along the carbon chain are attached to other atoms

Semiconductor. A solid crystalline material whose electrical conductivity lies between the conductivities of a conductor and an insulator. A semiconductor's conductivity can be significantly changed by exposure to light (photoconductivity), addition of small amounts of certain impurities (doping), or both.

Sensitizer. A chemical that lowers the activation energy of a reaction, thereby increasing the reaction rate

Singlet oxygen. Oxygen with no unpaired electrons. It is more reactive than triplet oxygen (oxygen with two unpaired electrons-the ground state).

Solar radiation. Electromagnetic radiation emitted by the sun

Steady state. The condition of a system during which system characteristics remain relatively constant with time after initial transients or fluctuations have disappeared

Superfund. A program established in 1980 by U.S. EPA to identify abandoned or inactive sites where hazardous substances have been or might be released to the environment in order to ensure that the sites are cleaned up by responsible parties or the government, evaluate damages to natural resources, and create a claim procedure for parties that have cleaned up sites or spent money to restore natural resources

Superfund Innovative Technology Evaluation Program. A program established by U.S. EPA to encourage development and implementation of innovative technologies for hazardous waste site remediation, monitoring, and measurement

Ultraviolet radiation. Electromagnetic radiation in the wavelength range of 4 to 400 nanometers

Unsaturated organic compound. An organic compound in which not all the available valence bonds along the carbon chain are attached to other atoms

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Executive Summary

Over the past two decades, environmental regulatory requirements have become more stringent because of increased awareness of the human health and ecological risks associated with environmental contaminants. Therefore, various treatment technologies have been developed over the last 10 to 15 years in order to cost-effectively meet these requirements. One such group of technologies is commonly referred to as advanced oxidation processes. These processes generally involve generation and use of powerful but relatively nonselective transient oxidizing species, primarily the hydroxyl radical (•OH) and in some cases the singlet oxygen. The •OH can be generated by both photochemical and nonphotochemical means to oxidize environmental contaminants. This handbook discusses the applicability of advanced photochemical oxidation (APO) technologies for treatment of contaminated water, air, and solids (soil, sediment, and ash).

The primary purpose of this handbook is to summarize commercial-scale APO system performance and cost data for treatment of contaminated water, air, and solids. In addition, it presents similar information drawn from pilot- and bench-scale evaluations of APO technologies as a supplement to the commercial-scale data. The handbook is intended to serve as an APO reference document for remedial project managers, on-scene coordinators, state and local regulators, consultants, industry representatives, and other parties involved in management of contaminated water, air, and solids. Specifically, it should assist these intended users in evaluating the applicability of APO technologies and in selecting one or more APO technologies for site-specific evaluation.

This handbook is not intended to summarize all the APO performance and cost data available in the literature. Rather, it is intended to present information on state-of-the-art APO technologies for treating contaminated environmental media. Commercial-scale APO system performance and cost data is presented in greater detail than pilot-scale results because the handbook is intended for practitioners, Similarly, pilot-scale results are presented in greater detail than bench-scale results. In addition, pilot- and bench-scale results are presented only where they supplement commercial-scale APO system evaluation results or where they fill information gaps, such as those associated with by-product formation.

This handbook presents an introduction (Section 1); provides background information on various APO technologies, typical commercial-scale APO systems, andsystem design and cost considerations (Section 2); and summarizes APO system performance and cost data for treating contaminated water, air, and solids (Sections 3, 4, and 5, respectively). References cited in each section are listed at the end of the section. APO technology vendor contact information is presented in the appendix.

This executive summary briefly describes the APO technologies and summarizes the commercial-scale system performance and cost data for treatment of contaminated water, air, and solids. Tables ES-1 and ES-2 at the end of the executive summary present commercial-scale performance and cost data for contaminated water and contaminated air treatment using various APO processes.

APO Technologies

APO technologies can be broadly divided into the following groups: (1) vacuum ultraviolet (VUV) photolysis, (2) ultraviolet (UV)/oxidation processes, (3) the photo-Fenton process, and (4) sensitized APO processes. These APO technologies and their variations are briefly described below.

VUV Photolysis

Photolysis of water using UV radiation of a wavelength shorter than 190 nanometers yields •OH and hydrogen radicals (H•). Contaminant degradation in water and in a relatively high-humidity air stream can be accomplished through oxidation by *OH or reduction by H• because VUV photolysis of water produces powerful oxidizing species (•OH) and reducing species (H•). Commercial-scale VUV photolysis systems are not currently available. However, bench-scale study results indicate that VUV photolysis is effective in treating contaminated water and humid air streams.

UV/Oxidation Processes

UV/oxidation processes generally involve generation of *OH through UV photolysis of conventional oxidants, including hydrogen peroxide (H_2O_2) and ozone (0,). Both UV/H_2O_2 and UV/O_3 processes are commercially available. Some APO technology vendors also offer variations of these processes (for example, $UV/O_3/H_2O_2$ and UV/H_2O_2/proprietary catalyst). The commercial-scale UV/oxidation systems available for contaminated water treatment include the (1) Calgon Carbon Corporation (Calgon) perox-pure™ and Rayox® UV/H_2O_2 systems; (2) Magnum Water Technology, Inc. (Magnum), CAV-OX® UV/H_2O_2 systems; (3) WEDECO UV-Verfahrenstechnik (WEDECO) UV/H_2O_2 and UV/O_3 systems; and (4) U.S. Filter/Zimpro, Inc. (U.S. Filter), $UV/O_3/H_2O_2$ system. The only commercial-scale UV/oxidation system available for contaminated air treatment is the Process Technologies, Inc. (PTI), UV/O_3 system. UV/oxidation treatment systems for contaminated solids generally treat contaminated slurry or leachate generated using an extraction process such as soil washing.

Photo-Fenton Process

Decomposition of H_2O_2 using ferrous iron (Fe(II)) or ferric iron (Fe(III)) under acidic conditions yields *OH. The rate of removal of organic pollutants and the extent of mineralization using the $Fe(II)/H_2O_2$ and $Fe(III)/H_2O_2$ reagents are improved considerably by irradiation with near-UV radiation and visible light. This process is called the photo-Fenton reaction, The only commercial-scale photo-Fenton system available is the Calgon Rayox® ENOX water treatment system.

Sensitized APO Processes

Sensitized APO processes can be broadly categorized as dye-sensitized and semiconductor-sensitized processes. These categories are described below.

In a dye-sensitized APO process, visible light is absorbed by a sensitizing dye, which excites the dye molecules to a higher energy state. The excited dye then transfers some of its excess energy to other molecules present in the waste stream, producing a chemical reaction. When dissolved oxygen accepts energy from the excited dye molecule (for example, methylene blue or rose bengal'), the dissolved oxygen is converted to singlet oxygen, a powerful oxidant. This APO process has not yet become commercially viable.

In a semiconductor-sensitized APO process, metal semiconductors are used to destroy environmental contaminants by means of light-induced redox reactions. These reactions, involve generation of conduction band electrons and valence band holes by UV irradiation of semiconductor materials such as titanium dioxide (TiO_2). In this process, the formation and availability of *OH are maximized by addition of oxidants such as H_2O_2 and 0,.

The Matrix UV/TiO_2 system is a commercial-scale sensitized APO system for contaminated water treatment. The 'commercial-scale sensitized APO systems for contaminated air treatment include the (1) Zentox Corporation (Zentox) UV/TiO_2 system; (2) Matrix Photocatalytic, Inc. (Matrix), UV/TiO_2 system; and (3) KSE, Inc. (KSE), Adsorption-Integrated-Reaction (AIR) UV/catalyst system.

Contaminated Water Treatment

APO has been shown to-be an effective technology for treatment of contaminated water. Matrices to which APO has been applied include the following: (1) contaminated groundwater, (2) industrial wastewater, (3) municipal wastewater, (4) drinking water, (5) landfill leachate, and (6) contaminated surface water. As shown below, a number of APO processes have been evaluated in terms of their effectiveness in treating various waterborne contaminants. Of these processes, UV/oxidation has been evaluated for the most contaminant groups, while VUV photolysis has been evaluated for the fewest.

Table ES-l at the end of this executive summary presents commercial-scale performance and cost data for contaminated water treatment using various APO processes. This table shows that UV/oxidation processes have been found to be effective in treating various contaminants. Other APO processes, including the photo-Fenton and sensitized APO processes, have also been found to be effective, but for only a limited number of contaminant groups. The treatment costs vary widely depending on the type and concentration of contaminants treated and the APO system used for treatment. The information sources cited in this handbook should be carefully reviewed before a cost comparison is made because the cost estimates presented in the literature were not made using a consistent set of assumptions.

Contaminant Group	APO Process Status for Contaminated Water Treatment			
	VUV Photolysis	UV/Oxidation	Photo-Fenton	Sensitized
Volatile Organic Compounds (VOC)	❑	★	★	★
Semivolatile Organic Compounds (SVOC)	❑	★	★	0
Polychlorinated Biphenyls (PCB)	❑	❑	cl	0
Pesticides and Herbicides	0	●	0	0
Dioxins and Furans	❑	❑	0	cl
Explosives and Their Degradation Products	❑	★	❑	0
Humic Substances	❑	❑	❑	0
Inorganics	❑	❑	❑	0
Dyes	cl	●	❑	0
Microbes	❑	★	❑	0

Notes: ★ = Commercial-scale, ● = Pilot-scale, 0 = Bench-scale, ❑ = Developmental

Contaminated Air Treatment

APO has been shown to be an effective technology for treatment of contaminated air. Matrices to which APO has been applied include the following: (1) soil vapor extraction (SVE) off-gas, (2) air stripper off-gas, (3) industrial emissions, and (4) automobile emissions. As shown below, a number of APO processes have been evaluated in terms of their effectiveness in treating various airborne contaminants. Of these processes, the sensitized APO processes have been evaluated for the most contaminant groups, while the VUV photolysis process has been evaluated for the fewest.

Table ES-2 at the end of this executive summary presents commercial-scale performance and cost data for contaminated air treatment using various APO processes. This table shows that sensitized APO processes have been found to be effective in treating various contaminants. One UV/oxidation process, the UV/O_3 process, has also been found to be effective, but only for VOCs. The table also shows that the available treatment cost information is limited.

Contaminant Group	APO Process Status for Contaminated Air Treatment		
	VUV Photolysis	UV/Oxidation	Sensitized
VOCs	O	★	★
svocs	cl	●	❑
Explosives and Their Degradation Products	❑	❑	★
Inorganics	❑	❑	0

Notes: ★ = Commercial-scale, ● = Pilot-scale, 0 = Bench-scale, ❑ = Developmental

Contaminated Solids Treatment

APO has been shown to be an effective technology for treatment of contaminated solids, primarily at the bench-scale level. Most evaluations involved generating a leachate or slurry by washing the contaminated solids with water, surfactant solution, or an organic solvent and then applying an APO process to treat the contaminated leachate or slurry in a manner similar to contaminated water treatment. Use of an APO process to treat contaminated slurry may require frequent APO system maintenance because solids in the slurry will coat the light source and inhibit transmission of light.

Solid matrices to which APO has been applied include the following: (1) contaminated soil, (2) contaminated sediment, and (3) contaminated ash. As shown below, a number of APO processes 'have been evaluated in terms of their effectiveness in treating various contaminated solids. Of these processes, the UV/oxidation, photo-Fenton, and sensitized APO processes have been evaluated to some extent, but little data is available on the effectiveness of VUV photolysis.

The commercial-scale performance data for contaminated solids treatment is limited to one UV/oxidation process, the UV/H_2O_2 process. A Calgon perox-pure™ system was used to treat soil contaminated with pesticides. The influent to the perox-pure™ system, which was generated by an on-site soil washing system, primarily contained 0.49, 1.1, and 3.9 mg/L of disulfoton, thiometon, and oxadixyl, respectively. A sand filter was used to remove suspended solids from the influent to the perox-pure™ system. The system achieved removals of up to 99.5 percent. No cost information is available. Based on the limited performance results, APO processes appear to show promise for treating contaminated solids.

Contaminant Group	APO Process Status for Contaminated Solids Treatment			
	VUV Photolysis	UV/Oxidation	Photo-Fenton	Sensitized
SVOCs	❑	❑	❑	**0**
PCBs	❑	❑	0	❑
Pesticides and Herbicides	❑	★	❑	0
Dioxins and Furans	❑	❑	❑	0

Notes: ★ = Commercial-scale, 0 = Bench-scale, ❑ = Developmental

Table ES-l. Contaminated Water Treatment

CONTAMINATED MATRIX	CONTAMINANT GROUP	PROCESS	SYSTEM	PERFORMANCE DATA Contaminant	Concentration	Percent Removal	APPROXIMATE COST (4998 U.S. Dollars)
UV/Oxidation Processes							
Contaminated Groundwater	VOCs	UV/H_2O_2	Calgon perox-pure™	Benzene	52 micrograms per liter (µg/L)	Greater than (>) 96	$0.08 [operation and maintenance (O&M)] to $1.50/cubic meter ($m^3$) (capital and O&M)
				Chlorobenzene	3,100 µg/L	>99.9	
				Chloroform	41 to 240 µg/L	93.6 to >97	
				I.I-Dichloroethane (DCA)	120 to 400 µg/L	>95.8 to >99.5	
				1,2-DCA	22 µg/L	>92	
				1,4-Dichlorobenzene	420 µg/L	>99.5	
				1,2-Dichloroethene (DCE)	200 to 11,000 µg/L	>99 to >99.9	
				Methylene chloride	8 µg/L	>86	
				Tetrachloroethene (PCE)	63 to 2,500 µg/L	>98.7 to >99.9	
				1,1,1-Trichloroethane (TCA)	110 to 130 µg/L	92.9	
				Trichloroethene (ICE)	21 to 1,700 µg/L	>93 to >99.9	
				Vinyl chloride (VC)	1,200 to 1,700 µg/L	>95.8 to >97	
			Calgon Rayox®	1,2-DCE	810 µg/L	91.4	$0.09/$m^3$ (O&M)
				TCE	14,700 µg/L	99.9	
		Granular Activated Carbon followed by UV/H_2O_2	Calgon Rayox®	Methylene chloride	6.9 µg/L	92.6	$0.31/$m^3$ (O&M)
		UV/H_2O followed by Air Stripper	Calgon Rayox®	Methylene chloride	60 µg/L	>98.3	Not available
				PCE	6,000 µg/L	>99.9	
				1,1,1-TCA	100 µg/L	>99	
		UV/H_2O_2	Magnum CAV-OX®	Benzene	250 to 500 µg/L	99.9	$0.32 (O&M) to $1.50/$m^3$ (capital and O&M)
				cis-1,2-DCE	250 µg/L	>99.9	
				trans-1,2-DCE	200 µg/L	>99.9	
				PCE	11 µg/L	>98	
				TCE	1,500 to 2,000 µg/L	99.9	
				Total petroleum hydrocarbons	190 milligrams per liter (mg/L)	99.9	
				VC	53 µg/L	>99.7	

Table ES-I. Contaminated Water Treatment (Continued)

CONTAMINATED MATRIX	CONTAMINANT GROUP	PROCESS	SYSTEM	PERFORMANCE DATA			APPROXIMATE COST (1998 U.S. Dollars)
				Contaminant	Concentration	Percent Removal	
UV/Oxidation Processes (Continued)							
Contaminated Groundwater Continued)	**VOCs** (Continued)	UV/H_2O_2	**Magnum CAV-OX® II**	Benzene	250 to 500 µg/L	99.8	**\$1.50/m^3** (capital and **O&M)**
				TCE	1,500 to 2.000 µg/L	99.8	
			WEDECO	Benzene	310 µg/L	93	**\$0.39/m^3 (O&M)**
				1,2-DCA	54 µg/L	9	
				cis-1,2-DCE	46 µg/L	**>87**	
				Ethylbenzene	**41** µg/L	92	
				VC	34 µg/L	86	
		UV/O_3	**WEDECO**	PCE	160 µg/L	96.6	\$0.19/m^3 (O&M)
				TCE	330 µg/L	99	
		UV/O_3/H_2O_2	U.S. Filter	**1,1-DCA**	9.5 to 13 µg/L	65	\$0.08 to **\$5.60/m^3** (O&M)
				1,1,1-TCA	2 to 4.5 µg/L	87	
				TCE	50 to 520 µg/L	99 to **>99**	
	SVOCs	UV/H_2O_2	Calgon **perox-pure™**	Pentachlorophenol **(PCP)**	15 **mg/L**	99.3	\$1**.20/m^3 (O&M)**
			Calgon **Rayox®**	**N-**nitrosodimethylamine (NDMA)	**20** µg/L	**>99.9**	**\$0.10/m^3** (O&M)
				Polynuclear aromatic hydrocarbons	1 to 2 **mg/L**	**>99.9**	
				Phenol	2 **mg/L**	**>99.9**	
	Explosives and Their Degradation Products	UV/H_2O_2	Calgon **perox-pure™**	Benzathiazole	20 µg/L	**>82**	**\$0.02/m^3** (O&M)
				1,4-Dithiane	200 µg/L	**>98**	
				1,4-Oxathiane	**82** µg/L	**>97**	
				Cyclonite	28 **mg/L**	**>82**	
				Thiodiglycol	480 µg/L	**>97**	
				1,3,5-Trinitrobenzene 1	5 µg/L	96	
			Calgon **Rayox®**	Nitroglycerin **(NG)**	1,000 **mg/L**	**>99.9**	**\$13 to \$34/m^3** (capital **and O&M)**
				Nitroguanidine	2,700 **mg/L**	**>99.9**	

Table ES-I. Contaminated Water Treatment (Continued)

CONTAMINATED MATRIX	CONTAMINANT GROUP	PROCESS	SYSTEM	PERFORMANCE DATA			APPROXIMATE COST 11998 U.S. Dollars)
				Contaminant	Concentration	Percent Removal	
UV/Oxidation Processes (Continued)							
ndustrial Wastewater	**VOCs**	UV/H_2O_2	Calgon perox-pure”	Acetone	20 mg/L	>97.5	\$1.10/m^3 (O&M)
				Isopropyl alcohol	20 mg/L	>97.5	
	SVOCS	UV/H_2O_2	Calgon Rayox®	Chemical oxygen demand (COD)	1,000 mg/L	Not available	\$0.83 to \$150/m^3 (capital and O&M)
				NDMA	30 µg/L to 1,400 mg/L	>98.3 to >99.9	
				Unsymmetrical dimethylhydrazine	6.000 mg/L	Not available	
			Magnum CAV-OX® II	Phenol	20 µg/L	>99.9	Not available
	Microbes	UV/H_2O_2	Magnum CAV-OX® II	*Salmonella*	1 million colony forming units per milliliter	>99.9	Not available
andfill Leachate	COD	UV/O_3	WEDECO	COD	900 mg/L	>90	\$6.80/m^3 (capital and O&M)
Photo-Fenton Process							
Contaminated Groundwater	svocs	Photo-Fenton	**Calgon Rayox® ENOX**	PCP	1,000 µg/L	Flow stream to be reinjected: 90 Flow stream to be discharged: 99	\$0.36/m^3 (O&M)
Industrial Wastewater	**VOCs**	Photo-Fenton	**Calgon Rayox® ENOX**	COD	3,000 mg/L	>98.4	\$44/m^3 (O&M)
Sensitized APO Process							
Contaminated Groundwater	VOCs	UV/TiO_2	Matrix	Benzene	400 to 1,100 µg/L	99	\$7.80/m^3 (capital and O&M)
				1,1-DCA	660 to 840 µg/L	21	
				1,1-DCE	120 to 160 µg/L	97	
				cis-1,2-DCE	78 to 98 µg/L	96	
				PCE	120 to 200 µg/L	82	
				1,1,1-TCA	680 to 980 µg/L	40	
				TCE	230 to 610 µg/L	93	
				Toluene	44 to 85 µg/L	>92	
				Total xylenes	55 to 200 µg/L	98	

Table ES-2. Contaminated Air Treatment

CONTAMINATED MATRIX	CONTAMINANT GROUP	PROCESS	SYSTEM	PERFORMANCE DATA			APPROXIMATE COST (1998 U.S. Dollars)
				Contaminant	Concentration	Percent Removal	
V/Oxidation Process							
VE Off-Gas	**VOCs**	**UV/O_3**	PTI	cis-1,2-DCE	22 parts per million by volume **(ppmv)**	74.0	**$3.80/pound** of **VOCs** removed (capital and O&M)
				PCE	31 ppmv	89.7	
				TCE	28 ppmv	80.8	
				Toluene	14 ppmv	93.1	
				Total **VOCs**	1,000 to 1,100 ppmv as carbon	95.9	
ensitized APO Processes							
VE Off-Gas	**VOCs**	**UV/Catalyst**	KSE AIR	Methane	2,000 to 4,000 ppmv	Minimal	Not available
				PCE	1 to 150 ppmv	**>99**	
		UV/TiO_2	Matrix	PCE	1,200 ppmv	95.2	Not available
				1,1,1-TCA	Not available	Not removed	
				TCE	160 ppmv	98.1	
ir Stripper **Off-** as	**VOCs**	**UV/Catalyst**	KSE AIR	**1,2-DCA**	0.9 to 3 ppmv	About 99	Not available
dustrial missions	**VOCs**	**UV/Catalyst**	KSE AIR	Total **VOCs**	2,000 ppmv	**>99**	**For a 1.8-standard cubic meter per minute (scmm) System** **$53,320 (capital)** **$376 (monthly energy)** **$1,672 (annual maintenance)**
				Pentane	2,100 ppmv	**>99.9**	**For a 4.4-scmm System** **$183,000 (capital)** $7,800 (annual operating)
	Explosives and Their Degradation Products	**$UV/TiO_2/O_3$**	Zentox	NG	1.7 ppmv	99.2	**For an 18-scmm System** **$175,000 to** $260,000 (capital)

Section 1
Introduction

Improper waste disposal practices have resulted in contamination of various environmental media. Over the past two decades, environmental regulatory requirements have become more stringent because of increased awareness of the human health and ecological risks associated with environmental contaminants. In many cases, conventional treatment technologies, such as air stripping, carbon adsorption, biological treatment, and chemical oxidation using ozone (0,) or hydrogen peroxide (H_2O_2), have limitations. For example, stripping and adsorption merely transfer contaminants from one medium to another, whereas biological treatment and conventional chemical oxidation have low removal rates for many environmental contaminants, including chlorinated organics. Therefore, various alternative treatment technologies have been developed over the last 10 to 15 years in order to cost-effectively meet environmental regulatory requirements. One such group of technologies is commonly referred to as advanced oxidation processes,

Advanced oxidation processes generally involve generation and use of powerful but relatively nonselective transient oxidizing species, primarily the hydroxyl radical (*OH); in some vapor-phase advanced oxidation processes, singlet oxygen or $O(^1D)$ has also been identified as the dominant oxidizing species (Loraine and Glaze 1992). Table 1-l shows that *OH has the highest thermodynamic oxidation potential, which is perhaps why *OH-based oxidation processes have gained the attention of many advanced oxidation technology developers. In addition, as shown in Table 1-2, most environmental contaminants react 1 million to 1 billion times faster with •OH than with O_3, a conventional oxidant. *OH can be generated by both photochemical processes (for example, ultraviolet [UV] radiation in combination with O_3, H_2O_2, or a photosensitizer) and nonphotochemical processes (for example, electron beam irradiation, 0, in combination with H_2O_2, or Fenton's reagent). This handbook discusses the applicability of advanced photochemical oxidation (APO) technologies for treatment of contaminated water, air, and solids (soil, sediment, and ash).

This section discusses the purpose and scope (Section 1 .1) and organization (Section 1.2) of this handbook.

Table 1-1. Oxidation Potential of Several Oxidants in Water

Oxidant	Oxidation Potential (eV)[a]
*OH	2.80
$O(^1D)$	2.42
O_3	2.07
H_2O_2	1.77
Perhydroxy radical	1.70
Permanganate ion	1.67
Chlorine dioxide	1.50
Chlorine	1.36
O_2	1.23

Note:

[a] Source: *CRC Handbook 1985*

1.1 Purpose and Scope

The primary purpose of this handbook is to summarize commercial-scale APO system performance and cost data for treatment of contaminated water, air, and solids, In addition, it presents similar information drawn from pilot- and bench-scale evaluations of APO technologies as a supplement to the commercial-scale performance and cost data. The handbook is intended to serve as an APO reference document for remedial project managers, on-scene coordinators, state and local regulators, consultants, industry representatives, and other parties involved in management of contaminated water, air, and solids. Specifically, it should assist these intended users in evaluating the applicability of APO technologies and in selecting one or more APO technologies for site-specific evaluation.

For the purposes of this handbook, commercial-, pilot-, and bench-scale systems are defined as follows:

- A commercial-scale system is a system manufactured by an APO technology vendor and available for purchase or leasing from the vendor.

Table 1-2. Rate Constants for 0, and *OH Reactions with Organic Compounds in Water

	Rate Constant $(M^{-1}s^{-1})^a$	
Compound Type	O_3	*OH
Acetylenes	50	10^8 to 10^9
Alcohols	10^{-2} to 1	10^8 to 10^9
Aldehydes	10	10^9
Alkanes	10^{-2}	10^6 to 10^9
Aromatics	1 to 10^2	10^8 to 10^{10}
Carboxylic acids	10^{-3} to 10^{-2}	10^7 to 10^9
Chlorinated alkenes	10^{-1} to 10^3	10^9 to 10^{11}
Ketones	1	10^9 to 10^{10}
Nitrogen-containing organics	10 to 10^2	10^8 to 10^{10}
Olefins	1 to 450×10^3	10^9 to 10^{11}
Phenols	10^3	10^9 to 10^{10}
Sulfur-containing organics	10 to 1.6×10^3	10^9 to 10^{10}

Note:

[a] Sources: Cater and Others 1990; Dussert 1997

- **A pilot-scale system** is a system designed and fabricated by an engineering firm to (1) estimate the performance and cost of a particular APO technology, (2) identify field operational problems of the technology and their resolutions, and (3) evaluate scale-up requirements for implementing the technology. A commercial-scale system is selected after the pilot-scale system proves to be successful.

- **A bench-scale system** is a system that (1) is of much smaller scale than commercial- and pilot-scale systems, (2) is used to evaluate the feasibility of a particular APO process, (3) is used to gain more insight into the process kinetics and mechanisms, and (4) .may be used to generate a preliminary cost estimate for comparison with the costs of alternative technologies. A pilot-scale evaluation of a system may follow successful performance by a particular APO process at the bench-scale level.

This handbook is not intended to summarize all the APO performance and ‘cost data available in the literature. Rather, it is intended to present information on state-of-the-art APO technologies for treating contaminated environmental media. Commercial-scale APO system performance and cost data is presented in greater detail than pilot-scale results because the handbook is intended for practitioners. Similarly, pilot-scale results are presented in greater detail than bench-scale results. In addition, pilot- and bench-scale results are presented only where they supplement commercial-scale APO system evaluation results or where they fill information gaps, such as those associated with by-product formation.

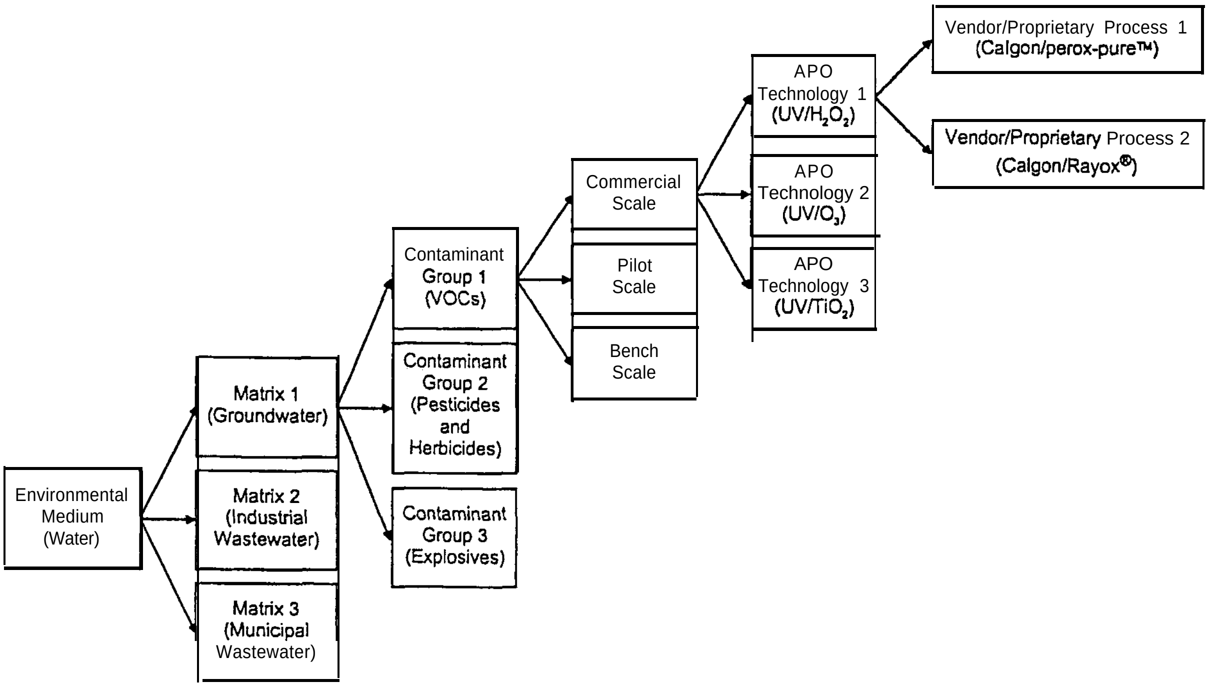
This handbook does not address nonenvironmental APO technology applications. For example, it does not discuss APO technology applications in (1) industrial processes (for example, use of a UV/O_3 process for surface cleaning to improve adhesive bonding) and (2) the manufacture of various products used in residential and commercial buildings and tunnels (for example, titanium dioxide [TiO_2]-coated ceramic tiles and glass). Poulis and others (1993) and Fujishima (1996) summarize such APO applications.

Finally, the information included in this handbook is derived from an extensive literature review, and thus the level of detail presented varies depending on the information sources available. Specifically, the treatment costs included should be considered only order-of-magnitude estimates because most of the references used do not state the assumptions made in estimating treatment costs. To facilitate quick APO technology comparisons, cost estimates from the literature were adjusted for inflation using implicit price deflators for gross national product and are presented in 1998 U.S. dollars herein. This approach has been proposed by the U.S. Department of Commerce and is used to estimate financial assurance requirements under Resource Conservation and Recovery Act Subtitle C as documented in *40 Code of Federal Regulations* 264.142(b). Cost estimates reported in currencies other than U.S. dollars were converted to U.S. dollars using the exchange rates for the appropriate years before adjusting them for inflation.

1.2 Organization

This handbook is divided into six sections and one appendix. Section 1 presents an introduction to the APO handbook. Section 2 provides background information on various APO technologies, typical commercial-scale APO systems, and system design and cost considerations. Sections 3, 4, and 5 summarize APO system performance and cost data for treating contaminated water, air, and solids, respectively. References cited in each section are listed at the end of the section. The appendix contains APO technology vendor contact information.

To facilitate user access to information, the handbook presents performance and cost data for each environmental medium by matrix, contaminant group, scale of evaluation, technology evaluated, and technology vendor or proprietary system (see Figure l-l). For example, where performance and cost data for water (the medium) is summarized, groundwater (matrix 1) is discussed before other matrices. For the groundwater matrix, volatile organic compounds (VOC) or contaminant group 1 is discussed before other contaminant groups. For the VOC contaminant group, commercial-scale applications are summarized before pilot- and bench-scale evaluations. Similarly, the commercial-scale applications are organized by APO technology and by vendor or proprietary process. If bench-scale results for a particular contaminant were derived using a synthetic matrix (for example, distilled water spiked with target contaminants), the results are included under the matrix that is described first. For example, in general, bench-scale results derived using synthetic wastewater are presented under the groundwater matrix because the groundwater matrix is the first matrix discussed in Contaminated Water Treatment (Section 3). However, bench-scale results for dye removal in synthetic wastewater are not presented under the groundwater matrix because no commercial- or pilot-scale results are available for dye removal in groundwater. Therefore, bench-scale results for dye removal in synthetic wastewater are appropriately presented under the industrial wastewater matrix.



Note: The information in parentheses represents a typical example.

Figure l-l. Performance and cost data organization.

1.3 References

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Section 2
Background

This section provides background information on APO technologies (Section 2.1), commercial-scale APO systems (Section 2.2), and APO system design and cost considerations (Section 2.3). The level of detail included in this section should be adequate to allow the user to comprehend the performance and cost data included in Sections 3, 4, and 5 of this handbook. For additional information, the references cited in Section 2 should be consulted.

2.1 APO Technologies

As described in Section 1, APO technologies use •OH generated by photochemical means to oxidize environmental contaminants. As implied by the term APO, light energy is one of the essential components of an APO technology. Depending on the type of APO technology employed, UV radiation (of wavelengths from 100 to 400 nanometers [nm]) or visible radiation (400 to 700 nm) is used to produce *OH.

The wavelength required to carry out an APO process is generally determined by the principle involved in production of •OH by the particular APO technology. For example, for a UV/TiO$_2$ technology, light of a wavelength shorter than 387.5 nm is required because TiO$_2$ (anatase form) has an energy band gap of 3.2 electron volts (eV) and can be activated by UV radiation of a wavelength shorter than 387.5 nm. Similarly, visible radiation can be used in a dye-sensitized APO technology because the wavelength at which dyes absorb significant radiation is in the visible radiation wavelength range (for example, 666 nm for methylene blue), In some cases, solar radiation may be used because it starts at a wavelength of about 300 nm at ground level. However, solar radiation may not be the best choice for a UV/TiO$_2$ technology because only a small portion of the total solar spectrum is in the 300 to 387.5 nm range.

APO technologies can be broadly divided into the following groups: (1) vacuum UV (VUV) photolysis, (2) UV/oxidation processes, (3) the photo-Fenton process, and (4) sensitized APO processes. These APO technologies and their variations are briefly described below.

2.1.1 VUV Photolysis

The UV spectrum is arbitrarily divided into three bands: UV-A (315 to 400 nm), UV-B (280 to 315 nm), and UV-C (100 to 280 nm) (Philips Lighting 1985). Of these' bands, UV-A and UV-C are generally used in environmental applications. UV-A radiation is also referred to as long-wave radiation, near-UV radiation, or black light. Most UV-A lamps have their peak emission at 365 nm, and some have their peak emission at 350 nm. UV-C radiation, which is also referred to as short-wave radiation, is used for disinfection of water and wastewater. The spectral output of the low-pressure mercury vapor lamps used for disinfection purposes is mostly at 254 nm, with only 5 to IO percent of the output at 185 nm. Often the 185-nm emission that leads to the in situ formation of 0, from oxygen (0,) in the surrounding atmosphere is cut off from the germicidal lamps; doped silica or a sodium barium glass sleeve is used to cut off radiation below 200 nm. However, in some photochemical applications, a high-quality quartz sleeve such as Suprasil that transmits the 185-nm radiation is used to take advantage of the high energy associated with the shorter wavelength (one mole of photons at 254 nm equals 471 kilojoules, whereas one mole of photons at 185 nm equals 647 kilojoules). According to Unkroth and others (1997), in general, the quantum yield of mercury vapor lamps is too low for most photochemical reactions to occur. Therefore, for some applications, more, efficient radiation sources such as excimer lasers (high-intensity pulsed radiation) and excimer lamps are evaluated as alternatives to conventional UV radiation sources.

The high energy associated with UV radiation of a wavelength shorter than 190 nm can photolyze water to yield *OH and hydrogen radicals (H•), a process referred to as VUV photolysis (Gonzalez and others 1994). Contaminant degradation in water and in a relatively high-humidity air stream can be accomplished through oxidation by *OH or reduction by H• because VUV photolysis of water produces powerful oxidizing species (*OH) and reducing species (H•). This process is particularly useful in treating waste streams contaminated with compounds that are difficult to oxidize. For example, the •OH reaction rate constant for chloroform is 5×10^6 liters per mole-second ($M^{-1}s^{-1}$), whereas the H• reaction rate constant for chloroform is 1.1×10^7 $M^{-1}s^{-1}$ (Buxton and others 1988).

Commercial-scale VUV photolysis systems are not currently available. However, bench-scale studies conducted using xenon-xenon excimer lamps with a peak emission of 172 nm indicate that VUV photolysis of water has significant potential for cleaning up contaminated water (Jacob and others 1993; Gonzalez and others 1994). In addition, VUV photolysis has been shown to be effective at the bench-scale level in treating humid air streams contaminated with halogenated methanes (Loraine and Glaze 1992).

2.1.2 UV/Oxidation Processes

Most commercial UV/oxidation processes involve generation of *OH through UV photolysis of conventional oxidants, including H_2O_2 and O_3. However, generation of *OH by photolysis of chlorine using UV-A and UV-C radiation, which has been observed by Nowell and Hoigné (1992), has yet to be commercialized. A summary of the chemistry of UV/H_2O_2 and UV/O_3 processes is presented below. More information is provided by Glaze and others (1987).

UV Photolysis of H_2O_2

Generation of *OH by UV photolysis of H_2O_2 is described by the following equation:

$$H_2O_2 + \text{light energy } (hv) \rightarrow 2{\bullet}OH \qquad (2\text{-}1)$$

Low-pressure mercury vapor UV lamps with a 254-nm peak emission are typically used to produce UV radiation, but these lamps may not be the best choice for a UV/H_2O_2 process because the maximum absorbance of UV radiation by H_2O_2 occurs at about 220 nm and because the molar absorption coefficient of H_2O_2 at 254 nm is low, only 19.6 liters per mole-centimeter ($M^{-1}cm^{-1}$). If low-pressure mercury vapor lamps are used, a high concentration of H_2O_2 is needed in the medium to generate sufficient •OH because of the low molar absorption coefficient. However, high concentrations of H_2O_2 may scavenge the •OH, making the UV/H_2O_2 process less effective. To overcome this limitation, some APO technology vendors use high-intensity, medium-pressure, broad band UV lamps; others use high-intensity, xenon flash lamps whose spectral output can be adjusted to match the absorption characteristics of H_2O_2 or another photolytic target.

UV Photolysis of 0,

UV photolysis of 0, in water yields H_2O_2, which in turn reacts with UV radiation or 0, to form *OH as shown below.

$$O_3 + hv + H_2O \rightarrow H_2O_2 + O_2 \qquad (2\text{-}2)$$

$$H_2O_2 + hv \rightarrow 2{\bullet}OH \qquad (2\text{-}3)$$

$$20, + H_2O_2 \rightarrow 2{\bullet}OH + 30, \qquad (2\text{-}4)$$

Photolysis of O_3 in wet air produces •OH as shown below.

$$0, + hv \rightarrow 0, + O(^1D) \qquad (2\text{-}5)$$

$$O(^1D) + H_2O \rightarrow 2{\bullet}OH \qquad (2\text{-}6)$$

Because the molar absorption coefficient of 0, is 3,300 $M^{-1}cm^{-1}$ at 254 nm, UV photolysis of 0, is not expected to have the same limitation as that of H_2O_2 when low-pressure mercury vapor UV lamps are used. In addition, if the 185-nm emission is not cut off from the low-pressure mercury vapor lamps, the 0, formed in situ is photolyzed to yield •OH (Bhowmick and Semmens 1994).

Both UV/H_2O_2 and UV/O_3 processes are commercially available. Some APO technology vendors also offer variations of these processes (for example, $UV/O_3/H_2O_2$ and UV/H_2O_2/proprietary catalyst).

2.1.3 Photo-Fenton Process

The dark reaction of ferrous iron (Fe(II)) with H_2O_2 known as Fenton's reaction (Fenton 1894), which is shown in Equation 2-7, has been known for over a century.

$$Fe(II) + H_2O_2 \rightarrow \text{ferric iron } (Fe(III)) + \text{hydroxide ion (OK)} + {*}OH \qquad (2\text{-}7)$$

The *OH thus formed either can react with Fe(II) to produce Fe(III) as shown below,

$$*OH + Fe(II) \rightarrow Fe(III) + OK \qquad (2\text{-}8)$$

or can react with and initiate oxidation of organic pollutants present in a waste stream. This process is effective at pH levels less than or equal to 3.0.

Decomposition of H_2O_2 is also catalyzed by Fe(III) (Walling 1975). In this process, H_2O_2 is decomposed to the water molecule (H_2O) and O_2, and a steady-state concentration of Fe(II) is maintained during the decomposition, as shown below.

$$\begin{aligned} Fe(III) + H_2O_2 &\rightleftarrows [Fe(III)\ldots O_2H]^{2+} + H^+ \\ &\rightleftarrows Fe(II) + HO_2\bullet + H^+ \qquad (2\text{-}9) \end{aligned}$$

$$HO_2\bullet + Fe(III) \rightarrow Fe(II) + H^+ + 0, \qquad (2\text{-}1\ 0)$$

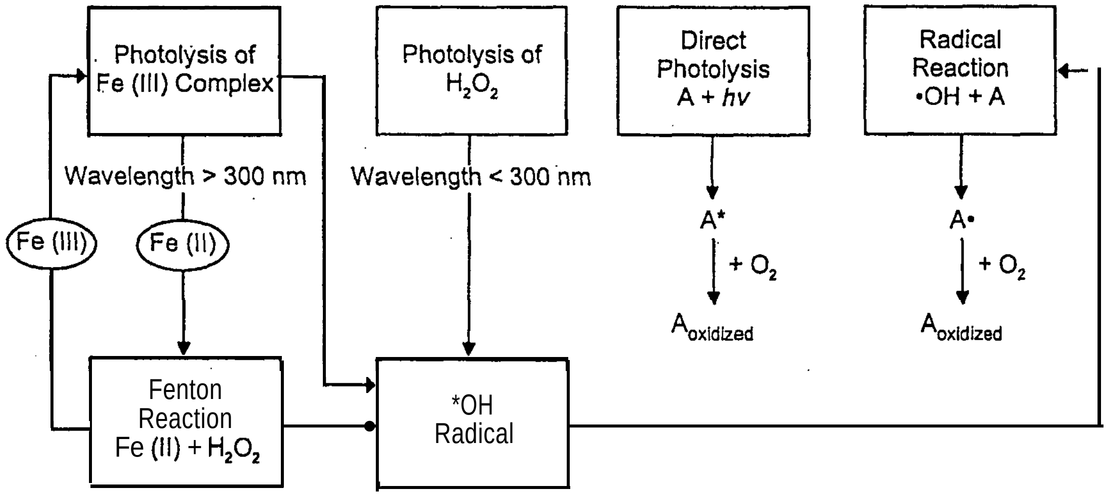
The Fe(II) ions react with H_2O_2 to generate *OH (see Equation 2-7), which then react with organic pollutants. However, the initial rate of removal of organic pollutants by the $Fe(III)/H_2O_2$ reagent is much slower than that for the $Fe(II)/H_2O_2$ reagent, perhaps because of the lower reactivity of Fe(III) toward H_2O_2. This process is only effective at an acidic pH level of about 2.8 (Pignatello 1992).

The rate of removal of organic pollutants and the extent of mineralization with the $Fe(II)/H_2O_2$ and $Fe(III)/H_2O_2$ reagents are improved considerably by irradiation with near-UV radiation and visible light (Ruppert and others 1993). This process is called the photo-Fenton reaction (see Figure 2-l). Photoenhancement of reaction rates is likely because of (1) photoreduction of Fe(III) to Fe(II); (2) photodecarboxylation of ferric carboxylate complexes; and (3) photolysis of H_2O_2, all of which are briefly described below.

1. Photoreduction of Fe(M) *to Fe(II):* Irradiation of the hydroxylated Fe(III) ion or ferrihydroxalate ($Fe(III)(OH)^{2+}$) in aqueous solution produces the Fe(II) ion and •OH (Faust and Hoigne 1990) as shown below.

$$Fe(III)(OH)^{2+} + hv \rightarrow Fe(II) + {}^*OH \qquad (2\text{-}11)$$

This is a wavelength-dependent reaction, and the quantum yields of *OH and Fe(II) ion formation decrease with increasing wavelength. For example, the quantum yield of •OH is 0.14 at 313 nm and 0.017 at 360 nm (Faust and Hoigne 1990). In addition to the •OH produced by the reaction shown in Equation 2-l 1, the photogenerated Fe(II) can participate in the Fenton reaction (see Equation 2-7), generating additional •OH and thus accelerating the rate of removal of organic contaminants.



Note: “A” is the target contaminant. “A*” and "A•" are reaction intermediates.

Figure 2-1. Scheme of chemical reactions in the photo-Fenton reaction (Source: Kim and Others 1997).

*2. Photodecarboxylafion of ferric carboxylate com***plexes:** **Fe(III) ions form** stable complexes and associated ion pairs with carboxylates and polycarboxylates (for example, anion of oxalic acid). These complexes are photochemically active and generate Fe(II) ions when irradiated, according to Balzani and Carassiti (1970), as shown below.

$$\mathrm{Fe(III)(RCO_2)^{2+}} + hv \rightarrow \mathrm{Fe(II)} + \mathrm{CO,} + \mathrm{R}\bullet \qquad (2\text{-}12)$$

The radical R• can react with dissolved 0, and degrade further. The Fe(II) ions can in turn participate in the Fenton reaction and generate additional •OH. Carboxylates are formed during photocatalyzed oxidation of organic pollutants; thus photodecarboxylation, as shown in Equation 2-12, is expected to play an important role in treatment and mineralization of organic contaminants.

*3. **Photolysis** of H_2O_2:* Some direct photolysis of H_2O_2 occurs (see Equation 2-l); however, in the presence of strongly absorbing iron complexes, this reaction contributes only in a minor way to photodegradation of organic contaminants.

Many wastewaters exhibit high absorbance at wavelengths below 300 nm. Competition for UV light from the wastewater and poor absorption of UV light at 254 nm by H_2O_2 make UV/H_2O_2 treatment less useful in some situations. In these cases, the UV-visible/ferrioxalate/H_2O_2 process (Equation 2-12) provides advantages, as ferrioxalate has a high molar absorption coefficient at wavelengths above 200 nm (see Figure 2-2), absorbs light strongly at longer wavelengths (up to 450 nm) and generates *OH with a high quantum yield. Zepp and others (1992) have shown that photolysis of ferrioxalate in the presence of H_2O_2 generates •OH that can react with and oxidize organic pollutants in solution, Safarzadeh-Amiri (1993) has shown that irradiation of a ferrioxalate/H_2O_2 mixture with UV-visible light is a very effective process for removal of various organic pollutants in water.

The Calgon Carbon Corporation (Calgon) Rayox® enhanced oxidation (ENOX 910) process takes advantage of the ferrioxalate photo-Fenton chemistry and supplements the UV/H_2O_2 process with a proprietary catalyst in some applications.

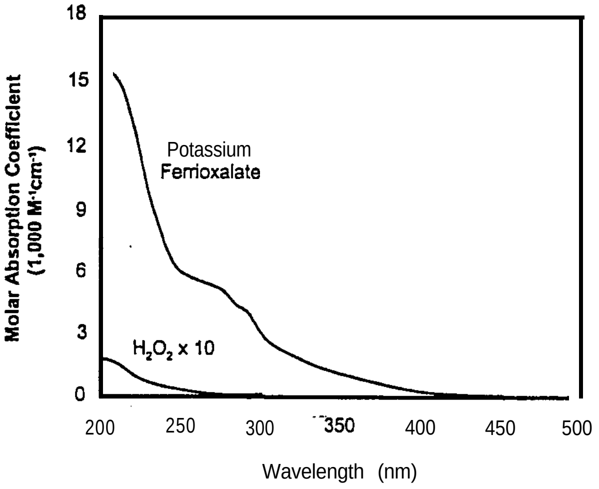


Figure 2-2. Absorption spectra of H_2O_2 and potassium ferrioxalate in aqueous solution (Source: **Safarzadeh-Amiri** and Others 1997).

2.1.4 Sensitized APO Processes

Sensitized APO processes can be broadly categorized as dye-sensitized and semiconductor-sensitized processes. These categories are described below.

Dye-Sensitized APO Processes

In a dye-sensitized APO process, visible light is absorbed by a sensitizing dye, which excites the dye molecule to a higher energy state. The excited dye then transfers some of its excess energy to other molecules present in the waste stream, producing a chemical reaction. When dissolved 0, accepts energy from a sensitizer (for example, methylene blue or rose bengal), the dissolved 0, is converted to O(^{1}D), an effective oxidant. This APO process has yet to become commercially viable, perhaps because of the difficulty associated with removing the dye from the treated waste stream (Li and others 1992).

Semiconductor-Sensitized APO Processes

Semiconductors are solids that have electrical conductivities between those of conductors and those of insulators. Semiconductors are characterized by two separate energy bands: a low-energy valence band and a high-energy conduction band. Each band consists of a spectrum of energy levels in which electrons can reside. The separation between energy levels within each energy band is small, and they essentially form a continuous spectrum. The energy separation between the valence and conduction bands is called the band gap and consists of energy levels in which electrons cannot reside.

Light, a source of energy, can be used to excite an electron from the valence band into the conduction band. When an electron in the valence band absorbs a photon,' the absorption of the photon increases the energy of the electron and enables the electron to move into one of the unoccupied energy levels of the conduction band. However, because the energy levels of the valence band are lower than those of the conduction band, electrons in the conduction band eventually move back into the valence band, leaving the conduction band empty. As this occurs, energy corresponding to the difference in energy between the bands is released as photons or heat. Semiconductors are said to exhibit photoconductivity because photons can be used to excite a semiconductor's electrons and allow easy conduction.

Semiconductors that have been used in environmental applications include TiO_2, strontium titanium trioxide, and zinc oxide (ZnO). TiO_2 is generally preferred for use in commercial APO applications because of its high level of photoconductivity, ready availability, low toxicity, and low cost. TiO_2 has three crystalline forms: rutile, anatase, and brookite. Studies indicate that the anatase form provides the highest *OH formation rates (Tanaka and others 1993).

TiO_2 exhibits photoconductivity when illuminated by photons having an energy level that exceeds the TiO_2 band gap energy level of 3.2 eV. For TiO_2, the photon energy required to overcome the band gap energy and excite an electron from the valence band to the conduction band can be provided by light of a wavelength shorter than 387.5 nm. When an electron in the valence band is excited into the conduction band, a vacancy or hole is left in the valence band. Such holes have the effect of a positive charge. The combination of the electron in the conduction band (e^-_{CB}) and the hole in the valence band (h^+_{VB}) is referred to as an electron-hole pair. The electron-hole pair within a semiconductor band tends to revert to a stage where the electron-hole pair no longer exists because the electron is in an unstable, excited state; however, the band gap inhibits this reversal long enough to allow excited electrons and holes near the surface of the, semiconductor to participate in reactions at the surface of the semiconductor.

A simplified TiO_2 photocatalytic mechanism is summarized in Figure 2-3. This mechanism is still being investigated, but the primary photocatalytic mechanism is believed to proceed as follows (Al-Ekabi and others 1993):

$$TiO_2 + hv \rightarrow e^-_{CB} + h^+_{VB} \qquad (2\text{-}13)$$

At the TiO_2 surface, the holes react with either H_2O or OH^- from water dissociation to form •OH as follows:

$$h^+_{VB} + H_2O \rightarrow {*}OH + H^+ \qquad (2\text{-}14)$$

$$h^+_{VB} + OH- \rightarrow {*}OH \qquad (2\text{-}15)$$

An additional reaction may occur if the electron in the conduction band reacts with 0, to form superoxide ions ($O_2{\bullet}^-$) as follows:

$$e^-_{CB}\ t\ 0, \rightarrow O_2{\bullet}^- \qquad (2\text{-}16)$$

The $O_2{\bullet}^-$ can then react with H_2O to provide additional •OH, OH-, and 0, as follows:

$$2O_2{\bullet}^- + 2H_2O \rightarrow H_2O_2 + 2OH^- + 0, \qquad (2\text{-}17)$$

$$H_2O_2 + e^-_{CB} \rightarrow OH^- + {\bullet}OH \qquad (2\text{-}18)$$

The OH- can then react with the hole in the valence band as shown in Equation 2-15 to form additional •OH. One practical problem with semiconductor photoconductivity is the electron-hole reversal process. The overall result of this reversal is generation of photons or heat instead of •OH. The reversal process significantly decreases the photocatalytic activity of a semiconductor. One possible method of increasing the photocatalytic activity of a semiconductor is to add irreversible electron acceptors (IEA) or oxidants to the matrix to be treated. Once IEAs accept an electron in the conduction band or react with $O_2{\bullet}^-$, the IEAs dissociate and provide additional routes for *OH generation. H_2O_2 is an IEA and illustrates the role that IEAs may play in APO processes. When the IEA H_2O_2 accepts an electron in the conduction band, it dissociates as shown in Equation 2-18. Therefore, H_2O_2 not only inhibits the electron-hole reversal process and prolongs the lifetime of the photogenerated hole, but it also generates additional •OH.

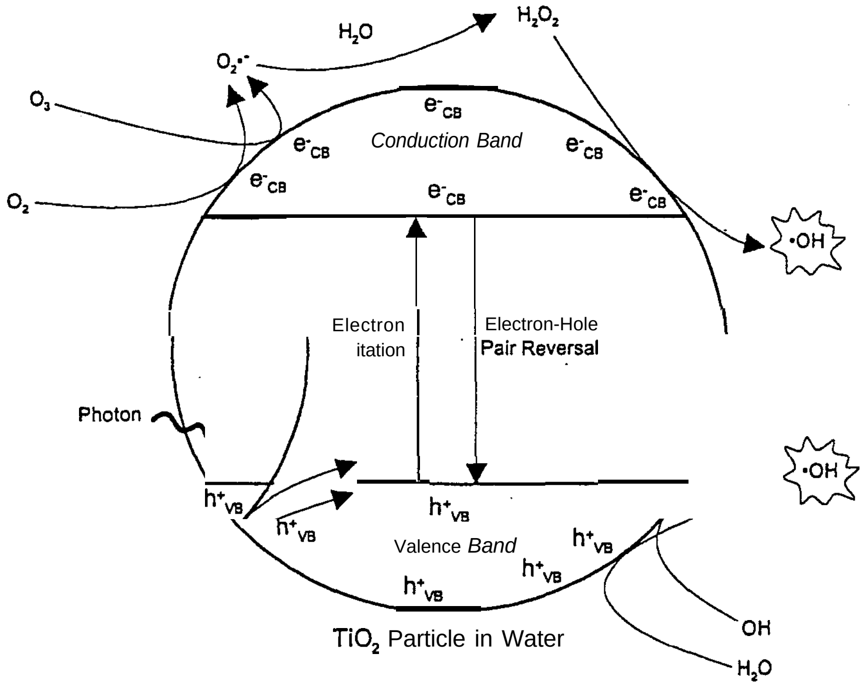


Figure 2-3. Simplified TiO_2 photocatalytic mechanism.

0, is also used as an IEA and may undergo the following reaction:

$$20, + 2e^-_{CB} \rightarrow 0, + 20,' \qquad (2\text{-l }9)$$

The 0, and $O_2^{\bullet -}$ can generate additional •OH in accordance with Equations 2-l 6 through 2-l 8.

Several commercial-scale semiconductor-sensitized APO systems are available for treating both contaminated water and air.

2.2 Com'mercial-Scale APO Systems

This section describes typical commercial-scale APO systems for water and air. No commercial-scale APO systems for solids are available. However, an APO system for water can be used to treat the contaminated leachate generated by leaching contaminants from soil using a soil washing process that is commercially available. The information included in this section was obtained from APO vendors or from published documents. The level of detail provided varies depending on the source of information used.

The commercial-scale APO systems for water described in this section include the (1) Calgon perox-pure™ and Rayox® UV/H_2O_2 systems; (2) Magnum Water Technology, Inc. (Magnum), CAV-OX® UV/H_2O_2 system; (3) WEDECO UV-Verfahrenstechnik (WEDECO) UV/O_3 systems; (4) U.S. Filter/Zimpro, Inc. (U.S. Filter), UV/O_3/H_2O_2 system; and (5) Matrix Photocatalytic, Inc. (Matrix), UV/TiO_2 system. The commercial-scale APO systems for air described in this section include the (1) Process Technologies, Inc. (PTI), UV/O_3 system; (2) Zentox Corporation (Zentox) UV/TiO_2 system; and (3) KSE, Inc. (KSE), Adsorption-Integrated-Reaction (AIR) UV/catalyst system.

Other commercially available systems, including (I) the Calgon Rayox® ENOX 510, 710, and 910 systems, photo-Fenton systems for water treatment, and (2) the Matrix UV/TiO_2 system for air treatment, are not described in this section because the vendors stated that these systems are very similar to their other APO systems and did not provide additional information. In addition, the WEDECO UV/H_2O_2 commercial-scale water treatment system is not described in this section because the vendor did not provide a system description. However, according to a case study narrative provided by WEDECO (1998), the UV/H_2O_2 system consists of (1) two UV reactors in series with one low-pressure mercury vapor lamp in each reactor and (2) an H_2O_2 dosing station. The narrative also states that the system is operated as a "once-through" system (no recirculation).

2.2.7 Calgon perox-pure™ and Rayox® UV/H_2O_2 Systems

The Calgon perox-pure™ and Rayox® UV/H_2O_2 treatment systems are designed to remove organic contaminants dissolved in water. These systems use UV radiation and H_2O_2 to oxidize organic compounds present in water at milligram per liter (mg/L) levels or less. These systems produce no air emissions and generate no sludge or spent media that require further processing, handling, or disposal. The systems use medium-pressure mercury vapor lamps to generate UV radiation. The principal oxidants in the systems, *OH, are produced by direct photolysis of H_2O_2 at UV wavelengths.

A typical Calgon UV/H_2O_2 system is assembled from the following portable, skid-mounted components: an oxidation unit, an H_2O_2 feed module, an acid feed module, and a base feed module. A schematic flow diagram of a typical Calgon UV/H_2O_2 system is shown in Figure 2-4. The oxidation unit shown in Figure 2-4 has six reactors in series with one 15-kilowatt (kW) UV lamp in each reactor and a total volume of 55 liters (L). Each UV lamp is mounted inside a UV-transmissive quartz tube in the center of each reactor such that wafer flows around the quartz tube.

In a typical application of the Calgon system, contaminated water is dosed with H_2O_2 before the water enters, the first reactor; however, a splitter can be used to add H_2O_2 at the inlet to any reactor in the oxidation unit. In some applications, acid is added to lower the influent pH and shift the carbonic acid-bicarbonate-carbonate equilibrium to carbonic acid. This equilibrium is important because carbonate and bicarbonate ions scavenge •OH. After chemical injections, the contaminated water flows through a static mixer and enters the oxidation unit. Water then flows through the six UV reactors. In some applications, base is added to the treated water to adjust the pH in order to meet discharge requirements, if necessary.

Solids may accumulate in this system as a result of oxidation of metals (such as iron and manganese), water hardness, or solids precipitation. Accumulated solids could eventually coat the quartz tubes, thus reducing treatment efficiency. Therefore, the quartz tubes encasing the UV lamps are equipped with wipers that periodically clean the tubes and reduce the impact of accumulated solids.

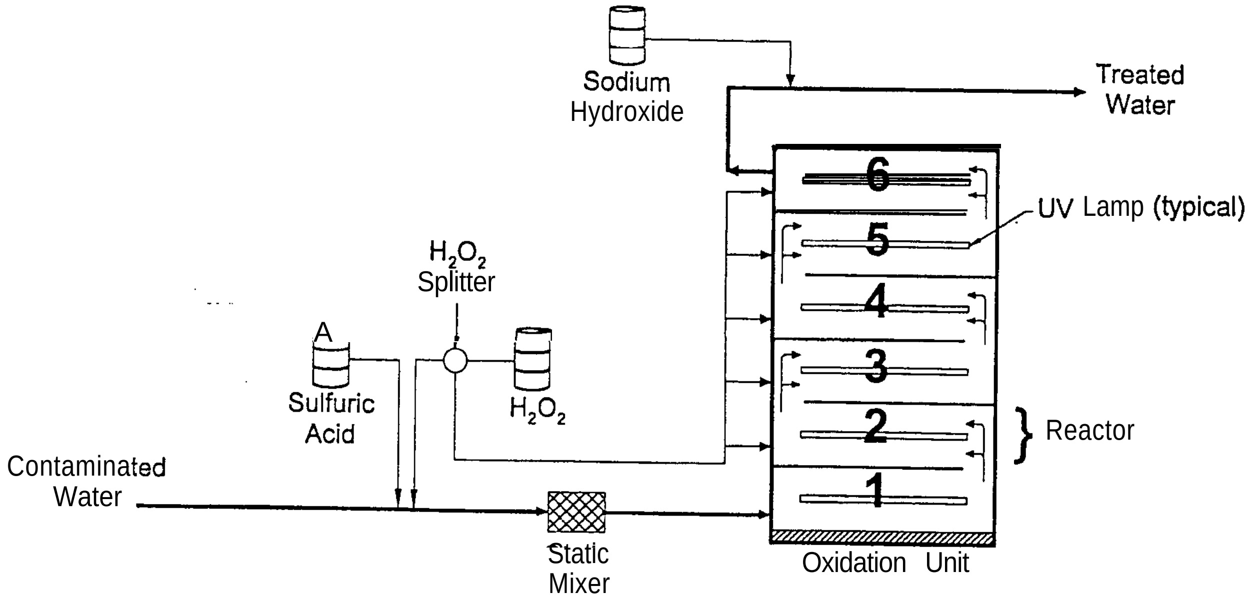


Figure 24. Flow configuration in a Calgon UV/H_2O_2 system.

2.2.2 Magnum CAV-OX® UV/H_2O_2 System

The CAV-OX® process was developed by Magnum to remove organic contaminants dissolved in water. The process uses hydrodynamic cavitation, UV radiation, and H_2O_2 to oxidize organic compounds present in water at mg/L levels or less. In the CAV-OX process, organic contaminants in water are oxidized by *OH and hydroperoxyl radicals produced by hydrodynamic cavitation, UV radiation, and H_2O_2.

A typical CAV-OX® UV/H_2O_2 system consists of a portable, truck- or skid-mounted module with the following components: a cavitation chamber, an H_2O_2 feed tank, and UV reactors (see Figure 2-5). Depending on the application, Magnum uses the CAV-OX® I (low-energy) or the CAV-OX® II (high-energy) process for treating contaminated water. The CAV-OX® I process uses one UV reactor with six 60-Watt (W), low-pressure UV lamps; the reactor is operated at 360 W. The CAV-OX® II process uses two UV reactors, each with one high-pressure UV lamp operated at 2.5 or 5 kW. The CAV-OX® process generates UV radiation using mercury vapor lamps. Each UV lamp is housed in a UV-transmissive quartz tube mounted entirely within the UV reactor. The low-energy reactor has a volume of about 40 L, and each high-energy reactor has a volume of about 25 L.

In a typical application of a CAV-OX® system, contaminated water is pumped to the cavitation chamber. Here the water undergoes extreme pressure variations, resulting in hydrodynamic cavitation. H_2O_2 is usually added to the contaminated water in-line between the cavitation chamber and the UV reactor. However, H_2O_2 may also be added to the contaminated water in-line before the cavitation chamber. Inside the UV reactor, H_2O_2 photolysis by UV radiation results in additional formation of *OH that rapidly react with the organic contaminants. Treated water exits the UV reactor for appropriate disposal.

2.2.3 WEDECO UV/O_3 Systems

WEDECO commercial-scale UV/O_3 system designs vary depending on the application. Figure 2-6 shows a system designed to remove chlorinated VOCs in water. This system consists of a UV reactor, an 0, generator, an 0, absorption tank, and a catalytic 0, decomposer. In a typical application, contaminated water first enters a UV reactor containing several UV-C lamps. The UV-irradiated water is recycled through the system for in-line 0, gas addition and then for 0, absorption in the 0, absorption tank. The ozonated water is then returned to the UV reactor after it is mixed with additional contaminated water. The chlorinated solvents present in the combined waste stream are removed by the •OH generated in the UV reactor. Until the system reaches steady state, 100 percent of the UV-irradiated water is recycled. Once the system reaches steady state, only a small portion of the UV-irradiated water is recycled, and the remaining water (treated water) is disposed of appropriately. Undissolved 0, present in the off-gas from the 0, absorption tank is decomposed to 0, in the catalytic 0, decomposer before the off-gas is emitted to the atmosphere.

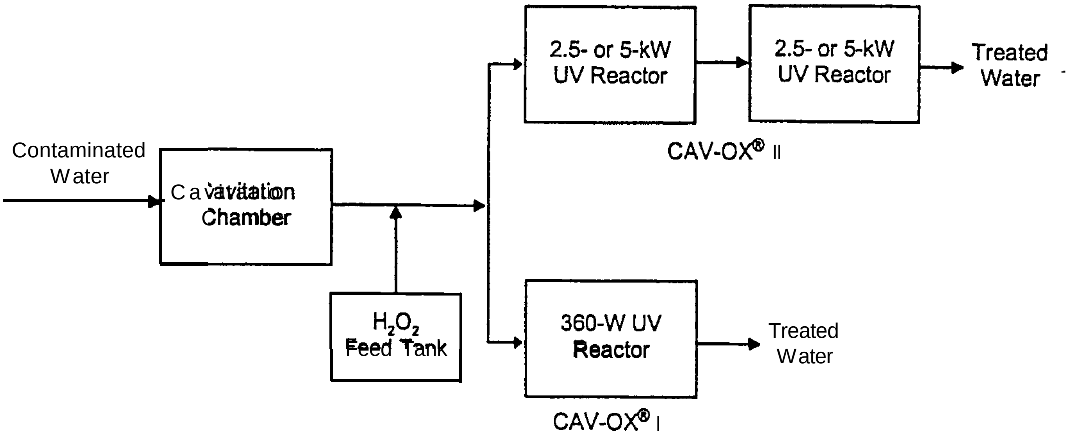


Figure 2-5. Flow configuration in a Magnum CAV-OX® UV/H_2O_2 system.

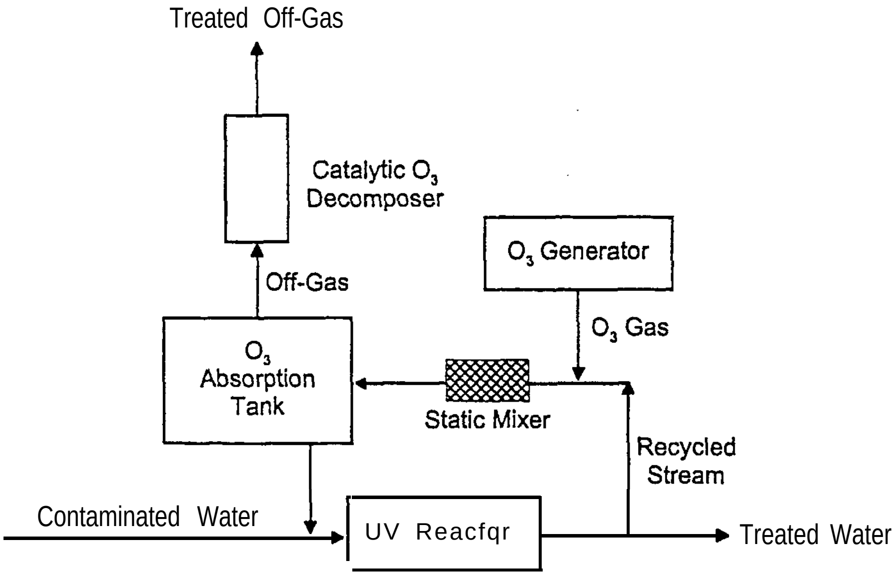


Figure 2-6. Flow configuration in a **WEDECO** UV/O_3 system for water contaminated with chlorinated **VOCs.**

Figure 2-7 shows a WEDECO system designed for chemical oxygen demand (COD) and adsorbable organic halide (AOX) removal from biologically treated landfill leachate. This system is similar to the system described above except that this system has two 0, absorption tanks and the contaminated water flows through the absorption tanks before it flows through the UV reactor.

2.2.4 U.S. 'Filter $UV/O_3/H_2O_2$ System

The U.S. Filter UV/oxidation treatment system uses UV radiation, O_3, and H_2O_2 to oxidize organics in water. This system was formerly known as the Ultrox system. The major components -of this system are the UV/oxidation reactor, 0, generator, H_2O_2 feed tank, and catalytic 0, decomposition (Decompzon) unit.

The UV/oxidation reactor shown in Figure 2-8 has a volume of 600 L and is 1 meter (m) long by 0.5 m wide by 2 m high. The reactor is divided by five vertical baffles into six chambers and contains 24 low-pressure mercury vapor lamps (65 W each) in quartz sleeves. The UV lamps are installed vertically and are evenly distributed throughout the reactor (four lamps per chamber).

Each chamber also has one stainless-steel sparger that extends along the width of the reactor. The spargers uniformly diffuse 0, gas from the base of the reactor into the contaminated wafer. H_2O_2 is introduced in the influent line to the reactor from a feed tank. An in-line static mixer is used to disperse the H_2O_2 into the contaminated water in the influenf feed.

In a typical operation, contaminated water first comes in contact with H_2O_2 as it flows through the influent line to the reactor. The water then comes in contact with UV radiation and 0, as it flows through the reactor at a rate selected to achieve the desired hydraulic retention time. As the 0, in the reactor is transferred to the contaminated water, •OH are produced. The *OH formation from 0, is catalyzed by UV radiation and H_2O_2. The treated water flows out of the reactor for appropriate disposal.

0, that is not transferred to the contaminated water will be present in the reactor off-gas. This off-gas 0, is subsequently removed by the Decompzon unit before the off-gas is vented to the atmosphere. The Decompzon unit uses a nickel-based proprietary catalyst to decompose reactor off-gas 0, to 0,. The Decompzon unit can accommodate flows of up to 900 standard cubic meter (m^3) per minute (scmm) and can reduce 0, concentrations in the range of 1 to 20,000 parts per million by volume (ppmv) to less than (<) 0.1 ppmv.

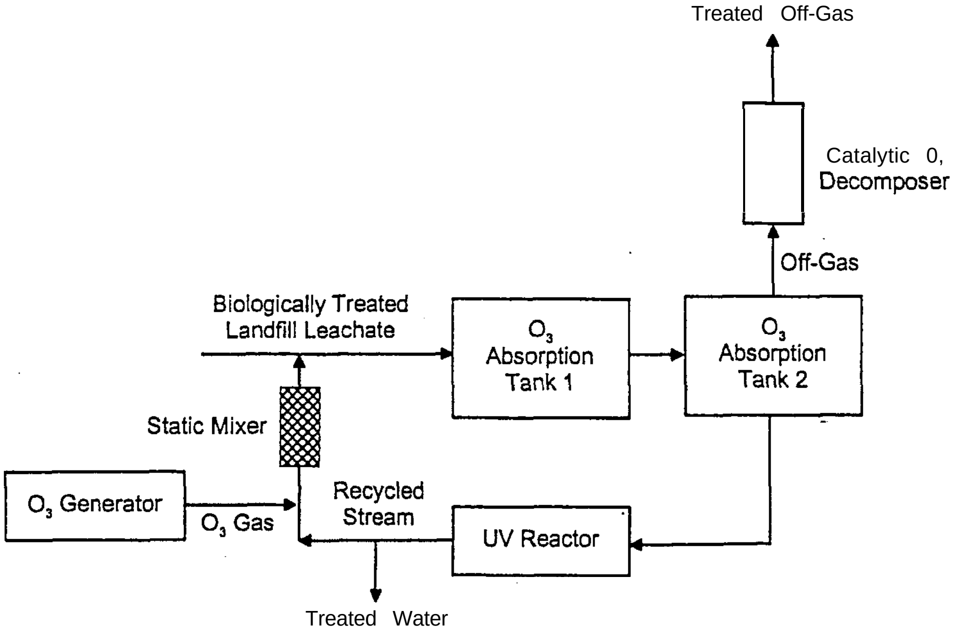


Figure 2-7. Flow configuration in a **WEDECO** **UV/O_3** system for biologically treated landfill leachate.

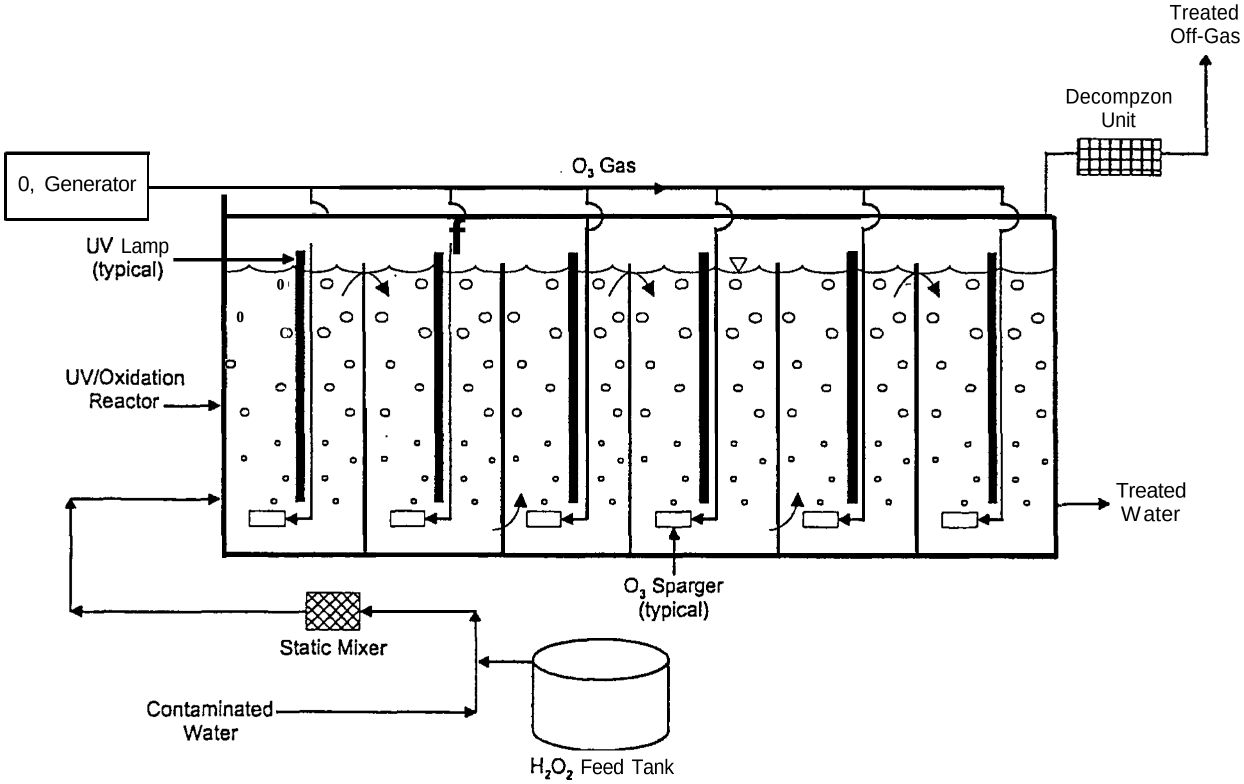


Figure **2-8.** Flow configuration in a U.S. Filter **UV/O_3/H_2O_2** system.

2.2.5 Matrix UV/TiO$_2$ System

The Matrix UV/TiO$_2$ system is designed to treat liquid wastes containing organic contaminants. The Matrix system uses UV light with its predominant emission at a wavelength of 254 nm, the anatase form of the TiO$_2$ semiconductor, and oxidants to generate •OH.

A typical Matrix treatment system contains many photocatalytic reactor cells; the exact number of cells varies depending on the application. Each cell is 1.75 m long and has a 4.5-centimeter (cm) outside diameter. A 75-W 254-nm UV light source is located coaxially within a 1.6-m-long quartz sleeve. The quartz sleeve is surrounded by eight layers of fiberglass mesh bonded with the anatase form of TiO$_2$ and is enclosed in a stainless-steel jacket. Each cell is rated for a maximum flow rate of about 0.8 liter per minute (L/min).

A typical Matrix treatment system consists of two units positioned side by side in a mobile trailer. Each unit consists of 12 wafers, and each wafer consists of six photocatalytic reactor cells joined by manifolds. A block placed in each wafer channels contaminated water into three reactor cells at a time. The flow configuration in a wafer is shown in Figure 2-9. The overall maximum flow rate for this configuration is 2.4 Umin. Each set of three cells along the path where the contaminated water flows is defined as a path length. Therefore, each wafer has two path lengths. Each unit has 24 path lengths, resulting in a total of 48 path lengths for the two units. The Matrix system can be operated with fewer path lengths than those available in a given system. H$_2$O$_2$ and 0, are injected at multiple path lengths throughout the Matrix system. The exact number of injection points varies depending on the application.

Figure 2-10 shows the flow configuration in the Matrix UV/TiO$_2$ treatment system. Beginning with the first wafer, contaminated water enters path length 1 (the first set of three reactor cells in Unit 1) and then path length 2 (the second set of three reactor cells in Unit 1). After treatment is completed in the first wafer, contaminated water flows to the second wafer and enters path length 3 (the first set of three reactor cells in Unit 2) and then path length 4 (the second set of three reactor cells in Unit 2). This process continues 'until the contaminated water has passed through all 24 wafers (48 path lengths). The treated water exiting path length 48 is disposed of appropriately.

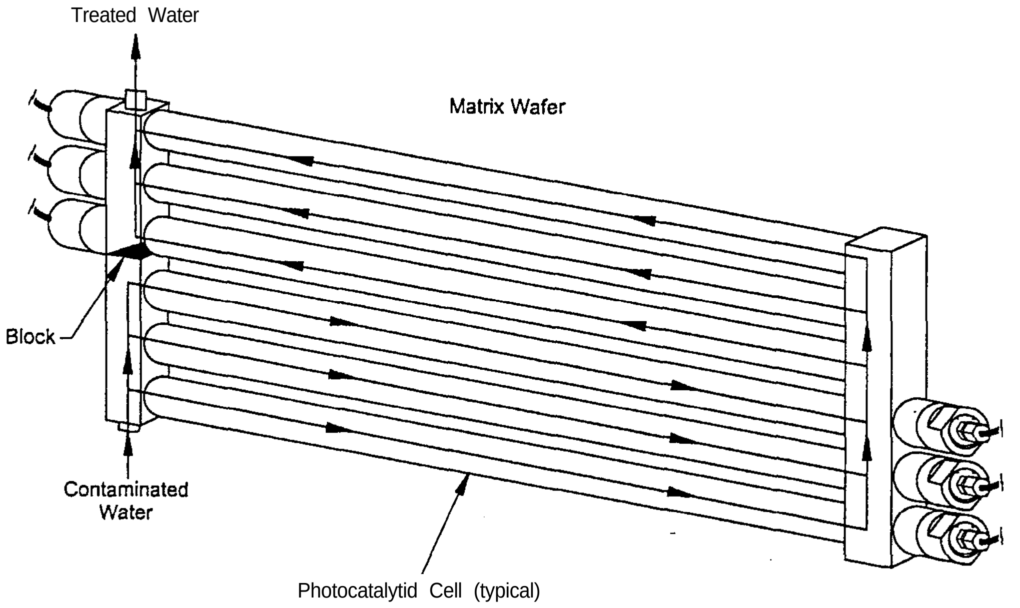


Figure 2-9. Flow configuration In a Matrix wafer.

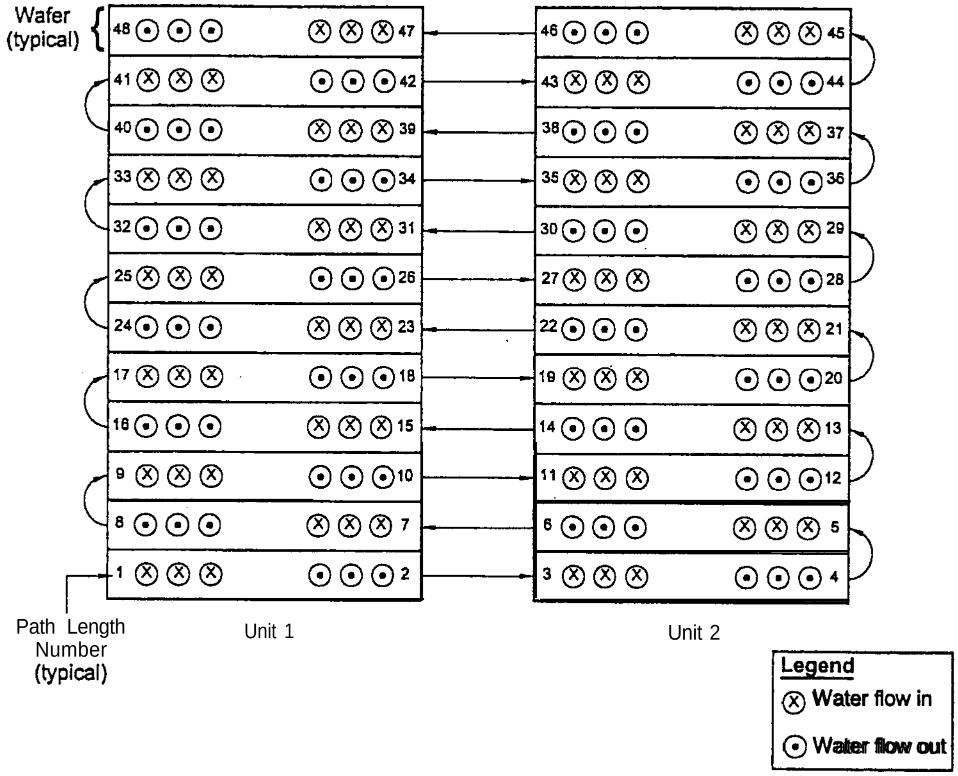


Figure **2-10.** Flow configuration in the Matrix **UV/TiO_2** system.

2.2.6 *PTI UV/O_3 System*

The PTI UV/O_3 system is designed to remove VOCs from contaminated air. Figure 2-11 shows the process flow of VOC-contaminated air through the system, which consists of a concentration unit (CU) and a photolytic destruction unit (PDU). The CU is best applied to high-flow, low-concentration VOC-contaminated vapor streams; conversely, the PDU is best applied to low-flow, high-concentration VOC-contaminated vapor streams. By sequentially combining the CU and PDU technologies, PTI has created a system that can treat a variety of VOC-contaminated vapor streams.

The CU consists of an adsorber, a desorber, and a condenser, The adsorber contains small Ambersorb® beads that capture the VOCs in the contaminated air. The treated air is discharged from the adsorber to the atmosphere. In the desorber, the VOC-laden beads are heated by steam to evaporate the VOCs in order to produce a concentrated VOC vapor stream and regenerate the beads. The concentrated VOC vapor stream from the desorber flows to the condenser, where organics and water vapor condense and are removed from the vapor stream. The noncondensable vapor stream from the condenser is then processed through the PDU. The regenerated beads are returned to the adsorber and reused.

The PDU uses a proprietary technology developed by PTI. The PDU consists of low-pressure mercury vapor UV lamps. These lamps, which are housed in photolytic reactors, produce UV light predominantly at the 254-nm wavelength and to a small extent at the O_3-producing 185-nm wavelength to destroy VOCs in the noncondensable vapor stream. In the PDU, VOCs are removed by direct UV photolysis and by oxidation using •OH, which are generated by the UV photolysis of the 0, formed in situ. A proprietary reagent material in close proximity to the UV lamps converts the reaction by-products to stable, inorganic salts. The treated gas from the PDU passes through a scrubber that removes acidic gases formed in the PDU. The off-gas from the scrubber is returned to the adsorber in the CU.

2.2.7 Zentox UV/TiO_2 System

The Zentox UV/TiO_2 system uses a semiconductor-sensitized process to remove organics in contaminated air. A typical Zentox reactor module is a 0.6-m-long, 0.6-m-wide, 1.2-m-high box containing up to 28 UV lamps with their predominant emission at a wavelength of 254 or 350 nm. The

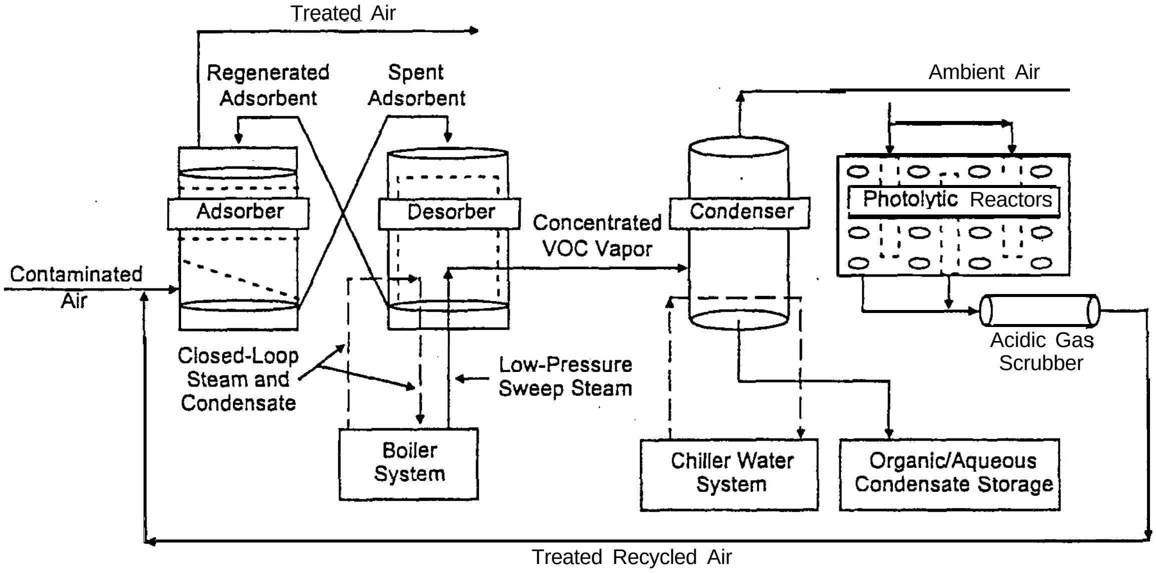


Figure 2-11. Flow configuration in the PTI UV/O_3 system.

modular design allows multiple modules to be connected. in series or in parallel in order to achieve the desired level of performance. Within a module, UV lamps are mounted inside quartz glass sleeves to isolate the lamps from the process gas and to allow cooling air flow over the lamps. Replaceable catalyst media are placed in the reactor through a removable side door. The catalyst consists of Degussa P25 TiO_2 applied to a proprietary support material that is designed to be chemically stable under Zentox system operating conditions and to provide low-pressure drop through the reactor. The system uses 0, as an IEA and UV lamps with their predominant emission at a wavelength of 254 or 350 nm. The 350-nm UV lamps are considered to be a good alternative for treating certain air streams that form a polymeric coating on 254-nm UV lamps. The Zentox system is designed for ambient temperature operation but is capable of running at temperatures up to 85 °C.

2.2.8 KSE AIR W/Catalyst System

The KSE AIR system combines two unit operations, adsorption and chemical oxidation, and uses UV light, a proprietary catalyst, and 0, present in the contaminated air to treat air streams containing VOCs, including chlorinated and nonchlorinated compounds, In a typical system application, the contaminated air stream containing VOCs flows into the photocatalytic reactor. The VOCs are trapped on the surface of a proprietary catalytic adsorbent. This adsorbent is continuously illuminated with UV light, removing the concentrated VOCs trapped on the surface by enhanced photocatalytic oxidation. Thus, the system at the same time removes VOCs and continuously regenerates the catalytic adsorbent. The system operates at ambient temperature, as the catalyst is activated by UV light. Treated air is discharged to ambient air or to a polishing unit if further treatment is required.

2.3 APO System Design and Cost Considerations

Bolton and others (1996) present a simple, practical scale-up approach for designing APO systems. This approach requires that information on key process variables, such as UV dose and concentrations of oxidants and catalysts, be generated by performing treatability studies. The approach assumes that contaminant removal follows first-order kinetics. The approach should therefore be appropriately modified when contaminant removal deviates from first-order kinetics.

As stated above, the UV dose (the amount of UV power to be radiated per unit volume of contaminated water treated) and the concentrations of oxidants and catalysts to be used are the primary design variables to be optimized when sizing an APO system. Treatability studies should be performed to measure the UV dose required to achieve a desired effluent contaminant concentration. The UV dose for a particular stream is determined in an iterative manner by examining the effects of selected process variables-such as pH, oxidant concentration, and choice of catalyst-on the treatment process.

Before determining the UV dose to achieve a specific percent contaminant removal, electrical energy required to achieve one order-of-magnitude contaminant removal per unit volume of waste treated (EE/O) should be determined from treatability studies, EE/O combines light intensity, hydraulic retention time, and contaminant percent removal into 'a single measure and is expressed in the units of kilowatt hour per cubic meter (kWh/m^3). The economics of APO are driven primarily by electrical power, flow rate, and percent removal, and EE/O provides a simple, fairly accurate tool for (1) sizing the full-scale system and (2) estimating capital and operating costs.

After the EE/O is determined through treatability studies, the UV dose required in a specific case is calculated using the following equation:

$$\text{UV dose} = \text{EE/O} \times \log (C_i/C_f) \qquad \textit{(2-20)}$$

where

C_i is the initial concentration (expressed in any units), and

C_f is the anticipated or required discharge standard (expressed in the same units as C_i).

Once the required UV dose is known, the electrical operating cost associated with supplying UV energy can be calculated as follows:

$$\text{Electrical cost } (\$/m^3) = \text{UV dose } (kWh/m^3) \times \text{power cost } (\$/\text{kilowatt-hour}) \qquad (2\text{-}21)$$

Lamp replacement costs typically range between 30 and 50 percent of the electrical cost (for preliminary costing purposes, a conservative value of 45 percent is used here). The next key parameter is the chemical reagent doses to be used. The chemical reagent dose (including the oxidant and any added catalyst) requirement depends on the compound to be treated and is based on treatability test results. Therefore, the total APO system operating cost can be calculated as follows.

$$\text{Total APO system operating cost } (\$/m^3) = (1.45 \times \text{electrical cost}) + \text{chemical reagent cost} \qquad \textit{(2-22)}$$

Capital cost is a function of system size, which in turn is a function of the UV power required to remove selected contaminants. The following equation can be used to determine the total UV power required:

$$\begin{aligned} \text{UV power (kW)} &= \text{EE/O} \times \text{flow (cubic meter per hour } [m^3/h]) \times \log (C_i/C_f) \\ &= \text{UV dose} \times \text{flow } (m^3/h) \end{aligned} \qquad \textit{(2-23)}$$

Once the required UV power is known, the associated capital cost can be estimated by obtaining price quotations from the APO system vendors.

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Section 3
Contaminated Water Treatment

APO has been demonstrated to be an effective technology for treatment of contaminated water. Matrices to which APO has been applied include the following: (1) contaminated groundwater, (2) industrial wastewater, (3) municipal wastewater, (4) drinking water, (5) landfill leachate, and (6) contaminated surface water. Collectively, APO has been applied to the following types of waterborne contaminants: VOCs, semivolatile organic compounds (SVOC), polychlorinated biphenyls (PCB), pesticides and herbicides, dioxins and furans, explosives and their degradation products, humic substances, inorganics, dyes, and microbes.

To assist an environmental practitioner in the selection of an APO technology to treat contaminated water, this section includes (1) commercial-scale system evaluation results for UV/H_2O_2,. UV/O_3, $UV/O_3/H_2O_2$, photo-Fenton, and UV/TiO_2 processes and (2) pilot-scale system evaluation results for UV/H_2O_2, photo-Fenton, $solar/TiO_2$, and $solar/TiO_2/H_2O_2$ processes. This section also summarizes supplemental information available from bench-scale studies of APO processes.

As described in Section 1.2, this handbook organizes performance and cost data for each matrix by contaminant group, scale of evaluation (commercial, pilot, or bench), and APO system or process, In general, commercial- and pilot-scale applications are discussed in detail. Such discussions include, as available, a system description, operating conditions, performance data, and system costs'presented in 1998 dollars. Bench-scale studies of APO processes are described in less detail and only if they provide information that supplements commercial- and pilot-scale evaluation results. At the end of each matrix section, a table is provided that summarizes operating conditions and performance results for each commercial- and pilot-scale study discussed in the text.

3.1 Contaminated Groundwater Treatment

The effectiveness of APO technologies in treating contaminated groundwater has been evaluated for various contaminant groups, including VOCs, SVOCs, PCBs, pesticides and herbicides, dioxins and furans, explosives and their degradation products, humic substances, and inorganics. This section discusses APO technology effectiveness with regard'to each of these contaminant groups.

3. I. 1 VOC-Contaminated Groundwater

This section discusses treatment of VOCs in groundwater using the UV/H_2O_2, UV/O_3, $UV/O_3/H_2O_2$, and UV/TiO_2 processes on a commercial scale. Additional information on VOC removal using the UV/H_2O_2, $solar/TiO_2$, and $solar/TiO_2/H_2O_2$ processes at the pilot scale and (2) UV/H_2O_2 and UV/TiO_2 processes at the bench scale is also included.

Commercial-Scale Applications

This section summarizes the effectiveness of the Calgon perox-pure" UV/H_2O_2, Calgon Rayox® UV/H_2O_2, Magnum CAV-OX® UV/H_2O_2, WEDECO UV/H_2O_2, WEDECO UV/O_3, U.S. Filter $UV/O_3/H_2O_2$, and Matrix UV/TiO_2 treatment systems in removing the following VOCs from contaminated groundwater.

APO Process'	VOCs Removed
UV/H_2O_2	Benzene; CB; chloroform; I ,1 -DCA; 1,2-DCA; 1,4-DCB; 1,2-DCE; ethylbenzene; methylene chloride; PCE; 1,1,1 -TCA; TCE; TPH; VC
UV/O_3	TCE, PCE
$UV/O_3/H_2O_2$	1,1-DCA; 1,1,1-TCA; TCE
UV/TiO_2	Benzene; 1 ,1-DCA; 1,1-DCE; cis-1,2-DCE; PCE; 1 ,1,1-TCA; TCE; toluene; xylenes

Calgon perox-pure™ UV/H_2O_2 Systems

A Calgon perox-pure" UV/H_2O_2 system' was demonstrated in September 1992 under the U.S. Environmental Protection Agency (U.S. EPA) Super-fund Innovative Technology Evaluation (SITE) program. This demonstration involved removing VOCs from groundwater at Lawrence Livermore National Laboratory, Site 300, in Tracy,. California (Topudurti and others 1994).

Trichloroethene (TCE) and tetrachloroethene (PCE) were the primary groundwater contaminants at Site 300, with concentrations ranging from 890 to 1,300 micrograms per liter (µg/L) and 71 to 150 µg/L, respectively. In addition, 1,1,l-trichloro-ethane (1,1,1-TCA); 1,1-dichloroethane (1,1-DCA); and chloroform were present in groundwater in trace amounts. Two sets of system test runs were conducted: Runs 1 through 8 used raw groundwater, while Runs 9 through 14 used groundwater spiked with about 150 µg/L of 1,1,1-TCA; 1,1-DCA; and chloroform each. Average influent total organic halide (TOX) and AOX concentrations were measured at 800 and 730 µg/L, respectively. A flow rate of 38 L/min was maintained in all runs except Runs 7 and 8, which had a flow rate of 150 Umin. The H_2O_2 dose ranged from 30 to 240 mg/L. The infiuent pH levels for Runs 1 and 2 were 8.0 and 6.5, respectively, while Runs 3 through 14 had an influent pH level of 5.0.

The system treated about 150 m^3 of VOC-contaminated groundwater at Site 300. For the spiked groundwater, optimum operating conditions were determined to be a flow rate of 38 L/min, an influent H_2O_2 concentration of 40 mg/L, an H_2O_2 dose of 25 mg/L in the influent to Reactors 2 through 6, and an influent pH of 5.0 (see Figure 2-4 for a system layout). TCE; PCE; and 1,1-DCA removals in groundwater exceeded 99.9, 98.7, and 95.8 percent, respectively. Also, 1,1,1-TCA and chloroform were removed by a maximum of 92.9 and 93.6 percent, respectively. TOX removal ranged from 93 to 99 percent, and AOX removal ranged from 95 to 99 percent.

The treated effluent met California drinking water action levels and federal drinking water maximum contaminant levels (MCL) for the abovementioned compounds at the 95 percent confidence level. Bioassay tests showed that, while the influent was not toxic, the effluent was acutely toxic to freshwater test organisms (the water flea [*Ceriodaphnia dubia*] and fathead minnow [*Pimephales promelas*]). The toxicity was attributed primarily to the H_2O_2 residual in the effluent.

Groundwater remediation costs were estimated for two scenarios. In Case 1 (raw groundwater), the groundwater was assumed to have only two contaminants that are relatively easy to oxidize (TCE and PCE). Groundwater remediation costs were $2.10/$m^3$ of water treated for a 190-L/min system, of which the Calgon perox-pure™ direct treatment cost totaled $0.89/$m^3$. In Case 2 (spiked groundwater), the groundwater was assumed to have five contaminants, two of which are relatively easy to oxidize (TCE and PCE), and three of which are difficult to oxidize (1,1,1-TCA; 1,1-DCA; and chloroform). Groundwater remediation costs were $3.30/$m^3$ of water treated for a 190-L/min system, of which the Calgon perox-pure™ direct treatment cost totaled $1.50/$m^3$.

In another field study, a Calgon perox-pure™ system was tested at the Old O-Field site at Aberdeen Proving Ground in Maryland in April and May 1991 (Topudurti and others 1993). The primary VOCs in the groundwater at the site included 1,2-dichloroethene (1,2-DCE); benzene; and chloroform, which were present at concentrations of 200, 52, and 41 µg/L, respectively. In addition, 1,2-DCA; TCE; and methylene chloride were present in the groundwater at concentrations of 22, 21, and 8 µg/L, respectively. Iron (120 mg/L) and manganese (2.5 mg/L) were also present in the groundwater at the site. Contaminated groundwater (a total of 140 m^3) was pumped from three wells to two holding tanks, where it was pretreated by a metals precipitation system. During the metals precipitation pretreatment process, iron and manganese were removed by 99.8 and 99.2 percent to levels of 0.2 and 0.02 mg/L, respectively. After pretreatment, the groundwater pH was adjusted to 7. Then the influent entered the UV/oxidation system. Four tests were conducted at a flow rate of 60 Umin; the hydraulic retention time was about 5 minutes. In Tests 1, 2, and 3, the H_2O_2 doses were 45, 90, and 180 mg/L, respectively; the doses were equally divided into three parts and added by a splitter at (1) the influent line to the first reactor, (2) the effluent line from the first reactor, and (3) the effluent line from the second reactor. In Test 4, a total H_2O_2 dose of 45 mg/L was added to the influent line to the first reactor; the splitter was not used.

The treated effluent met federal MCLs -for all compounds. Removals of 1,2-DCE; benzene; chloroform; 1,2-DCA; TCE; and methylene chloride were >99, >96, >97, >92, >93, and >86 percent, respectively. The influent to and effluent from the system passed the bioassay tests; the water was not acutely toxic to freshwater test organisms (the fathead minnow, *Daphnia magna,* sheepshead minnow, and mysid shrimp). Although specific process by-products were not identified, the effluent pH was observed to decrease by about one unit, indicating that some of the by-products were acidic. The study did not include a treatment cost estimate.

In another field test, a Calgon perox-pure™ UV/H_2O_2 system was used to evaluate the feasibility of applying APO to remediate VOC-contaminated groundwater at Kelly Air Force Base in San Antonio, Texas. Groundwater from two highly contaminated sites at Kelly Air Force Base, designated as Sites E-l and E-3 of Zone 2, was used in the test (Klink and others 1992).

The primary VOCs at Site E-l were 1,2-DCE; PCE; TCE; and vinyl chloride (VC), which were present at concentrations of 11,000; 2,500; 1,700; and 1,200 µg/L, respectively. Site E-3 groundwater was contaminated with chlorobenzene (CB); VC; 1,2-DCE; l,4-dichlorobenzene(1,4-DCB); and 1,1-DCA, which were present at concentrations of 3,100; 1,700; 430; 420; and 400 µg/L, respectively. Groundwater samples from both sites were pretreated using pre-oxidation with H_2O_2 followed by filtration through a 3-micron filter to remove dissolved contaminants such as iron and manganese and suspended solids, which can reduce transmission of UV light. The system was operated at flow rates of 490 (Site E-l) and 940 (Site E-3) Umin.

For Site E-l, an H_2O_2 concentration of 50 mg/L, a pH of 5.5, and a retention time of 2 minutes were selected as the preferred operating conditions. For Site E-3, an H_2O_2 concentration of 100 mg/L, a pH of 5.1, and a retention time of 4 minutes were selected as the preferred operating conditions. Removals at Site E-l were >99.9 percent for 1,2-DCE; PCE; and TCE and 95.8 percent for VC. At Site E-3, the removals of CB; VC; 1,2-DCE; 1,4-DCB; and 1 ,1 -DCA were >99.9, >97, >99.1, >99.5, and >99.5 percent, respectively.

The estimated capital cost of groundwater treatment to meet drinking water standards was $115,000 for Site E-l and $241,000 for Site E-3. These estimates assume a flow rate of 75 and 130 Umin for the systems at Sites E-l and E-3; respectively. Operation and maintenance (O&M) costs were projected to be $2,800 and $13,000 per month for Sites E-l and E-3, respectively. These O&M costs covered all required chemicals but not the pretreatment and groundwater extraction systems.

In 1989, a Calgon perox-pure” UV/H_2O_2 system was used to remove TCE from groundwater that served as a municipal drinking water source in Arizona. The drinking water well contained 50 to 400 µg/L of TCE. The Calgon perox-pure” Model SSB-30R system treated the groundwater at a flow rate of 510 Umin using 15 kW of power. TCE concentrations were reduced to <0.5 µg/L, which corresponds to >99.7 percent removal. In addition to meeting the target effluent level requirement, the system met the local community requirement for a low-visibility, quiet treatment system that could be operated in the middle of a large residential area.

The total O&M cost estimated by the vendor was about $0.08/$m^3$ of water treated, including electricity, H_2O_2, and general maintenance costs (U.S. EPA 1993).

Calgon Rayox® UV/H_2O_2 System

The Calgon Rayoxe UV/H_2O_2 system was used to treat groundwater contaminated with halogenated VOCs at the Groveland Wells Superfund site in Groveland, Massachusetts (Weir and others 1996). The primary VOCs of concern at the site were TCE and 1,2-DCE, which were present in the groundwater at concentrations of 4,700 and 810 µg/L, respectively. The optimal treatment conditions, based on the lowest system operating cost, were an H_2O_2 dose of 25 mg/L, a flow rate of 1.5 m^3/min, and use of a 60-kW system consisting of four 15-kW UV lamps, Under theseconditions, the technology effectively removed TCE and 1,2-DCE from groundwater at the site and met surface water discharge limits, achieving removals of 99.9 and 91.4 percent, respectively. -The estimated capital cost for the system was $110,000, and the O&M cost was $0.09/$m^3$.

The Calgon Rayoxe UV/H_2O_2 technology has been combined with more conventional water treatment systems, such as air stripping and granular activated carbon (GAC), in field studies to treat VOC-contaminated groundwater. Performance data for these hybrid systems is discussed below.

In a field test, a Calgon Rayox® UV/H_2O_2 system was combined with air stripping to remediate VOC-contaminated groundwater at the Millville Municipal Airport in New Jersey in, March 1994. The hybrid system consisted of two 90-kW Calgon Rayoxe units and a Low Profile Shallow Tray@ air stripper. The hybrid system was designed to treat up to 760 Umin of contaminated groundwater (Bircher and others 1996).

PCE was the primary VOC present in the groundwater, with concentrations of about 6,000 @g/L; also 1 ,1 , 1 -TCA and methylene chloride were present at concentrations of 100 and 60 µg/L, respectively. Adequate treatment was achieved using one 90-kW unit and a flow rate of 450 L/min. H_2O_2 was added to the influent at a concentration of 25 mg/L.

The combined Calgon Rayox®/air stripping system was able to almost completely degrade the VOCs in the groundwater. Specifically, while the Calgon Rayoxe UV/H_2O_2 system reduced the initial concentrations of PCE; 1 ,1 ,1 -TCA; and methylene chloride by 99.8, 20, and 16.7 percent, respectively, the final concentrations of these compounds in the air stripper effluent were all <1 µg/L, indicating >99.9, 99, and 98.3 percent removal, respectively. These results show that for an unsaturated compound such as PCE, most of the removal occurred in the Calgon Rayoxe system, while for the saturated compounds (1,1,1-TCA and methylene chloride), most of the removal occurred in the air stripper. No cost information was available.

In another field test, a Calgon Rayox® UV/H_2O_2 system was used to treat VOC-contaminated groundwater after treatment with GAC at the Fort Ord Remedial Action Site in Monterey, California (Bircher and others 1996). The Fort Ord site groundwater was contaminated with methylene chloride at concentrations up to 6.9 µg/L and other organics. The treatment system consisted of two 9,100-kilogram (kg) carbon adsorption units in series and four 90-kW Calgon Rayox® units in parallel. Groundwater was fed through the carbon adsorption units at flow rates of up to 2,700 L/min. The pH of the effluent from the carbon adsorption units was adjusted to 5.0 using sulfuric acid. The pH-adjusted water was then treated by the Calgon Rayoxe UV/H_2O_2 system.

Organics other than methylene chloride were removed primarily by the GAC, while methylene chloride was primarily removed by the Calgon Rayoxe UV/H_2O_2 system. The system reduced the concentration of methylene chloride to 0.5 µg/L, a removal of 92.6 percent, using the four 90-kW units. A total of eight 90-kW units would have been needed to achieve this percent removal if the Calgon Rayoxe UV/H_2O_2 system had been used alone. The capital cost of the combined GAC/Calgon Rayox® system was $730,000, compared to $1 million if the Calgon Rayoxe technology had been used alone. Operating costs were estimated to be $0.31/$m^3$ of water treated for the GAC/Calgon Rayoxe hybrid system, whereas the Calgon Rayoxe UV/H_2O_2 system alone would have cost $0.58/$m^3$ of water treated to operate.

Magnum CAV-OX® UV/H_2O_2 System

The Magnum CAV-OX® UV/H_2O_2 system was demonstrated at Edwards Air Force Base in California under U.S. EPA's SITE program in I993 to remove VOCs from groundwater (U.S. EPA 1994). The primary groundwater contaminants at the site were TCE and benzene. During the demonstration, influent concentrations of TCE and benzene ranged from 1,500 to 2,090 µg/L and 250 to 500 µg/L, respectively. Three configurations of the CAV-OX® UV/H_2O_2 system were demonstrated: (1) the CAV-OX® I low-energy system, which contained six 60-W UV lamps (broad band with a peak at 254 nm) and operated at a flow rate of 1.9 to 5.7 L/min; (2) the CAV-OX® II high-energy system operating at 5 kW and 3.8 to 15 L/min; and (3) the CAV-OX® II high-energy system operating at 10 kW and 3.8 to 15 L/min.

About 32 m^3 of contaminated groundwater was treated during the demonstration. The optimum operating conditions, percent removals, and estimated costs associated with the CAV-OX® I and II systems are as follows:

- CAV-OX® I: influent H_2O_2 concentration = 23 mg/L; flow rate = 2.3 Umin; average removal of TCE and benzene = 99.9 percent; groundwater remediation cost for 95-L/min system = $3.80/$m^3$ of water treated (of which CAV-OX® I direct cost = $1.50/$m^3$)
- CAV-OX® II: influent H_2O_2 concentration = *48* mg/L; flow rate = 5.3 Umin; average removal of TCE and benzene = 99.8 percent; groundwater remediation cost for 95-L/min system = $4.07/$m^3$ of water treated (of which CAV-OX® II direct cost = $1.50/$m^3$)

In 1990, the CAV-OX® I low-energy system was used at a former Chevron service station in Long Beach, California, to remediate groundwater contaminated by leaking underground storage tanks (U.S. EPA 1994). The system used at the site consisted of a cavitation chamber, a centrifugal pump, an H_2O_2 injection process, and 12 60-W UV lamps housed in two stainless-steel reaction chambers. The primary contaminant of concern in site groundwater was total petroleum hydrocarbons (TPH), which was present at 190 mg/L. Pretreated influent was pumped into the CAV-OX® system at a flow rate of 38 Umin. The H_2O_2 dose was maintained at 20 mg/L. About 2 years was required to remediate the site; during this period, the CAV-OX® I low-energy process was operational 99.9 percent of the time. After 2 years of operation, 99.9 percent of the TPH in the groundwater had been removed. The overall cost was $0.47/$m^3$ of water treated; however, it is unclear what is included in this cost.

In 1997, the CAV-OX® I UV/H_2O_2 system was used to treat VOC-contaminated groundwater at a military site; the name and location of the 'site are unavailable. The primary contaminant of concern was TCE, which was present in groundwater at an average concentration of 1,800 µg/L. Cis-1,2-DCE; trans-1,2-DCE; VC; and PCE were also present at concentrations of 250, 200, 53, and 11 µg/L, respectively. The system achieved the following removals for VOCs: 99.9 percent for TCE; >99.9 percent for cis-1,2-DCE; >99.9 percent for trans-1,2-DCE; >99.7 percent for VC; and >98 percent for PCE. The estimated total direct operating cost was \$0.32/m^3 of water treated, which includes \$0.06/m^3 for 30 mg/L of 35 percent H_2O_2 (at \$1.17/kg), \$0.15/m^3 for electricity (at \$0.08/kilowatt-hour), \$0.06/m^3 for maintenance, and \$0.05/m^3 for replacement of 12 lamps once per year (Magnum 1998).

WEDECO UV/H_2O_2 System

A commercial WEDECO UV/H_2O_2 system was used to treat VOC-contaminated groundwater. The primary contaminants in the groundwater were 1,2-DCA; cis-1,2-DCE; benzene; ethylbenzene; and VC, which were present at concentrations of 54, 46, 310, 41, and 34 µg/L, respectively. The 1,2-DCA concentration was reduced by only 9 percent. However, removals for cis-1,2-DCE; benzene; ethylbenzene; and VC were >87, 93, 92, and 86 percent, respectively. The total cost estimate for the WEDECO groundwater treatment system was \$0.39/m^3 of water treated, which includes \$0.15/m^3 for electricity, \$0.16/m^3 for system operation and UV lamp replacement, and \$0.08/m^3 for H_2O_2 (WEDECO 1998).

WEDECO UV/O_3 System

A commercial-scale WEDECO UV/O_3 system was used to treat groundwater contaminated with TCE and PCE at concentrations of 330 and 160 µg/L, respectively. The system was operated at a flow rate of 10 m^3/h, an 0, dose of 5 mg/L, and a UV-C light intensity of 30 milliwatt per liter (mW/L). Under these conditions, the system achieved 99.0 and 96.6 percent removals for TCE and PCE, respectively. The estimated treatment cost was \$0.19/m^3 of water treated; of this cost, \$0.08/m^3 was for electricity, \$0.04/m^3 was for O&M, and \$0.07/m^3 was for capital equipment (Leitzke and Whitby 1990).

U.S. Filter UV/O_3/H_2O_2 System

The U.S. Filter UV/O_3/H_2O_2 system, formerly known as the Ultrox system, was demonstrated at the Lorentz Barrel and Drum site in San Jose, California, under the U.S. EPA SITE program in February and March 1989 (Topudurti and others 1993). Primary contaminants in the groundwater at the site were TCE; 1,1-DCA; and 1,1,1-TCA, which were present at concentrations of 50 to 88 µg/L, 9.5 to 13 µg/L, and 2 to 4.5 µg/L, respectively. Eleven test runs were performed to evaluate the U.S. Filter UV/O_3/H_2O_2 system under various operating conditions. The flow rate was maintained at 0.14 m^3/min. Optimum conditions for treatment were an influent pH of 7.2, a retention time of 40 minutes, an 0, dose of 110 mg/L, an H_2O_2 dose of 13 mg/L, and use of 24 65-W UV lamps.

Under these conditions, the system achieved removals as high as 99 percent for TCE; 65 percent for 1,1-DCA; and 87 percent for 1,1,1-TCA. While most VOCs were removed by chemical oxidation, 1,1-DCA and 1,1,1-TCA were removed by 0, stripping in addition to oxidation. Specifically, stripping accounted for 12 to 75 percent of the total 1,1,1-TCA removal and 5 to 44 percent of the total 1,1-DCA removal. The off-gas treatment unit (Decompzon unit) reduced reactor off-gas 0, by more than 99.9 percent to levels <0.1 ppm. Capital costs for the UV/oxidation unit and 0, generator in the system were estimated to range between \$88,000 and \$320,000. O&M costs for the system can be as low as \$0.08/m^3 of treated water if only oxidant and electrical costs are considered or can exceed. \$5.6/m^3 of treated water if extensive pretreatment is required.

The U.S. Filter UV/O_3/H_2O_2 system was field-tested by the U.S. Department of Energy at the Kansas City Plant in Missouri in 1988. TCE was present in the groundwater at a concentration 520 µg/L. During the field test, the flow rate through the system ranged from 20 to 38 Umin. The TCE removal achieved by the system was >99 percent. Capital and O&M costs were estimated to be \$380,000 and \$5/m^3 of water treated, respectively (U.S. EPA 1990).

Matrix UV/TiO_2 System

Under U.S. EPA's SITE program, the Matrix UV/TiO_2 system was demonstrated to destroy VOCs in groundwater at the U.S. Department of Energy's K-25 Site on the Oak Ridge Reservation in Oak Ridge, Tennessee, in August and September 1995 (Topudurti and others 1998).

The primarygroundwater contaminants at the K-25 Site included 1,1-DCA; 1,1,1-TCA; xylenes; toluene; cis-1,2-DCE; and 1,1-DCE, which were present in concentrations ranging from 660 to 840 µg/L, 680 to 980 µg/L, 55 to 200 µg/L, 44 to 85 µg/L, 78 to 98 µg/L, and 120 to 160 µg/L, respectively. Groundwater was also spiked with TCE, PCE, and benzene—contaminants not present at high concentrations in groundwater at the Oak Ridge

Reservation but present at many Superfund sites-to produce system influent concentrations ranging from 230 to 610 µg/L; 120 to 200 µg/L; and 400 to 1 ,1 00 µg/L, respectively. H_2O_2 and 0, were added to the Matrix system influent at concentrations of 70 and 0.4 mg/L, respectively, in order to enhance treatment performance in certain runs. Influent flow rates varied from 3.8 to 9.1 Umin. Groundwater alkalinity ranged from 270 to 300 mg/L calcium carbonate, and the pH ranged from 6.5 to 7.2. The Matrix system did not require pH adjustment of groundwater prior to treatment. The groundwater also contained high concentrations of iron and manganese (about 16 and 9.9 mg/L, respectively). To prevent fouling of the photocatalytic reactor cells during the demonstration, an ion-exchange pretreatment system was used to remove Iron and manganese in the groundwater.

During the demonstration, the Matrix system (see Figure 2-l 0) treated about 11,000 L of contaminated groundwater. In general, at path length 48, removals of up to 99 percent were observed for benzene; toluene; xylenes; TCE; PCE; cis-1,2-DCE; and 1,1-DCE. However, low removals were observed for 1,1-DCA and 1,1,1-TCA, which were reduced by no more than 21 and 40 percent, respectively. The demonstration showed that the percent removals at path length 24 (halfway through the system) can be increased to match the removals at path length 48 by adding H_2O_2 at a dose of 70 mg/L. This finding indicates that the equipment cost and electrical energy cost could be reduced by 50 percent by adding H_2O_2 at a relatively low cost. The system effluent met the Safe Drinking Water Act MCLs for benzene; cis-1,2-DCE; and 1,1-DCE. However, the effluent did not meet the MCLs for PCE; TCE; 1,1-DCA; and 1,1,1-TCA. VOC removal was generally reproducible for most VOCs when the Matrix system'was operated on different occasions under identical conditions. Treatment by the Matrix system did not reduce groundwater toxicity to freshwater test organisms (the water flea [*Ceriodaphnia dubia*] and fathead minnow [*Pimephales promelas*]). The estimated groundwater remediation cost for the Matrix system is about $18/m^3 of water treated. Of this cost, the Matrix system direct treatment cost was about $7.60/m^3 of water treated.

Pilot-Scale Applications

VOCs in groundwater have been removed using APO processes on a pilot scale. This section presents pilot-scale evaluation results for the UV/H_2O_2, solar/TiO_2, and solar/TiO_2/H_2O_2 processes in removing the following VOCs.

APO Process.	VOCs Removed
• UV/H_2O_2	• Benzene
• Solar/TiO_2	• TCE
• Solar/TiO_2/H_2O_2	• BTEX

UV/H_2O_2

A UV/H_2O_2 system was pilot-tested by the Gateway Center Water Treatment Plant in Los Angeles, California, to treat groundwater contaminated with benzene prior to the groundwater's discharge to the Los Angeles River. The system consisted of an H_2O_2 injection unit; a 360-kW UV reactor; and two vessels containing 9,100 kg of activated carbon each. The average concentration of benzene in the untreated groundwater was 35 µg/L. The influent pH averaged 6.8, and the flow rate was maintained at about 3.2 m^3/min. Under these conditions, the UV/H_2O_2 system achieved 98 percent removal of benzene. The treated groundwater's pH was adjusted using sodium hydroxide to meet the discharge limit. No cost information was reported (Oldencrantz and others 1997).

Solar/TiO_2

A pilot-scale solar/TiO_2 system designed by researchers at the National Renewable Energy Laboratory and Sandia National Laboratory was field-tested at a Super-fund site at Lawrence Livermore National Laboratory in Tracy, California, to treat TCE-contaminated groundwater (Mehos and Turchi 1993). The system used at -Lawrence Livermore National Laboratory consisted of a concentrating solar collector and a mobile equipment skid.. The reactor for the study consisted of a 0.051 -cm-diameter borosilicate glass pipe that ran along the length of the solar collector at the focal line of the parabolic troughs. The influent TCE concentration was about 110 µg/L, and the raw groundwater's pH averaged 7.2. Powdered TiO_2 catalyst was added to the influent as a concentrated slurry at a dose of 800 to 900 mg/L. The flow rate was maintained at 15 Umin, corresponding to a retention time of 10 minutes.

The study results showed that lowering the pH of the influent groundwater significantly increased the percent removal of TCE by reducing the concentration of bicarbonate ion, a known scavenger of •OH. Lowering the pH from 7.2 to 5.6 increased TCE removals from 91 to 99 percent. The projected treatment cost for a full-scale, 380-m^3/day treatment system at the Lawrence Livermore National Laboratory site was $0.83/m^3 of water treated.

Solar/TiO_2/H_2O_2

In a pilot-scale field test at Tyndall Air Force Base in Florida, a solar/TiO_2/H_2O_2 batch system was used to treat jet fuel contaminants-specifically, 2 mg/L of total benzene, toluene, ethylbenzene, and xylene (BTEX)—in groundwater. The treatment unit consisted of a photoreactor area made up of 15 nonconcentrating solar panels. TiO_2 doses of 0.5 to 1 mg/L and an H_2O_2 dose of 100 mg/L were used. Removal rates for BTEX and total organic carbon (TOC) were slightly higher at pH levels of 4 and 5, suggesting that an acidic medium is beneficial. From about 50 to 75 percent of the BTEX was removed during the 3-hour studies. The TOC concentration, which ranged from 70 to 90 mg/L initially, remained relatively unchanged, suggesting that while parent compounds were destroyed, complete mineralization did not occur. The estimated treatment cost, including capital and O&M costs and based on a flow rate of 38 m^3/day, was \$20 to \$29/m^3 of water treated (Turchi and others 1993).

Bench-Scale Studies

This section summarizes the results of bench-scale studies of the effectiveness of APO processes for VOC removal from groundwater. The bench-scale results are summarized only for studies that provided information beyond the commercial- and pilot-scale applications summarized above. The level of detail provided varies depending on the source of information used. For example, VOC percent removals and test conditions are not specified for some of the bench-scale studies because such information is unavailable in the sources. Bench-scale study results on VOC removals and treatment by-products in groundwater and synthetic wastewater matrices for the following VOCs by UV/H_2O_2 and TiO_2 are discussed,

APO Process	**VOCs** Removed
• UV/H_2O_2	• Acetone, naphthalene, TCE, PCE
• UV/TiO_2	• Chloroform, ethylbenzene, nitrobenzene, MTBE

UV/H_2O_2

Hirvonen and others (1996) report on UV/H_2O_2 treatment of well water contaminated with TCE and PCE in a batch UV reactor. TCE and PCE concentrations were initially 100 and 200 μg/L, respectively. The UV dose was 1.2 W/L, the H_2O_2 dose was 140 mg/L, and the influent pH was 6.8. Treatment resulted in 98 and 93 percent removals of TCE and PCE, respectively, in 5 minutes. Chlorinated by-products formed included trichloroacetic acid and dichloroacetic acid.

A Calgon Rayox® UV/H_2O_2 bench-scale reactor was used to study degradation of acetone in synthetic wastewater. Acetone was present at concentrations of 30 to 300 mg/L. The H_2O_2 dose was varied from 100 to 544 mg/L. The initial concentrations of acetone and H_2O_2 significantly affected the initial rate of acetone degradation. At a high pH, by-products of acetone degradation-specifically, acetic acid, formic acid, and oxalic acid-accumulated, competed for *OH, and slowed down acetone removal (Stefan and others 1996).

By-product formation during naphthalene degradation by UV/H_2O_2 treatment was studied using synthetic wastewater. By-products of the reaction included naphthol; naphthoquinone; bicyclo[4,2,9]octa-1,3,5-triene; 2,3-dihydroxy-benzofuran; 1(3h)isobenzofuranone; benzaldehyde; phthalic acid; benzoic acid; phenol; hydroxybenzaldehyde; hydroxyacetophenone; and dimethylpentadiene (Tuhkanen and Beltran 1995).

UV/TiO_2

UV/TiO_2 degradation of chloroform in distilled water was studied using pure silver (Ag)-loaded TiO_2. At an initial chloroform concentration of 200 mg/L, 44 percent of the chloroform was removed when Ag-loaded TiO_2 was used, and 35 percent was removed when pure (unloaded) TiO_2 was used. The addition of Ag as a sensitizer improved the performance of the UV/TiO_2 process (Kondo and Jardim 1991).

UV/TiO_2 degradation of ethylbenzene was studied. The initial concentrations of ethylbenzene and TiO_2 were 0.32 to 5.4 mg/L and 1,000 mg/L, respectively. The reaction by-products identified include 4-ethylphenol, acetophenone, 2-methylbenzyl alcohol, 2-ethylphenol, and 3-ethylphenol. At an initial pH of 4.5, about 65 minutes was required for complete mineralization (Vidal and others 1994).

Minero and others (1994) studied photocatalytic degradation of nitrobenzene using the UV/TiO_2 process. Within 1 hour, >90 percent mineralization was achieved using 200 mg/L of TiO_2. The reaction by-products identified include 2-, 3-, and 4-nitrophenol and dihydroxybenzenes.

Photodegradation of methyl-*tert*-butyl ether (MTBE) in synthetic wastewater using the UV/TiO_2 process was studied. The optimum amount of catalyst was 100 mg/L, above which increased turbidity reduced

360 minutes of irradiation at a pH of 7.0 (Jardim and others 1997).

UV/ZnO

Richard and Boule (1994) studied photochemical oxidation of salicylic acid using the UV/ZnO process. At a ZnO dose of 2,000 mg/L and under O_2-saturated conditions, 2,5-dihydroxybenzoic acid; 2,3-dihydroxybenzoic acid; and pyrocatechol were identified as by-products.

3.1.3 PCB-Contaminated Groundwater

No commercial- or pilot-scale information was available on the effectiveness of APO in treating groundwater contaminated with PCBs. Two bench-scale studies for the following PCBs are summarized below.

APO Process	PCBs Removed
• Solar/diethylamine	• PCB congeners: 66, 101, 110, 118, 138 (Aroclor 1254)
• Solar/TiO_2	• Aroclor 1248

Lin and others (1995) studied photodegradation of five PCB congeners—66, 101, 110, 118, 138—under simulated sunlight in the presence of the sensitizer diethylamine. These congeners represent 45.5 percent of all Aroclor 1254 congeners. PCBs were present in synthetic wastewater at a concentration of 1 .O mg/L. With a diethylamine dose of 1 μg/L and a reaction time of 24 hours, congeners 66, 101, 110, 118, and 138 were degraded by 89, 99, 84, 98, and 78 percent, respectively. Congener 138 generated five congeners during photochemical oxidation; specifically, congeners 85, 87, 97, 99, and 118 were generated during 1 hour of treatment.

PCB removal from synthetic wastewater has also been studied using the solar/TiO_2 process in a bench-scale study by Zhang and others (1993). Aroclor 1248 was present in synthetic wastewater at a concentration of 320 mg/L. At a TiO_2 dose of 50,000 mg/L, 83 percent removal of Aroclor 1248 was observed in 4 hours.

3.7.4 Pesticide- and Herbicide-Contaminated Groundwater

No evaluations of commercial-scale APO processes for removing pesticides and herbicides from groundwater were available. However, one APO process (UV/O_3) has been evaluated at the pilot scale, and several such APO processes have been evaluated at the bench scale. The results of these evaluations are summarized below.

Pilot-Scale Application

Kearney and others (1987) conducted a UV/O_3 pilot-scale study involving treatment of pesticide in synthetic wastewater. The concentration of each contaminant (alachlor; atrazine; Bentazon; butylate; cyanazine; 2,4-dichlorophenoxyacetic acid [2,4-D]; metolachlor; metribuzin; trifluraline; carbofuran; and malathion) was varied at three levels: 1 0, 100, and 1,000 mg/L. The treatment unit used consisted of 66 low-pressure mercury vapor lamps with a total UV output of 455 W at 254 nm. The flow rate through the system was varied from 8 to 40 Umin. For pesticides at initial concentrations of 10 to 100 mg/L, >99.9 percent removal was observed. For the 1 ,000-mg/L initial concentrations, the removals ranged from 75 to 85 percent. The time required for 90 percent removal depended on the initial pesticide concentration and increased as the initial concentration increased (about 20 minutes for a 10-mg/L initial concentration and 60 minutes for a 1 00-mg/L initial concentration).

Bench-Scale Studies

Pesticides and herbicides in water have been removed using the VUV, UV/H_2O_2, UV/O_3, photo-Fenton, and UV/TiO_2 processes at the bench-scale level. This section summarizes bench-scale results for APO treatment of the following pesticides and herbicides; information on by-products and contaminant percent removals is provided where available.

APO Process	Pesticides and Herbicides Removed
• ❖◆❖	• Atrazine
· UV/H_2O_2	• 2,4-D
· UV/O_3	· Simazine
• Photo-Fenton	• Methyl parathion, metolachlor
· UV/TiO_2	• Alachlor; atrazine; Basagran; Bentazon; carbofuran; 2,4-D; 1,2-dibromo-3-chloropropane; dichlorvos; Diquat; Diuron; monocrotophos; Monuron; pendimethalin; propazine; propoxur; simazine

VUV

The VUV process was evaluated in terms of mineralization of atrazine (22 mg/L) in synthetic wastewater. By-products identified include ammelide, ammeline, and cyanuric acid. The yield of the by-products of atrazine degradation (for example, cyanuric acid) from VUV photolysis was found to be about half the yield obtained in UV/TiO_2 reactions (Gonzalez and others 1994).

UV/H_2O_2

Pichat and others (1993) studied UV/H_2O_2 treatment of 2,4-D in synthetic wastewater. The initial concentration of 2,4-D was 80 mg/L. At an H_2O_2 dose of 99 mg/L, mineralization of the compound was nearly complete (>99 percent) within 3 hours.

UV/O_3

The UV/O_3 process was evaluated in oxidation of simazine in synthetic wastewater. The initial concentration of simazine was 4 mg/L. The retention time in the reactor was 15 minutes. Complete oxidation of the compound was observed when 34 milligrams per minute of 0, was applied at a pH of 7.2. By-products of the reaction included chlorodiamino s-triazine, aminochloro ethylamino s-triazine, diaminohydroxy s-triazine, aminodihydroxy s-triazine, and cyanuric acid (Lai and others 199.5).

Photo-Fen ton

The photo-Fenton reaction was used to treat metolachlor(2-chloro-N-[2-methyl-6-ethylphenyl]-N-[2-methoxy-1 -methylethyl]acetamide) and methyl parathion in synthetic wastewater. The initial concentrations of metolachlor and methyl parathion ranged from 28 to 57 mg/L and 26 to 53 mg/L, respectively. The doses of H_2O_2 and Fe(III) used were 340 and 350 mg/L, respectively. Under a black light, metolachlor was completely mineralized to carbon dioxide in 6 hours; details on methyl parathion degradation were not available. Organic by-products of the metolachlor reaction included chloroacetate, oxate, formate, and serine. By-products of methyl parathion degradation included oxalic acid; 4-nitrophenol; dimethyl phosphoric acid; and traces of O,O-dimethyl-4-nitrophenyl phosphoric acid (Pignatello and Sun 1995).

UV/TiO_2

The UV/TiO_2 process was evaluated for treating synthetic wastewater containing 2,4-D and propoxur at 50 mg/L each. At a pH of 4 and with a TiO_2 dose of 180 mg/L, 2,4-D and propoxur concentrations were reduced by 97 and 73 percent, respectively. The primary by-products of 2,4-D degradation were formaldehyde; 2,4-DCP; and 2,4-DCP formate. According to the Microtox test, which measures toxicity based on the quantity of light emitted by the luminescent bacterium *Photobacterium phosphoreum* before and after exposure to an aqueous sample, 2,4-D by-products are more toxic than the parent compounds after partial degradation. These results indicate the importance of completely destroying the by-products during treatment (Lu and Chen 1997).

UV/TiO_2 was applied to treatment of synthetic wastewater containing dichlorvos at an initial concentration of 50 mg/L. The UV/TiO_2 process was tested at pH levels of 4 and 8 for 3 hours. Greater removal was observed at a pH of 4. However, the toxicity of the solution increased 2.5 times that of the parent compound during the irradiation period. At a pH of 8, although the percent removal was lower than it was -at a pH of 4, toxicity decreased during the illumination period (Lu and others 1993).

The UV/TiO_2 process was tested in terms of oxidation of atrazine (22 mg/L), simazine (20 mg/L), and propazine (23 mg/L) in synthetic wastewater. The by-products of UV/TiO_2 photodegradation of all three compounds were ammeline; ammelide; and 1,3,5-triazine-2,4-diamine-6-chloro. Cyanuric acid was the final product of the reactions (Pelizzetti and others 1992).

The California Department of Health Services, Sanitation and Radiation Laboratory tested the UV/TiO_2 process in destruction of 1,2-dibromo-3-chloropropane (DBCP) in contaminated groundwater taken from a polluted well in the vicinity of Fresno, California. The initial DBCP concentration of 2.9 μg/L was decreased to 0.4 μg/L (an 86 percent removal) using 0.25 percent TiO_2 catalyst on silica gel and UV light (a 1-kW xenon lamp) in about 6 hours (Halmann and others 1992).

Degradation of carbofuran (220 mg/L) in synthetic wastewater was studied using a UV/TiO_2 process. Under a 400-W medium-pressure mercury lamp and TiO_2-coated glass plates (with a surface coverage of 2.5 x 10^{-5} g/cm^2), complete mineralization was achieved after 15 hours of irradiation at a pH of 6. A fluorescent compound appeared as an intermediate during photooxidation. The degradation rate was relatively low at high pH values (Tennakone and others 1997).

Hua and others (1995) photodegraded monocrotophos using the UV/TiO_2 process. At a flow rate of 0.030 liter per minute (L/min) and an initial monocrotophos concentration of 11,000 mg/L, 51 percent of the compound degraded after 1 hour. Addition of H_2O_2 to the UV/TiO_2 system significantly enhanced degradation, For example, when 62 mg/L of H_2O_2 was added to a solution containing 10,000 mg/L of monocrotophos, 10 percent more degradation was observed after 1 hour than was the case with UV/TiO_2 alone.

Kinkennon and others (1995) studied UV/TiO_2 degradation of the herbicides Basagran, Diquat, and Diuron in synthetic wastewater at a concentration of 10 mg/L each. Under a 1 -kW high-pressure xenon lamp, Basagran, Diquat, and Diuron concentrations were reduced by 95 percent in 1 hour, 90 percent in 90 minutes, and 90 percent in 1 hour, respectively.

Pramauro and others (1993) applied the UV/TiO_2 process to degrade Monuron, or 3-(4-chlorophenyl)-l-l -dimethylurea, in synthetic wastewater. Light was provided by a 1,500-W xenon lamp. With an initial Monuron concentration of 20 mg/L, 100 mg/L of TiO_2 catalyst, and a pH of 5.5, >99.9 percent removal of the contaminant took place in 30 to 40 minutes. The compound 4-chlorophenyl isocyanate was identified as an intermediate that was decomposed after about 35 minutes of irradiation.

UV/TiO_2 treatment of pendimethalin and alachlor at initial concentrations of 100 and 51 mg/L, respectively, was evaluated. Using a 120-W, high-pressure mercury lamp and a TiO_2 dose of 250 mg/L, 60 percent removal was achieved for pendimethalin in 3 hours compared to only 10 percent degradation in the absence of TiO_2. Alachlor was degraded much more quickly under the same conditions (95 percent removal in 20 minutes). The by-products of pendimethalin degradation were 2,6-dinitro 3,4-dimethylaniline and 6-nitro 3,4-dimethylaniline. The byproducts of alachlor degradation were hydroxyalachlor and ketolachlor (Moza and others 1992).

Pelizzetti and others (1989) studied degradation of the herbicide Bentazon, or 3-isopropyl-2,1 ,3-benzothiadiazin-4-one-2,2-dioxide, using the UV/TiO_2 process in a batch system. Using a 1,500-W xenon lamp and 50 mg/L of TiO_2, the initial Bentazon concentration of 20 μg/L was reduced to <0.1 μg/L (>99.5 percent removal) after 10 minutes of irradiation.

3.1.5 Dioxin- and Furan-Contaminated Groundwater

Dioxins and furans have been removed-from synthetic wastewater using the photo-Fenton process at the bench-scale level. Pignatello and Huang (1993) studied the fate of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) contaminants in the herbicide 2,4,5-trichlorphenoxyacetic acid (2,4,5-T) during photo-Fenton treatment. PCDD and PCDF were initially present at concentrations of 2.3 and 0.0016 μg/L, respectively. The highest removals were observed in aerated solutions at a pH of 2.8 and with an H_2O_2 dose of 1,700 mg/L. Under these conditions, 89 to >99.9 percent removal of the PCDD and PCDF was achieved in 1 hour except for octachloro-dibenzofuran, which was degraded by 66 percent.

3.7.6 Explosive- and Degradation Product-Contaminated Groundwater

Explosives and their degradation products in groundwater have been treated using the UV/H_2O_2 process at the commercial scale. Removal of explosives and their degradation products from groundwater using the UV/TiO_2 process has been evaluated at the bench scale. The results of the commercial- and bench-scale evaluations are discussed below.

Commercial-Scale Applications

This section presents performance data from field studies using the Calgon perox-pure™ and Calgon Rayox® UV/H_2O_2 treatment systems to remove the following explosives and their degradation products from groundwater.

APO Process	Explosives and Their Degradation Products Rbmoved
UV/H_2O_2	Benzathiazole; 1,4-dithiane; NG; NQ; 1,4-oxathiane; RDX; thiodiglycol; 1,3,5-TNB

Calgon perox-pure™ UV/H_2O_2 System

A Calgon perox-pure™ UV/H_2O_2 system was used to treat contaminated groundwater at the Old O-Field Site of Aberdeen Proving Ground in Maryland. The groundwater contaminants at the Old O-Field site included thiodiglycol; 1,4-dithiane; and 1,4-oxathiane at concentrations of 480, 200, and 82 μg/L, respectively. Benzathiazole and 1,3,5-trinitrobenzene (TNB) were also present in the groundwater at concentrations of 20 and 15 μg/L, respectively. Four tests were conducted at a flow rate of 60 L/min; the hydraulic retention time was about 5 minutes. In Tests 1, 2, and 3, the H_2O_2 doses used were 45, 90, and 180 mg/L, respectively; the doses in these tests were equally divided into three parts and added by the splitter at (1) the influent line to the first chamber, (2) the effluent line from the first chamber, and (3) the effluent line from the second chamber. In Test 4, a total H_2O_2 dose of 45 mg/L was added to the influent line to the first reactor; the splitter was not used. The treated effluent met federal MCLs for all compounds. Removals of thiodiglycol; 1,4-dithiane; 1,4-oxathiane; benzathiazole; and 1,3,5-TNB were >97, 98, 97, 82, and 96 percent, respectively. No cost information was provided for the system (Topudurti and others 1993).

Also, a Calgon perox-pure™ UV/H_2O_2 system was used to treat groundwater at the former Nebraska Ordnance Plant in Mead, Nebraska. Site groundwater contained 28 μg/L of cyclonite (RDX), the primary ordnance compound used at the site. The 30-kW system used at the site consisted of six 5-kW lamps, each mounted horizontally above one another in separate 6-inch reactor chambers. The groundwater flowed in series in a serpentine pattern to each reactor chamber. The field study was performed at a (1) flow rate of 310 L/min, (2) pH of 7.0, (3) H_2O_2 dose of 10 mg/L, and (4) UV dose of 0.53 kWh/m^3. The RDX concentration was reduced by more than 82 percent. The total operating cost for a system with a flow rate of 29,000 Umin was estimated to be \$0.02/m^3 of water treated, which includes the costs of power, lamp replacement, and H_2O_2 (Calgon 1998).

Calgon Rayox® UV/H_2O_2 System

A Calgon Rayox® UV/H_2O_2 system was installed at the Indian Head Division, Naval Surface Warfare Center, in Indian Head, Maryland, to treat nitroglycerin (NG) production wastewater and nitroguanidine (NQ) wastewater. The system reduced NQ levels from 2,700 to 1 mg/L (>99.9 percent removal) and NG levels from 1,000 to 1 mg/L (>99.9 percent removal) using a UV dose of 450 kWh/m^3. By-products of NG degradation included 1,2-dinitroglycerin (DNG); 1,3-DNG; mononitroglycerin (MNG); nitrogen; nitrate; nitrite; and ammonia. By-products of NQ degradation included nitrate, nitrite, and ammonia. The treatment cost for NG production wastewater was estimated to be \$13/m^3 of water treated, and the cost for treating NQ wastewater was estimated to be \$34/m^3 of water treated (Hempfling 1997).

Bench-Scale Studies

Schmelling and Gray (1995) examined UV/TiO_2 photodegradation of 2,4,6-trinitrotoluene (TNT) in a slurry reactor. When a 50-mg/L solution of TNT was treated using UV/TiO_2 in the presence of O_2, about 90 percent of the TNT was oxidized to carbon dioxide in 2 hours. Oxidative by-products included trinitrobenzoic acid, trinitrobenzene, and trinitrophenol. In a subsequent study, the same reaction was tested under conditions typically observed in field applications. Schmelling and others (1997) compared TNT degradation rates in the UV/TiO_2 process at pH levels of 5.0 and 8.5. The degradation rate was higher at a pH of 5.0, where >90 percent removal was observed in 1 hour; 3 hours was needed to achieve the same removal at a pH of 8.5. When varying concentrations of humic acids (1, 10, and 20 mg/L representative of low, medium, and high values observed in natural waters) were added to TNT solutions, degradation rates increased with increasing concentrations of humic acid.

3.1.7 Humic Substance-Contaminated Groundwater

A UV/TiO_2 process was used to remove a brown discoloration in synthetic wastewater introduced by humic acid, which was present at a concentration of 0.1 mg/L. The batch reaction took place under a 250-W, medium-pressure mercury lamp. During the reaction, the discoloration decreased by half in about 12 minutes. However, it took 1 hour to mineralize only 50 percent of the humic substances to carbon dioxide and H_2O. Some of the reaction by-products were highly fluorescent (Eggins and others 1997).

3.1.8 Inorganic-Contaminated Groundwater

Bench-scale treatment of cyanide (2.6 mg/L) in synthetic wastewater (2.6 mg/L) was conducted using a UV/ZnO process. At a pH of 11, and using a ZnO dose of 8,000 mg/L, more than 95 percent of cyanide was destroyed in 9 minutes. Reaction by-products include cyanogen and the cyanate ion (Domenech and Peral 1988).

Table 3-1. Contaminated Groundwater Treatment

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional Information		
OCs (Commercial Scale)						
JV/H_2O_2 Calgon erox-pure™)	<u>Raw Groundwater</u> TCE: 890 to 1,300 µg/L PCE: 71 to 150 µg/L <u>Spiked Groundwater</u> TCE: 690 to 1,000 µg/L PCE: 63 to 92 µg/L 1,1-DCA: 120 to 170 µg/L 1,1,1-TCA: 110 to 130 µg/L Chloroform: 140 to 240 µg/L	Flow rate: 38 to 150 L/min Reactor volume: 57 L (total) Light source: six 5-kW mercury lamps Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 30 to 240 mg/L Influent pH: 8.0, 6.5, 5.0	TCE: >99.9 PCE: >98.7 1 ,I-DCA: >95.8 1,1,1-TCA: 92.9 Chloroform: 93.6	Effluent acutely toxic to freshwater test organisms	<u>Case 1: Raw Groundwater</u> Remediation cost: $2.10/m^3 Calgon perox-pure" cost: $0.89/m^3 <u>Case 2: Spiked Groundwater</u> Remediation cost: $3.30/m^3 Calgon perox-pure™ cost: $1 .50/m^3	Topudurti and others 1994
IV/H_2O_2 algon erox-pure™)	1,2-DCE: 200 µg/L Benzene: 52 µg/L Chloroform: 41 µg/L 1 ,2-DCA: 22 µg/L TCE: 21 µg/L Methylene chloride: 8µg/L	Flow rate: 60 L/min Reactor volume: 300 L Light source: four 15-kW mercury lamps Wavelength: broad band with a peak at 254 nm H_2O_2 doses: 45, 90, 180 mg/L Retention time: 5 min	1,2-DCE: >99 Benzene: >96 Chloroform: >97 1,2-DCA: >92 TCE: >93 Methylene chloride: >86	Effluent not toxic to freshwater test organism	Not available	Topudurti and others 1993
V/H_2O_2 algon erox-pure™)	<u>Site E-1</u> 1 ,2-DCE: 11,000 µg/L PCE: 2,500 µg/L TCE: 1,700 µg/L vc: 1,200 µg/L	<u>Site E-1</u> Flow rate: 490 L/min Light source: 90-kW system Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 50 mg/L Influent pH: 5.5 Retention time: 2 min	Site 1,2-DCE: >99.9 PCE: >99.9 TCE: >99.9 VC: >95.8	None	<u>Site E-1:</u> <u>For a 75-L/min System</u> Equipment cost: $115,000 O&M cost: $2,800/month	Kllnk and others 1992
	Site CB: 3,100 µg/L vc: I.700 µg/L 1 ,2-DCE: 430 µg/L 1.6DCB: 420 µg/L 1,1-DCA: 400 µg/L	<u>Site E-3</u> Flow rate: 940 L/min Light source: 270-kW system Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 100 mg/L Influent pH: 5.1 Retention time: 4 min	Site CB: >99.9 vc: >97 1,2-DCE: >99.1 1,4-DCB: >99.5 I ,1-DCA: >99.5	None	<u>Site 3 :</u> <u>For a 130-L/min System</u> Equipment cost: $241,000 O&M cost: $13,000/month	
V/H_2O_2 algon rox-pure™)	TCE: 50 to 400 mg/L	Flow rate: 510 L/min Reactor volume: not available tight source: one 15-kW UV lamp Wavelength: broad band with a peak at 254 nm H_2O_2 dose: not available	>99.7	None	O&M cost: $0.08/m^3	U.S. EPA 1993

Table 3-1. Contaminated Groundwater Treatment (Continued)

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional Information		
VOCs (Commercial Scale) (Continued)						
UV/H_2O_2 (Calgon Rayox®)	TCE: 4,700 μg/L 1,2-DCE: 810 μg/L	Flow rate: 1.5 m^3/min Light source: four 15-kW UV lamps Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 25 mg/L	TCE: 99.9 1,2-DCE: 91.4	None	Equipment cost: $110,000 O&M cost: $0.09/$m^3$	Weir and other: 1996
UV/H_2O_2 Followed by Air Stripper (Calgon Rayox®)	PCE: 6.000 μg/L 1,1,1-TCA: 100 μg/L Methylene chloride: 60 μg/L	Flow rate: 450 L/min Light source: one 90-kW UV lamp Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 25 mg/L	Before Air Stripper PCE: 99.8 1,1,1-TCA: 20 Methylene chloride: 16.7	Percent Air Stripper PCE: >99.9 1,1,1-TCA: >99 Methylene chloride: >98.3	Not available	Bircher and others 1996
GAC Followed by UV/H_2O_2 [Calgon Rayox®)	Methylene chloride: 6.9 μg/L	Flow rate: 2,700 Umin (total) Light source: four 90-kW UV lamps Wavelength: broad band with a peak at 254 nm H_2O_2 dose: not available Influent pH: 5.0	92.6	None	For a 2,700 L/min Rayox®/GAC System Equipment cost: $730,000 O&M cost: $0.31/$m^3$	Bircher and others 1996
JV/H_2O_2 (Magnum CAV-OX®)	TCE: 1,500 to 2,000 μg/L Benzene: 250 to 500 μg/L	CAV-OX I System Flow rate: 2.3 L/min Light source: six 60-W UV lamps Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 23 mg/L	CAY-OX I System TCE: 99.9 Benzene: 99.9	None	CAV-OX-I System Remediation cost: $3.80/$m^3$ Magnum cost: $1.50/$m^3$	U.S. EPA 1994
		CAV-OX II system Flow rate: 5.3 Umin Light source: 5-kW and 10-kW Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 48 mg/L	CAV-OX II System TCE: 99.8 Benzene: 99.8	None	CAV-OX II System Remediation cost: $4.07/$m^3$ Magnum cost: $1.50/$m^3$	U.S. EPA 1994
JV/H_2O_2 Magnum CAV-OX®)	TPH: 190 mg/L	Flow rate: 38 Umin Light source: 12 60-W UV lamps Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 20 mg/L	99.9	None	CAV-OX I System $0.47/$m^3$	U.S. EPA 1994

Table 3-1. Contaminated Groundwater Treatment (Continued)

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional Information		
VOCs (Commercial Scale) (Continued)						
UV/H_2O_2 (Magnum CAV-0X®)	TCE: 1.800 µg/L cis-1 ,2-DCE: 250 µg/L trans-1,2-DCE: 200 µg/L vc: 53 µg/L PCE: 11 µg/L	Flow rate and retention time: not available Reactor volume: not available Light source: six 60-W UV lamps Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 30 mg/L of 35 percent H_2O_2	TCE: 99.9 cis-1 ,2-DCE: >99.9 trans-1,2-DCE: >99.9 vc: >99.7 PCE: >98	None	CAV-OX I System $\$0.32/m^3$ (includes H_2O_2, electricity, maintenance, and lamp replacement costs)	Magnum 1998
UV/H_2O_2 (WEDECO)	1,2-DCA: 54 µg/L cis-1 ,2-DCE: 46 µg/L Benzene: 310 µg/L Ethyl Benzene: 41 µg/L vc: 34 µg/L	Flow rate: 3.8 to 15 L/min Reactor volume: not available Light source: two low-pressure mercury lamps Wavelength: broad band with a peak at 254 nm H_2O_2 dose: not available	1,2-DCA: 9 cis-1 ,2-DCE: >87 Benzene: 93 Ethylbenzene: 92 vc: 86	None	$\$0.39/m^3$ (includes electricity, O&M, lamp replacement. and H_2O_2 costs)	WEDECO 1998
UV/O_3 (WEDECO)	TCE: 330 µg/L PCE: 160 µg/L	Flow rate: 10 m^3/h Light source: UV-C 30-mW/L H_2O_2 dose: 5 mg/L	TCE: 99 PCE: 96.6	None	$\$0.19/m^3$ (includes electricity, O&M, and equipment costs)	Leitzke and Whitby 1990
$UV/O_3/H_2O_2$ (U.S. Filter)	TCE: 50 to 88 µg/L 1,1-DCA: 9.5 to 13 µg/L 1,1,1-TCA: 2 to 4.5 µg/L	Flow rate: 0.14 mg^3/min Light source: 24 65-W UV lamps Wavelength: broad band with a peak at 254 nm 0, dose: 1 10 mg/L H_2O_2 dose: 13 mg/L Influent pH: 7.2 Retention time: 40 min	TCE: 99 1,1-DCA:.65 1,1,1-TCA: 87	1,1-DCA and 1.1 ,1-TCA removal due to stripping by 0, and oxidation	Equipment cost: \$88,000 to \$320,000 O&M cost: \$0.08 to $\$5.60/m^3$ (depending on pretreatment requirements)	Topudurti and others 1993
$UV/O_3/H_2O_2$ (U.S. Filter)	TCE: 520 µg/L	Flow rate: 20 to 38 L/min Reactor volume: 2,700 L Light source: 72 65-W lamps Wavelength: broad band with a peak at 254 nm Oxidant doses: not available	>99	None	Equipment cost: \$380,000 O&M cost: $\$5/m^3$	U.S. EPA 1990

Table 3-1. Contaminated Groundwater Treatment (Continued)

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional Information		
/OCs (Commercial Scale) (Continued)						
JV/TiO$_2$ Matrix)	1 ,1 -DCA: 660 to 840 μg/L 1,1,1 -TCA: 680 to 980 μg/L Total xylenes: 55 to 200 μg/L Toluene: 44-85 μg/L cis-1,2-DCE: 78 to 98 μg/L 1,1-DCE: 120 to 160 μg/L TCE: 230 to 610 μg/L PCE: 120 to 200 μg/L Benzene: 400 to 1,100 μg/L	Flow rate: 3.8 to 9.1. Umin Light source: 144 75-W UV lamps Wavelength: 254 nm Influent pH: 6.5 to 7.2 H_2O_2 dose: 22 mg/L 0, dose: 0.4 mg/L	1,1-DCA: 21 1,1,1-TCA: 40 Xylenes: 98 Toluene: >92 cis-1,2-DCE: 96 1 ,1-DCE: 97 TCE: 93 PCE: a2 Benzene: 99	Aldehydes and haloacetlc acids No acute toxicity reduction for fathead minnows and water fleas 50 percent reduction in equipment and electrical energy costs realized through H_2O_2 addition	Treatment cost: $18/m^3 Matrix direct cost: $7.60/m^3	Topudurti and others 1998
VOCs (Pilot Scale)						
UV/H_2O_2	Benzene: 35 μg/L	Flow rate: 3.2 m^3/min Light source: 360-kW reactor Wavelength: broad band with a peak at 254 nm H_2O_2 dose: not available Influent pH: 6.8	98	Effluent pH adjusted with sodium hydroxide	Not available	Oldencrantz and others 1997
Solar/TiO$_2$	TCE: 100 mg/L	Flow rate: 15 Umin Light source: solar (>300 nm) TiO$_2$ dose: 800 to 900 mg/L Influent pH: 5.6 and 7.2 Retention time: 10 minutes	TCE: 99 at pH 5.6; 91 at pH 7.2	None	For 380-m^3/day System $0.83/m^3	Mehosand Turchi 1993
Solar/TiO$_2$/H_2O_2	Total BTEX: 2 mg/L	Flow rate: 38 m^3/day Reactor volume: 530 L Light source: not available Wavelength: 380 nm TiO$_2$ dose: 0.5 to 1 .0 mg/L H_2O_2 dose: 100 mg/L Influent pH: 4-5 Retention time: 3 hours	50 to 75	None	$20 to $29/m^3 (including capital and O&M costs)	Turchi and others 1993

Table 3-1. Contaminated Groundwater Treatment (Continued)

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional Information		
SVOCs (Commercial Scale)						
UV/H_2O_2 (Calgon perox-pure™)	PCP: 15 mg/L	Flow rate: 260 Umin Reactor volume: not available Light source: 180-kW system Wavelength: not available H_2O_2 dose: 150 mg/L Influent pH: 5 Retention time: not available	99.3	None	For a 260-L/min System O&M cost: \$1.20/m^3 (including electricity, chemical, and general maintenance costs)	U.S. EPA 1993
UV/H_2O_2 (Calgon Rayox®)	PAH: l-2 mg/L Phenol: 2 mg/L	Flow rate: 380 Umin Reactor volume: not available Light source: not available Wavelength: not available H_2O_2 dose: not available	PAH: >99.9 Phenol: 799.9	None	Not available	Cater and others 1990
UV/H_2O_2 (Calgon Rayox®)	NDMA: 20 µg/L	Flow rate: 2,300 Umin Reactor volume: not available Light source: proprietary UV lamps H_2O_2 dose: not available	799.9	None	For a 2,300-L/min System Operating cost: \$0.10/m^3	Calgon 1996
Photo-Fenton (Calgon Rayox® ENOX)	PCP: 1,000 µg/L	Flow rate: 450 L/min Reactor volume: not available Light source: 60-kW system Wavelength: not available H_2O_2 dose: not available ENOX catalyst dose: not available	Flow stream to be reinjected: 90 Flow stream to be discharged: 99	None	Operating cost: \$0.36/m^3	Calgon 1996
Pesticides and Herbicides (Pilot Scale)						
UV/O_3	Pesticides: 10; 100; 1,000 mg/L (alachlor; atrazine; Bentazon; butylate; Cyanazine; 2,4-D; metolachlor; metribuzin; trifluraline; carbofuran; malathion)	Flow rate: 8-40 Umin Light source: 66 UV lamps: 450 W Wavelength: 254 nm 0, dose: not available Influent pH: not available Retention time: 20 to 60 min	Pesticides with initial concentrations of 10 to 100 mg/L: >99.9 Pesticides with initial concentrations of 1,000 mg/L: 75 to 85	None	Not available	Keamey and others 1987
Explosives and Their Degradation Products (Commercial Scale)						
UV/H_2O_2 Calgon perox-pure™)	Thiodiglycol: 480 µg/L 1,4-Dithiane: 200 µg/L 1,4-Oxathiane: 82 µg/L Benzathiazole: 20 µg/L 1,3,5-TNB: 15 µg/L	Flow rate: 60 Umin Reactor volume: 300 L Light source: four 15-kW mercury lamps Wavelength: not available H_2O_2 doses: 45, 90, and 180 mg/L Retention time: 5.3 min	Thiodiglycol: >97 1,4-Dithiane: >98 1,4-Oxathiane: >97 Benzathiazole: >82 1,3,5-TNB: 96	Vendor: Calgon perox-pure ™ Site: Old O-Field Site Aberdeen Proving Ground, Maryland	Not available	Topudurti and others 1993

Table 3-1. Contaminated Groundwater Treatment (Continued)

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional Information		
Explosives and Their Degradation Products (Commercial Scale) (Continued)						
UV/H_2O_2 (Calgon perox-pure™)	RDX: 28 μg/L	Flow rate: 310 Umin Reactoivolume: not available Light source: six 5-kW lamps UV dose: 0.53 kWh/m^3 Wavelength: not available H_2O_2 dose: 10 mg/L pH = 7.0	>82	Former Nebraska Ordnance Plant. NE	For a 29,000 L/min System $0.02/$m^3$ (induding power, lamp replacement, H_2O_2, and general maintenance)	Calgon 1998
UV/H_2O_2 (Calgon Rayox®)	NG: 1,000 mg/L NQ: 2,700 mg/L	Flow rate: not available (batch) Reactor volume: not available UV dose: 450 kWh/m^3 Wavelength: not available H_2O_2 dose: not available	799.9	By-products NG: 1,2-DNG; 1,3-DNG; MNG; nitrogen; nitrate; nitrite; ammonia NQ: nitrate, nitrite, and ammonia	NG: $13/$m^3$ NQ: $34/$m^3$	Hempfling 1997

3.2 Industrial Wastewater Treatment

The effectiveness of APO technologies in treating industrial wastewater has been evaluated for various contaminant groups, including VOCs, SVOCs, dyes, inorganics, and microbes. This section discusses the APO technology effectiveness with regard to each of these contaminant groups.

3.2.1 VOC-Contaminated Industrial Wastewater

This section discusses treatment of VOCs in industrial wastewater using the UV/H_2O_2 and photo-Fenton processes on a commercial scale. Information on VOC-contaminated industrial wastewater treatment using the UV/H_2O_2 and semiconductor-sensitized processes at the bench-scale level is also included.

Commercial-Scale Applications

This section summarizes the effectiveness of the Calgon perox-pure™ UV/H_2O_2 and Calgon Rayox® photo-Fenton (ENOX) treatment systems in removing the following VOCs from industrial wastewater.

APO Process	VOCs Removed
• UV/H_2O_2	• Acetone, isopropyl alcohol
• Photo-Fenton	• Various solvents (individual VOCs not measured)

Calgon perox-pure™ UV/H_2O_2 System

In 1992, a Calgon perox-pure™ UV/H_2O_2 system was installed at the Kennedy Space Center in Florida to treat industrial wastewater. The primary contaminants in the wastewater included acetone (20 mg/L) and isopropyl alcohol (20 mg/L). A 10-kW Calgon perox-pure™ system initially treated 19,000- to 23,000-L batches of contaminated water at the site. The system was subsequently converted to a flow-through mode and was operated at a flow rate of 19 L/min and with an H_2O_2 dose of 100 mg/L. The system achieved >97.5 percent removal for acetone and isopropyl alcohol, meeting the treatment facility discharge requirement. The total estimated O&M cost reported by the vendor was at $\$1.10/m^3$ of water treated, which includes the costs of electricity ($\$0.61/m^3$), H_2O_2 ($\$0.18/m^3$), and general maintenance ($\$0.31/m^3$) (U.S. EPA 1993).

Calgon Rayox® Photo-Fenton (ENOX) System

The Calgon Rayox® photo-Fenton (ENOX) system was used to treat wastewater from a liquid crystal display equipment manufacturing plant in Puerto Rico. The wastewater contained various solvents used to clean electronic components; no information on the specific chemicals and their concentrations was available. The wastewater COD level was 3,000 mg/L; its pH level was 11.1; and its alkalinity level was 1,100 mg/L as calcium carbonate. A 30-kW Rayox® photo-Fenton system was used to treat the wastewater. At a UV dose of 160 kWh/m^3, the COD level was reduced to <50 mg/L, a >98.4 percent removal. The total operating cost of the treatment system was $\$44/m^3$ of water treated, which includes the costs of electricity, lamp replacement, H_2O_2, ENOX catalyst, and pH adjustment (Calgon 1998).

Bench-Scale Studies

This section summarizes the results of bench-scale studies of the effectiveness of UV/H_2O_2 and semiconductor-sensitized processes in removing the following VOCs from industrial wastewater.

APO Process	VOCs Removed
* UV/H_2O_2	• Various chlorinated VOCs (individual VOCs not measured)
• Solar/TiO_2; Solar/ZnO	• Chloroform, dimethylamine, methanol

UV/H_2O_2

Smeds and others (1994) evaluated the effectiveness 'of the UV/H_2O_2 process in treating spent chlorination wastewater from a kraft pulp mill. The wastewater contained various chlorinated organics and was characterized by measuring AOX (1,300 g per ton of pulp processed). The highest AOX removal (86 percent) was achieved at a temperature of 100 °C over a pH range of 2 to 12; pH had no significant effect on AOX removal;

Semiconductor-Sensitized Processes

Peyton and DeBerry (1981) evaluated the effectiveness of semiconductor-sensitized processes (solar/TiO_2 and solar/ZnO) in treating wastewater contaminated with dimethylamine, methanol, and chloroform. At the end of a 6-hour reaction period, multiple combinations of semiconductors and reaction pH levels yielded various percent removals for the three VOCs: (1) TiO_2 at a pH of 10 reduced the dimethylamine concentration by 55 percent, (2) TiO_2 at a pH of 7 reduced the methanol concentration by 51 percent, and (3) ZnO at a pH of 7 reduced the chloroform concentration by 50 percent.

3.2.2 SVOC-Contaminated Industrial Wastewater

This section discusses treatment of SVOCs in industrial wastewater using the UV/H_2O_2 process on a commercial scale. Information on SVOC removal (1) at the pilot-scale level using the photo-Fenton process and (2) at the bench-scale level using the UV/O_3, photo-Fenton, and semiconductor-sensitized processes is also included.

Commercial-Scale Applications

This section summarizes the effectiveness of the Calgon Rayox® and Magnum CAV-OX® UV/H_2O_2 systems in removing the following SVOCs from industrial wastewater.

APO Process	SVOCs Removed
• UV/H_2O_2	• NDMA, phenol, UDMH

Calgon Rayox® UV/H_2O_2 System

A Calgon Rayox® UV/H_2O_2 system was used to treat NDMA-contaminated wastewater from a rubber manufacturing company. The initial NDMA concentration in the wastewater was 30 μg/L. The Calgon Rayox® system, which was operated at a flow rate of 45 L/min, reduced the NDMA concentration in the wastewater by more than 98.3 percent. The treatment cost was estimated to be $0.83/m^3 of water treated, but details of this estimate were unavailable (Calgon 1996).

In another Calgon Rayox® UV/H_2O_2 system application, NDMA-contaminated process wastewater from a specialty chemicals manufacturing company was treated using a 380-L/min system. The wastewater contained 600 μg/L of NDMA and 1,000 mg/L of COD. The system achieved >99.9 percent removal of NDMA; no information was available on COD removal. The treatment cost was estimated to be $1 .10/m^3 of water treated, but details of this estimate were unavailable (Calgon 1996).

Aerospace industry wastewater contaminated with NDMA and unsymmetrical dimethylhydrazine (UDMH) at 1,400 and 6,000 mg/L, respectively, was treated using a Calgon Rayox® UV/H_2O_2 system. The system treated about 1,500 Uday of wastewater (in batch mode) and removed more than 99.9 percent of the NDMA from the wastewater. The treatment cost was estimated to be $1 50/m^3 of water treated, but details of this estimate were unavailable (Calgon 1996).

Magnum CAV-OX® UV/H_2O_2 System

The Magnum CAV-OX® II high-energy UV/H_2O_2 system was field-tested to treat effluent from a pharmaceutical plant. The wastewater contained phenol at 20 μg/L. Three tests were conducted at flow rates of 7.6, 15, and 23 L/min. H_2O_2 was used at a dose of 60 mg/L. At flow rates of 7.6, 15, and 23 L/min, the percent removal of phenol was >99.9, 99, and 96 percent, respectively. No treatment cost information was available (U.S. EPA 1994).

Pilot-Scale Application

This section summarizes removal of 3,4-xylidine from industrial wastewater at the pilot-scale level using the photo-Fenton process. Wastewater containing 3,4-xylidine at an initial concentration of 2,700 mg/L was treated using the photo-Fenton process in a recirculating batch reactor. A total of 500 L of wastewater was treated in each batch. With a UV dose of 20 W/L, an H_2O_2 dose of 4,200 mg/L, a ferrous sulfate dose of 3,000 mg/L, and a pH of 3, more than 99.9 percent of the 3,4-xylidine had been removed after 30 minutes of treatment. The H_2O_2 concentration had less effect than the ferrous sulfate concentration on 3,4-xylidine removal (Oliveros and others 1997).

Bench-Scale Studies

This section summarizes the results of bench-scale studies of the effectiveness of UV/O_3, photo-Fenton, and semiconductor-sensitized processes in removing the following SVOCs from industrial wastewater.

APO Process	SVOCs Removed
- UV/O_3	- 4-CP, phenol, several reactive azo dyes, several unspecified svocs
- Photo-Fenton	- 4-CP, several reactive azo dyes
- Solar/ZnO	- Phenol

UV/O_3

Beltran and others (1997a, 1997b) evaluated the UV/O_3 process's effectiveness in treating distillery and tomato processing plant wastewaters containing phenols and other chemicals. The UV/O_3 process achieved 90 percent COD removal from tomato processing plant wastewater compared to 30 to 50 percent using ozonation alone. The UV/O_3 process also achieved the highest COD removal for distillery wastewater; the percent removal was not reported. For both wastewaters, the UV/O_3 process was found to be significantly more effective than UV photolysis and UV/H_2O_2 processes.

Photo-Fenton

Industrial dye wastewater containing 4-CP and a mixture of reactive azo dyes was used to compare the effectiveness of UV/O_3, UV/H_2O_2, UV/TiO_2, and photo-Fenton processes. Under laboratory conditions, 4-CP had been degraded by 75 percent after 90 minutes of wastewater treatment in the photo-Fenton process; this process was also found to be the most effective mineralizing 4-CP (Ruppert and others 1994).

Chen and others (1997) evaluated various APO processes, including the UV/H_2O_2 and photo-Fenton processes, for phenol and COD removal from industrial wastewaters. They concluded that the photo-Fenton process achieved the highest phenol and COD removal rates of the processes evaluated. Phenol at an initial concentration of 25 mg/L was reduced by more than 99.9 percent in 10 minutes under the following test conditions: a UV-A light intensity of 4 kilowatts per liter; H_2O_2 dose of 70 mg/L; and ferric chloride dose of 8.1 mg/L. No details on COD removal were available.

Semiconductor-Sensitized Processes

Peyton and DeBerry (1981) evaluated the effectiveness of semiconductor-sensitized processes (solar/TiO_2 and solar/ZnO) in treating wastewater contaminated with phenol. At the end of a 6-hour reaction period, the highest phenol removal (53 percent) was achieved using ZnO at a pH of 7.

3.2.3 Dye-Contaminated Industrial Wastewater

Dyes have been removed from industrial wastewater using UV/H_2O_2, UV/O_3, and semiconductor-sensitized processes. This section describes the use of these processes in pilot-scale applications and bench-scale studies.

Pilot-Scale Applications

This section summarizes the removal of the following dyes from industrial wastewater at the pilot-scale level using the UV/H_2O_2 process.

APO Process	Dyes Removed
- UV/H_2O_2	- Reactive Blue 21, Reactive Red 195, unspecified

A pilot-scale UV/H_2O_2 system was installed at a pulp and paper mill in South Carolina to remove colored organics from industrial wastewater. The wastewater also contained chlorinated organics; the specific chemicals and their concentrations are unknown. A UV dose of 80 milliwatts per square centimeter-second (mW/cm^2-sec) was maintained. An 80 percent color removal was achieved at an H_2O_2 dose of 840 mg/L and a flow rate of 190 L/min. In general, increasing H_2O_2 concentration resulted in an increase in color removal. Color reduction was not influenced by pH, indicating that the bleaching operation wastewater did not have to be pretreated for pH adjustment. Specific treatment cost estimates were not available (Smith and Frailey 1990).

Also on the pilot scale, the UV/H_2O_2 process was applied to spent reactive dyebath wastewater containing Reactive Blue 21 and Reactive Red 195 at initial concentrations of 300 and 20 mg/L, respectively. The highest removals were achieved at H_2O_2 doses of 3,000 and 1,000 mg/L for Reactive Blue 21 and Reactive Red 195, respectively. The UV/H_2O_2 process was 'most effective with a neutral pH. Specific percent removals were not available (Namboodri and Walsh 1996).

Bench-Scale Studies

This section summarizes information on removal of the following dyes from actual and simulated industrial wastewaters at the bench-scale level using

UV/H_2O_2, UV/O_3, and semiconductor-sensitized processes.

APO Process	Dyes Removed
• UV/H_2O_2	• Acid Black 1, Reactive Black 5, Reactive Orange 16, Vat Blue 6, Vat Red 10
• UV/O_3	• Several unspecified dyes
• UV/TiO_2	• Acid Blue 40, Basic Yellow 15, Direct Blue 87, Direct Blue 160, Reaction Red 120, several unspecified dyes
• $UV/TiO_2/SnO_2$	• Acid Orange 7

UV/H_2O_2

Shu and others (1994) evaluated the effect of pH on UV/H_2O_2 process effectiveness in treating synthetic wastewater containing azo dyes; they used Acid Black 1 as the model compound. Optimum degradation was observed in the pH range of 3.0 to 5.2. Other information, such as percent removal data, was unavailable.

Unkroth and others (1997) used an excimer laser as an alternative to mercury lamps in treating commercial coloring agents for linen. The laser was used to irradiate four dyes-Reactive Orange 16, Reactive Black 5, Vat Red 10, and Vat Blue 6-at UV wavelengths of 193 nm (argon-fluorine) and 248 nm (krypton-fluorine). Greater decolorization was achieved at the shorter wavelength. When laser irradiation at 193 nm was coupled with use of H_2O_2, almost complete oxidation of the dyes was achieved with 2 to 7 times less energy. Vat dyes, which need about 10 times higher energy doses for removal than do reactive dyes, were reduced from 25 mg/L to about 2 mg/L, a 92 percent removal. Irradiation with mercury lamps heated the wastewater to 60 °C, while laser irradiation did not alter the wastewater's temperature.

UV/O_3

Biologically pretreated paper mill wastewater containing 70 to 600 mg/L of COD as a result of dye processes was treated using the UV/O_3 process. Reaction by-products formed include sulfuric acid and oxalic acid. High temperatures (40 °C) and high pH values (9 and above) resulted in high O_3 consumption. A temperature increase from 25 to 40 °C and variations in pH levels did not significantly affect the process's effectiveness. The estimated UV/O_3 treatment cost, based on biologically pretreated effluent with 400 mg/L of COD and 80 percent COD removal, was \$2.38/m^3 of water treated, which includes electricity, capital, and maintenance costs (Oeller and others 1997).

Semiconductor-Sensitized Processes

Li and Zhang (1996) evaluated the effectiveness of the UV/TiO_2 process in treating synthetic wastewater containing eight dyes at an initial concentration of 100 mg/L each. Under a black light in a batch reactor and with a TiO_2 dose of 1,000 mg/L, color removal was >95 percent after 4 to 6 hours of treatment. COD and TOC removals from the wastewater ranged from 30 to 70 percent, depending on the dyes present. Biochemical oxygen demand (BOD) increased as COD and TOC decreased, suggesting that UV/TiO_2 photooxidation may enhance the biodegradability of the wastewater and may require postbiological treatment.

Tang and An (1995a, 1995b) studied UV/TiO_2 treatment of synthetic wastewater containing five commercial dyes: Acid Blue 40, Basic Yellow 15, Direct Blue 87, Direct Blue 160, and Reaction Red 120. The initial concentration of each dye was about 100 mg/L. More than 5 hours was required to completely mineralize the dyes. At higher dye concentrations, reaction rates and percent removals were lower. The oxidation rate decreased as the number of azo linkages in a dye molecule increased.

A UV/TiO_2 process was used in batch studies to remove COD in and decolorize the wastewater from 5-fluorouracil manufacturing. Complete decolorization and significant COD removal were achieved in 20 hours of reaction time. Addition of H_2O_2 to the UV/TiO_2 system significantly increased the decolorization and COD removal rates. Diluting the wastewater also increased the COD removal rate. Direct photolysis resulted in no COD reduction but did achieve color reduction (Anheden and others 1996).

Textile dye effluent containing Acid Orange 7 was treated using UV/TiO_2/tin oxide (SnO_2) process. At an initial concentration of 42 mg/L, the dye was degraded by 95 percent after irradiation for. 30 minutes. The optimum mass ratio of the two semiconductors for fastest degradation of Acid Orange 7 was 2:1, SnO_2 to TiO_2 (Vinodgopal and Kamat 1995).

3.2.4 Inorganic-Contaminated Industrial Wastewater

This section presents information on the following inorganics removal from industrial wastewater at the bench-scale level using semiconductor-sensitized processes. No commercial- or pilot-scale information is available.

APO Process	Inorganics Removed
- Solar/TiO_2	- Free and complexed cyanide, hexacyanate
- UV/TiO_2	- Ferricyanide

Rader and others (1993) achieved >99.9 percent cyanide removal in 11 days while using a solar/TiO_2 process to treat hexacyanate solution. In a later study, Rader and others (1995) were able to achieve >99.9 percent free and complex cyanide removal from precious metal mill effluent containing cyanide at 48 mg/L in 3 days. In both cases, nitrate formation was observed, indicating complete oxidation of cyanide.

Aqueous ferricyanide solution (26 mg/L as cyanide) was treated using TiO_2 and a 4-W UV lamp or solar radiation in a bench-scale study. The highest removal rate was observed at a pH of 10. Photodegradation of ferricyanide using a 4-W UV lamp resulted in 93 percent degradation after 9 hours, while with solar radiation, more than 99.9 percent of the ferricyanide was removed in 1.5 hours (Bhakta and others 1992).

3.2.5 Microbe-Contaminated industrial Wastewater

This section discusses removal of microbes (Salmonella) from industrial wastewater at the commercial-scale level using a Magnum CAV-OX® UV/H_2O_2 system. No' pilot- or bench-scale information was available.

The Magnum CAV-OX® UV/H_2O_2 system was evaluated during treatment of pathogens in wastewater associated with chicken farming. The primary contaminant of concern in the wastewater was the bacterium Salmonella. The concentration of this bacterium in the influent was about 1 million colony-forming units per milliliter (cfu/mL). Tests were conducted at Perdue Farms in Bridgewater, Virginia, using a CAV-OX® I low-energy unit and a CAV-OX® II high-energy unit. The wastewater was processed through the CAV-OX® units at a flow rate of 3.8 L/min. The CAV-OX® I unit was operated with six 60-W UV lamps, and the CAV-0X® II unit was operated with two UV lamps of 2.5 to 5-kW intensity. The H_2O_2 dose was 80 mg/L. Under these conditions, the CAV-OX® II unit performed much better than the CAV-OX® I unit. The final concentration of *Salmonella* exiting the CAV-OX® II unit was 0.01 cfu/mL (>99.9 percent removal). No cost information was provided (U.S. EPA 1994).

Table 3-2. Industrial Wastewater Treatment

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional information		
VOCs (Commercial Scale)						
UV/H_2O_2 (Calgon perox-pure™)	Acetone: 20 mg/L Isopropyl alcohol: 20 mg/L	Flow rate: 19 Umin Light source: 10-kW Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 100 mg/L	Acetone: >97.5 sopropyl alcohol: >97.5	Treatment of Kennedy Space Center wastewater	\$1.10/m³ (including electricity, H_2O_2, and maintenance costs)	I.S. EPA 1993
Photo-Fenton (Calgon Rayox® ENOX)	COD: 3,000 mg/L Individual VOC concentrations unknown	Flow rate: batch/recycle Reactor volume: not available UV dose: 160 kWh/m³ Wavelength: not available H_2O_2 dose: not available Influent pH: 11.1 Alkalinity: 1,100 mg/L as calcium carbonate	>98.4	Treatment of electronics industry wastewater Met COD regulatory limit	\$44/m³ (including electricity, lamp replacement, H_2O_2, ENOX catalyst, and pH adjustment costs)	algon 1998
SVOCs (Commercial Scale)						
UV/H_2O_2 (Calgon Rayox®)	NDMA: 30 µg/L	Flow rate: 45 Umin Reactor volume: not available Light source: proprietary UV lamps Wavelenath: not available H_2O_2 dose: not available	>98.3	Treatment of rubber manufacturing industry wastewater	\$0.83/m³	Calgon 1996
UV/H_2O_2 (Calgon Rayox®)	NDMA: 600 µg/L COD: 1,000 mg/L	Flow rate: 380 L/min Reactor volume: not available Light source: proprietary UV lamps Wavelength: not available H_2O_2 dose: not available	NDMA: >99.9 COD: not available	Treatment of specialty chemical industry wastewater	\$1.10/m³	Calgon 1996
UV/H_2O_2 (Calgon Rayox®)	NDMA: 1,400 mg/L UDMH: 6,000 mg/L	Flow rate: not applicable (batch) Reactor volume: not available Light source: proprietary UV lamps Wavelength: not available H_2O_2 dose: not available	NDMA: >99.9 JDMH: not available	Treatment of aerospace industry wastewater	\$150/m³	Calgon 1996
UV/H_2O_2 (Magnum CAV-OX® II)	Phenol: 20 µg/L	Flow rate: 7.6 L/min Reactor volume: not available Light source: 2 UV lamps of 2.5 to 5-kW intensity Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 60 mg/L	>99.9	Treatment of pharmaceutical industry wastewater	Not available	J.S. EPA 1994

Table 3-2. Industrial Wastewater Treatment (Continued)

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional Information		
SVOCs (Pilot Scale)						
Photo-Fenton	**3,4-Xylidine:** 2,700 mg/L	Flow rate: not applicable (recirculating batch) Reactor volume: 500 L Reaction time: 30 minutes Wavelength: not available UV dose: 20 W/L H_2O_2 dose: 4,200 mg/L Ferrous sulfate dose: 3,000 mg/L Influent pH: 3	>99.9	Not available	Not available	Oliveros and o[illegible]ers 1997
Dyes (Pilot Scal						
UV/H_2O_2	Colored and chlorinated organics: not available	Flow rate: 190 Umin Reactor volume: not available Light source: two Teflon-based UV lamps Wavelength: 254 nm UV dose: 80 mW/cm^2-sec H_2O_2 dose: 840 mg/L Influent pH: 10-11	Color: 80 Chlorinated organics: not available	None	Not available	Smith and Frailey 1990
Microbes (Comn ercial Scale)						
UV/H_2O_2 (Magnum CAV-OX® II)	*Salmonella:* 1 million cfu/mL	Flow rate: 3.8 L/min Reactor volume: not available Light source: 2 UV lamps of 2.5- to 5-kW intensity Wavelength: broad band with a peak at 254 nm H_2O_2 dose: 80 mg/L	>99.9	Treatment of poultry industry wastewater	Not available	U.S. EPA 1994

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Section 4
Contaminated Air Treatment

APO has been demonstrated to be an effective technology for treatment of contaminated air. Matrices to which APO has been applied include the following: (1) soil vapor extraction (SVE) off-gas, (2) air stripper off-gas, (3) industrial emissions, and (4) automobile emissions. Collectively, APO has been applied to the following types of airborne contaminants: VOCs, SVOCs, explosives and their degradation products, and nitrogen oxides (NO,).

To assist an environmental practitioner in the selection of an APO technology to treat contaminated air, this section includes (1) commercial-scale system evaluation results for the UV/O_3, UV/catalyst, and UV/TiO_2 processes and (2) pilot-scale system evaluation results for the UV/TiO_2, solar/TiO_2, and UV/O_3 processes. This section also presents supplemental information from bench-scale studies of APO processes.

As described in Section 1.2, this handbook organizes the performance and cost data for each matrix by contaminant group, scale of application (commercial, pilot, or bench), and APO system or process used. In general, commercial- and pilot-scale applications are discussed in detail. Such discussions include, as available, a system description, operating conditions, performance data, and system costs. Bench-scale studies of APO processes are described in less detail and only if they provide information that supplements commercial- and pilot-scale evaluation results. At the end of each matrix section, a table is provided that summarizes operating conditions and performance results for each commercial- and pilot-scale study discussed'in the text.

4.1 SVE Off-Gas Treatment

APO has been shown to be an effective treatment technology for VOC-contaminated off-gas from SVE systems. Treatment systems based on UV/O_3, UV/catalyst, and UV/TiO_2 processes have been developed at the commercial scale. A treatment system based on the UV/TiO_2 process has been demonstrated at the pilot-scale level. Bench-scale studies of the VUV, UV/O_3, and UV/TiO_2 processes also have been performed. Commercial- and pilot-scale VOC treatment system performance and cost data, where available, are provided below. Summaries of the bench-scale studies follow the commercial- and pilot-scale system discussions.

Commercial-Scale Applications

Treatment of VOC-contaminated SVE off-gas using APO has been demonstrated at the commercial scale at a wide range of concentrations (1 to 4,000 ppmv). This section discusses the effectiveness of the PTI UV/O_3, KSE AIR UV/catalyst, and Matrix UV/TiO_2 treatment systems in removing the following VOCs from SVE off-gas.

APO Process	VOCs Removed
• UV/O_3	. cis-1,2-DCE; PCE; TCE; toluene; total VOCs
·UV/Catalyst	. Carbon tetrachloride, methane, PCE, TCE, toluene, trimethylbenzene, xylene
· UV/TiO_2	• PCE; 1,1,1-TCA; TCE

In application of these systems, removals exceeding 90 percent for TCE; PCE; 1,1,1-TCA; and toluene have been achieved. Removals of cis-1,2-DCE and methane have not met with the same success. As discussed below, VOC removal is a function of the system used as well as the contaminant type and concentration. Of the three systems that have been demonstrated, cost data was available only for PTI's UV/O_3 system.

PTI UV/O_3 System

A PTI UV/O_3 system was field-tested using VOC-contaminated off-gas drawn from an SVE system at Site 9 of Naval Air Station North Island in San Diego County, California (PTI 1998). Feed gas for the PTI system was supplied by a slipstream of off-gas from the SVE system. Before entering the PTI system, the SVE off-gas passed through an air-water separator to remove any free moisture. Make-up air was also used to vary the flow and concentration of contaminants.

The primary contaminants in the SVE off-gas at Site 9 included PCE; TCE; cis-1,2-DCE; and toluene. Total VOCs entering the PTI system ranged in concentration from 1,000 to 1,100 ppmv as carbon. The primary VOCs in the feed gas were as follows: PCE (31 ppmv); TCE (28 ppmv); cis-1,2-DCE (22 ppmv); and toluene (14 ppmv). For the test, the

PTI system operated at steady state for about 18 days, during which time the system achieved 89 percent on-line availability. The maximum flow rate treated was 12 scmm.

During the field test, the average removal for total VOCs was 95.9 percent. Average removals for primary VOCs were as follows: 89.7 percent for PCE; 80.8 percent for TCE; 74.0 percent for cis-1,2-DCE; and 93.1 percent for toluene. Reaction by-products analyzed for during the test included hydrochloric acid (HCI), chlorine, phosgene, and carbon monoxide (CO). HCI, chlorine, and phosgene were measured at the PTI system outlet at 0.18, 0.04, and 11 parts per billion by volume (ppbv), respectively. The amount of CO produced in the PTI system was determined to be between 31 and 56 ppmv.

Although PTI did not report treatment costs for the system demonstrated, it used results from the test to scale up costs for an 85-scmm system; 85 scmm was the flow capacity of the SVE system at Site 9. PTI's estimated equipment and operating cost at the site was $3.80/pound of VOC treated, assuming (1) use of an 85-scmm system; (2) treatment of 95,000 pounds of VOCs per year for 3 years; and (3) 95 percent removal of the VOCs treated.

KSE *AIR UV/Catalyst Sysfem*

The KSE AIR UV/catalyst system was demonstrated using VOC-contaminated off-gas from an SVE system at Loring Air Force Base in Aroostook County, Maine (Kittrell and others 1996a). This demonstration was conducted in coordination with the U.S. EPA SITE Emerging Technology Program. KSE's AIR system contains KSE's proprietary catalyst and 60 UV lamps. Information on the composition of the catalyst and the wavelength of the UV lamps was not available.

The primary contaminants in the SVE off-gas included PCE and methane. Over a 30-day period of system evaluation, PCE concentrations in the SVE off-gas varied significantly, diminishing from 150 ppmv during the first few days to <1 ppmv at the end of the demonstration. Methane concentrations ranged from 2,000 to 4,000 ppmv throughout the demonstration. Additional VOCs identified at low levels <1 ppmv in the off-gas included toluene, xylene, TCE, trimethylbenzene, and carbon tetrachloride. The flow rates treated ranged from 1.4 to 2.0 scmm.

For most of the demonstration, the KSE system achieved >99 percent removal of PCE, while methane removal was minimal. KSE attributed the minimal methane removal to the catalyst composition, which had been selected for PCE removal.

Matrix UV/TiO$_2$ System

The Matrix UV/TiO$_2$ system was field-tested using VOC-contaminated off-gas drawn from an SVE system located at the U.S. Department of Energy Savannah River Superfund site in Aiken, South Carolina (Anonymous 1995). The Matrix system consisted of a fluorescent lamp (with UV output of 300 to 400 nm) encased by a fiberglass mesh sleeve coated with TiO$_2$ catalyst. Before entering the system, SVE off-gas passed through a cyclone separator . and filter to remove moisture and particulates, respectively.

The primary contaminants in the SVE off-gas at the site included TCE; PCE; and 1 ,1 ,l-TCA. TCE and PCE concentrations in the SVE off-gas ranged from 110 to 190 ppmv and 700 to 1,200 ppmv, respectively. The feed stream concentration of 1 ,1,1-TCA was not reported. The flow rates treated for the test ranged from 0.0028 to 2.8 scmm; however, performance data is available for only three flow rates: 0.71, 1.4, and 2.1 scmm.

VOC removals varied widely during the test period. For instance, TCE removal varied from 49.5 to 98.1 percent. The highest TCE removal (98.1 percent) was achieved when. the feed stream TCE concentration was 160 ppmv and the flow rate was 0.71 scmm. Similarly, PCE removals varied widely,. ranging from 52.7 to 95.2 percent. The highest PCE removal (95.2 percent) was achieved when the feed stream PCE concentration was 1,200 ppmv and the flow rate was 0.71 scmm. The Matrix system did not remove 1 ,1,1 -TCA.

Small quantities of carbon tetrachloride, chloroform, dichloroacetyl chloride (DCAC), hexachloroethane, methylchloroformate, pentachloroethane, and trichloroacetyl chloride were identified as reaction by-products. The chemical-specific concentrations were not available.

Pilot-Scale Application

A pilot-scale UV/TiO$_2$ system developed by researchers at the University of Wisconsin in Madison was field-tested using VOC-contaminated off-gas drawn from an SVE extraction well in the M area of the Savannah River site in Aiken, South Carolina (Read and others 1996). The UV/TiO$_2$ system consisted of two photoreactor flow cells (each 9.2 x 10^{-4} m^3) packed with TiO_2 catalyst. Positioned in the middle of each flow cell was a long-wave, 40-W fluorescent UV black light lamp. The UV output was not reported.

The primary contaminants in the SVE off-gas included TCE (56 to 290 ppmv) and PCE (2,300 to 3,860 ppmv). Additional VOCs present at lower levels were 1,1,I-TCA (up to 38 ppmv) and 1,1-DCE (up to 150 ppmv). System performance was also evaluated using diluted VOC concentrations. Dilution of the SVE off-gas was achieved by adding ambient air to the feed stream upstream from the UV/TiO_2 system. Dilution resulted in the following chemical-specific feed stream concentrations: <80 ppmv for TCE; <800 ppmv for PCE; below detection limit (1 ppmv) for 1,1,1-TCA and 1,1-DCE. During 8 days of system operation, system temperature ranged from 75 to 110 °C, and the flow rate ranged from 5.0 x 10^{-4} to 6.0 x 10^{-3} scmm. 0, was added to the system at 5.0 x 10^{-4} scmm near the end of the field test to evaluate its effect on system performance.

Under both undiluted and diluted feed stream conditions, removals exceeding 97 percent were observed for TCE; PCE; 1,1,1-TCA; and 1,1-DCE. Treatment of the undiluted off-gas, however, yielded significantly more reaction by-products. The reaction by-products identified included phosgene, chloroform, carbon tetrachloride, pentachloroethane, and hexachloroethane. After the feed stream was diluted with ambient air to reduce the total VOC concentration to below 1,000 ppmv, reaction by-products identified under undiluted conditions, except for hexachloroethane, were reduced to below 1 ppmv; hexachloroethane was detected at concentrations of <10 ppmv. The highest VOC removals occurred when supplemental 0, was added to the system. Specifically, TCE and PCE removals exceeded 99.9 percent when their concentrations in the feed stream were 66 and 502 ppmv, respectively. The concentrations of all reaction by-products previously identified, including hexachloroethane, were reduced ‘to <1 ppmv. However, according to Read and others (1996), addition of 0, would not be cost effective for a full-scale system.

Bench-Scale Studies

The treatment of VOCs using VUV, UV/O_3, and UV/TiO_2 processes has been evaluated at the bench-scale level using synthetic matrices. Many bench-scale studies have been conducted to evaluate the effect of several key UV/TiO_2 process variables. In contrast, the VUV and UV/O_3 processes have received much less attention despite bench-scale results indicating that these processes provide effective treatment of certain types of contaminants. This section provides information that supplements commercial- and pilot-scale evaluation results for removing the following VOCs from contaminated air matrices including SVE off-gas,.

APO Process	VOCs Removed
• ❖◆❖	• Carbon tetrachloride, chloroform, trichlorofluoroethane
• UV/O_3	• Carbon tetrachloride; chloroform; PCE; 1,1,1-TCA; TCE
• UV/TiO_2	• Acetic acid, acetyl aldehyde; acetone; benzene; 1-butanol; butylraldehyde; ethanol; formaldehyde; formic acid; methyl mercaptan; PCE; 2-propanol; 1,1,1-TCA; TCE; toluene; xylenes

VUV Photolysis

Treatment of three halogenated methanes (carbon tetrachloride, chloroform, and trichlorofluoroethane [CFC-113]) was studied by Loraine and Glaze (1992) using a VUV system. For this study, VUV conditions were established using a xenon-xenon excimer lamp with a maximum UV output at 172 nm. The study showed that carbon tetrachloride and chloroform were removed by a pseudo-first-order process, while CFC-113 was removed by a zero-order process. Removals of 95 percent were achieved for all three VOCs using the following run times: 25 minutes for carbon tetrachloride, 16 minutes for chloroform, and 238 minutes for CFC-113. The initial VOC concentrations and reaction by-products were not reported.

UV/O_3

The removal kinetics of three saturated VOCs (carbon tetrachloride; 1,1,1-TCA; and chloroform) and two unsaturated VOCs (TCE and PCE) using the UV/O_3 process were studied by Bhowmick and Semmens (1994). For this study, two UV lamps were used: one UV lamp with its predominant output at 254 nm and with a small output at 185 nm (about 5 percent), and one UV lamp with output only at 254 nm. For the saturated VOCs, the study showed that removal rates were higher for the lamp with output at 254 and 185 nm and that the rates were unaffected by addition of 0,. The removal rates were also higher for unsaturated VOCs using the lamp with output at 245 and 185 nm; however, addition of 0, improved the removal rates for TCE and PCE up to 30 and 12 percent, respectively. 0, was most effective for removing the unsaturated compounds at concentrations between 2 and 3 mg/L. Removals of both the unsaturated and saturated VOCs followed first-order kinetics, and the rate constants were an order of magnitude higher for the unsaturated VOCs than for the saturated VOCs. In addition, moisture was found to favor the chloroform; 1,1,1-TCA; and TCE removal kinetics but had no impact on the PCE and carbon tetrachloride removal kinetics. Phosgene was identified as a reaction by-product.

UV/TiO$_2$

Treatment of VOCs using the UV/TiO$_2$ process at the bench-scale level has received significant attention. Bench-scale studies of interest have focused on evaluating the effects of the following key process variables: supplemental oxidants (0,, O_3, and H_2O_2), water vapor, co-catalysts, reaction pressure, and co-contaminants. Additional bench-scale UV/TiO$_2$ studies have evaluated removal of high-level VOC concentrations and formation of reaction by-products. Summaries of these bench-scale UV/TiO$_2$ studies are provided below. Some of the studies evaluated more than one process variable; such studies are described with emphasis on the process variable for which supplemental information is called for herein.

Effect of Supplemental Oxidants

Several bench-scale studies have demonstrated that oxidants such as O_2, O_3, and H_2O_2 can enhance VOC removals by the UV/TiO$_2$ processes. For instance, Wang and Marinas (1993) evaluated the effect of adding 0, on removal of TCE by the UV/TiO$_2$ process. This study was conducted with reactor inlet TCE and 0, concentrations ranging from 5 to 7 ppmv and 24 to 2,700 ppmv, respectively, and in the absence of humidity. The study showed that TCE removals increased from 30 to 88 percent with increasing 0, concentrations up to 500 ppmv. At higher 0, concentrations, TCE removal remained relatively constant, ranging from 86 to 91 percent.

Similarly, supplemental 0, and H_2O_2 were shown to enhance removal of VOCs (2-propanol, benzene, toluene, xylene, and ethanol) by the UV/TiO$_2$ process (Nimlos and others 1995). In this study, removal of 2-propanol increased from 39 percent without 0, to >99.7 percent with supplemental 0,. When subjected to a mixture of benzene, toluene, and xylene, the TiO$_2$ catalyst was deactivated: however, once 0, was added, removals of 79, 95, and >99.7 percent were achieved for benzene, toluene, and xylene, respectively. The individual effects of supplemental 0, and H_2O_2 on removal of ethanol by the UV/TiO$_2$ process were also evaluated. The study showed that ethanol removal increased by more than an order of magnitude (to >90 percent removal) after individual additions of 0, and H_2O_2. Information on the initial VOC concentrations and on the concentrations of 0, and H_2O_2 additions was not clearly provided.

Effect of Water Vapor

Based on studies conducted at the bench-scale level, water vapor appears to have differing effects on removal of VOCs by the UV/TiO$_2$ processes. In general, the effects appear to depend on the water vapor concentration as well as the type and concentration of the target VOC. For instance, Anderson and others (1993) observed that the presence of water vapor in the reactant gas stream decreased the initial reaction rates of TCE (specific values were not reported) below the rates observed under water-free conditions; however, water vapor was required to maintain photocatalytic activity for extended periods. For the water-free reactant stream, the TCE reaction rate decreased by 50 percent after 2 hours of irradiation. The decrease in photocatalytic activity was attributed to fewer OH• in a water-free environment to adsorb on the surface of the TiO$_2$ catalyst, as OH• is the primary oxidant for photochemical oxidation of TCE. The reaction rate of TCE was independent of water vapor over the water vapor/TCE mole ratio of 4.2 x 10^{-4} to 0.027. Raupp and others (1994) also observed that the presence of water vapor in reactant gas streams decreased the initial reaction rates of TCA, benzene, and acetone below the rates observed under water-free conditions; however, water was required to maintain photocatalytic activity for extended periods.

The effect of water vapor on removal of TCE at various concentrations by a UV/TiO$_2$ process was evaluated by Berman and Dong (1994). The study showed that when the initial TCE concentration was 800 ppmv, TCE removal exceeded 99.9 percent as water vapor concentrations increased up to 50,000 ppmv; however, when the initial TCE concentration was 4,500 ppmv, TCE removal decreased from about 98 to 87 percent as water vapor concentrations increased over the same range. The negative effect of water vapor on TCE removal was attributed to competition between TCE and water vapor for sites on the TiO_2 catalyst.

Peral and Ollis (1992) observed that the effect of water vapor on removal of VOCs (acetone, 1-butanol, butyraldehyde; and m-xylene) using the UV/TiO_2 process also depends on the type of chemical being treated. For acetone at an initial concentration of about 84 ppmv, the study showed that water vapor inhibits acetone removal. Specifically, the removal rate for acetone decreased from about 1 to 0.16 μg/cm^2-min as the water vapor concentration was increased from about 40 to 14,000 ppmv. In contrast, the removal rate for m-xylene was found to increase from about 0.12 to 0.20 μg/cm^2-min as the water vapor concentration increased from 0 to about 1,400 ppmv. At higher water vapor concentrations (7,500 ppmv) the removal rate decreased, reaching about 0.07 μg/cm^2-min. Variations in water vapor concentration were shown to have no significant effect on the removal rates of I-butanol and butyraldehyde. The initial concentrations for m-xylene, 1-butanol, and butyraldehyde were not clearly reported.

Effect of Co-Cat&.&

The effect of co-catalysts and various fluorescent light sources on VOC removal by the UV/TiO_2 process was investigated by Watanabe and others (1993). For this study, the individual effects of various metals, including copper (II), Fe(II), platinum (II), strontium (II), cobalt (II), nickel (II), and palladium (II), coated on a TiO_2 catalyst at 0.1 to 1 molar percent were evaluated with regard to methyl mercaptan removal under various fluorescent light sources. Under black light conditions, addition of platinum (II), strontium (II), cobalt (II), nickel (II), or palladium (II) as a co-catalyst was demonstrated to diminish removal of methyl mercaptan, while addition of copper (II) and Fe(II) enhanced removal. The highest methyl mercaptan removal was achieved after addition of copper (II). The study also showed that the percent removal of methyl mercaptan in the absence of light, under pink light, and under regular fluorescent light was an order of magnitude lower than under black light. Under black light conditions, removal of methyl mercaptan was shown to increase from about 15 percent without a co-catalyst to about 90 percent with addition of copper (II) as a co-catalyst at 1.0 molar percent.

Effect of Reaction Pressure

The effect of reducing reaction pressure on TCE removal in a UV/TiO_2 system was evaluated by Annapragada and others (1997). The initial concentrations of TCE and water vapor were adjusted for reaction pressure changes such that their initial concentrations under standard conditions were the same in all experiments. For example, 7.2 micromoles per liter (μmol/L) of TCE and 1,400 μmol/L of water vapor at 21.5 pounds per square inch absolute pressure (psia) are equivalent to 1.6 μmol/L of TCE and 320 μmol/L of water vapor at 4.9 psia; both conditions would correspond to 4.9 μmol/L of TCE and 980 μmol/L of water vapor under standard conditions. The study showed that as reaction pressure was reduced from 21.5 to 4.9 psia, TCE removal increased from 59 to 85 percent. The increase in TCE removal was attributed to reduced competition between TCE and water vapor for adsorption sites on the TiO_2 catalyst. At reduced pressure, the amount of water vapor that condenses is less, resulting in relatively more adsorption sites for TCE.

Competitive Effect of Co-Contaminants

The single-contaminant and multiple-contaminant kinetics of TCE and toluene were studied using the UV/TiO_2 process by Luo and Ollis (1996). In a gas stream containing TCE at concentrations up to 140 ppmv, >99.9 percent TCE removal was achieved. In a gas stream containing toluene, 20 to 8 percent removals were achieved for concentrations ranging from about 20 to 140 ppmv, respectively. Study of TCE and toluene mixtures revealed a strong promotion-inhibition behavior in which TCE enhances toluene removal and toluene reduces TCE removal. When the TCE concentration was 140 ppmv and the toluene concentration was below 26 ppmv, almost complete removal was achieved for both toluene and TCE. When the toluene concentration was increased to levels above 42 ppmv, TCE was hardly removed, and toluene removal exhibited only a slight increase. When the TCE concentration was decreased to 42 ppmv, toluene and TCE removals both dropped significantly (to >60 percent).

Removal of High-Level VOC Concentrations

Several bench-scale studies indicate that the ability to remove VOCs using the UV/TiO_2 process depends strongly on the type and concentration of the compound being treated. For example, Al-Ekabi and others (1993) observed chemical- and concentration-dependent effects on photochemical oxidation of high-level TCE and PCE concentrations. The study showed >99 percent removal of TCE for initial TCE concentrations ranging from 7,400 to 11,000 ppmv. TCE removal decreased and varied from 92 to 94 percent for initial TCE concentrations ranging from 17,000 to 23,000 ppmv. Similarly, >99 percent removal of PCE was observed for an initial PCE concentration of 3,100 ppmv, but for initial PCE concentrations ranging from 4,600 to 9,200 ppmv, PCE removal was reduced and varied from 93 to 96 percent. In addition, Holden and others (1993) observed that benzene removal increased from 10 to 73 percent in a UV/TiO_2 system after the initial concentration of benzene was reduced from 140,000 to 2,200 ppmv.

Reaction By-Product Formation

A quantitative and qualitative evaluation of TCE reaction by-products in a UV/TiO_2 system as a function of flow rate (retention time) was conducted by Holden and others (1993). For this study, the reaction by-products from complete removal of TCE, which was present at an initial concentration of 24,500 ppmv, were evaluated after the flow rates through the reactor were set at 1×10^{-4}, 5×10^{-5}, 2.5×10^{-5}, and 1.0×10^{-5} scmm. For each of the flow rates evaluated, the following by-products were identified in varying distributions: DCAC, phosgene, carbon dioxide, chlorine, CO, HCl, and oxides of chlorine. The study showed that as the flow rates decreased (1.0 × 10” to 2.5×10^{-5} scmm), phosgene concentrations increased and DCAC concentrations decreased, indicating that DCAC was being converted to phosgene. When the flow rate was further decreased from 2.5×10^{-5} to 1.0×10^{-5} scmm, DCAC was completely removed, and the phosgene concentration was relatively lower. Collectively, this change in distribution suggests that DCAC is the primary reaction by-product of TCE photochemical oxidation. This change also suggests that at sufficiently low flow rates, both DCAC and phosgene may not be present as final by-products of TCE photochemical oxidation.

Reaction by-products formed during ethanol removal were studied by Nimlos and others (1996) using the UV/TiO_2 process. The study revealed that removals exceeding 99 percent could be achieved for ethanol concentrations ranging from 40 to 200 ppmv. Acetyl aldehyde, formaldehyde, and carbon dioxide were identified as the primary reaction by-products; acetic acid, formic acid, ethyl acetate, methyl formate, ethyl formate, and methyl acetate were identified at lower concentrations. To better examine the kinetics of ethanol, the study also evaluated (in individual tests) by-product formation from UV/TiO_2 photolysis of acetyl aldehyde, formaldehyde, acetic acid, and formic acid. For acetyl. aldehyde concentrations ranging from 50 to 200 ppmv, >99 percent removal was achieved; identified by-products included formaldehyde, acetic acid, and methyl formate. Removal of formaldehyde concentrations ranging from 80 to 400 ppmv exceeded 80 percent; formic acid, methyl formate, and methanol were identified as reaction by-products. Acetic acid removal exceeded 99 percent for concentrations ranging from 80 to 180 ppmv; reaction by-products included primarily formaldehyde. Carbon dioxide was identified as the reaction by-product of formic acid.

Table 4-1. SVE Off-Gas Treatment

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional Information		
VOCs (Commercial Scale)						
UV/O_3 (PTI)	Total VOCs: 1,000 to 1.100 ppmv as carbon PCE: 31 ppmv TCE: 28 ppmv cis-1,2-DCE: 22 ppmv Toiuene: 14 ppmv	Flow rate: 12 scmm Reactor volume: not available Light source: low-pressure UV lamps with output at 185 to 254 nm	Total VOCs: 95.9 PCE: 89.7 TCE: 80.8 cis-1,2-DCE: 74.0 Toluene: 93.1	Reaction By-products HCl: 0.18 ppbv Chlorine: 0.04 ppbv Phosgene: 1 1 ppbv CO: 31 to 56 ppmv	For an 85-scmm System $3.80/pound of VOCs treated	PTI 1998
UV/Catalyst (KSE AIR)	PCE: 150 to 1 ppmv Methane: 2,000 to 4,000 ppmv	Flow rate: 1.4 to 2.0 scmm Reactor volume: not available Light source: 60 UV lights; intensity and wavelength not available	PCE: >99 Methane: minimal	Not available	Not available	Kittrell and others 1996a
UV/TiO_2 [Matrix]	PCE: 1,200 ppmv TCE: 160 ppmv 1,1,1-TCA: not available	Flow rate: 0.71 scmm Reactor volume: not available Light source: one fluorescent lamp with UV output at 300 to 400 nm	PCE: 95.2 TCE: 98.1 1,1,1-TCA: not removed	Reaction By-products Carbon tetrachioride Chloroform DCAC Hexachioroethane Methylchloroformate Pentachloroethane Trichioroacetyl chloride	Not available	Anonymous 1995
VOCs (Pilot Scale)						
UV/TiO_2	TCE: 66 ppmv PCE: 502 ppmv 1,1-DCE: below detection limit 1.1,1-TCA: below detection limit	Flow rate: 5.0 x 10^{-4} scmm Reactor volume: two 9 2 x 10^{-4} m^3 flow cells Light source: two 40-W fluorescent UV black light lamps Temperature: 100 °C O_2 addition: 5.0 x 10^{-4} scmm	TCE: >99.9 PCE: >99.9 1,1-DCE: not available 1,1,1-TCA: not available	Reaction By-products Phosgene: <1 ppmv Chloroform: <1 ppmv Carbon tetrachlortde: <1 ppmv Pentachioroethane: <1 ppmv Hexachloroethane: <1 ppmv	None	Read and others 1996

4.2 Air Stripper Off-Gas Treatment

APO has been shown to be an effective treatment technology for air stripper off-gas contaminated with low-level VOC concentrations. At the commercial scale, KSE's AIR UV/catalyst system has achieved nearly 99 percent removal of low-level 1,2-DCA concentrations. At the pilot-scale level, a UV/TiO_2 system achieved 93 percent removal of low-level ethanol concentrations. Cost information was not available for either of these two systems. Bench-scale studies of VOC removal using the UV/TiO_2 process are described in Section 4.1. The commercial- and pilot-scale systems that have been used to treat VOCs in air stripper off-gas are described below.

Commercial-Scale Application

This section discusses the effectiveness of the KSE AIR UV/catalyst commercial-scale treatment system in removing VOCs from air stripper off-gas. The KSE system was demonstrated using air stripper off-gas contaminated -with low-level 1,2-DCA concentrations at Dover Air Force Base in Delaware (Kittrell and Quinlan 1995a). KSE's system consisted of a single vessel containing a proprietary catalyst and varying numbers of black light UV lamps (the system had a 60-lamp capacity). The composition of the catalyst and the wavelength and intensity output of the UV bulbs were not reported. The system received contaminated air via a slipstream directly from the combined effluent of two air stripping towers without further treatment.

During the 1 O-week period of system operation, the inlet air stream was saturated with water vapor and contained 1,2-DCA concentrations ranging from 0.9 to 3 ppmv. The flow rate through the reactor ranged from 1.4 to 1.7 scmm and averaged 1.2 scmm. During the initial stages of the demonstration when 30 of the 60 black light UV lamps were illuminated, 1,2-DCA removal averaged 96 percent. By illuminating additional lamps in the later stages of the demonstration, KSE was able to increase 1,2-DCA removal; specifically, when seven and later eight more lamps were illuminated, 1,2-DCA removal averaged >96 percent and about 99 percent, respectively. Reaction by-products were not analyzed for during the demonstration.

Pilot-Scale Application

This section discusses the effectiveness of a pilot-scale UV/TiO_2 system in removing VOCs from air stripper off-gas. A pilot-scale UV/TiO_2 system was field-tested by National Renewable Energy Laboratory (NREL) researchers using ethanol-contaminated off-gas from an air stripper at the Coors Brewery in Golden, Colorado (Nimlos and others 1995). The waste treatment areas at the facility contained several holding pits that held beer-laden wastewater prior to biological treatment. The UV/TiO_2 system was tested using a sidestream of off-gas from a blower assembly that had been installed to strip ethanol from one of the pits. The system, a recirculating batch reactor, consisted of a series of three 8-inch Pyrex tubes coated on the inside with TiO_2 and illuminated with four banks of black lights with their UV output at 360 nm (the intensity was not reported),

For this study, which was conducted over 2 days, the inlet off-gas was saturated with water vapor (to achieve 100 percent relative humidity) and contained initial concentrations of ethanol ranging from 6.4 to 40 ppmv. Ethanol removal over this concentration range varied from about 78 to 93 percent. The highest ethanol removal (93 percent) was observed at an initial concentration of 15 ppmv and with a retention time of 0.4 second.

Table **4-2.** Air Stripper Off-Gas Treatment

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	‘TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional Information		
VOCs (Commercial Scale)						
UV/Catalyst (KSE AIR)	1 **,2-DCA:** 0.9 to 3 ppmv	Flow rate: 1.4 to 1.7 **scmm** Reactor volume: not available Light source: about 45 UV black light lamps; intensity not available Water vapor: 100 percent relative humidity	About 99	Not available	Not available	Kittrell and Quinlan 1995a
VOCs (Pilot Scale)						
UV/TiO_2	**Ethanol:** 15 ppmv	Flow rate: not available (recirculating batch) Reactor volume: three **8-inch** Pyrex tubes Light source: four banks of UV lamps with UV output at 360 nm; intensity not available Water vapor: 100 percent relative humidity Retention time: 0.4 second	**About** 93	**Not** available	Not available	Nimlos and others 1995

4.3 Industrial Emissions Treatment

Although only a limited number of applications have been developed, APO has been shown to be an effective treatment technology for VOCs, SVOCs, and explosives in industrial emissions. At the commercial-scale level, APO systems based on UV/catalyst and UV/TiO_2 processes have been developed for treatment of VOCs and explosives and their degradation products, respectively. Pilot-scale systems for treatment of VOCs using the solar/TiO_2 process and SVOCs using the UV/O_3 process have been demonstrated. Bench-scale studies of VOC removal using UV/TiO_2 and UV/O_3 processes are described in Section 4.1. In addition to performance data, system cost information is available for commercial-scale systems designed to treat VOCs and explosives. The commercial- and pilot-scale systems available to treat industrial emissions are described below.

4.3. 1 VOC-Confaining Indusfrial Emissions

This section discusses removal of VOCs in industrial emissions using the UV/catalyst process at the commercial scale. Additional information on VOC removal using the solar/TiO_2 process at the pilot-scale level is also included.

Commercial-Scale Applications

This section discusses the effectiveness of the KSE AIR UV/catalyst treatment system in removing the following VOCs from industrial emissions.

APO Process	VOCs Removed
• UV/Catalyst	• Aliphatic hydrocarbon, pentane

KSE's AIR system was demonstrated using high-level VOC (aliphatic hydrocarbon) concentrations in emissions from the Chering-Plough Corporation contact lens manufacturing facility in Cidro, Puerto Rico (Kittrell and others 1996b). The source of the VOCs was an aliphatic hydrocarbon (Shell Sol B HT) solvent used in the lens vats within the facility. KSE's AIR system contains a proprietary catalyst and UV lamps. The number of lamps and their wavelength and intensity were not reported. The system received contaminated air from exhaust hoods that drew solvent vapor emissions from the surface of the vats.

Over the 2-week demonstration period, the system achieved high removals (>99 percent) for feed stream total VOC concentrations ranging from 1,900 to 2,000 ppmv. The flow rate through the system ranged from 0.3 to 0.8 scmm and corresponded to retention times <1 second. The highest VOC removal was achieved with an initial feed stream total VOC concentration of 2,000 ppmv and a flow rate of 0.3 scmm. Using gas chromatography, KSE observed that no reaction by-products were formed during the demonstration. Compound-specific detectors were used to monitor for CO, formaldehyde, and acetaldehyde, and none of the compounds was detected.

KSE's estimated capital cost for a 1.8-scmm system with a percent removal >99 percent was $53,320. Monthly energy and annual maintenance costs for the system at the Chering-Plough Corporation facility were estimated at <$376 and $1,672, respectively.

KSE's AIR UV/catalyst system was also demonstrated using pentane emissions from an expandable polystyrene plant (Kittrell and others 1996b). During this demonstration, high pentane removals (99.2 to 99.9 percent) were achieved for feed stream pentane concentrations ranging from 340 to 3,600 ppmv at 20 percent relative humidity. The rate of flow through the system ranged from 0.3 to 0.9 scmm and corresponded to retention times <1 second. The demonstration showed that relative humidity, which varied from 20 to 100 percent, had no impact on system performance. Specifically, when KSE increased the relative humidity to 100 percent, pentane removal exceeded 99.9 percent with an initial pentane concentration of 2,100 ppmv and a system flow rate of 0.8 scmm. Using gas chromatography, KSE observed that no reaction by-products were formed during the demonstration. Compound-specific detectors were used to monitor for CO, formaldehyde, and acetaldehyde, and none of the compounds was detected.

Based on the demonstration, KSE's estimated capital cost for a 4.4-scmm system with pentane removal >99 percent was $183,000. Annual operating costs were estimated at $7,800.

Pilot-Scale Application

This section discusses the effectiveness of a pilot-scale solar/TiO_2 system in treating VOC-contaminated industrial emissions. A pilot-scale system was field-tested by NREL researchers using VOC-laden paint booth emissions at E/M Corporation's North Hollywood painting plant (Nimlos and others 1995). VOCs identified-in the emissions included ethanol, toluene, and methyl ethyl ketone. The system used for the study was a modified version of the recirculating batch reactor used by NREL for treating air stripper off-gas contaminated with ethanol (see Section 4.2, Pilot-Scale Application). Specifically, the system was modified to use sunlight as the UV light source, and supplemental 0, was added to the feed gas at concentrations ranging from 500 to 2,600 ppmv. The study showed that 99 percent removal of total VOCs ranging in concentration from 250 to 350 ppmv was achieved in 3 to 4 seconds when the concentration of 0, exceeded 1,000 ppmv.

4.3.2 SVOC-Containing Industrial Emissions

This section discusses the effectiveness of a pilot-scale UV/O_3 system in treating SVOC-contaminated industrial emissions. A pilot-scale UV/O_3 system was field-tested using chlorophenol emissions from a plant making selective weed killers (Barker and Jones 1988). The system (a gas scrubber) consisted of a 150-L spray section and a 15-L sump section. Located in the sump were I I I S-W low-pressure mercury lamps supplying 1 I W/L. The UV output of the low-pressure mercury lamps was not reported. 0, was supplied to the sump section by an 0, generator. The sump liquor was maintained at a pH of 5 to 6 and a temperature of 40 to 50 "C. The feed gas was supplied to the interface of the sump and spray sections at a flow rate of either I .2 or 2.0 scmm.

The demonstration showed that UV light had very little effect on removal of chlorophenol. In the presence of UV light and O_3, whose concentration varied from IO to 30 g/m^3, removals exceeding 99 percent were achieved for chlorophenol concentrations ranging from I to 130 ppmv. The highest chlorophenol removal (>99.9 percent) was achieved when the inlet chlorophenol and 0, concentrations were 34 ppmv and 30 g/m^3, respectively. Chlorophenol removals in the absence of UV light still exceeded 99 percent for inlet concentrations ranging from 3 to 5 ppmv and with 0, concentrations ranging from 10 to 30 g/m^3. Based on TOC analyses, however, the study revealed that the combination of UV light and 0, was important for removing compounds other than chlorophenol in the feed stream.

4.3.3 Explosive- and Degrada tidn Product-Containing Industrial Emissions

This section discusses the effectiveness of the Zentox UV/TiO_2 commercial-scale treatment system in removing NG from industrial emissions. Zentox's system was demonstrated using NG-containing emissions from a propellant annealing oven at the U.S. Naval Surface Warfare Center, Indian Head Division Extrusion Plant (Turchi and Miller 1998). Stack gas from the heating process was drawn from the oven stack to the Zentox system.

Days I and 2 of the 4-day demonstration were used to (I) determine whether addition of supplemental 0, improves NG removal and (2) evaluate the relative advantages of germicidal lamps (50 W with UV output at 254 nm) and black light lamps (64 W with UV output at 350 nm). Results indicated that 0, addition at 45 to 120 ppmv in combination with either germicidal or black light lamps was required to achieve rapid oxidation of NG to NO,. Black lights, however, were found to perform better in converting NG to nitrogen dioxide. Use of the germicidal lamps resulted in formation of an organic film on the lamps because of direct photolysis of higher molecular weight compounds present in the feed gas. Based primarily on these results, black lights and supplemental 0, were selected for subsequent tests under steady-state conditions during days 3 and 4.

Results from days 3 and 4 demonstrate that the Zentox system is capable of achieving high (>97 percent) NG removals. On day 3, the system was operated with 28 lamps, four catalyst banks, and a flow rate of 1.4 scmm. 0, concentrations in the feed gas were maintained at 140 ppmv, and inlet NG concentrations ranged from 1.6 to 2.1 ppmv. Under these conditions, NG removal exceeded 97 percent. The highest removal (99.2 percent) was observed when the initial NG concentration was I .7 ppmv. The target removals for the demonstration were 80 to 85 percent, so Zentox increased the loading rate on day 4 by increasing the flow through the reactor to 2.1 scmm, reducing the number of catalyst banks by half, and reducing the number of UV lamps to 17. 0, concentrations in the feed gas were maintained at 45 ppmv, and inlet NG concentrations ranged from 1.7 to 3.3 ppmv. Under these conditions, NG removal exceeded 80 percent. On both days 3 and 4, NO, was observed as a reaction by-product at concentrations <25 ppmv.

Zentox's estimated capital costs for a 650-scmm full-scale system with an NG percent removal >97 percent range from $175,000 to $260,000. Estimated capital costs for the same size system with an NG percent removal >80 percent range from $100,000 to $150,000. Operating costs were not reported. According to Zentox, the capital costs are expected to be lower once more field tests have been conducted to identify the optimum 0, feed concentration and catalyst formation.

Table 4-3. Industrial Emissions Treatment

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional Information		
/OCs (Commercial Scale)						
JV/Catalyst KSE AIR)	Total VOCs: 2,000 ppmv	Flow rate: 0.3 scmm Reactor volume: not available Light source: UV lamps (wavelength and intensity not available) Retention time: <1 second	>99	Treatment of emissions from a contact lens manufacturing plant Reaction by-products not detected	For a 1.8-scmm System with >99 Percent Removal Capital cost: $53.320 Energy cost: $376/month Maintenance cost: $1,672/year	Kittrell and others 1996b
	Pentane: 2,100 ppmv	Flow rate: 0.8 scmm Reactor volume: not available Light source: UV lamps (wavelength and intensity not available) Retention time: <1 second Relative humidity: 100 percent	>99.9	Treatment of emissions from an expandable polystyrene plant Reaction by-products not detected	For a 4.4-v >99 Percent Removal Capital: $183,000 Annual operating: $7,800	Kittrell and others 1996b
'OCs (Pilot Scale)						
olar/TiO_2	Total VOCs (ethanol, toluene, and methyl ethyl ketone): 250 to 350 ppmv	Flow rate: not available (recirculating **batch)** Reactor volume: three 8-inch Pyrex tubes Light source: sunlight 0, addition: >1 ,000 ppmv Retention time: 3 to 4 seconds	99	Treatment of paint booth emissions	Not available	Nimlos **and** other: 1995
VOCs (Pilot Scale)						
IV/O_3	Chlorophenol: 34 ppmv	Flow rate: 1.2 or 2.0 scmm Reactor volume: not available Spray section: 150 L Sump section: 15 L Light source: 11 15-W low-pressure mercury lamps 0, addition: 30 g/m^3 pH: 5 to 6 Temperature: 40 to 50 °C	>99.9	Treatment of emissions from a chemical weed killer manufacturer	Not available	Barker and Jones 1988
xplosives and Their Degradation Products (Commercial Scale)						
$V/TiO_2/O_3$ 'entox)	NG: 1.70 ppmv	Flow rate: 1.4 scmm Reactor volume: not available Light source: 28 64-W black lights with output at 350 nm Temperature: ambient 0, addition: 140 ppmv	99.2	Treatment of NG emissions from an annealing oven Reaction By-product NO,: <25 ppmv	Capital Cost for a 650-scmm System with >97 Percent Removal $175,000 **to $260,000**	Turchi and Miller 1998

Water and *Air.* Cincinnati, Ohio. October 26 through 29, 1996.

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Watanabe, T., A. Kitamura, E. Kojima, C. Nakayama, K. Hashimoto, and A. Fujishima. 1993. "Photocatalytic Activity of TiO_2 Thin Film under Room Light." *Photocatalytic Purification and Treatment of Wafer and Air.* Edited by D.F. Ollis and H. Al-Ekabi. Elsevier Science Publishers B.V. Amsterdam. Pages 747 through 751.

Section 5
Contaminated Solids Treatment

APO has been demonstrated to be an effective technology for treating contaminated solids, primarily at the bench-scale level. Most evaluations involved generation of a leachate or slurry by washing the contaminated solids with water, surfactant solution, or an organic solvent and then applying an APO process to treat the contaminated leachate or slurry in a manner similar to contaminated water treatment. Use of an APO process to treat contaminated slurry may require frequent APO system maintenance because solids in the slurry will coat the light source and inhibit transmission of light.

Solid matrices to which APO has been applied include the following: (1) contaminated soil, (2) contaminated sediment, and (3) contaminated ash. Collectively, APO has been applied to the following types of contaminants: (1) svocs, (2) PCBs, (3) pesticides and herbicides, and (4) dioxins and furans. One commercial-scale application of an APO process (Calgon perox-pure™ UV/H_2O_2) for treating contaminated solids is reported in the literature. This section describes the commercial-scale application of this process and several bench-scale evaluations of APO processes for treating contaminated solids. A table summarizing operating conditions and performance results for the commercial-scale Calgon perox-pure™ UV/H_2O_2 system is included this section.

5.1 Contaminated Soil Treatment

The effectiveness of APO technologies in treating contaminated soil has been evaluated for various contaminant groups, including SVOCs, PCBs, pesticides and herbicides, and dioxins and furans. This section discusses APO treatment technology effectiveness with regard to each of these contaminant groups.

5.7.7 SVOC-Contamina ted Soil

SVOCs in soil have been treated using sensitized photochemical processes at the bench-scale level. The effectiveness of these processes in removing the following SVOCs from contaminated soil is described below.

APO Process	SVOCs Removed
· Photo sensitization	• Anthracene, biphenyl, 9H-carbazole, m-cresol, fluorene, PCP, phenanthrene, pyrene, quinoline
· UV/TiO_2	• Acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, 2-CP, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, pyrene

Dupont and others (1990) evaluated the effectiveness of various sensitizers (methylene blue, riboflavin, peat moss, diethylamine, and anthracene) under UV or visible light in removing SVOCs from contaminated slurries at the bench-scale level. The study also evaluated the effectiveness of the UV/H_2O_2 process in decontaminating the slurries. Three types of soil (silty clay, sandy loam, and silty loam) were spiked with several SVOCs, including anthracene, biphenyl, 9H-carbazole, m-cresol, fluorene, PCP, phenanthrene, pyrene, and quinoline, at 500 milligrams per gram each. Soil slurries were generated by mixing the contaminated soils with methylene chloride and water. Anthracene was found to be the most effective sensitizer; other APO processes did not show a statistically significant improvement over direct photolysis. On the contrary, diethylamine inhibited photodegradation of other SVOCs. The study concluded that soil type is a significant factor in photodegradation of compounds, indicating the need for site-specific assessments of soil-phase photodegradation.

In another bench-scale study, Ireland and others (1995) evaluated the effectiveness of the UV/TiO_2 process in decontaminating soil slurries containing 16 PAHs, including fluoranthene, pyrene, benzo(a)-anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a)pyrene. Soil contaminated with motor oil (1) was spiked with the PAHs at concentrations ranging from 1.6 to 6.4 milligrams per kilogram, (2) extracted using triethylamine, and (3) slurried using water. The concentrations of PAHs in the slurry varied from 580 to 660 mg/L. Two 15-W bulbs providing light with wavelengths from 300 to 400 nm were placed 1 cm from a 40-milliliter slurry aliquot. Within 24 hours of irradiation, all PAHs except chrysene and pyrene were degraded by more than 85 percent; chrysene and pyrene were degraded by 33 and 66 percent, respectively.

Pelizzetti and others (1992) evaluated the effectiveness of UV/TiO_2 process in treating soil slurries contaminated with 2-CP at 20 mg/L. At a colloidal TiO_2 dose of 500 mg/L and after 60 minutes of UV irradiation, about 95 percent of the 2-CP was removed.

5.1.2 PCB-Contaminated Soil

PCBs in contaminated soil have been treated using the photo-Fenton process at the bench-scale level. McLaughlin and others (1993) investigated the effect of temperature on removal of PCBs in diatomaceous earth slurries using the photo-Fenton process. PCB congener (2,2',5-trichlorobiphenyl and 2,2',4,5,5'-pentachlorobiphenyl) removals were studied at two temperatures (27 and 60 “C). At an H_2O_2 dose of 0.8 mg/L, an Fe(II) dose of 2 mg/L, and a pH of 3, and in 5 hours of reaction time, the investigators observed (1) 2,2',5-trichlorobiphenyl removals of 84 and 96 percent at 27 and 60 °C, respectively; and (2) 2,2',4,5,5'-pentachlorobiphenyl removals of 80 and 85 percent at 27 and 60 °C, respectively. They concluded that the rate of the PCB removal is a function of PCB concentration in solution and the number of chlorine atoms in the PCB (the removal rate decreases with an increasing number of chlorine atoms).

5.7.3 Pesticide- and Herbicide-Contaminated Soil

This section discusses treatment of the following pesticides and herbicides in soil using (1) the UV/H_2O_2 process on a commercial-scale level and (2) the UV/TiO_2 process at the bench-scale level,

APO Process	**Pesticides and Herbicides Removed**
• UV/H_2O_2	• Disulfoton, oxadixyl, parathion, propetamphos, thiometon
• UV/TiO_2	• Atrazine

A 180-kW Calgon perox-pure™ UV/H_2O_2 system was used to treat soil contaminated with disulfoton, thiometon, parathion, propetamphos, and oxadixyl. The influent to the perox-pure™ system, which was generated by an on-site soil washing system, primarily contained 0.49, 1.1, and 3.9 mg/L of disulfoton, thiometon, and oxadixyl, respectively. Parathion and propetamphos were present in the influent at relatively low levels (0.8 mg/L or less). The perox-pure™ system was operated at flow rates ranging from 6 to 20 m^3/h (corresponding to retention times of 12 to 3 minutes), an H_2O_2 dose of 50 mg/L, and a pH of 7. A sand filter was used to remove suspended solids from the influent to the perox-pure™ system. The system achieved removals of up to 99.5 percent. However, suspended solids that were not captured by the filter caused frequent scaling of UV lamps, which resulted in frequent shutdown of the system (Egli and others 1994).

At the bench-scale level, atrazine was found to be effectively removed in soil slurries (about 2 percent solids) using the UV/TiO_2 process. In soil slurries containing 20 mg/L of atrazine, at a colloidal TiO_2 dose of 500 mg/L, and after 60 minutes of UV irradiation, atrazine removal of about 95 percent was achieved (Pelizzetti and others 1992).

5.1.4 Dioxin- and Furan-Contaminated Soil

Dioxins and furans in soil have been treated using UV/TiO_2 and UV/anthracene processes at the bench-scale level. The effectiveness of these processes in removing the following dioxins and furans from contaminated soil is described below.

APO Process	**Dioxins and Furans Removed**
• UV/TiO_2	• 2,7-Dichlorodibenzodioxin
• UV/ Anthracene	• Dibenzofuran

Pelizzetti and others (1992) evaluated the effectiveness of the UV/TiO_2 process in degrading 2,7-dichlorodibenzodioxin in soil slurries (about 2 percent solids) at the bench-scale level. At an initial concentration of 10 mg/L and a TiO_2 dose of 500 mg/L, about 90 percent of the 2,7-dichlorodibenzodioxin was removed in about 15 hours of UV irradiation.

In another bench-scale study, Dupont and others (1990) found that dibenzofuran could be removed from soil slurries using UV irradiation and anthracene, a sensitizer. In this process, the half-life of dibenzofuran was estimated to be about 80 days. More information on use of sensitizers is included in Section 5.1 .1.

Table 5-1. Contaminated Soil Treatment

PROCESS (SYSTEM)	CONTAMINANT CONCENTRATION	TEST CONDITIONS	RESULTS		COST (1998 U.S. Dollars)	REFERENCE
			Percent Removal	Additional Information		
Pesticides and Herbicides (Commercial Scale)						
UV/H_2O_2 (Calgon perox-pure™)	Disulfoton: 0.49 mg/L Thiometon: 1.1 mg/L Oxadixyl: 3.9 mg/L	Reactor volume: 1 m^3 Flow rate: 6 to 20 m^3/h Light source: high-pressure mercury vapor lamps (180 kW) Wavelength: not available H_2O_2 dose: 50 mg/L Reaction time: 3 to 12 min pH: 7	Disulfoton: 97.9 Thiometon: 99.1 Oxadixyl: 99.5	Suspended solids in influent coated the UV lamps, causing frequent system shutdown	Not available	Egli and others 1994

5.2 Contaminated Sediment Treatment

Limited information is available on the effectiveness of APO in treating contaminated sediment. No commercial- or pilot-scale results were available. This section describes the effectiveness of a UV/TiO_2 process in treating PCB-contaminated sediment at the bench-scale level.

Chiarenzelli and others (1995) evaluated the effectiveness of the UV/TiO_2 process in decontaminating sediment collected from a shallow embayment of the St. Lawrence River near Massena, New York. The sediment was contaminated with PCBs at concentrations of 27 to 38 milligrams per kilogram. The UV/TiO_2 process achieved about 88 percent PCB removal when the contaminated sediment slurry was irradiated for about 48 hours using UV-A light in the presence of TiO_2.

5.3 Contaminated Ash Treatment

Limited information is available on the effectiveness of APO in treating contaminated ash. No commercial- or pilot-scale results were available. This section describes the effectiveness of a UV/TiO_2 process in treating PCB-contaminated ash at the bench-scale level.

Chiarenzelli and others (1995) evaluated the effectiveness of the UV/TiO_2 process in decontaminating a slurry consisting of furnace ash, core sands, and slag from an aluminum foundry. The initial concentration of PCBs in the slurry was about 220 mg/L. Only 45 percent PCB removal was observed when the slurry was irradiated for about 24 hours using UV-A light in the presence of TiO_2. However, 88 percent removal was achieved when UV-C light was used instead of UV-A light. The inability of UV-A irradiation to achieve high removals suggests that the $solar/TiO_2$ process may not be an effective alternative to the UV/TiO_2 process for treating some wastes, particularly ash to which PCBs are strongly bound.

5.4 References

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APPENDIX

TECHNOLOGY VENDOR CONTACT INFORMATION

Vendor’	Contact Person	Address	Phone No.
Calgon Carbon Oxidation Technologies	Robert Abernethy	130 Royal Crest Court Markham, ON L3R 0A1 Canada	(905) 477-9242
KSE, Inc.	J. R. Kittrell	P.O. Box 368 Amherst, MA 01004	(413) 549-5506
Magnum Water Technology	Dale Cox or Jack Simser	600 Lairport Street El Segundo, CA 90254	(310) 322-4143 or (310) 640-7000
Matrix Photocatalytic, Inc.	Bob Henderson	22 Pegler Street London, Ontario N5Z 2B5 Canada	(519) 660-8669
Process Technologies, Inc.	John Ferrell or Michael Swan	1160 Exchange Street Boise, ID 83716-5762	(208) 385-0900
U.S. Filter/Zimpro, Inc.	Rick Woodling	2805 Mission College Blvd. Santa Clara, CA 95054	(408) 727-7740
WEDECO	H. Sprengel	Diamlerstraße 5 D-4900 Herford Germany	(05221) 391 1
Zentox Corporation	Rich Miller	2140 NE 36th Ave. Suite 100 Ocala, FL 34470	(353) 867-7482