The UV/Oxidation Handbook

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Solarchem Environmental Systems

Introduction

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

INTRODUCTION

Continued advances in UV/Oxidation have made it the EPA proven technology of choice in an ever increasing number of ground and process wastewater applications. The last five years have seen the number of full-scale UV/Oxidation installations increase from a handful to over 150.

UV/Oxidation is an example of Advanced Oxidation Processes (AOP), which are radical initiated means of oxidizing small amounts of toxic organic compounds present in ground and wastewaters. AOP usually involve the use of an oxidant such as hydrogen peroxide or ozone with or without a catalyst, and in most cases irradiating the resulting solution with ultraviolet light.

UV/Oxidation's key advantage is its inherent destructive nature; contaminants are destroyed with no requirement for disposal of secondary products such as spent carbon. There is no transfer of contaminants from one medium to another. Furthermore, UV systems in combination with hydrogen peroxide have no vapor emissions, hence no air permit is required. The equipment is quiet, compact, and unobtrusive, and preventative maintenance and operating requirements are low in a carefully designed system.

This handbook provides information on the photochemistry, economics, testing, and design of Advanced Oxidation Processes, with a focus on UV/Oxidation systems. It is designed to provide engineers and earth scientists with a basic understanding of the technology. For specific applications or for further information, please feel free to contact Solarchem.

Chapter 1
Questions and Answers

This chapter provides quick answers to the most commonly asked questions about UV/Oxidation. The remaining chapters of this handbook have been structured to answer these questions in greater detail.

1. What is UV/Oxidation and how does it work? (Chapter 2)

Ultraviolet Oxidation is a generic name for a family of Advanced Oxidation Processes (AOP) that use ultraviolet light in conjunction with standard oxidants such as hydrogen peroxide and ozone to achieve greatly increased treatment performance over that obtained with either hydrogen peroxide or ozone alone. The most common UV/Oxidation process (and the process this handbook concentrates on) is the use of UV with hydrogen peroxide. Ultraviolet light is used to split the hydrogen peroxide molecule, producing very reactive hydroxyl radicals ($\bullet$OH). These hydroxyl radicals then quickly react with organic contaminants in the water, eventually breaking them down into carbon dioxide and water.

2. What are the breakdown products? (Chapter 2)

UV/Peroxide can completely break down (mineralize) any organic compound to carbon dioxide and water. In most applications this level of treatment is not necessary, as when the treatment objective for the target contaminant is reached, the oxidation products (typically low molecular weight aldehydes or carboxylic acids) pose no problem from a toxicity or regulatory viewpoint and, as well, are readily biodegradable.

3. For what contaminants and concentrations is UV/Oxidation most economic? (Chapter 3)

Experience and knowledge of the economics of alternative processes have shown that UV/Oxidation can economically treat a broad range of contaminants in concentrations ranging from several hundred ppb to several hundred ppm. In certain instances, UV/Oxidation, when used in conjunction with photocatalysts, can be competitive for contaminant concentrations of several thousand ppm. UV/Oxidation is particularly effective for chloroalkenes such as TCE and vinyl chloride and aromatic compounds such as toluene and benzene. Experience and cost comparisons have shown that for contaminants such as 1,4-dioxane, NDMA, and iron cyanide, UV/Oxidation is the only practical choice. UV/Peroxide can treat saturated compounds such as TCA, methylene chloride, and chloroform, but reaction rates are much slower. However, Solarchem has patented a UV/Reduction process that increases reaction rates of this group of compounds by 10 times, making it very competitive against traditional technologies such as activated carbon.

4. What is the EE/O design parameter and why do you not use residence time? (Chapter 4)

Unlike chemical oxidation, which requires lengthy residence times, UV/Oxidation uses hydroxyl radicals that react much more rapidly (typically 10^6 to 10^3 times faster than ozone). Residence time is not the key design variable in sizing a UV system. The most important design parameter is the amount of energy applied to produce sufficient hydroxyl radical for further reaction. EE/O stands for Electrical Energy consumption per Order of (decade) magnitude reduction in contaminant concentration (treatment) in 1000 US gallons of water. The EE/O gives the number of kilowatt hours of electricity necessary to reduce the concentration of a contaminant in 1000 US gallons by one order of magnitude. It combines light intensity, residence time, and percent destruction into a single measure. Since the economics of UV/Oxidation systems are driven by electrical power, flowrate, and percent removal rather than the size of a retention tank, the EE/O allows for easy and accurate scale-up to full-scale design and cost.

5. What pretreatment is necessary? (Chapter 5)

UV/Oxidation will efficiently treat a wide range of industrial and process waters without the need for any pretreatment. However, under some conditions, pretreatment may be required. Typical forms of pretreatment that may be required include removal of suspended solids, free phase oil and grease, and iron concentrations greater than 100 ppm.

6. Can you guarantee the treatment performance of your system? (Chapter 5)

It is always recommended that a design test or treatability study be conducted for each application. This allows the vendor to fully characterize the water and optimize treatment performance. Since EE/Os are obtained empirically from design tests, they are used to very accurately predict full-scale system size, and thus treatment performance is guaranteed on the completion of a design test.

7. How many UV/Oxidation processes are there? (Chapter 6)

Although UV/Peroxide and UV/Ozone are the most common UV-enhanced processes available, Solarchem has developed and patented a family of eight UV/Oxidation processes using treatment-enhancing (**ENOX**) catalysts that significantly improve performance for specific applications. Four of these processes are proprietary and are patented by Solarchem.

8. What is the difference between the various UV/Oxidation vendors? (Chapter 8)

When comparing various UV/Oxidation vendors, a user should consider:

- Recommended power and reagent dosage requirements. Differences in the lamp's UV spectral output or proprietary

catalysts can reduce the power required and consumption of chemicals and will therefore reduce capital and operating costs.

- System reliability and customer service through reference checks of several existing installations.

- Design and historical effectiveness of the protective quartz sleeve wiping mechanism.

- The level of process automation used to provide on-line diagnostics, ease of operation and safety, along with minimum downtime.

- The knowledge base of their staff.

Chapter 2
Chemistry of Advanced Oxidation

The chapter describes the principles of Advanced Oxidation, starting with simple explanations of photolysis and the nature of oxidation reactions. A general description of the reaction mechanism is also provided, and the differences between first and second generation systems are explained.

PHOTOLYSIS

Photolysis involves the interaction of light with molecules to bring about their dissociation into fragments. Light is composed of tiny energy packets called *photons*, whose energy E is inversely proportional to the wavelength, λ, of the light.

$$E = \frac{hc}{\lambda}$$

where h is Planck's constant and c is the speed of light.

If the absorption of a photon by a molecule is to cause photolysis (dissociation), the photon energy must exceed the energy of the bond to be broken. This requires that the wavelength be in the ultraviolet region of the spectrum for most photolytic reactions. Compounds that absorb UV light and have high quantum yields of photolysis are good candidates for photodegradation. Examples of these classes of compounds include N-nitrosodimethylamine (NDMA) and chlorinated alkenes. Figure 2.1 shows the UV absorption spectra for some commonly encountered groundwater contaminants.
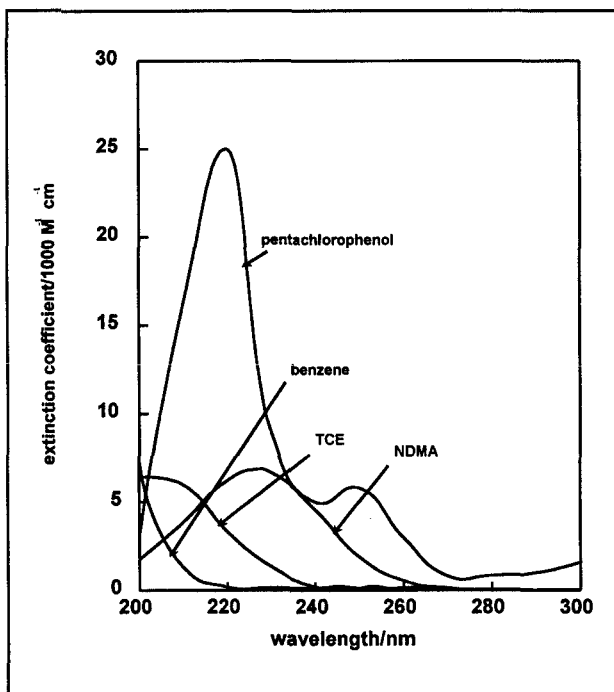

Figure 2.1
UV Absorption Spectra of Several Typical Organic Pollutants.

Figure 2.2 illustrates the application of **Rayox®** technology to a groundwater contaminated with NDMA. In this case, no oxidants were required as NDMA undergoes direct photolysis with a low electrical energy consumption of 2.5 kWh to destroy 90% of the NDMA in 1000 gallons.
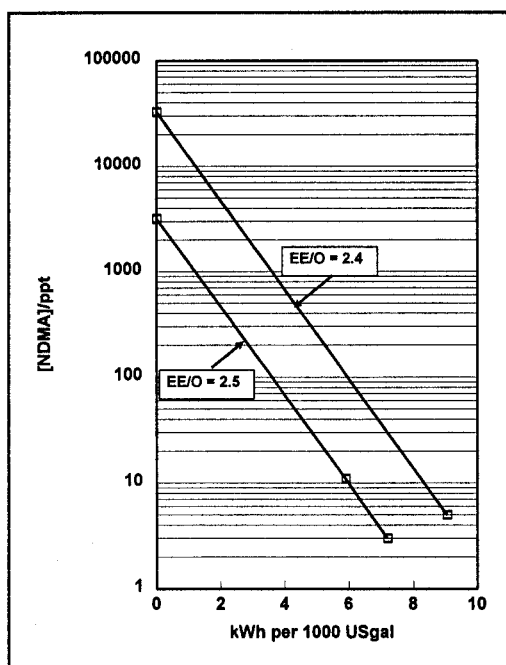
Figure 2.2

Rayox® Treatment of a Groundwater Containing 3000 and 30,000 ppt of N-nitrosodimethylamine (NDMA). This process does not require any oxidants.

Direct irradiation of organic micropollutants by high-intensity UV light provides a significant destruction pathway. For contaminants such as TCE, up to 30% of the reaction occurs via direct photolysis during typical UV/Oxidation (UV/H_2O_2) treatment. Direct photolysis is especially important for refractory compounds such as carbon tetrachloride, chloroform, and chlorinated alkanes, which react relatively slowly by hydroxyl radical attack alone.

Destruction by photolysis highlights the importance of using a UV lamp with the highest possible output in the UV region below 240 nm where most organic toxins strongly absorb light energy and where the photolysis quantum yield is typically higher.

OXIDATION

Oxidation is the chemical conversion of a contaminant to more oxygenated forms by means of reactions with oxidizing agents, such as oxygen (O_2), ozone (O_3), hydrogen peroxide (H_2O_2), or sodium hypochlorite (NaOCl). The following equation represents a general oxidation process:

Chlorinated	O_2, O_3	Oxygenated
Organic	→→→→→→	Intermediates
Molecules	H_2O_2 or NaOCl	

$$\begin{array}{lll}
\text{Oxygenated} & O_2, O_3 & \\
\text{Intermediates} & \rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow & CO_2 + H_2O + Cl^- \\
& H_2O_2 \text{ or } NaOCl &
\end{array}$$
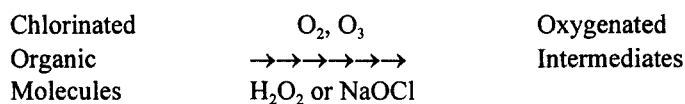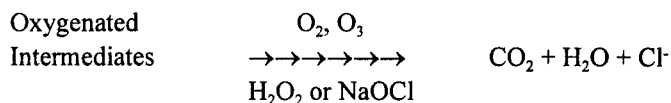
The multiple arrows indicate multi-step processes. Simple oxidation involves the addition of oxidizing agents such as O_2, O_3, H_2O_2, or NaOCl; however, the overall oxidation rates are usually too slow to be applied broadly for wastewater treatment.

ADVANCED OXIDATION PROCESSES (AOP)

In Advanced Oxidation Processes, the overall rate of oxidation of a contaminant is greatly increased over that obtained by the simple addit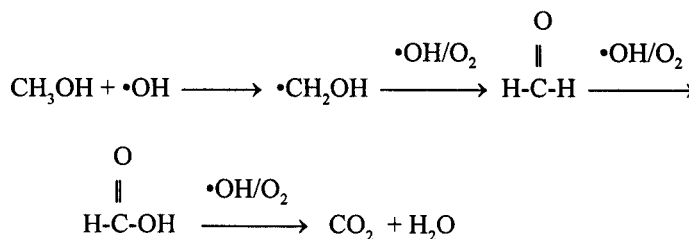ion of oxidizing agents. The main reason is the much greater involvement of highly reactive initiators (radicals) such as the hydroxyl radical (•OH) created in Advanced Oxidation Processes. Table 1.1 compares the reaction rates of various organic contaminants with ozone and the hydroxyl radical. The hydroxyl radical reacts typically a million to a billion times faster than ozone and hydrogen peroxide, resulting in greatly reduced treatment costs and system size.

Table 1.1
Reaction Rate Constants (k, in L mole^{-1} s^{-1})
of Ozone vs. Hydroxyl Radical

Compound	O_3	•OH
Chlorinated Alkenes	10^{-1} to 10^3	10^9 to 10^{11}
Phenols	10^3	10^9 to 10^{10}
N-containing Organics	10 to 10^2	10^8 to 10^{10}
Aromatics	1 to 10^2	10^8 to 10^{10}
Ketones	1	10^9 to 10^{10}
Alcohols	10^{-2} to 1	10^8 to 10^9
Alkanes	10^{-2}	10^6 to 10^9

Once generated, the hydroxyl radicals aggressively attack virtually all organic compounds. Depending upon the nature of the organic species, two types of initial attack are possible: the hydroxyl radical can abstract a hydrogen atom to form water, as with alkanes or alcohols, or it can add to the contaminant, as is the case for olefins or aromatic compounds.

• *Hydrogen Abstraction*

$$CH_3OH + \bullet OH \xrightarrow{} \bullet CH_2OH \xrightarrow{\bullet OH/O_2} \overset{\displaystyle O}{\underset{}{H\text{-}\overset{\|}{C}\text{-}H}} \xrightarrow{\bullet OH/O_2}$$

$$\overset{\displaystyle O}{\underset{}{H\text{-}\overset{\|}{C}\text{-}OH}} \xrightarrow{\bullet OH/O_2} CO_2 + H_2O$$

- ***Addition***
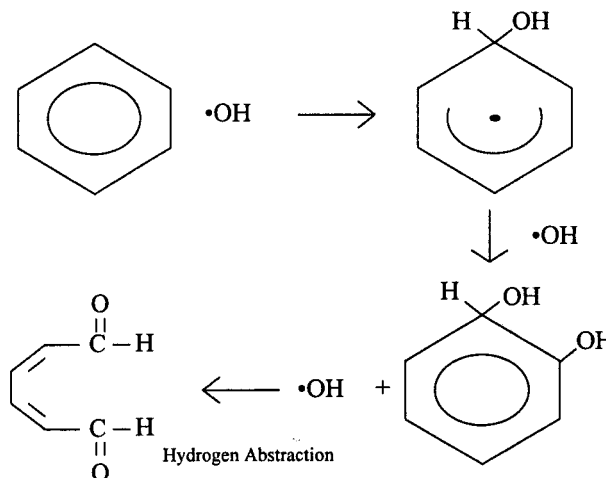
The attack by the hydroxyl radical, in the presence of oxygen, initiates a complex cascade of oxidative reactions leading to mineralization. As a rule of thumb, the rate of destruction of a contaminant is approximately proportional to the rate constant for the contaminant with the hydroxyl radical. From Table 1.1 we can see that chlorinated alkenes treat most efficiently because the double bond is very susceptible to hydroxyl attack. Saturated molecules (i.e., alkanes) have much smaller rate constants and therefore are more difficult to oxidize.

There are several methods for generating hydroxyl radicals that can be utilized. These include both photochemical and non-photochemical methods.

NON-PHOTOCHEMICAL OXIDATION

There are three well-known methods for generating hydroxyl radicals without using light energy. Two of the methods involve the reaction of ozone while the third uses the Fe^{+2} ion.

- Ozone at high pH

$$2\,O_3 + H_2O \xrightarrow{\text{OH}^-} \bullet OH + O_2 + HO_2$$
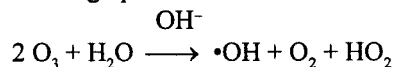
- Ozone + Hydrogen Peroxide

$$O_3 + H_2O_2 \longrightarrow \bullet OH + O_2 + HO_2$$

- Fenton's Reaction

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + \bullet OH$$

As will be discussed in more detail in Chapter 6, there are many different ultraviolet light-enhanced treatment processes available. The following are the two most common.

- *Photolysis of Ozone*

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$

$$O(^1D) + H_2O \rightarrow (2 \; \bullet OH) \rightarrow H_2O_2$$
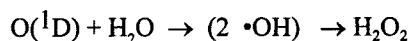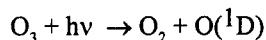
In aqueous solution, photolysis of ozone has been shown to lead to hydrogen peroxide in quantitative yields. Photolysis of ozone therefore appears only to be an expensive way to make hydrogen peroxide that is subsequently photolyzed to •OH radicals. The use of ozone can be quite effective from an operating cost standpoint, especially for waters with high background UV absorbance, but capital cost, stripping, ozone destruction, and health and safety problems can make ozone less desirable.

- *Photolysis of Hydrogen Peroxide*

In the UV/Peroxide process, a high-powered lamp emits UV radiation through a quartz sleeve into the contaminated water. Hydrogen peroxide is added, which is activated by the UV light to form oxidizing hydroxyl radicals:

$$H_2O_2 + h\nu \rightarrow 2 \; \bullet OH$$
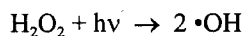
The following equation represents the simplified statement of the oxidation process:

Chlorinated Organic Molecule	O_2 $\rightarrow\rightarrow\rightarrow$ •OH	Intermediates (aldehydes /carboxylic acids)	O_2 $\rightarrow\rightarrow\rightarrow$ •OH	$CO_2 + H_2O + Cl^-$
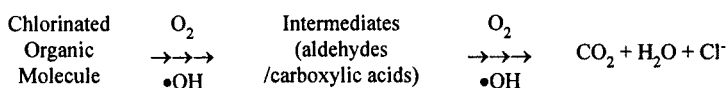
If allowed to proceed to completion, the end products are mainly carbon dioxide and water, with small amounts of chloride, nitrate, or sulfate ions depending on the contaminants. This oxidative treatment is called *mineralization* of the dissolved contaminants and means that secondary pollution or waste disposal is not required. In certain applications, catalysts, which are photo-active and non-toxic, are added to significantly enhance the system's performance. A UV/Oxidation system can be designed to meet any discharge requirement.

Since it is possible to generate hydroxyl radicals without UV light (for example, ozone/peroxide), what are the reasons for using UV light?

1. Photolysis: It is possible to photolyze compounds directly. This is very important for compounds that react slowly with hydroxyl radicals.

2. Avoids the use of ozone. Ozone increases capital costs, complexity, and health and environmental concerns and requires air permits.

3. Increased reaction rate contents. This results in "instantaneous" reactions and hence negates the need for large holding tanks and makes the systems very compact.

4. Avoids drastic pH changes. Ozone may require significant changes in pH to be effective. This adds operating and capital costs as well as complexity.

5. Increases flexibility. Can use a variety of oxidants and conditions when light is used.

6. Lower operating cost due to lower power consumption to generate hydroxyl radicals, as long as most of the light is absorbed by the peroxide.

SECOND GENERATION AOP

Since the introduction of first-generation UV systems in the late 1970s, many new features have been developed to overcome the deficiencies of these early systems:

1. First-generation systems relied on the use of low-power, low-pressure, monochromatic mercury UV lamps. The use of extra high-intensity and efficiency medium-pressure lamps with improved UV spectral output has led to more compact systems and lower treatment costs.

2. The development of new processes using Enhanced Oxidation (**ENOX**) catalysts have significantly improved treatment performance for specific applications such as elevated chemical oxygen demand (COD) levels and the treatment of chloroalkanes.

3. A proven wiping mechanism for keeping the quartz sleeve between the lamp and water clean has allowed for worry-free operation in waters containing high concentrations of iron and other fouling agents.

4. System reliability, failsafe operation, and process automation were greatly improved by the use of programmable logic controllers to operate the systems.

Chapter 3
UV/Oxidation vs. Competing Technologies

The following chapter compares advantages, disadvantages, and costs of UV/Oxidation treatment with more conventional technologies such as air stripping, activated carbon, and biological oxidation. Screening criteria are also outlined to help one quickly determine which technologies are most applicable for a specific application.

UV/OXIDATION SYSTEM

A typical UV/Oxidation system is shown in Figure 3.1. Reagents such as hydrogen peroxide and various photocatalysts are injected upstream of the reactor and mixed using metering pumps and an in-line static mixer. The contaminated water then flows sequentially through one or more UV reactors where treatment occurs. Within each reactor is one medium-pressure mercury lamp ranging in power from 1 kW to as high as 30 kW. It is separated from the water by a quartz sleeve, which is cleaned by a pneumatically driven wiper.

The UV lamp inside the reactor is operated at high voltage, typically between 1000 and 3000 volts. Safety interlocks are fitted to protect personnel from both the UV radiation and the high voltage supply. The control panel contains a Programmable Logic Controller (PLC), which can be used to control the entire system including feed pumps, reagent delivery systems, and ancillary equipment such as sensors, switches, and valves. PLC control allows for features such as remote diagnostics via a telephone modem and program customizing to accommodate changes in operation throughout the remediation cycle.

In most groundwater applications, the material specified for the UV reactor is 316L stainless steel, which protects against the oxidants and the UV light, while providing excellent resistance to corrosion.

UV systems in combination with hydrogen peroxide produce no vapor emissions or byproducts requiring disposal. Therefore, there are no air permits required, and stacks, noise, and long-term liability issues are also avoided. The equipment is quiet, compact, unobtrusive, with a high degree of system availability (>95%) well, preventative maintenance and operating requirements are low in a carefully designed system.

The following sections compare the advantages and disadvantages of air stripping, activated carbon, and biological treatment relative to UV/Oxidation.
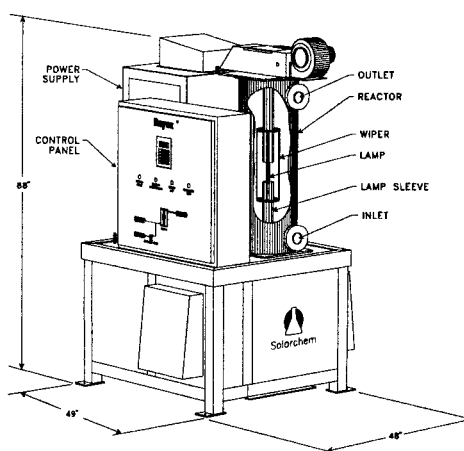
Figure 3.1
Typical UV/Oxidation System (30 kW unit).

AIR STRIPPING

Air stripping involves the transfer of volatile organics from the liquid phase to the air phase by greatly increasing the air/water contact area. Typical aeration methods include packed towers, diffusers, trays, and spray aeration.

Advantages: Air stripping is a more established and more widely understood technology than UV/Oxidation. It can be accurately designed from theory and experience without the need for design tests. If air emissions are not regulated, air stripping is by far the simplest and cheapest solution for the removal of volatile compounds from water (refer to Figure 3.2).

Disadvantages: The tower packing material is very susceptible to iron and biological fouling, which can significantly increase operating and maintenance costs. Air stripping does not destroy the contaminant, but only transfers it to the vapor phase. Treatment efficiency for semi-volatile components is greatly reduced, leading to much larger systems and increased capital and operating costs. If air emissions are regulated, off-gas treatment by activated carbon or incineration (catalytic/regenerative) will be required, increasing capital and operating costs and system complexity. Air strippers are typically large, loud, and obtrusive. Air permitting can be lengthy and complicated and is always changing.

ACTIVATED CARBON

This technology involves the passing of contaminated water or air through a bed of highly porous carbon. Contaminants collect and adhere to the carbon surface as a result of weak Van der Waals forces. Once the carbon is consumed (measured by the breakthrough of a specific contaminant), it is usually either disposed of or regenerated off-site.

Advantages: Liquid and vapor phase activated carbon treatment are well-established and understood technologies. Operation is usually simple and is often unattended. It can economically treat a wide variety of contaminants at low concentration (see Figure 3.3). The capital cost

of carbon systems is almost always less than UV/Oxidation systems for the same flowrate.

Disadvantages: At concentrations above 10 ppm, carbon replacement costs tend to become uncompetitive against UV/Oxidation regardless of contaminant. Liquid phase granulated activated carbon (LGAC) operation is susceptible to water matrix problems such as high iron, high COD, and biological fouling. Economic analysis should include the added cost of handling and disposal or regeneration of the spent carbon, analysis and monitoring for breakthrough, and the potential future liability associated with disposal. Some compounds such as vinyl chloride, NDMA, chloroform, and 1,4-dioxane do not adsorb efficiently at any concentration and cannot be treated using activated carbon.

BIOLOGICAL OXIDATION

Fixed film bioreactors such as rotating biological contactors and trickling filters use a microbial population attached to an inert support to aerobically digest organic matter to produce new cells.

Advantages: Most effective process for efficiently treating biological oxygen demand (BOD) concentrations in the hundreds of ppm.

Disadvantages: Metals removal is usually required to avoid poisoning the microbes or fouling the system. Skilled operators are usually required to start and maintain systems which are easily upset by variations in flow or water quality. Volatile organics are susceptible by the process because of the aeration involved in getting oxygen to the microbes. Solid residuals from the sludge handling process may require treatment and/or hazardous disposal.

AIR STRIPPING/CARBON MATRIX

Figure 3.2 is a plot of Henry's Law Constants (a measure of relative volatility) and Freundlich Coefficients (a measure of relative carbon adsorption) for over 150 chemicals. The plot has been divided into nine regions ranging from region 1, which contains contaminants considered to be both poor adsorbers and poor strippers, to region 9, which contains contaminants considered to be both good adsorbers and good strippers.

The regions were divided based on the following criteria:

> poor adsorber - loads at < 4 mg/g carbon
> average adsorber - loads at between 4 and 50 mg/g carbon
> good adsorber - loads at > 50 mg/g carbon
>
> poor stripper - Henry's Law Constant (HLC) < 10 atm/mol fraction
> average stripper - HLC between 10 and 200 atm/mol fraction
> good stripper - HLC > 200 atm/mol fraction

The lower the region number the more competitive UV/Oxidation treatment becomes for that contaminant. By locating which region a contaminant falls in, one can quickly gauge how applicable each technology will be. UV/Oxidation is clearly competitive for chemicals in region 1. Contaminants located in regions 5 to 9 can be effectively

treated by either air stripping or carbon (see note below). Regions 2 to 4 mark the competitive grey area. For regions 2 to 4, determining the lowest cost treatment will require more detailed information about the application. In many instances, UV/Oxidation will be the most competitive alternative.

Note: This matrix does **not** take into account other important considerations such as air emission regulations that would require some form of off-gas treatment. If off-gas treatment is required after air stripping, UV/Oxidation becomes a much more competitive treatment option for contaminants located in regions 4 and 5.

UV/OXIDATION CHECKLIST

The following checklist and matrix were developed in order to better understand which contaminants are most amenable to UV/Oxidation treatment. Potential applications can be quickly screened with yes or no answers to the following checklist questions.

1. Is a destruction technology preferred?

2. Are there any restrictions on air discharge?

3. Does the principal contaminant air strip poorly, such as phenol (i.e., Henry's Law Constant <200 atm/mole fraction)?

4. Do any of the principal contaminants load poorly on activated carbon in the liquid phase, such as vinyl chloride (i.e., <50 mg/g carbon @ 1 ppm)?

5. Does the background water chemistry interfere with carbon operation and adsorption of selected contaminants and therefore require unusually large amounts of liquid phase activated carbon (e.g., high iron or high COD)?

6. Are there handling or disposal concerns associated with loading contaminants on to activated carbon such as those associated with PCP and TNT?

If the answer is yes three or more times, then UV/Oxidation should definitely be considered. A preliminary cost estimate for a UV/Oxidation system can be made using the design parameters provided in Chapter 4. If the preliminary cost estimate looks favorable, your next step should be to arrange for a design test as described in Chapter 5 to confirm costs.
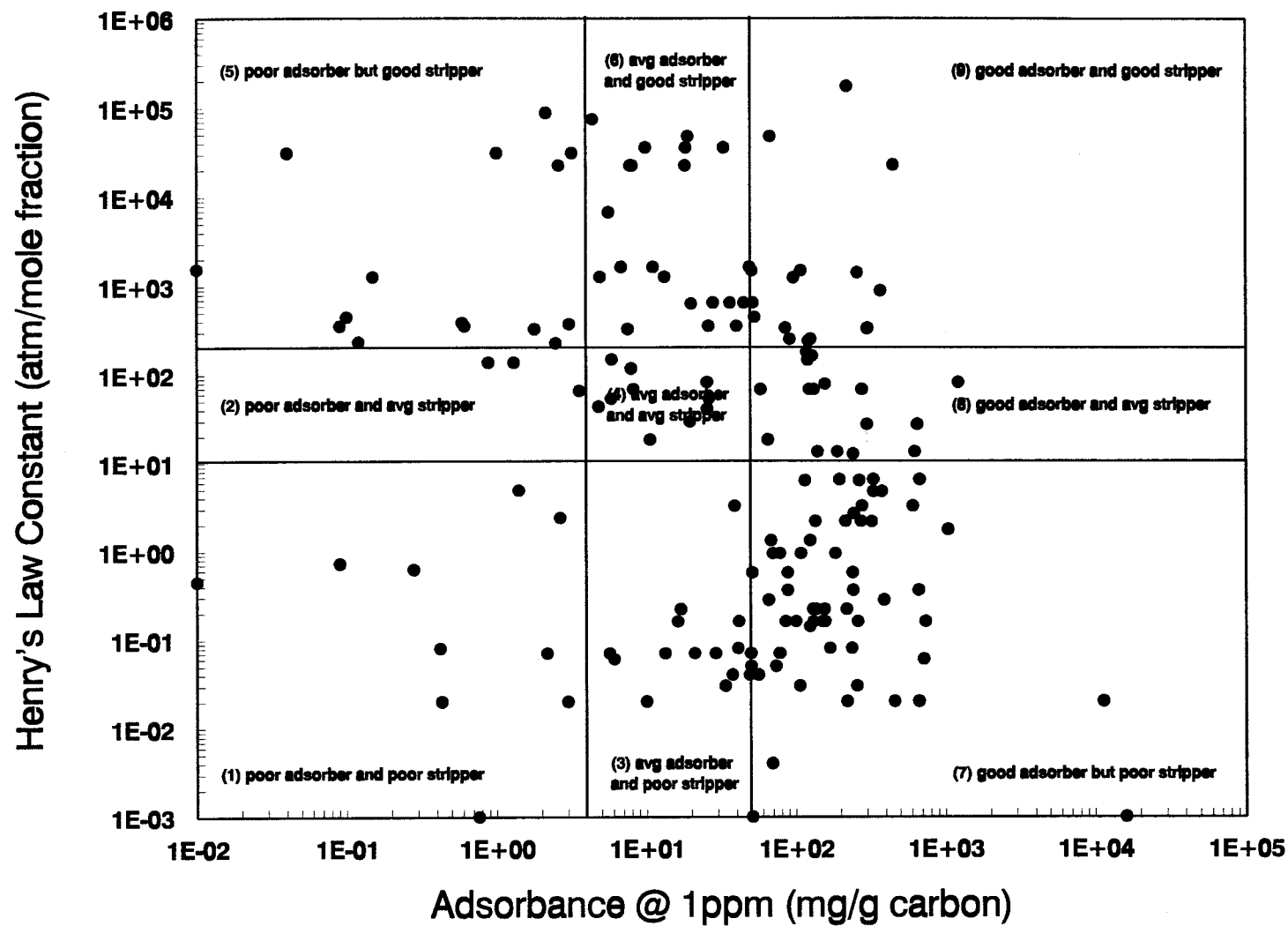
Figure 3.2
Air Stripping / Activated Carbon Matrix

Figure 3.2 - Continued

REGION	COMPOUND	k (mg/g carbon)	H (atm/mole fraction)	REGION	COMPOUND	k (mg/g carbon)	H (atm/mole fraction)	REGION	COMPOUND	k (mg/g carbon)	H (atm/mole fraction)
8	ACENAPHTHENE	140.00	13.39	5	DICHLOROETHYLENE,1,1-	0.15	1270.00	8	NAPHTHALENE	123.00	68.27
8	ACENAPHTHENE	190.00	13.39	6	DICHLOROETHYLENE,1,1-	4.91	1270.00	8	NAPHTHALENE	132.00	68.27
8	ACENAPHTHENE	626.00	13.39	5	DICHLOROETHYLENE,1,2-TRANS-	3.05	370.70	8	NAPHTHALENE	277.00	68.27
7	ACENAPHTHYLENE	115.00	6.33	2	DICHLOROMETHANE	0.88	137.60	4	NAPTHALENE	8.18	68.27
7	ACENAPHTHYLENE	266.00	6.33	7	DICHLOROPHENOL,2,4-	85.16	0.16	7	NITROBENZENE	68.00	1.32
1	ACETONE	2.65	2.38	3	DICHLOROPHENOL,2,4-	16.20	0.16	7	NITROBENZENE	124.69	1.32
1	ACRYLONITRILE	1.40	4.89	3	DICHLOROPHENOL,2,4-	41.40	0.16	7	O-CRESOL	50.07	0.05
8	ALDRIN	299.60	27.56	7	DICHLOROPHENOL,2,4-	131.00	0.16	9	P-XYLENE	85.00	336.90
8	ALDRIN	651.00	27.56	7	DICHLOROPHENOL,2,4-	157.00	0.16	8	PCB 1221	242.00	12.67
7	ANTHRACENE	330.00	4.78	4	DICHLOROPROPANE,1,2-	5.86	148.60	7	PENTACHLOROPHENOL	100.00	0.16
7	ANTHRACENE	376.00	4.78	3	DIELDRIN	38.90	3.24	7	PENTACHLOROPHENOL	150.00	0.16
5	BENZENE	0.04	309.00	7	DIELDRIN	277.66	3.24	7	PENTACHLOROPHENOL	260.00	0.16
5	BENZENE	1.00	309.00	7	DIELDRIN	606.00	3.24	7	PENTACHLOROPHENOL	736.57	0.16
5	BENZENE	3.18	309.00	7	DIMETHYLPHENOL,2,4-	78.00	0.94	7	PHENANTHRENE	135.00	2.18
3	BENZO(a)PYRENE	33.60	0.03	7	DIMETHYLPHENOL,2,4-	108.00	0.94	7	PHENANTHRENE	215.00	2.18
1	BENZOIC ACID	0.76	0.00	7	DIMETHYLPHENOL,2,4-	70.00	0.94	7	PHENANTHRENE	273.00	2.18
7	BENZOIC ACID	51.00	0.00	7	DIMETHYLPHENOL,2,4-	184.00	0.94	1	PHENOL	2.17	0.07
7	BHC,gamma-LINDANE	256.00	0.03	3	DINITRO-O-CRESOL,4,6-	41.00	0.08	3	PHENOL	13.30	0.07
1	BIS(2-CHLOROETHYL)ETHER	0.09	0.72	7	DINITRO-O-CRESOL,4,6-	237.00	0.08	3	PHENOL	21.00	0.07
7	BIS(2-ETHYLHEXYL)PHTHALATE	11300.00	0.02	1	DINITRO-o-CRESOL,4,6-	0.42	0.08	3	PHENOL	29.00	0.07
4	BROMOFORM	19.60	29.56	7	DINITRO-o-CRESOL,4,6-	169.00	0.08	3	PHENOL	49.80	0.07
6	CARBON TETRACHLORIDE	6.80	1634.00	3	DINITROPHENOL,2,4-	9.87	0.00	3	PHENOL	50.00	0.07
6	CARBON TETRACHLORIDE	11.10	1634.00	3	DINITROPHENOL,2,4-	18.40	0.00	7	PHENOL	77.40	0.07
6	CARBON TETRACHLORIDE	49.03	1634.00	3	DINITROPHENOL,2,4-	33.00	0.00	7	PHENOL	78.10	0.07
7	CHLORDANE	245.00	2.66	1	DIOXANE,1,4-	1.73	0.00	2	PHENOL PH 11.3	5.66	0.07
7	CHLORO-m-CRESOL,p-	124.00	0.14	7	DIPHENYLHYDRAZINE,1,2-	16000.00	0.00	3	PROPYLPHENOL,4-	19.00	0.47
9	CHLOROBENZENE	91.00	252.10	7	DIPHENYLHYDRAZINE,1,2-	16000.00	0.00	7	PROPYLPHENOL,4-	67.20	0.47
9	CHLOROBENZENE	125.40	252.10	7	ENDRIN	456.50	0.02	7	PYRENE	65.60	0.28
4	CHLORODIBROMOMETHANE	4.80	43.50	7	ENDRIN	666.00	0.02	7	PYRENE	389.00	0.28
5	CHLOROETHANE	0.59	384.40	1	ETHANOL	0.01	0.45	8	STYRENE	120.00	146.30
5	CHLOROFORM	2.60	22520.00	5	ETHYLBENZENE	0.10	446.80	8	TETRACHLOROETHANE,1,1,2,2-	64.96	18.34
6	CHLOROFORM	7.80	22520.00	9	ETHYLBENZENE	53.00	446.80	4	TETRACHLOROETHANE,1,1,2,2-	10.60	18.40
6	CHLOROFORM	8.04	22520.00	7	FLUORANTHENE	88.10	0.36	9	TETRACHLOROETHYLENE	50.80	1492.00
6	CHLOROFORM	18.20	22520.00	7	FLUORANTHENE	242.00	0.36	9	TETRACHLOROETHYLENE	108.17	1492.00
7	CHLOROPHENOL,2-	51.00	0.57	7	FLUORANTHENE	664.00	0.36	5	TOLUENE	0.09	353.10
7	CHLOROPHENOL,2-	88.00	0.57	7	FLUORENE	196.00	6.50	5	TOLUENE	0.61	353.10
7	CHLOROPHENOL,2-	240.00	0.57	7	FLUORENE	330.00	6.50	6	TOLUENE	26.10	353.10
2	CHRYSENE	6.07	0.06	7	FLUORENE	674.00	6.50	6	TOLUENE	40.20	353.10
7	CHRYSENE	716.00	0.06	4	HEPTACHLOR	25.54	82.22	8	TRICHLOROBENZENE,1,2,4-	157.00	78.89
7	CRESOL,2-	73.40	0.05	8	HEPTACHLOR	1220.00	82.22	4	TRICHLOROETHANE	25.55	41.00
3	CRESOL,3-	37.50	0.04	7	HEPTACHLOR EPOXIDE	1040.00	1.76	5	TRICHLOROETHANE,1,1,1-	2.48	226.67
7	CRESOL,3-	56.00	0.04	9	HEXACHLOROBENZENE	450.00	22890.00	4	TRICHLOROETHANE,1,1,2-	5.81	53.37
1	CRESOL,4-	2.98	0.02	9	HEXACHLOROBUTADIENE	258.00	1422.22	4	TRICHLOROETHANE,1,1,2-	26.20	53.37
3	CRESOL,4-	9.97	0.02	9	HEXACHLOROCYCLOPENTADIENE	370.00	888.89	6	TRICHLOROETHYLENE	28.00	648.20
7	DDT,p,p'-	322.00	2.16	9	HEXACHLOROETHANE	96.50	1243.00	6	TRICHLOROETHYLENE	36.30	648.20
1	DI BUTYL PHTHALATE	0.43	0.02	1	HYDROXYBENZOIC ACID,4-	2.14	0.00	6	TRICHLOROETHYLENE	45.00	648.20
7	DI-n-BUTYL PHTHALATE	220.00	0.02	1	ISOPROPANOL	0.28	0.62	9	TRICHLOROETHYLENE	51.62	648.20
7	DIBENZO(a,h)ANTHRACENE	69.30	0.00	7	LINDANE	106.02	0.03	6	TRICHLOROMONOFLUOROMETHANE	5.60	6765.00
8	DICHLOROBENZENE,1,2-	129.00	163.90	3	M-CRESOL	48.87	0.04	3	TRICHLOROPHENOL,2,4,6-	16.95	0.22
8	DICHLOROBENZENE,1,3-	118.00	180.10	6	MERCURY	20.00	633.33	7	TRICHLOROPHENOL,2,4,6-	130.10	0.22
9	DICHLOROBENZENE,1,4-	121.00	240.50	3	METHOXYPHENOL,4-	4.38	0.74	7	TRICHLOROPHENOL,2,4,6-	219.00	0.22
4	DICHLOROBROMOMETHANE	7.90	117.78	2	METHYLENE CHLORIDE	1.30	137.60	7	TRICHLOROPHENOL,2,4,6-	137.00	0.22
6	DICHLOROETHANE,1,1,1-	7.51	326.20	4	METHYLTERBUTYLETHER (MTBE)	4.30	16.3	7	TRICHLOROPHENOL,2,4,6-	155.00	0.22
5	DICHLOROETHANE,1,1-	1.79	326.20	1	N-NITROSODIMETHYLAMINE (NDMA)	0.01	0.00	5	VINYL CHLORIDE	0.01	1544.44
2	DICHLOROETHANE,1,2-	3.57	65.44	7	N-NITROSODIPHENYLAMINE	220.00	0.00	5	XYLENE,o-	0.12	232.50
6	DICHLOROETHYLENE,1,1-	13.25	1270.00	8	NAPHTHALENE	58.00	68.27	9	XYLENE,p-	303.00	336.90

Sources: EPA RREL Treatability Database and Chemical Engineering (November 1991)

The unit treatment costs of UV/Oxidation vs. liquid phase activated carbon as a function of influent concentration are compared in Table 3.1. The data are shown graphically in Figure 3.3. The cost region for poor carbon adsorbers was based on an isotherm k coefficient of less than 4 mg/g carbon at 1 ppm of concentration. The cost region for good carbon adsorbers was based on a k coefficient of greater than 50 mg/g carbon at 1 ppm. The wedge-shaped area represents the cost region for UV/Oxidation treatment.

Practical rule of thumb considerations when performing a cost comparison analysis include:
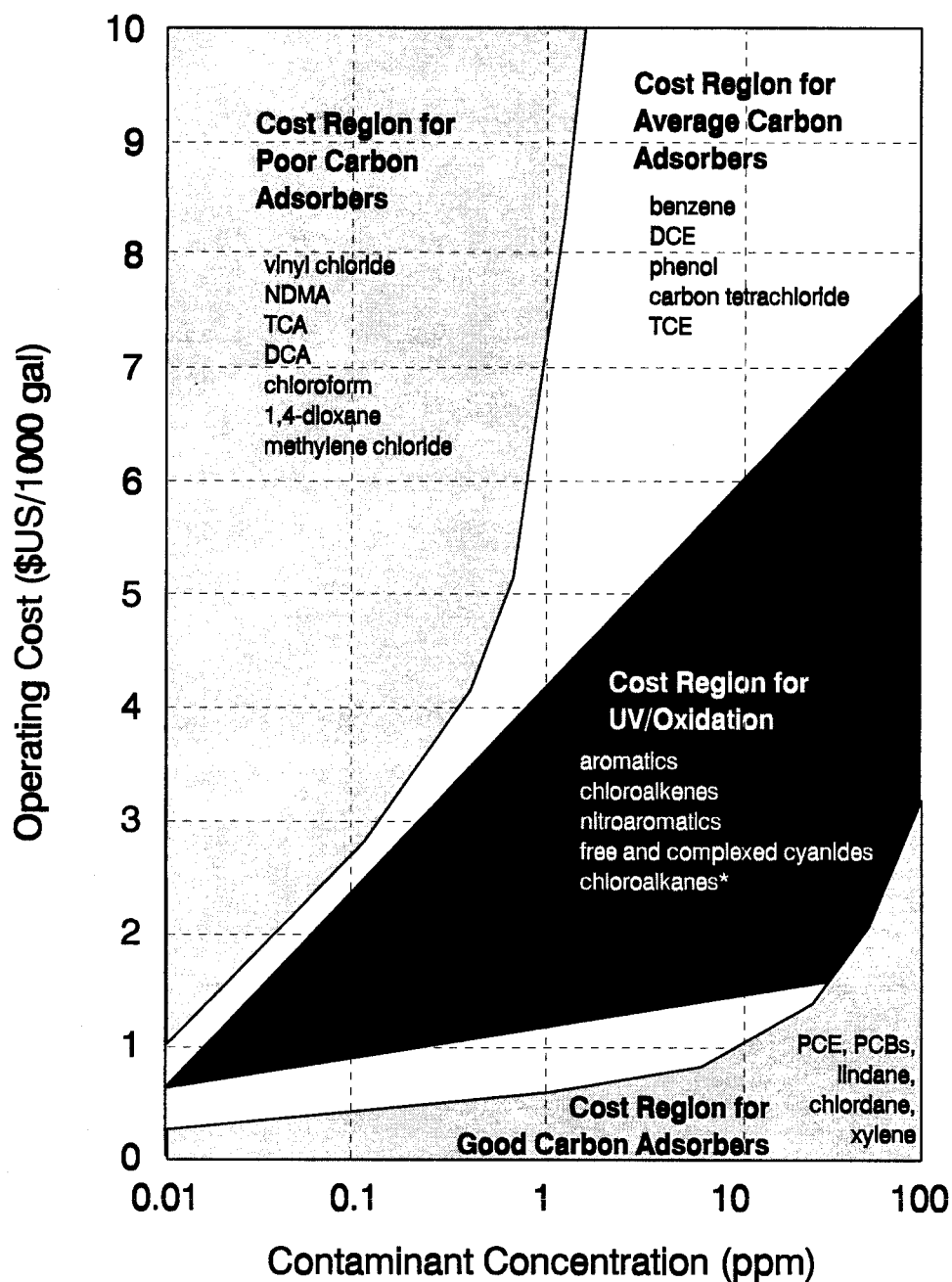
- Unit operating costs for UV/Oxidation treatment increase much more slowly with increasing influent concentrations than activated carbon. Even though activated carbon absorbs more strongly at higher concentrations, at concentrations above 50 ppm, activated carbon becomes uneconomic for even good carbon adsorbers.

- UV/Oxidation treatment costs are almost always less for contaminants that are poor carbon adsorbers regardless of concentration.

- For average carbon adsorbers, the most economical technology must be chosen on a case-by-case basis.

- UV/Oxidation capital costs are typically two to three times that of activated carbon. Therefore, longer term projects favor UV/Oxidation where the cumulative savings in operating costs offset the higher capital expense.

Table 3.1
Operating Cost Comparison between UV/Oxidation and Activated Carbon($US, 1995)

Contaminant Concentration (ppm)	UV/Peroxide ($/1000 USgal)	Poor Carbon Adsorbers ($/1000 USgal)	Average Carbon Adsorbers ($/1000 USgal)	Good Carbon Adsorbers ($/1000 USgal)
0.1	$0.5 - $2.5	>$3	$0.5 - $3	<$0.5
1	$1.5 - $4	>$10	$0.7 - $10	<$0.7
10	$2 - $6	>$50	$1 - $50	<$1
Typical Contaminants	aromatics, chloroalkenes, nitroaromatics, free and complexed cyanides, chloroalkanes*	vinyl chloride, NDMA, chloroform, TCA, DCA, methylene chloride, 1,4-dioxane	benzene, DCE, phenol, carbon tetrachloride, TCE	lindane, chlordane, xylene, PCE, PCBs

* based on use of a proprietary reduction catalyst

Figure 3.3
Operating Cost Regions for LGAC and UV/Oxidation.($US,1995)

The discussion so far has compared costs of stand-alone systems in each technology. Experience and economic analysis have shown that in some instances where concentrations of target contaminants are greater than 10 ppm, a combination of treatment systems provides the most economic solution. The most common example of this has been the use of UV/Oxidation as a pretreatment step before a final polish with activated carbon. Figure 3.4 compares operating costs as a function of percent mass removal. UV/Oxidation is particularly effective at reducing much of the initial mass loading (60% to 80% removal) while activated carbon is a very economical polishing step. When the two systems are combined, the results are much lower overall operating costs.
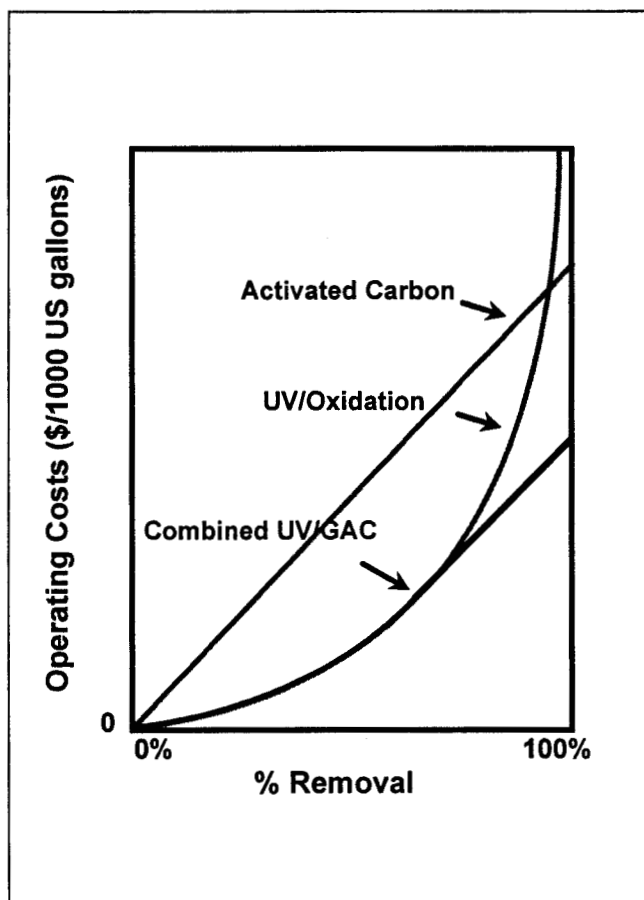

Figure 3.4
Operating Cost as a Function of % Mass Removal for Activated Carbon, UV/Oxidation, and Combined Systems.

A second example of combining systems to reduce overall costs and meet discharge requirements has been the use of UV/Oxidation as a pretreatment step followed by air stripping. In this case, UV/Oxidation reduces mass loading to the point where the remainder can be air stripped without violating the most stringent air emission mass restrictions.

Chapter 4
System Sizing and Cost Calculations

This chapter focuses on the methodology and treatment parameters for estimating preliminary capital and operating costs for UV/Peroxide systems (the most common UV/Oxidation arrangement).

The two primary design variables that must be optimized in sizing a UV/Peroxide system are the UV power radiated per unit volume of water treated, more commonly referred to as UV dose, and the concentration of hydrogen peroxide.

UV DOSAGE

UV dose, when applied to AOP, is a measure of the total lamp electrical energy applied to a fixed volume of water. The units are usually measured in kWh/1000 US gallons. This parameter combines flowrate, residence time, and light intensity into a single term. The dose of light, peroxide, and/or proprietary catalysts required per unit volume of water treated varies from one type of contaminated stream to the other. However, the dosage can be set to destroy virtually all types of contaminants to any level required. The calculation for either batch or flowthrough treatment is as follows:

Batch:
$$\text{UV Dose} = \frac{\text{lamp power (kW) x time (hrs) x 1000}}{\text{batch volume (gal.)}}$$

Flowthrough:
$$\text{UV Dose} = \frac{\text{1000 x lamp power (kW)}}{\text{flow (gpm) x 60}}$$

Design tests are performed to measure the UV dosage required to achieve the desired effluent concentration. The dosage to be applied to a particular stream is determined in an iterative manner by examining the effect on treatment of selected process variables such as pH, oxidant concentration, and choice of catalyst. Figure 4.1 is an example of the typical UV/Oxidation treatment curve resulting from a single test run. It is a plot of the contaminant concentration (on a log scale) as a function of UV dose. Although the reaction between the target compound and the •OH radical is bimolecular, the latter is produced at a constant, steady state rate. Therefore, the contaminant concentration becomes the limiting reagent and hence pseudo-first-order reaction kinetics apply. By measuring the inverse slope of this destruction curve, one has a very accurate and easily comparable measure of treatment performance, which we have termed the EE/O, (or electrical energy per order). The steeper the slope, the smaller the EE/O and the faster the treatment.
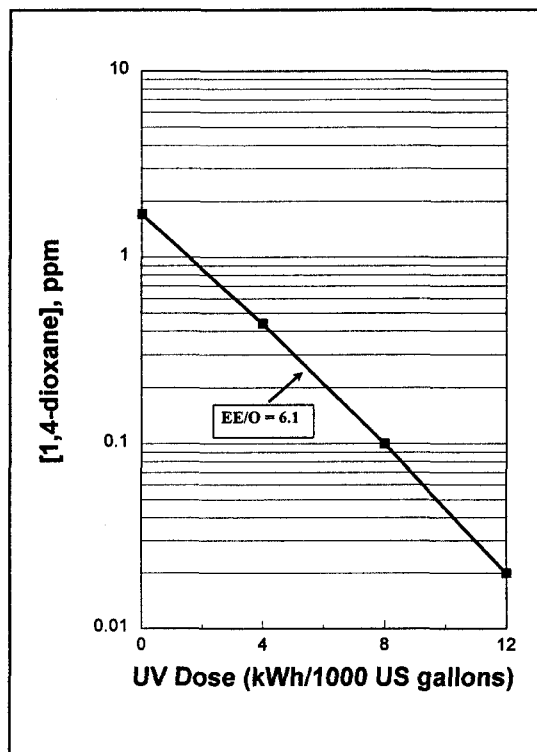
Figure 4.1
Typical UV/Oxidation Destruction Curve.

ELECTRICAL ENERGY PER ORDER (EE/O)

The key design variables of exposure to UV radiation and the number of orders of magnitude of contaminant concentration removed are combined into a single function, the Electrical Energy per Order or EE/O. The EE/O is a powerful scale-up parameter and is a measure of the treatment obtained in a fixed volume of water as a function of exposure to UV light. It is defined as:

"The kilowatt hours of electricity required to reduce the concentration of a compound in 1000 gallons by one order of magnitude (or 90%). The unit for EE/O is kWh/1000 US gallons/order."

For example, if it takes 10 kWh of electricity to reduce the concentration of a target compound from 10 ppm to 1 ppm (one order of magnitude or 90%) in 1000 gallons of groundwater, then the EE/O is 10 kWh/1000 gal/order for this compound. It will then take another 10 kWh to reduce the compound from 1 ppm to 0.1 ppm, and so on.

The linear relationship between UV dose and the log of contaminant concentration has important implications. First, a single number (EE/O) can completely describe the UV treatment characteristics of a contaminant. This makes the comparison of treatment performance as simple as comparing EE/Os. The lower the EE/O the more efficient the treatment. Second, as the previous example illustrates, it takes the same amount of energy to treat the first 90% of the contaminant as it does to treat the subsequent 90% of the remaining contaminant. Thus, UV treatment is very efficient at reducing the mass loading of a contaminant and can be used as a very cost-effective pretreatment step.

The EE/O measured in a design test is specific to the water tested and to the compound of interest, and it will vary for different applications. Typical EE/Os for a range of organic contaminants are provided in Table 4.1. EE/O makes the scale-up and comparison of relative treatment performance very simple. For example, from Table 4.1, atrazine has an EE/O of 30 while 1,4-dioxane has an upper EE/O of 6. Atrazine requires five times more energy for the same level of destruction as 1,4-dioxane. Therefore, under similar influent and effluent conditions, the treatment system for atrazine would require five times the UV power of that treating 1,4-dioxane for the same flowrate.

Table 4.1
Typical EE/Os for Contaminant Destruction

Compound	EE/O (kWh/1000 USgal/order)
1,4-Dioxane	2 - 6
Atrazine	30
Benzene	2 - 5
Chlorobenzene	5
Chloroform	15*
DCA	15*
DCE	2 - 5
Freon	10*
Iron Cyanide	40
NDMA	2 - 5
PCE	3 - 8
PCP	10
Phenol	5
TCE	2 - 4
Toluene	2 - 5
Xylene	2 - 5
TCA	15*
TNT	12
Vinyl Chloride	2 - 3

* Reduction catalyst required

With the EE/O determined, either through design tests or estimated by using Table 4.1, the UV dose (i.e., the amount of electrical energy required to treat 1000 gallons) required in a specific case is simply calculated using the following equation:

(1) UV Dose = EE/O * $\log(C_i/C_f)$, [where C_i is the specified starting concentration (any units), and C_f is the anticipated or required discharge standard (same units as C_i)]

Note: For streams with several contaminants, the required energy is not additive but determined by the contaminant requiring the greatest UV dose (see calculation example 2).

OPERATING COSTS

Once the required UV dose is known, the electrical operating cost associated with supplying the UV energy can be calculated using the following equation:

(2) Electrical Cost $(\$/1000 \text{ USgal})$ = UV Dose $(\text{kWh}/1000 \text{ USgal})$ * Power Cost $(\$/\text{kWh})$

The second key parameter from the design test is the concentration (ppm) of chemical reagents used, specifically hydrogen peroxide and any catalyst added to improve performance. The peroxide dose is based on the UV absorbance and COD of the water and is typically in the range 25 to 200 ppm (mg/L). For the purpose of a preliminary cost estimate, the simplest rule of thumb for estimating the amount of peroxide necessary is the greater of 25 ppm or twice the COD concentration. The cost of the hydrogen peroxide varies from $0.005 to $0.008 per ppm concentration/1000 USgal ($US,1995). If a catalyst is required, its selection and concentration will vary with the target compound and will be based on design test results. Lamp replacement costs typically range from 30% to 50% of the electrical cost. For preliminary costing purposes, a conservative value of 45% has been used.

Therefore,

(3) Total Operating Cost $(\$/1000 \text{ USgal})$ = 1.45 * Electrical Cost + Peroxide Cost,

where Peroxide Cost = $(H_2O_2 \text{ conc. in ppm})$ * ($0.005/\text{ppm}/1000 \text{ USgal}$).

CAPITAL COSTS

Capital cost is a function of system size, which is a function of the UV power required to destroy the selected contaminants. Using the EE/Os provided in Table 4.1, the following equation is used to determine the total UV power (kW) required:

(4) UV Power (kW) $= \dfrac{EE/O * 60 * \text{Flow(USgpm)} * \log(C_i/C_r)}{1000}$

$= \dfrac{\text{UV Dose} * 60 * \text{Flow (USgpm)}}{1000}$

Once the required UV power is known, Figure 4.2 can be used to look up the associated capital cost. The capital costs are given as ranges to allow for the actual number of discrete reactors that will be required along with any additional system options required.

The total UV power varies proportionally with flowrate and orders of magnitude of concentration of contaminant removed. For example, doubling the flowrate doubles the UV power required. Similarly, to extend treatment from 1 ppm to 0.1 ppm from a starting concentration of 10 ppm will also double the UV Power required. The equation can theoretically be used to obtain total UV Power for any combination of flowrate or concentration, but its accuracy depends on the EE/O, which for a single contaminant can vary significantly from those listed depending on the water matrix and initial concentration.

It is important to note that the total UV power is influenced much more by a change in flowrate than by a similar change in concentration. The reason being, that UV power has only a logarithmic dependence on concentration through the log (C_i/C_r) term, and a linear dependence on flowrate.

These are the most accurate cost figures possible without performing actual design tests. The design tests consist of batch treatment runs of sampled water while varying UV dosage and reagent concentrations. Capital and operating costs are optimized over the lifetime of the remediation project by selecting the combination of total UV power and reagent concentration where the most economical treatment is obtained.
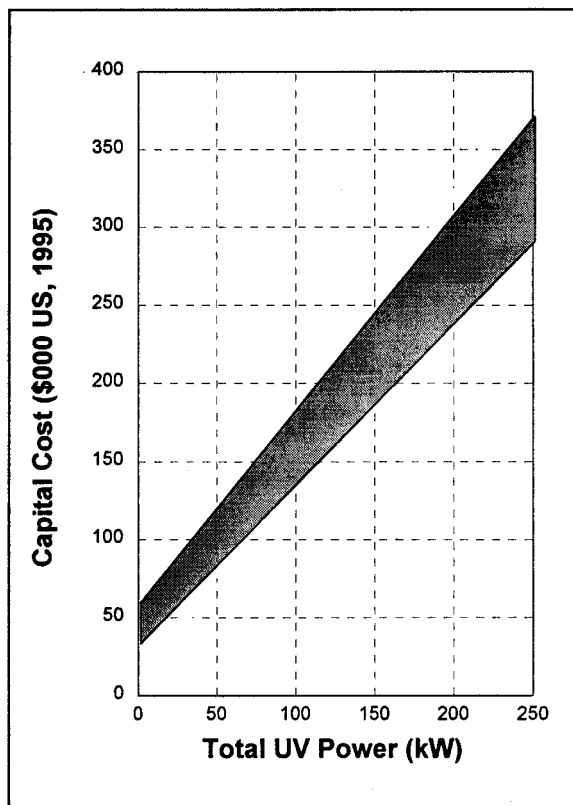

Figure 4.2
UV/Oxidation Capital Costs as a Function of UV Power.

Calculation Example 1 - single contaminant:

In a recent application, UV/Oxidation was considered for the treatment of groundwater contaminated with 1.8 ppm of 1,4-dioxane, a solvent used widely in the chemical industry. A hydrogeological survey at the remediation site specified a flowrate of 125 USgpm. Analysis of the water showed a COD of 18 ppm and a pH of 6.9. The target effluent concentration for discharge of 1,4-dioxane was 0.03 ppm.

Operating Costs:

Using an EE/O of 6 kWh/1000 USgal/order for 1,4-dioxane from Table 4.1, the electrical cost can be simply calculated using Equations 1 and 2:

Assuming a power cost of $0.06 US/kWh,

Electrical Cost = 6 kWh/1000 USgal/order * log (1.8/0.03) * $0.06/kWh = $0.64/1000 USgal

For this case the peroxide required will be approximately 2 * 18 = 36 ppm (i.e., greater than 25 ppm).

Therefore, using Equation 3:

Total Operating Cost = 1.45 * Electrical Cost + Peroxide Cost

$$= 1.45 * \$0.64/1000 \text{ USgal} + (36 \text{ ppm} * \$0.005/\text{ppm}/1000 \text{ USgal})$$

$$= \underline{\$1.11/1000 \text{ USgal}.}$$

Capital Cost:

The EE/O is also used to calculate the total UV power required in the full-scale system using Equation 4:

$$\text{UV Power (kW)} = \frac{6 * 60 * 125 \text{ (USgpm)} * \log (1.8/0.03)}{1000} = \underline{80 \text{ kW}}$$

Using Figure 4.2, the capital cost estimate for the 80 kW UV/Oxidation system required will typically range between US $125,000 and US $160,000.

Payback:

Assuming an activated carbon system is already in place, one can quickly calculate the payback of the UV/Oxidation system capital cost from the operating cost savings. Figure 3.3 can provide an estimate of the operating cost of the activated carbon system. Since 1,4-dioxane loads relatively poorly on carbon, its operating costs for this influent concentration will be greater than $10/1000 gal. Assuming year-round, 24 hour operation, yearly operating cost savings will equal:

Yearly Operating Savings = (carbon operating cost - UV operating cost) * flowrate per year / 1000 USgal

$$= (\$10 - \$1.11) * 125 * 60 * 24 * 365 / 1000 = \$584,000 \text{ per year}$$

Payback (yr) = Initial Capital ($) / operating cost savings ($/yr)

$$= \$130,000 / \$584,000 \text{ per year}$$

$$= \underline{0.22 \text{ yrs } (< 3 \text{ months})}$$

Calculation Example 2 - mixed contaminants

The following application consists of simultaneously treating four chlorinated solvents in groundwater. Influent and effluent concentrations are as follows with an expected flowrate of 50 gpm:

Compound	Influent (ppb)	Effluent (ppb)	EE/O	No. of Orders $\log(C_i/C_i)$	UV Dose (kWh/1000gal)
TCE	1500	<5	4	2.5	10
DCE	600	<70	5	0.9	4.5
PCE	30	<5	8	0.8	6.4
Vinyl Chloride	10	<2	3	0.7	2.1

Using EE/Os taken from Table 4.1 and calculating the number of orders of removal, required UV dosages to treat each contaminant have been calculated. The treatment of TCE requires the largest UV dose and therefore dictates the overall system size.

Using Equation 2 and assuming a Power Cost of $0.06/kWh:

Electrical Cost = UV Dose * Power Cost = 10 kWh/1000 USgal* $0.06/kWh = $\underline{\$0.60/1000 \text{ USgal}}$

Since the COD is not known, an estimate of the peroxide required can be obtained by summing the influent concentrations and multiplying by three times.

Therefore,

Hydrogen Peroxide required = 3 * (1.5 + 0.6 + 0.03 + 0.01) = 6.4 ppm (or less than 25 ppm)

Total Operating Cost = 1.45 * Electrical Cost + Peroxide Cost

= 1.45 * $0.60/1000 USgal + (25 ppm * $0.005/ppm/1000 USgal)

= $1.00/1000 USgal.

Using Equation 4:

$$UV\ Power\ (kW) = \frac{10 * 60 * 50\ (USgpm)}{1000} = 30\ kW$$

Using Figure 4.2, the capital cost estimate for a 30 kW UV/Oxidation system will typically range between US $70,000 and US $90,000.

BATCH SYSTEMS

At low influent flowrates greater treatment efficiency can be achieved by a batch system that has been well designed to reduce the inefficiency inherent in batch systems. Theoretically, the most efficient way to run a UV reactor is in a flowthrough mode but at low flowrates other factors will adversely affect the efficiency of the system. For example, at low flowrates there is almost no horizontal mixing as the water passes through the reactor. The water that is close to the lamp in the reactor will stay close to the lamp and will be over- treated. Water that is far away from the lamp will stay far away and will be under-treated by the lamp. Therefore, this lack of mixing at low flows will result in poor treatment of the water.

Another problem that can be encountered with low flowrates is over-heating. Medium pressure UV lamps generate heat energy and as the water passes slowly through the reactor, the temperature rise can be significant. In batch treatments, a heat exchanger is often added to remove the heat generated by the UV reactor.

Another consideration is the number of lamp starts and stops required. Frequent lamp starts will reduce the life of the UV lamps, so batch systems should be designed with batch volumes and treatment times that allow for continuous operation in order to reduce the number of lamp starts and stops.

Chapter 5
Design Tests

Design tests are carried out on a water sample, which is representative of the water to be treated, in order to confirm the preliminary capital and operating cost estimates that were based on the characterization of the subject water. They also enable the design engineer to optimize the UV/Oxidation system for each particular application.

Typically, a design test constitutes a series of runs on a pilot-scale UV batch reactor, where the effect on treatment of

- pre-conditioning the sample water,
- adjusting the concentration of hydrogen peroxide and any catalyst, and
- varying the applied UV dose

is determined until the optimum set of conditions is found. The optimum choice of factors varies from one contaminated water to another, and they can almost always be adjusted in the field to provide more effective treatment.

Upon completion of the design test, a report is issued that would typically include:

- an assessment of the treatment alternatives evaluated and a selection of the preferred UV treatment process
- a fixed price quotation for the proposed system
- a statement of the performance guarantee and warranty for the system
- an estimate of the operating costs
- a schematic flow diagram of the proposed system

REQUIREMENTS

Characterizing the contaminated water to determine the key process parameters is the first stage in the design process. Flowrate, contaminant concentration, and UV absorbance are the most critical design parameters. The chemical oxygen demand (COD), alkalinity, hardness, the concentration of certain metal ions (e.g., iron), and the total suspended solids (TSS) are also important.

In order to undertake a design test, the following are required:

- adequate volume of a representative sample of the water to be treated, (at least 5 gallons, typically 55 gallons)
- discharge objectives/requirements
- all available analytical data on the actual subject water
- any specific analytical methods that may be unique to the project
- variation in flowrate (minimum, normal, maximum)
- estimated operating hours per year
- specifics of geographical location
- electrical power cost in $/kWh

Before beginning a design test, the water must be characterized by performing a number of tests:

- measure the UV absorbance spectrum, COD, pH, alkalinity
- determine if solids, high levels of iron, chloride or any other suspected interfering species, are present.

UV Absorbance Spectrum: The UV absorbance is a measure of the transparency of the water between a wavelength of 200 nm and 400 nm. The lower the total absorbance of a water, the easier it is to treat. It is desirable to have absorbance values no greater than 0.2-0.5 per centimeter, which are the absorbances often found in groundwaters or drinking waters. High absorbances lead to competition for the UV light from non-target species. For waters with very high absorbance (>10/cm), all of the light is absorbed in the first millimeter or less from the quartz sleeve that surrounds the lamp. This results in slower treatment since untreated water must continuously be brought into contact with the quartz. Good mixing is therefore very important in these circumstances.

COD: The chemical oxygen demand (COD) gives the total amount of oxidizable compounds present in the water. The higher the COD of the water, the slower the treatment of a specific compound. COD values of under 100 ppm are considered low for **Rayox®** applications and are not of serious concern (eg., a COD of 100 ppm will decrease treatment efficiency of 15 ppm benzene by about 20%; a COD of 200 ppm will decrease treatment efficiency by 100%). Some non-organic compounds contribute to COD, eg., Fe^{+2}, H_2O_2.

pH: The optimum pH will be different for each treatment choice. For example, ozone treatment is generally more effective at basic pH, UV/Peroxide treatment is generally more effective at acidic pH. The discharge pH of a water is usually regulated between 6 and 9.

Alkalinity: Alkalinity is a measurement of the amount of bicarbonate and carbonate present. It usually is present only in groundwaters to any significant extent. The usual range in groundwaters is 200-300 mg/L. A low level is less than 100 and a high level is above 300 mg/L. Bicarbonate and carbonate compete with the pollutants for hydroxyl radicals. Carbonate is the much more reactive of the two and therefore the effect is more noticed at higher pH. In high alkalinity waters, treatment improves at pH<6.5 with a pH of 5 about optimum. The H_2CO_3/HCO_3^- buffer occurs at pH 6.5; the HCO_3^-/CO_3^{-2} buffer is at pH 10.

Suspended Solids: Suspended solids have two effects on **Rayox®** treatment. They reflect and/or absorb UV light, which means that less light reaches the contaminant or hydrogen peroxide. The solids also adsorb organics. Since only dissolved organics will react, adsorbed organics slow down treatment. The UV/Oxidation process first destroys the dissolved component, causing a shift in the phase equilibrium. As the adsorbed organics begin to dissolve into solution, they are quickly oxidized. The new rate determining step is the rate of desorption, which is much slower than the rate of oxidation. This effect is most

severe for hydrophobic compounds such as PCBs and PAHs. A 100 ppm level of suspended solids slows down treatment of 100 ppm 1,4-dioxane by 30%.

Oil and Grease: Soluble oil and grease levels slow down treatment by competing with hydroxyl radicals and increasing the UV absorbance of the water. Insoluble oil and grease must be removed with an oil/water separator. Hydrophobic organic compounds like benzene will preferentially dissolve in the oil droplets or emulsions and will not be treated by AOP processes.

Iron: High levels of iron (> 50 ppm) will strongly absorb UV light and thus compete with target contaminants and H_2O_2 for UV energy. This decreases treatment efficiency. However, UV/Oxidation can benefit from dissolved iron due to Fenton's chemistry. Therefore, if iron is present in the water at greater than 5 ppm, it is beneficial to maintain the iron in the solution by operating at a reduced pH.

Note: Soluble iron will precipitate during treatment (if the pH is not reduced), but quartz fouling is not a problem, provided that the UV reactor employed has a proven and powerful cleaning mechanism.

High Chloride: High levels of chloride can compete with hydroxyl radicals at low pH or lead to corrosion problems (> 10%). At pH values above 5, chloride has little effect but at pH values of 2 or 3, chloride can drastically reduce treatment efficiency.

PRETREATMENT

Pretreatment may be required before AOP treatment is applied, depending on the level of interferences such as suspended solids or oil and grease. There are two major methods of pretreatment:

Filtering: If suspended solids are a problem (> 50 ppm), then filtering should be considered. There is an economical and operational trade-off between filter size and treatment efficiency. A finer filter will increase UV treatment efficiency but will result in more frequent filter changeouts or increased backwash. Generally, a 10 to 30 μm filter is recommended although other porosities can be tried.

Clarification: Suspended solids and/or oil droplets can be removed using a clarifier. Often a coalescing surface, such as an inclined plate or coalescing filter medium, is required and sometimes a flocculant such as alum, or other commercial polymer is required to aid in the separation.

Note: The added costs and handling problems associated with the sludge or filter cake generated from pretreatment should be carefully weighed against the costs of decreased treatment efficiency.

INTERFERENCES

It is also important that the water be tested for any species that may significantly reduce UV treatment efficiencies. Species leading to reduced treatment efficiency can be classified into three groups:

1. **UV Interferences** - species that absorb UV light and convert it into heat, leaving fewer photons available for absorption and photolysis by hydrogen peroxide to yield hydroxyl radicals.

2. **Hydroxyl Scavengers** - species that readily react with and consume hydroxyl radicals, leaving fewer of them available to react with target contaminants.

3. **Suspended Solids** - although fouling is not a concern for **Rayox®** systems, high SS levels will foul other commercially available UV treatment systems. The suspended solids will also form a surface upon which hydrophobic compounds will adsorb and therefore slow their treatment rates.

Table 5.1 summarizes factors that can reduce treatment efficiency and at what concentrations they begin to become a concern.

Table 5.1
Factors Affecting UV/Oxidation Treatment

Factors Affecting Treatment	Concentration of Concern
UV Interferences:	
Nitrate (NO_3^-)	> 10 ppm
Nitrite (NO_2^-)	> 10 ppm
Phosphate (PO_4^-)	> 1%
Chloride Ion (Cl^-)	> 1%
COD	> 1000 ppm
Ferrous Ion (Fe^{+3})	> 50 ppm
Hydroxyl Scavengers:	
Chloride Ion (Cl^-)	> 1000 ppm
Nitrite (NO_2^-)	> 10 ppm
Carbonates (HCO_3^-/CO_3^{-2})	> 300 ppm
Sulphites (SO_3^{-2})	> target contaminant
Sulphides (S^{-2})	> target contaminant
Precipitates:	
Calcium (Ca^+)	> 50 ppm
Ferrous Ion (Fe^{+3})	> 50 ppm
Magnesium (Mn)	> 1000 ppm

Most of these concerns are addressed during design tests and can be overcome by proper selections of pretreatment, UV treatment process, oxidant, catalyst, and pH. In cases where UV interferences are too high, a non-photochemical AOP pretreatment step may be more cost effective.

NON-PHOTOCHEMICAL AOP

The non-photochemical pretreatment options are ozone at high pH, ozone plus peroxide, along with several other proprietary Solarchem processes.

Ozone/high pH: The ozone treatment is run at around pH 9-12 where the reaction between the hydroxide ion and ozone results in the formation of hydroxyl radicals (see page. 8 in Chapter 2) which causes the decomposition of ozone into hydroxyl radicals. A 1:1 molar ratio of ozone to target contaminants is a typical minimum. Complete destruction requires much greater ratios, up to about 5:1 or sometimes higher and hence becomes more costly. Ozone injection devices include diffusers, in-line mixers, and ventures. For costing purposes, first calculate the dose of ozone required (in pounds) based on a molar ratio of between 1:1 and 5:1 of O_3 to contaminant. Then using 10 kWh/lb of ozone generated (which includes air prep), calculate the power and subsequent electrical cost required. The capital cost of ozone treatment can be high and also have complexities with regards to air/water separation, off-gas treatment and health, safety, and environmental concerns.

Ozone/peroxide: The combination of ozone with hydrogen peroxide is an AOP treatment alternative for low organic concentrations of several hundred parts per billion or less. The pH is maintained at between 7 and 8. At higher pH values, the reaction of ozone with hydroxide ion predominates and the peroxide has little benefit. The optimum molar ratio of ozone to peroxide is about 2:1, although this may differ for various waters.

Other Pretreatment Processes: If a water stream requires pretreatment for the economical removal of organics, consult Solarchem for available options and the possibility of applying these options to a full-scale process.

OTHER CONSIDERATIONS

Representative Water Sample: The initial and final concentrations of the target compounds used in the design test should be similar to those expected in the actual application. To ensure representative contaminant concentrations, procedures such as minimizing drum head space during transport and test procedures to reduce VOC losses should be followed. To obtain accurate final concentrations, the reduction in concentration should be analyzed throughout each run in order to determine the consistency of the treatment.

Initial Concentration: The initial concentration of pollutant usually has an effect on the treatment rate. At higher concentrations, the EE/O values are higher (treatment efficiency is lower). The exact decrease in efficiency depends on the complexity of the organic. Small molecules with only one or two carbon atoms show little or no effect on initial concentration. For example, chloroform and NDMA do not appear to have any concentration effect and thus the amount of UV energy to give 90% destruction is the same for a wide range of initial concentrations of pollutant. Pollutants with more carbon atoms, such as benzene or 1,4-dioxane, show a significant relationship between initial concentration and treatment performance. For example, the EE/O for benzene at 3 ppm is 4.5 and at 15 ppm it is 7. Treatment of 100 ppm of 1,4-dioxane with 200 ppm H_2O_2 requires an EE/O of 11.6 whereas treatment of 200 ppm of 1,4-dioxane with 500 ppm H_2O_2 requires an EE/O of 17.9.

One reason for the increase in EE/O at higher initial contaminant concentrations is that higher concentrations of intermediate byproducts are formed that absorb UV light. Since the same intensity of UV light is present regardless of the pollutant concentration, the amount of photons absorbed by the pollutant must decrease if the concentration of a co-absorber(s) is increased. The intermediate byproducts also slow reaction rates by competing for hydroxyl radicals.

Batch vs. Flowthrough: Most frequently, design tests are conducted in batch mode. This offers the most reproducible method of treatment since levels of additives can easily be controlled. Since most full scale systems are flowthrough, the batch testing must be properly designed to get accurate figures for scale-up purposes. Some precautionary measures include:

1. Using a low-power lamp at high flowrates. It is best to use the 1 kW lamp at flows of around 20 USgpm. This should result in almost no error in converting the data to a flowthrough configuration unless the EE/O is below 5, e.g., low initial concentrations of NDMA or TCE.

2. In batch mode, it is possible that some volatile compounds can be air stripped in the batch tank. This is usually not seen for most compounds treated (BTX, TCE). However, low boiling (higher vapor pressure) compounds such as Freon-11 and vinyl chloride can easily be volatilized. Therefore, it is advisable to include a "mixing-only" control run in the design test, so that the data are available to account for any volatilization.

3. Ensure proper mixing. If flowthrough tests are being performed, wait till at least three reactor volumes have passed with the lamp on at full power before taking the first treated sample. If peroxide is being metered in, make sure that it is being adequately mixed before entering the reactor.

Chapter 6
UV Treatment Options

The major treatment options employing UV light are:

- **Rayox®** (UV Only)
- **Rayox®** (UV/ H_2O_2)
- **Rayox®-F** (UV/Fentons)
- **Rayox®-O** (UV/Ozone)
- **Rayox®-R** (UV/Reduction)
- **Rayox®-A** (UV/Visible/Peroxide)

Note: The Solarchem lamp is of a proprietary nature. Its characteristics and comparison to other lamps will be covered in a later section. The following discussion pertains to use with the Solarchem lamp only and may not be valid for UV lamps in general.

RAYOX® (UV ONLY)

This process involves the use of high-intensity UV lamps only with no oxidant or catalyst. It is limited to compounds that strongly absorb light between 200 and 300 nm and photodegrade with good efficiency. A good example where this applies is the treatment of NDMA. Usually it is practical only for treatment of a single compound in water. It may be advisable to add a small amount of peroxide to help oxidize any byproducts, such as nitrite produced from UV treatment of NDMA. Complete mineralization usually does not occur with photolysis only.

RAYOX® (UV/ H_2O_2)

Please refer to Chapter 2.

RAYOX®-F (UV/FENTONS)

This is a patented Solarchem process, which involves the addition of a small amount of iron (II) catalyst (about 10 ppm) to the water, adjustment of the pH to between 2-4, followed by treatment with UV. For aromatic and olefinic compounds up to five fold enhancement in treatment rate is possible. The costs of pH adjustment and the added complexity of the **Rayox®-F** process versus UV/Peroxide (**Rayox®**) must be considered in evaluating this treatment alternative.

RAYOX®-O (UV/OZONE)

Since photolysis of ozone gives hydrogen peroxide, UV/Ozone is really a combination of UV/Peroxide (**Rayox®**) and ozone/peroxide. However, there are a few instances where the contaminant strongly absorbs UV and forms a sufficiently long-lived excited state that reacts directly with the ozone, resulting in treatment costs that are lower than UV/Peroxide. It is sometimes advantageous to use a two-stage approach: ozone at high pH followed by photolysis or UV/Peroxide. Note that air stripping of volatile waterborne contaminants will occur with the use of ozone and should be avoided for waters with high VOCs. The use of ozone can be quite effective from an operating cost standpoint, especially for waters with high background UV absorbance, but capital cost, stripping, ozone destruction, and health, safety, and environmental considerations can make ozone less desirable.

One case where ozone is cost effective is in the treatment of trinitrotoluene (TNT) contaminated water. The treatment of TNT with UV/Peroxide or ozone alone generates a toxic byproduct, trinitrobenzene (TNB), which is refractory and difficult to treat. UV/Ozone treatment of water contaminated with TNT can avoid the production of TNB and so the resulting treated water stream is non-toxic.

RAYOX®-R (UV/REDUCTION)

Halogenated alkanes, such as carbon tetrachloride, chloroform, methylene chloride, dichloroethane (DCA), trichloroethane (TCA), pentachloroethane (PCA), and chlorofluorocarbons (Freons), are an important class of pollutants, which are found in a number of contaminated groundwaters and industrial wastewaters. Many of these pollutants adsorb poorly on activated carbon and treat slowly with UV/Oxidation and thus represent a unique treatment problem.

Solarchem has developed a patented *Ultraviolet Reduction Process*, called **Rayox®-R**, which is able to treat saturated halogenated organics (e.g., chloroalkanes) with much improved performance over standard UV/Oxidation treatment. This new process involves the photochemical generation of hydrated electrons (e_{aq}^-) via a proprietary catalyst, **ENOX 710**:

$$\text{ENOX 710} \xrightarrow{\ h\nu\ } e_{aq}^- + H^+$$
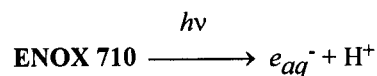
The hydrated electron is a very strong reducing agent and reacts with halogenated organics to generate inorganic halide ions. For example, the initial reaction step for TCA is as follows:

$$CCl_3CH_3 + e_{aq}^- \longrightarrow \bullet CCl_2CH_3 + Cl^-$$

Table 6.1 compares the •OH and e_{aq}^- rate constants for several common chloroalkanes and chloroalkenes. Chloroalkanes react from 1000 to over 16,000 times faster with the hydrated electron than with the hydroxyl radical.

Table 6.1
Reaction Rate Comparison

Pollutant	Rate Constant/$10^9 M^{-1} s^{-1}$	
	Hydrated Electron	Hydroxyl Radical
CH_2Cl_2	6.3	0.058
$CHCl_3$	30	0.005
CCl_4	16	0.001
$CH_2 = CCl_2$	23	6.8
$CHCl = CCl_2$	19	4.2
$CCl_2 = CCl_2$	13	2.6

Figure 6.1 compares UV/Peroxide (**Rayox®**) and UV/Reduction (**Rayox®-R**) treatment of 20 ppm of chloroform in tap water. The

amount of energy required to treat the same amount of contaminant is reduced by a factor of four. This directly affects both operating and capital costs for treatment. Operating costs for contaminants such as TCA have been reduced by as much as 85%.
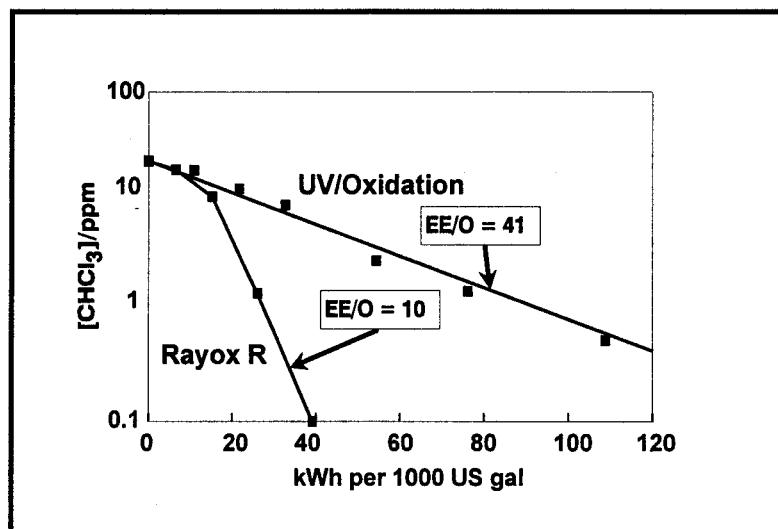

Figure 6.1
Comparison of Chloroform Treatment Using UV/Reduction vs.
UV/Oxidation.

Rayox®-R is effective for the treatment of not only halogenated alkanes but *also* halogenated alkenes (e.g., TCE, DCE, and vinyl chloride). Thus, in a waste stream that contains a variety of halogenated contaminants, both saturated and unsaturated, all will be treated equally well by **Rayox®-R**.

RAYOX®-A
(UV/VISIBLE/PEROXIDE)

H_2O_2 is a relatively weak absorber in the 200-300 nm wavelength band. In waters with a high background UV absorbance (i.e., COD > 500 ppm) H_2O_2 must compete with other UV absorbers for photons. Therefore, the production of hydroxyl radicals becomes less efficient.

To overcome this problem, Solarchem has developed the **Rayox®-A** process using a proprietary photocatalyst, **ENOX 910**. **ENOX 910** strongly absorbs both UV and visible light from 200 to 500 nm wavelengths. Figure 6.2 compares the relative absorbance of **ENOX 910** and hydrogen peroxide.
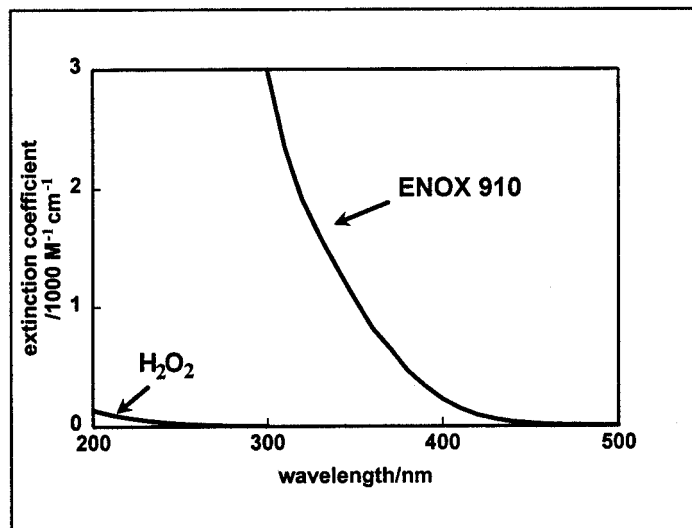
Figure 6.2

Comparison of UV Absorbance Spectra for ENOX 910 and Hydrogen Peroxide.

Unlike H_2O_2 which absorbs light only in the UV region, the **ENOX 910** photocatalyst makes use of significantly more of the lamp energy available to generate hydroxyl radicals.

The following is a simplified reaction mechanism for the **Rayox®-A** process:

$$ENOX\ 910 \xrightarrow{h\nu} ENOX\ 910^*$$

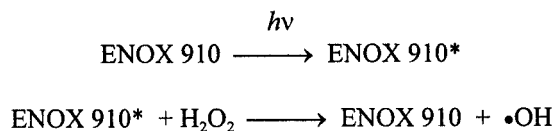$$ENOX\ 910^* + H_2O_2 \longrightarrow ENOX\ 910 + \bullet OH$$

Figure 6.3 is a comparison of treatment rates of total BTEX (benzene, toluene, ethylbenzene, and xylenes) in tank bottom water from bulk terminals.
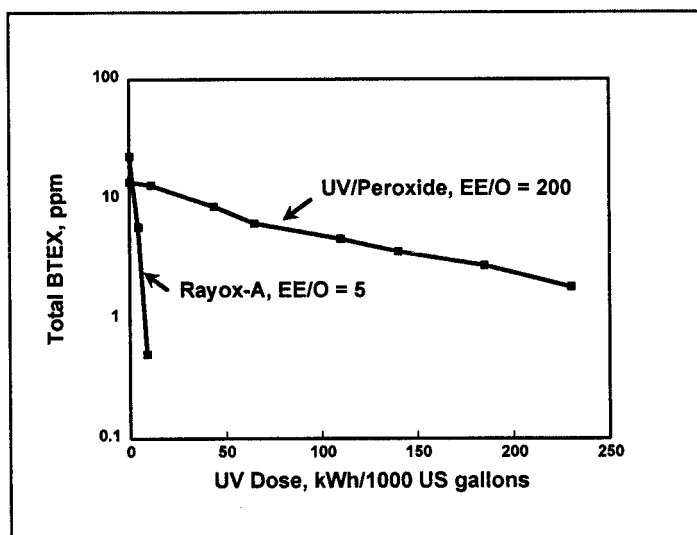

Figure 6.3

Comparison of Rayox®A and UV/Peroxide for BTEX.

6-4

In this application, the contaminated water has a chemical oxygen demand (COD) of about 1000 ppm and absorbs significantly in the UV and near UV region. It could not be treated efficiently using the standard process of UV catalysed peroxide, which would require a UV dose of 200 kWh/1000 US gallons to destroy the first 90% of contaminants.

However, the **Rayox®-A** process is able to treat this water efficiently and economically with an electrical consumption of 5 kWh/1000 US gallons to achieve the first 90% destruction of the BETX compounds. Thus, the electrical energy required to reduce the concentration of pollutants is reduced by 95%.

Any organic pollutant that has a reasonable reactivity towards hydroxyl radicals can be treated by the **Rayox®-A** process. These include aromatic and haloaromatic compounds, chloroalkenes and alkanes, ethers, alcohols, carboxylic acids, and ketones.

SEQUENTIAL TREATMENT

The treatment selectivity of the various **Rayox®** processes makes it possible to treat sequentially with **Rayox®-R** and **Rayox®**. Figure 6.4 shows the treatment of a mixture of 1,1,1-trichloroethane (TCA) and toluene. In the **Rayox®-R** phase the TCA disappears rapidly, but the toluene hardly changes at all. Then in the **Rayox®** phase, the toluene, plus any products from the treatment of the TCA, is removed. This example demonstrates the versatility of the treatment options available.
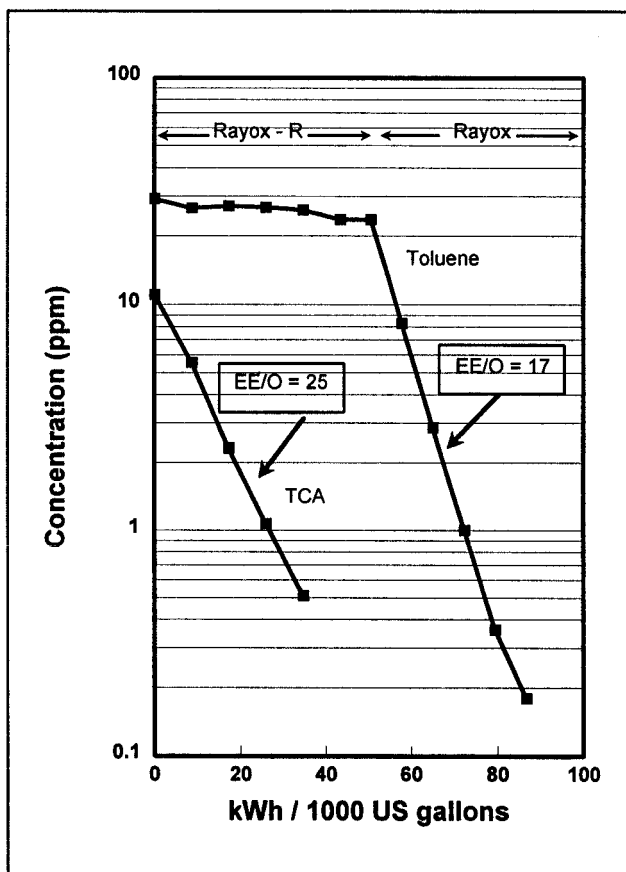

Figure 6.4
Sequential Rayox®-R and Rayox® Treatment of TCA and Toluene.

PROCESS SUMMARY

The following table summarizes the various UV treatment options available, with a list of contaminants they most effectively treat.

Table 6.2

Summary of UV Enhanced Treatment Processes

Solarchem Process	Type of Treatment	Typical Contaminants
Rayox®	Direct UV Photolysis	NDMA
Rayox®	UV catalyzed peroxide	TCE, PCE, vinyl chloride, BTEX, 1,4-dioxane
Rayox®-F (patented)	UV and Iron catalyzed peroxide	aromatics and phenols
Rayox®-T (patent pending, not discussed in chapter 6)	Catalytically enhanced peroxide	aromatics and chloroalkenes in high COD waters
Rayox®-A (patented)	UV and Visible light catalyzed peroxide	aromatics, ketones, ethers, chloroalkenes and alkanes, TOC in waters with high background UV absorbance
Rayox®-R (patented)	Ultraviolet Reduction	TCA, DCA, chloroform, carbon tetrachloride, dichloromethane
Rayox®-O	UV/Ozone	TNT, color removal, PCP

Chapter 7
Specific Treatment Examples

This chapter contains examples of the **Rayox**® treatment of specific classes of compounds. Several possible treatments are discussed under each heading. In each case, the preferred treatment is based on a combination of operating cost, capital cost, and process simplicity.

BTEX

BTEX refers to benzene, toluene, ethylbenzene, and xylene. These are aromatic compounds found primarily in gasoline. As common groundwater and tank bottom contaminants, their concentrations are found in the range from low ppb levels to 100 ppm. The typical discharge requirement is 5 ppb. The major application for treatment is in leaking underground gasoline storage tanks and ballast clean-out water from the petroleum industry.

The type of treatment depends on the initial concentrations and on the total pollutant load of the water. For waters that have moderately low UV absorbance, COD less than 100 mg/L and BTEX concentrations less than 25 ppm, UV/Peroxide is the best option, resulting in EE/O values of 2-10. Operation at pH 5 or lower will give a small improvement (20% - 30%) in EE/O. **Rayox**®-**F** will give EE/O values of around 2. The EE/O values are strongly concentration dependent, and for higher concentration waters, COD > 500 ppm, Solarchem's proprietary **Rayox**®-**T** or **Rayox**®-**A** processes may be necessary to find a cost-effective solution.

Ozone-based treatment is not recommended, since significant air stripping occurs.

MTBE

MTBE (methyl t-butyl ether) is a gasoline additive. Due to its high solubility in water, it tends to be found in much higher concentrations (hundreds or thousands of ppm) than BTEX. At these higher concentrations, alternative technologies such as activated carbon become very expensive and in most cases uneconomical.

MTBE is more difficult to treat than BTEX, with EE/O values of around 10 and hence can be the deciding factor in the treatment of gasoline containing waters, depending on the relative concentrations and the discharge requirements of each compound. The same treatment options are used as with BTEX.

DCE, TCE, PCE, VC

These compounds are dichloroethylene, trichloroethylene, perchloroethylene, and vinyl chloride. They are found in most contaminated groundwaters in the ppb and low ppm level. TCE has been identified as the most common pollutant in groundwater. These compounds have seen extensive use as cleaning solvents in a number of applications.

These compounds are easy to treat with EE/O values in the range of 1-10. The concentration effect is not as strong as with BTEX. The major treatment options are **Rayox®** (UV/Peroxide) or **Rayox® F**.

DCA, DCM, TCA, CHCl₃, CCl₄

These compounds, dichloroethane, dichloromethane (methylene chloride), trichloroethane, chloroform, and carbon tetrachloride are examples of chlorinated alkanes. They are found in many groundwaters in the low ppb to 10-1000 ppm range. They are considered refractory compounds, in that they are hard to treat by advanced oxidation. DCA and DCM are the easiest of the group to treat by UV/Peroxide with an EE/O value around 15-20 for relatively clean waters. TCA and chloroform have EE/O values generally of 30 or higher. The actual EE/O values are very strongly influenced by the UV absorbance and the total organic loading of the water. Easy-to-treat compounds are oxidized before refractory compounds, so frequently the DCA, TCA, and chloroform levels will go down very slowly until the other organics are treated and then the DCA, TCA, and chloroform will be oxidized.

There are two treatment choices. **Rayox®** (UV/Peroxide) will give EE/O values as stated above. A pH of 5 or less will give about double the rate of treatment than at a pH of 7 or more. The alternative and preferable treatment option is **Rayox®-R**, which gives much better treatment than UV/Peroxide with EE/O values of around 5-20. A water with many types of pollutants would require a combination of UV/Peroxide stage and **Rayox®-R**.

NDMA

NDMA an oxidation product of UDMH (unsymmetrical dimethylhydrazine) and a product of dimethylamine interacting with nitrite. It is found in some groundwaters and wastewaters from chemical plants usually in ppb levels. UV light is the only effective method of treatment.

NDMA can be readily treated with **Rayox®** by UV only with an EE/O of 2 (see Table 4.1). This is a preferred treatment option for clean groundwater. The rate of treatment of spiked tap water is increased almost two-fold by the photolysis at pH 2-4. In wastewaters NDMA can be an initial byproduct if UDMH or dimethylformamide are present. In this case, all of the UDMH and dimethylformamide must be treated before the NDMA will be destroyed. In heavily contaminated water this may require a non-photochemical treatment.

PHENOL AND PCP

Phenols are found in wood treating operations in both wastewater and groundwater. Levels range from ppb to hundreds of ppm. There are several treatment options. For low concentration of phenols, **Rayox®** (UV/Peroxide) or **Rayox®-F** (UV/Fentons) can be used, with EE/O values in the 5-10 region (see Table 4.1). At higher concentrations, the EE/O values become very large since the byproducts absorb UV light very strongly. In this case, **Rayox®-T** or **Rayox®-A** can be used for successful treatment. UV/Ozone is also a good treatment option for phenols.

NITRO-ORGANICS

Nitro-organics are primarily used as explosives. Examples include TNT (trinitrotoluene), DNT (dinitrotoluene), and NG (nitroglycerine). Low levels (low ppm) of TNT can be treated with **Rayox®** (UV/Peroxide) or UV, however, this generates high levels of; trinitrobenzene (TNB), which is refractory to hydroxyl radical initiated oxidation. This can usually be the deciding factor in the choice of treatment options. The TNB is toxic to fish and hence **Rayox®** (UV/Peroxide) treatment of TNT water will leave toxic species unless very high UV doses are employed. Treatment with ozone does not give increased levels of TNB and hence is the usual preferred treatment option. Either UV/Ozone or ozone at high pH can be used.

ETHERS

Ethers include 1,4-dioxane and tetrahydrofuran. These are used as solvents and are formed as byproducts in certain chemical processes. They are found in some wastewaters and groundwaters in ppb to ppm levels. These compounds do not load on activated carbon efficiently and thus the usual preferred treatment is **Rayox®** (UV/Peroxide) with EE/O values of 2-20. There is a concentration effect on the EE/O. **Rayox®-F** and **Rayox®-A** are typically not cost-effective except in high concentration cases. (See also MTBE).

CYANIDES

Cyanide (CN⁻) contaminated waters are produced from mining and electroplating operations. There are several type of cyanides, which can be classified as easy, medium, and difficult to treat by conventional oxidation processes. Free cyanides, such as sodium or potassium cyanide, are easy to oxidize and can be treated with bleach, peroxide, or ozone only. Weak acid dissociable cyanides, such as copper or zinc cyanide, are of medium difficulty to treat. Complexed cyanides such as iron cyanide do not treat using an oxidizing agent by itself. UV/Bleach is the preferred treatment and is about twice as effective as UV/Peroxide. The EE/O is between 40 and 80. Mechanistically, the iron cyanide is photolyzed to give free cyanide and iron hydroxide. The free cyanide is then oxidized by the bleach to give cyanate, OCN⁻, which is then further oxidized to CO_2 and NO_3^- (or perhaps N_2).

ACETONE

Acetone is a very common solvent and is found in many contaminated groundwaters, usually in low ppm levels. Acetone is a difficult compound to treat by advanced oxidation. Oxidation of acetone will not commence until virtually all of the other organics have been removed. The EE/O under best conditions is around 30-40 for 20 ppm acetone, using **Rayox®** (UV/Peroxide) at pH 5. The EE/O values increase dramatically as the acetone concentration increases. In dirty waters the EE/O can be several hundred. **Rayox®-A** is the most cost-effective AOP process for destroying waterborne acetone.

COD AND TOC

COD (Chemical Oxygen Demand): This is a measure of the amount of oxygen consumed during oxidation of the compound with potassium dichromate. The method measures organic plus inorganic compounds that are oxidized.

TOC (Total Organic Carbon): The TOC is the amount of carbon present as organically bound carbon. It is measured by the release of CO_2 upon oxidation of the compound with either high temperature catalyst or UV/Persulphate. The methodology can measure volatile carbon, inorganic carbon, and total carbon. COD is typically about two to three times higher than TOC. COD and TOC represent the total pollution level of a water. Basically, to reduce the values of COD or TOC requires a conversion of the contaminant to CO_2 and water. COD is usually a little easier to remove by advanced oxidation since non-organics, e.g., Fe^{+2} contribute and you do not need quite as complete an oxidation to see a reduction $\cong$ COD. As a rough approximation, EE/O values of 50-100 are necessary to obtain removal of TOC from initial concentrations up to 100 ppm. The best treatment is usually **Rayox®** (UV/Peroxide) at pH 5, where competition of carbonate/bicarbonate is minimized. For waters with high COD or TOC levels, **Rayox® A** or **Rayox® T** treatment is recommended.

BOD

BOD (Biochemical Oxygen Demand): BOD is the amount of oxygen consumed during a five-day biological oxidation test. BOD is always smaller than COD and it is harder to reduce in value than COD because some compounds, such as chlorinated organics, give low BOD values but their oxidation products give high BOD values, as the oxidation products are more biodegradable. Therefore, BOD can actually increase during the early stages of treatment. Advanced oxidation alone is generally not a good choice for treatment of water for the purpose of BOD reduction. BOD reduction is best dealt with by a combination of **Rayox®** followed by biological oxidation.

AOX/TOX

AOX (Adsorbable Organic Halogen): AOX measures the amount of organically bound halogen, X (usually chlorine), in a compound. TOX (total organic halogen) and AOX are interchangeable terms. Reduction of AOX by enhanced oxidation is easier than COD or TOC since the halogens tend to come off the organic compound in the early stages of treatment. The EE/O for AOX reduction is similar to the EE/O for the specific halogenated compound (see Table 4.1, Chapter 4).

Chapter 8
Solarchem Environmental Systems

Since 1988, we at Solarchem have been marketing our **Rayox®** family of advanced oxidation processes and now have over 80 full-scale industrial installations in North America, Europe, and Australasia treating a wide variety of groundwater and wastewater streams.

Over the past three years, Solarchem has carried out an extensive development program to bring on stream emerging technology to improve its treatment approach. This has involved not only enhancements of equipment dependability and efficiency, with the introduction of improved lamps, power supplies, and quartz lamp sleeve cleaning systems, but also process improvements resulting in the ability to treat refractory pollutants and pollutant mixtures, with the introduction of new processes such as UV/Reduction (**Rayox®-R**).

SOLARCHEM LAMP

Most UV photodegradation processes occur with the absorption of UV light in the 200-300 nm range. However, commercially available high-power UV lamps have an energy efficiency of only ~15%. In co-operation with our lamp supplier, we have been able to improve this efficiency to over 30%, with a substantial output below 240 nm, where many pollutants absorb UV directly. As an example, Figure 8.1 compares the treatment rate per kW under identical conditions of pollutant concentration, flowrate, and temperature of 1,4-dioxane, dichloromethane, and pentachlorophenol with Solarchem's 1 kW lamp and a commercial medium-pressure mercury lamp. As can be seen, the efficiency of Solarchem's lamp is two to three times greater than the standard commercial lamp, even when allowance is made for the different electrical powers. **Rayox®** systems use these lamps in 10 and 30 kW sizes.

Figure 8.2 shows the spectral outputs for some of the various types of mercury lamps commercially available. The Solarchem lamps are specialized high-temperature mercury lamps that have 30% output between 200 and 300 nm, which is significantly better than conventional medium-pressure mercury lamps and pulsed xenon flashlamps. The efficiency is similar to the low-pressure mercury lamps with the added benefits of having a broad band emission extending below 200 nm, and with much larger lamp powers available. Consequently, one 30 kW Solarchem lamp can replace 200 to 500 low-pressure lamps, resulting in systems that require much less maintenance and space.
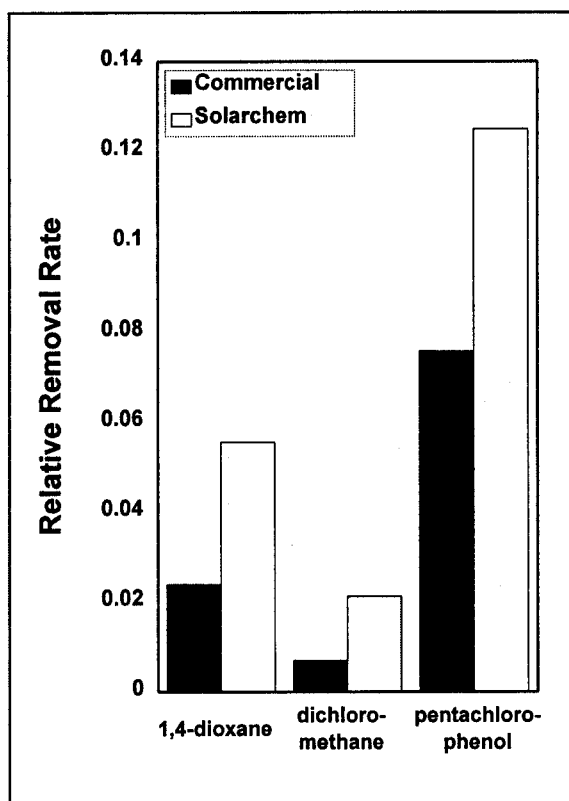
Figure 8.1
Comparison of Relative Removal Rate per kW for a Commercial Medium-Pressure Hg Lamp and a Solarchem Lamp.
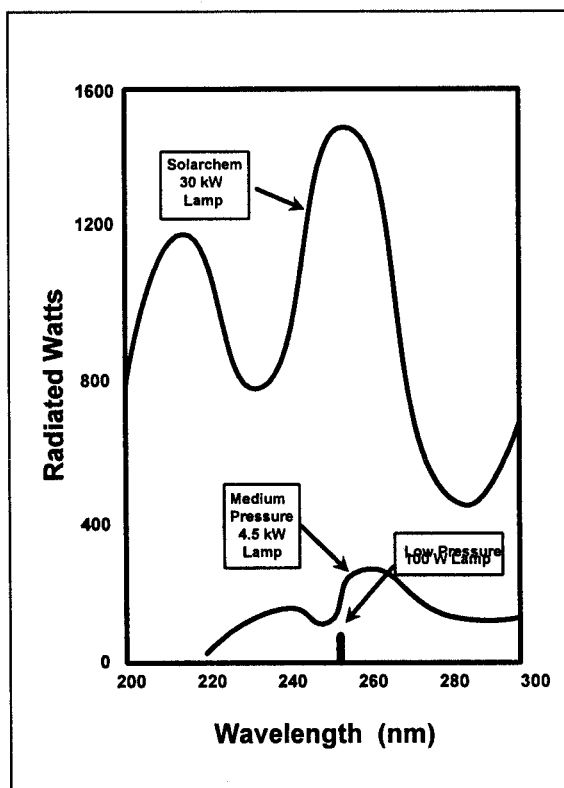

Figure 8.2
Comparison of UV Output for Commercially Available Mercury Lamps.

ENOX PHOTOCATALYSTS

Solarchem offers eight different UV treatment processes that can be tailored to a specific application. For a full description of each of these processes and photocatalysts, refer to Chapter 7.

POWER SUPPLY

Advanced oxidation is an energy-intensive method of water treatment. Use of an energy-efficient power supply has positive consequences on the operating costs of commercial systems. For this reason, Solarchem's developmental efforts on lamp power supplies have centered on achieving an excellent match between the inductive load represented by the lamp and the power supply. Over 90% of the mains power delivered by the power supply is received by the lamp. Power factor correction produces a power factor better than 0.9, thus avoiding a potential low power factor surcharge by the utility.

QUARTZ SLEEVE WIPER

The **Rayox®** reactor has a single UV lamp at the center separated from the water by a cylindrical quartz sleeve. Each **Rayox®** reactor has a patented wiper (called transmittance controller) for the quartz sleeve around the lamp. This device consists of a concentric stainless steel brush assembly that is automatically driven over the surface of the quartz sleeve by a pneumatically driven impeller. Iron-containing groundwaters can be a particular problem, as metal oxide coatings deposit on the quartz sleeve. Without the transmittance controller, treatment efficiency may be very good at first, but deteriorates over a period of days or weeks, or even hours in some instances. Figure 8.3 shows the performance of a **Rayox®** groundwater installation, running at 500 gpm, for 32 weeks. This was possible only as a result of the installation of the transmittance controller on each reactor. Without the transmittance controller, fewer than six hours of operation in iron containing groundwater would severely block UV light transmittance into the reactor, with a consequent reduction in treatment efficiency.
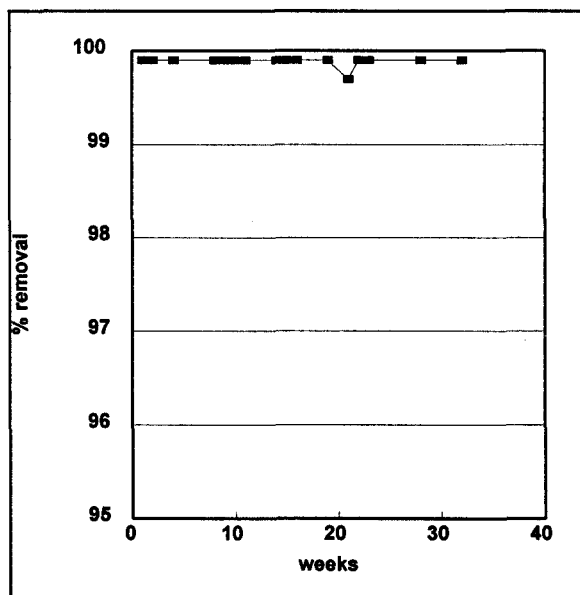

Figure 8.3
*Operational Results for a **Rayox®** Groundwater Installation Equipped with Solarchem's Quartz Cleaner.*

SUMMARY

Continuing research and development efforts have enabled Solarchem to bring on stream many new advances to UV/Oxidation technology. The improvements can be summarized as follows:

1. The development of UV lamps, which have an electrical efficiency of over 30% for the emission of UV light in the 200-300 nm range.

2. Design and implementation of power supplies with over 90% efficiency in delivering electrical power to the UV lamps.

3. Development of a robust wiper for keeping the quartz sleeve clean at all times, ensuring the integrity of the treatment.

4. Development of new and effective photocatalysts and UV treatment options not offered by any other UV/Oxidation vendor.

Appendix I

UV/Oxidation System Specifications

SOLARCHEM ENVIRONMENTAL SYSTEMS, INC.
UV/OXIDATION SYSTEM SPECIFICATION

CONTENTS   **PAGE**

THIS SPECIFICATION DOCUMENT CONFORMS TO THE CSI RECOMMENDED FORMAT

PART 1-GENERAL

1.01 DESCRIPTION

A. Scope

1. This specification covers the equipment and installation requirements for a UV/Oxidation system, which shall include factory assembled reactor(s), power supply(ies), reagent delivery system(s), and process control components.

2. The UV/Oxidation system shall be designed to provide treatment of the ____water stream to the treatment targets specified herein. The manufacturer shall assume complete responsibility for conformance with these specifications.

B. Related Work Specified Elsewhere

1. Electrical work is included in Division 16.

2. Piping is in Section _____. All process piping shall be stainless steel 316L

3. Painting and Finishing is in Division 9.

1.02 QUALIFICATIONS

A. Experience

1. Only equipment of the type described in this Section of the Specifications which has been in service for a period of not less than three (3) years in a minimum of five (5) installations shall be considered. To show compliance with this requirement, the manufacturer shall provide, with the submittals, a list of similar installations including the date placed in operation and unit description.

2. Equipment submitted for approval which does not meet the specified experience period shall be considered if the Equipment Supplier or Manufacturer provides a bond or cash deposit which shall guarantee replacement in the event of failure to comply with design criteria. The amount of the guarantee bond or cash deposit shall be for 150% of the purchase price of the equipment. The time for which the guarantee bond or cash deposit is required shall be equal to the warranty period.

B. Acceptable Manufacturers

1. The UV/Oxidation system shall be the **Rayox**® - ( ) process and equipment as manufactured by Solarchem Environmental Systems, Inc., Markham, Ontario.

2. _____

1.03 PERFORMANCE REQUIREMENTS

A. The manufacturer shall provide a guarantee that the equipment shall continuously meet the specified performance requirements under the following conditions:

System Size	: _____ kW	
Design Flowrate	: _____ gpm (For Treatment)	
Maximum Flowrate	: _____ gpm (Hydraulic)	
Minimum Flowrate	: _____ gpm (Turndown)	
Max. Inlet Pressure	: _____ psig	
Max. Pressure Drop	: _____ psi @ _____ gpm	
Effluent Temperature	: _____ deg. F (max)	
Power Supply	: 3ph / 60Hz / 480V	

Contaminant	Influent, ppb	Effluent, ppb

The UV/Oxidation system shall be supplied with a minimum electrical capacity to power UV lamps of _____ kW. In cases where a minimum UV power is not specified by the client, the UV/Oxidation manufacturer must state the UV power of the proposed system, and shall provide the results of treatability tests and calculations which clearly support the scale-up to the proposed system.

The operating cost in $/1000 gallons at the design flowrate shall be provided. This shall consist of the cost of UV power (@ $___/kWh), lamp replacement, and chemical additives (@ $___/lb).

1.04 SUBMITTALS

A. In accordance with the requirements set forth in Section _____, submit general arrangement drawings and manufacturer's data covering installation instructions, dimensions, weight, detailed specifications, materials of construction, parts, devices and any and all other information required to verify compliance with these specifications. Submittals shall be made approximately 4 weeks after receipt of written purchase order.

B. Submit drawings showing placement of the UV/Oxidation system relative to external piping, valves and other equipment that must be interfaced.

C. In accordance with the requirements set forth in Section _____, submit a complete operating and maintenance manual on delivery of the equipment.

1.05   DELIVERY, STORAGE, AND HANDLING

A.   Comply with the requirements in Section _____ of these Specifications. Delivery shall be in ___ weeks following receipt of purchase order.

B.   The manufacturer and purchaser shall protect the equipment from structural damage. For equipment that shall be stored for greater than two months prior to installation and operation, it must be maintained in accordance with manufacturer's long term storage instructions contained in the operation and maintenance manual.

C.   Package all spare parts or spare part assemblies in separate, sturdy, waterproof containers clearly marked with the name of the part or assembly, and the name of the unit of which it is a component.

1.06   WARRANTY

A.   Provide an equipment warranty in accordance with Section _____.

B.   The equipment manufacturer shall warrant the equipment for a period of twelve (12) months from shipment.

PART 2 - PRODUCTS

2.01   UV/OXIDATION SYSTEM

A.   The manufacturer shall furnish all tools, materials, labor, and appurtenances necessary for the complete fabrication, testing and shipment of the UV/Oxidation system.

B.   All equipment shall be new and unused, except for final check-out testing.

C.   The UV/Oxidation system shall consist of skid mounted reactor assembly(ies), power supply(ies), reagent delivery equipment, and programmed process control system. The reactor assembly shall be factory assembled and tested and ready for installation.

D.   Each UV/Oxidation skid shall be capable of completely independent operation from other skids.

2.02   REACTOR SKID ASSEMBLY

A.   The reactor skid shall consist of one or more UV reactors, each containing one or more UV lamps. Each lamp shall be protected from the water stream by a quartz cylinder. The reactors shall be designed for turbulent plug flow behavior to ensure

axial mixing for optimum photon absorption and at the same time eliminating short circuiting.

B. The UV lamps used in the UV/Oxidation reactor shall be specifically designed to provide a broad spectrum of light emission between 200 and 300 nm. to maximize photochemical destruction of waterborne pollutants. A minimum of 30% of the total lamp output must be below 300 nm. The lamps must be capable of providing 3000 hours of operation with no more than a 20% decrease in emissions in the 200 to 300 nm. spectrum. To produce a constant UV output throughout the useful lifetime, the lamp power must be automatically controlled to progressively increase electrical current in order to compensate for the decrease in UV emissions.

C. A cleaning mechanism shall be provided for each quartz tube to maintain efficient transmittance of UV light. The mechanism shall be constructed of materials which are not affected by high intensity UV radiation. The cleaning system must operate automatically with an adjustable time interval. Limit switches must be provided at both ends of wiper travel for fail-safe indication of proper operation. If limit switches are not provided, a UV intensity detector must be provided to ensure the transmittance of UV light through the quartz sleeve. Operation of the cleaning mechanism must not reduce the effectiveness of the treatment. If flow reversal is used as the motive force for the cleaning mechanism, equipment must be provided to enable the motive water to be collected and reworked prior to discharge.

D. Sample valves will be provided at the end of each reactor skid.

2.03 POWER SUPPLY

A. A power supply shall be provided for each UV lamp. The power supply(ies) shall be installed in a NEMA 1 ventilated and drip-proof enclosure, and all internal wiring must comply with NEC and be certified by a US OSHA accredited Nationally Recognized Testing Laboratory (NRTL). Efficiency of the power supply(ies) must be at least 92% and the power factor must be greater than 0.9 at full power.

B. The power supply lamp starting sequence will be set to ensure an extended lamp life and to minimize inrush starting current. A system shall be provided to control lamp power through feedback of operating current and voltage to compensate for variations in supply voltage, system temperature changes, and lamp aging (see also Section 2.02B).

C. The power supply system shall be provided with cooling fans, thermal protection, safety access interlock, lamp run meters, lamp ammeters, lamp voltmeters, and main power disconnect.

D. The power supply shall be equipped with transformers isolated from ground to provide inherent safety from electrical shock. Ground fault protection is not

acceptable as it is not intrinsically safe, and requires periodic checking to ensure continued safe operation.

E.   Each skid shall be wired for a single 480 VAC power drop. A 480 VAC/120 VAC transformer shall be provided to supply low voltage control devices. All control and interlocking circuitry shall be a maximum of 24 VDC.

2.04   UV/OXIDATION REACTOR CONTROL SYSTEM

A.   The UV/Oxidation system shall be controlled by a programmable logic device featuring a built-in watchdog timer to ensure integrity of operation. The programmable logic controller (PLC) shall be factory programmed and tested prior to shipment. The UV/Oxidation reactor control system must be certified by an NRTL.

B.   The system shall be operated from a main control console with system status and operational data shown on an interface display with an alphanumeric screen. The control system shall permit testing of all equipment while the system is off line for maintenance. This should include, but not be limited to, operation of quartz wiper mechanisms and interlocks, and all reagent pumps.

C.   The PLC shall have sufficient capacity and contacts for control and interface with all standard and optional features and equipment provided with the UV/Oxidation system. PLC memory must be protected by a continuously charged lithium battery in case of power outage.

D.   Each UV/Oxidation skid shall have an individual PLC and control panel to permit completely independent operation.

E.   The control panel(s) shall be NEMA 12 enclosure(s).

F.   Interlocks will be provided to alarm and/or shutdown the UV/Oxidation system under the following conditions:

- High temperature in lamp drive enclosure
- Low flowrate
- High temperature in the UV/Oxidation reactor
- Leak from UV/Oxidation reactor
- Lamp failure
- High voltage cabinet door is open
- Reactor access covers are open
- Low reagent flowrate
- Quartz wiper failure

G.   A magnetic flow meter with a digital flow indicator and flow totalizer calibrated in gpm shall be provided.

2.05   REAGENT DELIVERY SYSTEMS

A.   A chemical feed system shall be provided for the delivery of (hydrogen peroxide), (acid), (caustic), (other reagents), etc. to the UV/Oxidation system. Where appropriate, each feed system shall include a metering pump, rotometer, check valve at point of injection, pulsation damper, electronic solid state low flow switch, and an automatic priming or bleed valve. The operation of the chemical feed pumps shall be controlled by the PLC.

B.   Each delivery system shall be skid mounted on an epoxy coated mild steel assembly. Surface preparation and protective coatings are to be in accordance with System _____ described in Division 9.

2.06   ANCILLIARY EQUIPMENT (OPTIONAL)

A.   Reagent storage tanks sized to hold three (3) months supply at the design flowrate of _____ gpm.

B.   Reciprocating air compressor

C.   Modem

1.   A modem shall be installed to allow remote monitoring and diagnosis by the manufacturer, and to allow for programming changes to the system.

D.   Autodialer

1.   An autodialer shall be installed with the capacity to store and dial up to eight (8) telephone numbers. The autodialer must also have the capability of storing and delivering up to three (3) prerecorded messages pertaining to the nature of a fault condition.

E.   Recycle system

1.   A recycle system shall be installed to automatically recycle effluent during start-up or operating upsets. The recycle system shall consist of a recycle valve(s) and recycle/equalization tank of _____ gallon capacity.

PART 3 - EXECUTION

3.01   INSTALLATION

A.   Installation shall be in accordance with manufacturer's printed instructions.

B.   The contractor or installer shall provide certification from the manufacturer that the equipment has been properly installed.

C.   The UV/Oxidation system shall be suitable for installation on a sealed or painted concrete floor in an industrial indoor environment maintained between 40 deg. F and 95 deg. F.

3.02   MANUFACTURERS SERVICE

A.   The manufacturer shall provide the start-up services of a qualified field service representative for the purpose of installation inspection, system commissioning, and instruction of facility personnel in the proper operating and maintenance procedures. The proposal shall include an estimate of the number of mandays and the per diem cost for these start-up services.

3.03   ANCILLIARY SERVICES (OPTIONAL)

The vendor is requested to bid as an option:

A.   Periodic Maintenance Contract

The optional Periodic Maintenance Contract must include as a minimum:

- Visits on a quarterly basis to perform preventative maintenance, (i.e., check the performance of, examine, adjust and calibrate, as may be required, the UV/Oxidation system), and change out of the lamps if needed.

- Emergency service including all non-scheduled repair labor. Travel, labor and expenses for non-scheduled visits are invoiced to Purchaser's account.

- All parts and labor (other than emergency or non-scheduled labor) for maintenance of the system including replacement UV lamps.

Case Histories

Solarchem currently has over 90 **Rayox®** installations worldwide treating a variety of contaminants in process wastewater, groundwater, and drinking water. The following is a summary of a few of those installations:

Description	Location	Water	Contaminant(s)
Aerospace Company	Florida	P	Hydrazine, NDMA
Aerospace Company	California	P	Methyl Ethyl Ketone (MEK)
Aircraft parts manufacturer	New Jersey	G	Trichloroethylene (TCE)
Chemical Manufacturer	North Carolina	G	1,4-Dioxane, Benzene
Chemical Manufacturer	Minnesota	G	TCE
Chemical Manufacturer	Ontario	G	NDMA
Chemical Manufacturer	New Jersey	G	TCE
Chemical Manufacturer	France	G	TCE
Chemical Manufacturer	Ontario	P	Phenol
Chemical Manufacturer	Ontario	P	NDMA
Dry Cleaning Operation	California	G	Perchloethylene (PCE)
Explosives Manufacturer	Canada	P	TNT
Fabric Manufacturer	California	G	Chlorotoluene, Vinyl Chloride (VC)
Filtration Membranes Manufacturer	Michigan	G	1,4-Dioxane
Indian Reserve Drinking Water	Ontario	D	NDMA
Municipal Drinking Water Authority	Ontario	G	NDMA
Nuclear Power Plant	Quebec	P	TOC
Oil Refinery	Ontario	G	VC, DCE, TCE
Petroleum Terminal	New York	P	Benzene, Toluene, Xylene
Petrochemical Company	Ontario	G	BTEX
Rocket Engine Testing Center	Colorado	P	NDMA
Rubber Manufacturer	Ontario	P	NDMA
Service Station (LUST)	North Carolina	G	Benzene, MTBE
Service Station (LUST)	New York	G	BTEX
Service Station (LUST)	Nevada	G	Benzene
Superfund Air Force Base	Texas	G	DCE, Chlorobenzene, TCE, PCE, VC
Superfund Air Force Base	Texas	G	VC, DCA, TCA
Superfund Site	Massachusetts	G	DCE, TCE, VC
Superfund Site	California	G	TCE, DCE, TCA, DCA
US Navy	Maryland	P	Nitro Glycerin
Wood Treater	Missouri	G	Pentachlorophenol (PCP)
Wood Treater	Alabama	G	PAH's, PCP
Wood Treater	Alabama	P	PCP
Wood Treater	Ontario	P	PCP, Phenols

P = Process Wastewater   G = Groundwater   D = Drinking Water

BTEX - Service Station Groundwater Treatment
Unocal Corporation - Carson City, Nevada

Case History

In early 1991 Unocal needed to treat groundwater laden with BTEX at an abandoned service station in Carson City, Nevada. The flow from the wells varied greatly with precipitation, and the location was subject to climatic extremes.

A 30 kW **Rayox**® system was selected for the application and installed in September 1991. The system was designed to treat 30,000 gallons per day on an intermittent basis under the control of a programmable logic controller. There was no GAC polish, and the system was installed inside a heated enclosure.

The system operated until November 1992 and successfully treated 1.5 million gallons of water. Solarchem monitored the system operation from Las Vegas with a modem, and was completely responsible for maintenance and operation including hydrogen peroxide supply.

The system has now been relocated and is being modified for batch operation at another Unocal service station in Fremont, California.

Site Characteristics

Application:
- Contaminated groundwater from leaking underground storage tank

Location:
- Carson City, Nevada

Flow:
- 2 - 10 gpm (intermittent)

Influent:
- BTEX - 5 ppm
- TPH - 4 ppm

Effluent:
- BTEX < 5 ppb
- TPH, < 1 ppm

Special:
- Non-Operating Site
- <2 yr operating life

System Specifications:
- Model 30 - 1, 30 kW system

Special Features:
- skid mounted
- PLC controlled
- remote diagnostics
- lamp wiper
- remote alarm/auto dialer

Operating Cost:
- $2.25/1000 gallons

Solarchem Environmental Systems

Nashville	*Los Angeles*	*San Francisco*	*Houston*	*Toronto*
1-800-677-6918	1-310-803-1002	1-707-435-9390	1-713-362-1005	1-800-263-2476

NDMA - Ultraviolet Photolysis
Summary of Rayox® Installations Treating Nitrosamines

Although NDMA may seem like a new problem, we have been providing NDMA solutions for more than 3 years.

UV photolysis is the proven technology of choice for the treatment of NDMA in process and ground waters. Solarchem has 8 installations in North America treating NDMA using the **Rayox®** process. Flowrates range from as little as 400 gallons per day up to 600 gallons per minute including the largest single installation treating NDMA in the world. A brief summary of some of our installations is provided in the table below.

The Problem

NDMA is polar, highly water soluble compound, and therefore has a low partition coefficient in water. It is not amenable to treatment by conventional technologies because it does not adsorb onto activated carbon, will not efficiently air or steam strip from water, and is resistant to biodegradation.

EPA has just recently promulgated treatment standards for NDMA dischargers under the Clean Water Act which will eventually be incorporated into your NPDES permit. Are you prepared?

The Solution

The key to the success of UV/Photolysis for the destruction of NDMA is that the NDMA molecule absorbs UV light energy at the same wavelengths that are emitted from Solarchem's proprietary UV lamps. The following figure compares NDMA's UV absorbance spectra to the ultraviolet output of the Solarchem lamp. NDMA absorbs UV light very strongly in the 200 to 260 nm band and readily photo dissociates to form dimethylamine and nitrite.
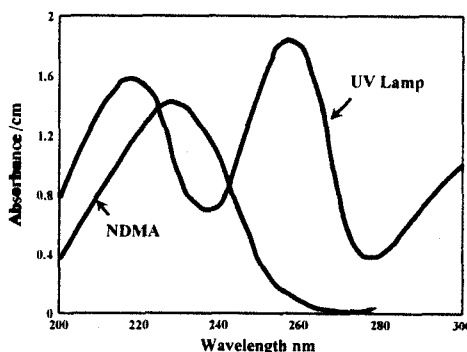
UV photolysis is a destruction technology, with no pollutant transfer or continuing liability. The **Rayox®** treatment system is compact, reliable, and unobtrusive, with considerable cost savings over more conventional treatment technologies.

Please contact us to find out if we have a solution to your NDMA treatment requirements.

Company	Description	Flowrate	NDMA Influent Conc.	NDMA Effluent Conc.	Operating Cost ($/1000gal)
Rubber Manufacturer	Dimethylamine (DMA) in extruded rubber reacting with nitrite in curing bath. NDMA showing up in wash water	12 gpm	30 ppb	< 500 ppt	$3/1000 gal
Specialty Chemicals Manufacturer	NDMA formed as byproduct from use of Dimethylamine (DMA) and shows up in process wash waters	100 gpm	600 ppb + 1000 ppm of COD	< 500 ppt	$4/1000 gal
Regional Water Authority	NDMA contaminated groundwater threatening water supply	600 gpm	20 ppb	< 14 ppt	$0.35/1000 gal
Aerospace	Unsymetrical Dimethylhydrazine (UDMH) in rocket fuel lines reacting with oxygen to form NDMA then showing up in water from pipe flushing	400 gpd (batch)	1400 ppm, 6000 ppm of hydrazine	< 200 ppt	$150/1000 gal

Pesticides - Soil Wash Water Treatment
Brown & Bryant Superfund Site - Arvin, California

Case History

From May through August 1991 Solarchem together with Roy F. Weston performed an on-site Emergency Removal Action using its **Rayox®** technology at the 5 acre Brown and Bryant Superfund Site, in Arvin, California. This represented part of one of the first fully successful on site remediations of a Superfund Site.

In early 1991, the soil washing of several hundred cubic yards of soil containing numerous banned pesticides including DDT, DCP, and Dinoseb was completed. This operation resulted in 100,000 gallons of soil wash water requiring treatment. The wash water contained 400 - 600 ppm of Dinoseb and was being stored in four - 30,000 gallon Baker Tanks on site.

Roy F. Weston Inc., in conjunction with the USEPA, chose Solarchem for the project. The **Rayox®** Advanced Oxidation process chosen (based on Solarchem's treatability study), destroyed the waterborne Dinoseb from 400 - 600 ppm to less than 100 ppb. Treatment was conducted in 1000 gallon batches utilizing ozonation followed by UV/peroxide. Greater than 99.9% destruction of Dinoseb and various other contaminants was achieved. Throughout the operation Solarchem provided continuous on site operation and maintenance support.

Site Characteristics
Application:
• Pesticide contaminated water from soil washing operation
Location:
• Arvin, California
Flow:
• 1000 gallon batches every 12 hr's
Influent:
• Dinoseb - 600 ppm
Effluent:
• Dinoseb < 100 ppb
Special:
• Emergency Removal Action performed on time and on budget
• continuous on-site operation and maintenance support

System Specifications
• Model 3 - 6, 18 kW system
Special Features:
• 14 lb./day ozone generator
• PLC controlled
• lamp wiper
• batch operation
Operating Cost:
• $40/1000 gallons

Solarchem Environmental Systems

Nashville	*Los Angeles*	*San Francisco*	*Houston*	*Toronto*
1-800-677-6918	1-310-803-1002	1-707-435-9390	1-713-362-1005	1-800-263-2476

Rayox®- F - Clean Up of PCP Contaminated Groundwater
Wood Treating Facility, Missouri

Case History

A wood treating facility, in operation since 1937, uses various oils and creosote to preserve railway ties and telephone poles. The past disposal of creosote and PCP (pentachlorophenol) laden wastewater to their surface impoundment (standard practice of the time) led to the inadvertent contamination of the underlying aquifer.

After an initial assessment of various treatment technologies, UV/Oxidation became the clear choice, due to the problems and costs associated with the use of activated carbon. PCP laden activated carbon is not accepted for regeneration because of the dioxins produced during the regeneration of the carbon. The added costs of disposing and purchasing only virgin carbon coupled with future RCRA liability concerns made this option unattractive.

Solarchem performed initial treatability tests in 1991 followed by a 5 week on-site trial. Conventional UV/peroxide was tested as well as several of Solarchem's patented photocatalysts. Solarchem's Rayox® F process, which involves the addition of a proprietary oxidation enhancing catalyst (**ENOX** 510), was found to be the most economic treatment option. The **ENOX** 510 catalyst reduced operating costs by 30% and capital costs by 40% over a conventional UV/peroxide process.

The system was designed to treat 120 gpm of groundwater with a PCP influent concentration of 1000 ppb. The system was delivered in early 1993 and is meetimg or exceeding performance requirements.

Site Characteristics
Application:
- PCP contaminated groundwater at a wood treatment facility

Flow:
- 120 gpm total (90 gpm to be re-injected to the aquifer, 30 gpm discharged to POTW)

Influent:
- PCP - 1000 ppb

Effluent:
- PCP - <100 ppb (90 gpm)
- PCP - <10 ppb (30 gpm)

System Specifications:
- **Rayox® F**
- Model 30 - 2, 60 kW system

Special Features:
- **ENOX** 510 photocatalyst
- PLC controlled
- automated lamp wiper
- skid mounted
- fully adjustable lamp power

Operating Cost:
- $1.30/1000 gallons

TCE, DCE, Vinyl Chloride Groundwater Treatment
Kelly Air Force Base, San Antonio, Texas

Case History

UV/Oxidation was the selected technology to remediate DCE, TCE contaminated groundwater at Kelly Air Force Base. A major engineering company was contracted by the USAF to assess various technologies including air stripping and activated carbon. UV/Oxidation was selected because the contaminants included vinyl chloride which ruled out air stripping and activated carbon due to prohibitive operating costs. Vinyl chloride adsorbs very poorly on carbon but treats readily using UV/Oxidation.

Solarchem was awarded a contract to lease a 30 kW trailer mounted **Rayox®** unit to demonstrate UV/Oxidation at several well sites on the base. The results would form the basis of full scale design.

The Air Force proceeded with groundwater remediation at two well sites on the base. Solarchem was awarded the contract for both treatment systems on the basis of cost and technical merit. Zone 1 required >95% destruction of DCE, while the destruction of 1,1-DCA controlled the design of Zone 2. The systems were delivered in the summer of 1993. Solarchem has on-site operating and maintenance responsibility for the equipment.

Site Characteristics - Zone 1
Flow: • 130 gpm **Influent:** • DCE - 1200 ppb • TCE - 130 ppb • Vinyl Chloride - 120 ppb **Effluent:** • DCE - <70 ppb cis, <100 ppb trans • TCE - <5 ppb • Vinyl Chloride - <2 ppb **System:** Model 30 - 3, 90 kW system **Operating Cost:** (includes Maintenance) $1.34/1000 gallons

Site Characteristics - Zone 2
Flow: • 250 gpm **Influent:** • 1,1 DCA - 60 ppb • DCE - 300 ppb • PCE - 200 ppb • Vinyl Chloride - 240 ppb **Effluent:** • 1,1 DCA - <3.5 ppb • DCE - <70 ppb cis, <100 ppb trans • PCE - <5 ppb • Vinyl Chloride - <2 ppb **System:** Three Model 30 - 3's, 270 kW system **Operating Cost:** (includes Maintenance) $1.98/1000 gallons