Photocatalysis: An Analysis of Its Applications and Market Potential

TR-111898

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REPORT SUMMARY

Electric utilities can create value for their customers and revenues for themselves by promoting advanced technologies that exploit the versatility and controllability of electricity. This report focuses on one such electrotechnology, photocatalysis, the use of ultraviolet light and a metal oxide catalyst to create aggressive oxidizing hydroxyl radicals to disinfect and decontaminate water, wastewater, and gas streams. The report describes the current state of this technology and its economic prospects and explores how utilities can benefit from increased marketplace acceptance of photocatalysis.

Background

In recent years interest has surged in the class of technologies collectively known as Advanced Oxidation Technologies (AOTs), whose most common application is destroying organic contaminants in gases and liquids. AOTs are excellent examples of electrotechnologies because electricity use is the major cost factor in their economics. This report deals with one AOT, photocatalysis. Another promising AOT, ozonated laundry, is explored in EPRI report TR-111899.

Objective

To describe the applications of photocatalysis and analyze their competitive benefits and economics; to estimate the current and potential size of the photocatalysis market and identify key market players; to explore ways in which promotion of photocatalysis can help utilities increase revenues and retain customers.

Approach

After conducting a literature search and consulting experts and vendors, the project team described the applications of photocatalysis, analyzed the economics of photocatalysis market, estimated its size and future prospects, and identified the key manufacturers of photocatalysis systems. The team explored the potential benefits of photocatalytic technologies for electric utilities and suggested several options utilities can use to leverage photocatalysis applications for their customers.

Results

The purpose of photocatalysis is to generate the hydroxyl radical, an extremely powerful oxidant capable of destroying organic contaminants in water and gas streams. The hydroxyl radical oxidizes organic contaminants at a reaction rate that is one million to one billion times faster than rates achieved by a traditional oxidant such as ozone.

Photocatalysis involves the use of ultraviolet light (UV) with metal-oxide catalysts such as titanium oxide to generate hydroxyl radicals from an oxidizing agent such as hydrogen peroxide or ozone or from a source of hydroxyl radicals such as water vapor. Photocatalysis has been used successfully for the disinfection and decontamination of water, wastewater, and gas streams.

The AOT industry in the United States consists of one or two major players and a host of small, minimally-capitalized companies working on the development of advanced technologies. Since 1996, some consolidations have been consummated as companies strive to attain the critical mass necessary to develop the market. In addition, a substantial amount of research has been completed in the past decade in universities and private laboratories in the United States and around the world.

Increased marketplace acceptance of photocatalysis will have two main benefits for utilities. A direct benefit, in terms of revenues, is the increased use of electricity associated with the high-intensity UV lighting required for the process. Associated benefits include the demonstration of electricity's ability to provide highly controllable, flexible, and reliable process features, and the electric power industry's ability to provide innovative and progressive technologies and services to customers with specialized needs.

EPRI Perspective

A utility wishing to leverage photocatalysis applications for its customers has a number of options. A utility can simply become informed about the technology and provide advice on it potential applications to meet specific, perhaps somewhat specialized customer requirements. Another approach is to assess the technology and build relations with equipment vendors to provide customers with documentation on successful applications and a list of potential suppliers. Or a utility can also form strategic alliances with the "best-of-breed" suppliers to market and distribute the technology to its own and other utilities' customers as a business development endeavor.

TR-111898

Interest Categories

Market research
Pricing, costing and rate design
Market forecasting
Strategic market assessment

Keywords
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INTRODUCTION

The U.S. electric industry is transitioning to competition over the next several years. This market is very large, generating over $200 million in revenues, and is therefore attracting a significant number of new entrants. However, the market is not growing very much, and thus incumbent utilities and the new entrants will be vying for existing customers, for the most part. It is expected that utility profit margins and energy commodity market prices will decrease over time as competition unfolds.

For all practical purposes, utilities are starting into this transition with about 100% market share, and their short-term objective is to maximize their market share or retain as much of their customer base as possible. In addition, some utilities are competing against other utilities and the new entrants for profitable commercial and industrial customers outside of their traditional service area.

The initial competition is taking place around higher-volume customers in the industrial and commercial sector, especially those customers that are energy-intensive. Three distinct competitive strategies are emerging to retain existing customers and acquire new ones: “cost leadership”, in which the utility prices its product at the lower end of the price-point spectrum, “total solutions”, in which the utility provides a branded bundle consisting of the energy commodity and energy-related services, and “ultra-service”, in which the utility provides highly-tailored energy and other services to selected market segments with high potential profitability.

The latter two strategies in particular require that the utility develop a more detailed understanding of the operations of its customers in order to provide a slate of services that closely match the customers’ needs. This mutual exchange of information and building of mutual understanding between the utility and these customers increases customer loyalty and thus retention.

What better way can an electric utility create value for its customers than through specialized applications of the product its knows best? The class of technologies known as electrotechnologies provides the vehicle for these applications. These advanced technologies are enabled by the versatility and controllability of electricity. Typical examples in radiation applications include the use of infra-red, microwave, ultrasound, plasma, electron beam, and ultraviolet (UV) in industrial and commercial operations. Because the technologies are new, there are often tradeoffs between costs and performance. Utilities have for years been demonstrating many of these applications in actual customer situations, and many utilities have established elaborate technology applications centers where customers can come to see demonstrations, test their products, or address difficult problems.

This report focuses on one specific electrotechnology -- photocatalysis. This technology is part of a class called Advanced Oxidation Technologies (AOT), all of which are used to create powerful oxidizing atmospheres for a broad range of applications. Photocatalysis uses UV light and a metal oxide, sometimes with the addition of an oxidant, to create aggressive oxidizing hydroxyl radicals that transform the chemical composition of gaseous and aqueous streams.

The objective of this report is to summarize the salient features of photocatalysis and its applications. First, the technology will be described in some detail, including its stage of development. Then, a broad range of applications including real situations will be presented and discussed. The economics of photocatalysis applications will be compared to competitive technologies and the potential market size for the applications will be estimated. The market analysis will continue with a review of the key players today, from those offering commercial products today to those engaged in prototype development. Finally, a value proposition for utilities to use with photocatalysis applications will be presented.

2

PHOTOCATALYSIS

Advanced Oxidation Technologies (AOTs)

In recent years there has been a surge of interest in a class of technologies collectively called Advanced Oxidation Technologies (AOTs) (1, 2, 3, 4). Note that the level of activity in photocatalysis in Japan far exceeds that in the U.S.(although it is difficult to obtain information about the activities). A recent symposium on photocatalysis at Tokyo University had 500 attendees, 400 of which were from industry.

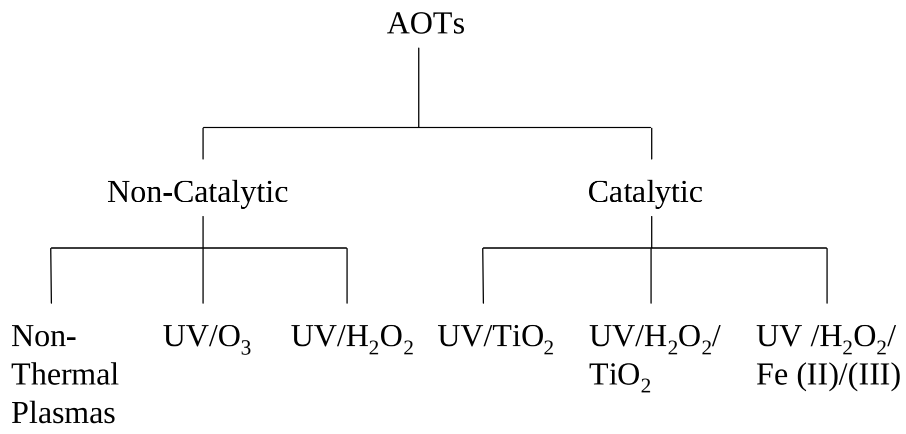
The purpose of AOTs is to generate one of the most powerful oxidants, the hydroxyl radical (•OH), that is capable of destroying organic contaminants in water and gas streams. This radical oxidizes organic contaminants at a reaction rate that is one million to one billion times faster than rates achieved by a traditional oxidants such as ozone as shown in the following table:

Table 2-1
Reaction Rate Constants (k, in L/mole/s) of Ozone vs. Hydroxyl Radical

Compound	Ozone	Hydroxyl Radical
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}

AOTs usually generate the hydroxyl radicals from oxidizing agents such as ozone or hydrogen peroxide using ultraviolet light (UV) and sometimes a metal oxide catalyst, the most effective to date being titanium oxide.

The commonly-used AOTs can be divided into catalytic and non-catalytic applications as shown in Figure 2-1.



TMS

Figure 2-1
Common AOTs

In Figure 2-1, Fe (II) and Fe (III) are iron ions denoting Fenton-like reagents.

AOTs are excellent examples of electrotechnologies because they are driven by electricity, and electricity use is the major cost factor in their economics. In fact, for aqueous stream applications, a figure-of-merit based on electricity use as a function of amount of contaminant removed has been developed to compare the overall economics of different remediation and clean-up applications (4).

In this report, we will focus on catalytic AOTs, defined as photocatalysis.

Photocatalysis

General Description

Photocatalysis involves the action of UV light on an oxidizing agent such as hydrogen peroxide or ozone or on a source of hydroxyl radicals such as water vapor, in the presence of a catalyst. The most often-used catalyst today is titanium oxide. A wide range of other semiconductors and other materials have been tested for photocatalytic activity, but in general they have been found to be less active than titanium oxide (5).

A high-powered medium pressure UV lamp is used to provide UV radiation with wavelengths in the 200 nm to 400 nm range through a quartz sleeve into the contaminated water or gas stream. Since AOT systems were first introduced in the late 1970s, one of the major improvements has been in the lamp area. The original low-pressure, low power (1 - 30 kW) mercury lamps have been substituted by high intensity (15 - 30 kW), medium pressure lamps with better UV spectral output and equipped with a sleeve-wiping mechanism to improve light penetration in aqueous solutions with high concentrations of scaling compounds. The new systems are more compact and less expensive.

The UV light provides photons of sufficient energy to liberate the hydroxyl radicals from the oxidants. Using hydrogen peroxide as the oxidant, the chemical kinetics scheme of interest is as follows:

H_2O_2 + h v (UV Light) = 2 •OH (hydroxyl radical)
• OH + Organic Pollutant = Mineralized products

The mineralization of the contaminants means that there are no secondary pollutants created nor is waste disposal required. Hydrogen peroxide absorbs light with wavelengths under 250 nm, and provides a quantum yield of unity, i.e., for every photon of light absorbed, one hydroxyl radical is created. The catalyst is suspended in aqueous solution or fixed onto a rigid supporting matrix. UV radiation produces hydroxyl radicals on the surface of the catalyst particles. However, while titanium oxide is photoactive, absent any oxidant in the aqueous solution, its quantum yield is very low at about 8% at the upper end (6). A promising new catalyst, ferrioxalate, which absorbs UV and visible light as high as 500 nm in wavelength, is being marketed by Calgon Carbon (9). The system can absorb 18% of the solar spectrum and has a quantum yield greater than unity.

Sunlight can also be used instead of UV lamps, although the quantum yield decreases as the radiation wavelength increases. The National Renewable Energy Laboratory has completed a great deal of research, development, and demonstrations of the sunlight-induced photocatalysis (5). Some other photoreactive catalysts such as Fenton’s Reagent (a chemical combination of ferrous ions and hydrogen peroxide) and a proprietary compound containing potassium ferrioxalate can absorb visible light up to wavelengths of 500 nm (1).

Technology Status

Photolysis (no catalyst used) and photocatalysis has been used successfully for the disinfection and decontamination of water, wastewater, and gas streams.

For aqueous solutions, typical contaminant concentrations treated using photolysis and photocatalysis are between 1 ppm and 100 ppm.

For drinking water disinfection, UV/hydrogen peroxide treatment works well without a catalyst (i.e., homogenous photolysis). Powerful (30 kW) lamps are used to irradiate water into which hydrogen peroxide had been added. For UV wavelengths in the 200 - 300 nm, the peroxide is photolyzed with a quantum yield of one hydroxyl radical per photon absorbed.

The wastewater applications are often more challenging, because of the potential for high UV absorbency and high chemical oxygen demand in the mixture. Adding a catalyst can speed the chemical destruction, although the susceptibility of the catalyst to fouling is a problem. Much work has been done to test various reactor designs that improve the mixing of the catalyst with the contaminated solution and to increase the residence time of the contaminant in waste-water streams, but the results to date have not justified the commercialization of a process because quantum yields are low, mass transfer is low, inorganics inhibit the catalyst, and the catalyst is susceptible to the deposition of surface solids (7, 8, 10).

For gaseous streams, typical contaminant levels range from 100 parts per million (ppm) down to parts per billion (ppb) for indoor air quality applications. Gaseous streams successfully treated to date include volatile hydrocarbons produced during the air-stripping operation in soil remediation and in industrial processes, and indoor air in commercial and residential situations, including the destruction of bacteria, viruses, fungi, and allergens.

According to reference (5), photocatalysis has been applied successfully to over 270 organic and inorganic compounds, with the most common being organic. A detailed exposition of applications to date is provided later in this report.

Energy Use

Because of the key role of UV, the driving factor in the economics of photocatalysis systems is electricity. A substantial amount of work has been done to characterize the electricity requirements in the treatment of aqueous streams. Each stream needs to be tested in order to determine the required dosage of UV. The dosage units are usually measured in terms of kWh/1,000 U.S. gallons. The dosage is determined in an iterative manner, testing the effect on treatment performance of variables such as alkalinity, oxidant concentration and catalyst choice (4). A reasonable approximation is that first-order kinetics apply to the destruction reaction, and thus the destruction curve (ppm of contaminant on a log scale versus the UV dose) is linear. Figure 2-2 provides an example of data for a 1,4-dioxane contaminated stream.

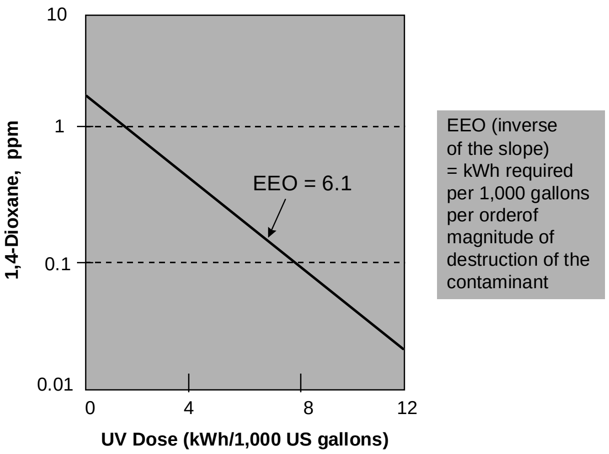


Figure 2-2
UV/Oxidation Destruction Curve for 1,4-Dioxane

The slope of the destruction curve becomes the measure of treatment performance, and is easily comparable across different contaminated streams. The steeper the slope, the faster the treatment. Calgon Carbon has proposed that the inverse slope of this curve be called the EEO (4) , defined as the electrical energy required to reduce the concentration of a compound in 1,000 gallons of water by one order of magnitude. The EEO completely determines the treatment characteristics of the contaminated water. The following table provides typical examples of EEOs for contaminant destruction:

Table 2-2
Typical EEOs for Contaminant Destruction

Compound	EEO (kWh/1000 US gals/order)
1,4-Dioxane	2-6
Atrazine	10-30
Benzene	2-5
Iron Cyanide	10-40
PCE	2-8
PCP	5-10
Phenol	5
TNT	12
Vinyl Chloride	2-3

From this table, it can be deduced that the treatment system for iron cyanide will take about five times as much UV power as that for treating perchlorethylene. Note that once the EEO is known, the kWh required for treatment, which comprises most of the operating costs, can be calculated. Since the UV dosage also determines system size, the EEO can also be used to calculate the capital costs of the treatment system.

3

APPLICATIONS OF PHOTOCATALYSIS

Photocatalysis applications can be divided into two major categories: gaseous and aqueous.

For gaseous streams, three broad areas of photocatalysis applications have been demonstrated:

- Indoor air quality: destruction of pollutants, bacteria, viruses, fungi, allergens, dust motes, and odors in office buildings, health-care facilities, aircraft, and residences

- Remediation of polluted sites: destruction of gaseous pollutants from air-strippers and off-gas systems

- Industrial processes: destruction of volatile hydrocarbons from such operations as paint booths.

All of these gaseous applications have received a significant amount of attention and resources.

For aqueous streams, there are four broad areas of photocatalysis applications:

- Industrial wastewater streams: destruction of a wide variety of hydrocarbons including gasoline, pesticides, and “pink” water

- Drinking water disinfection: eliminating harmful levels of pollutants (e.g., substituting for chlorination)

- Household applications: drinking water cleansing through thin coatings on glass kitchenware, self-cleaning bathroom tiles and windows, non-fogging mirrors

- Ultra-pure water: polishing of water to undetectable levels of impurities

The first two applications for aqueous streams dominate developments to date. The third, household applications, are commercial products on the market in Japan, but have yet to attract attention in U.S. markets. The last aqueous-phase application is a specialized one related to the space program.

The next subsections provide details of actual applications in the above areas.

Gaseous Applications

Indoor Air Quality

Though the focus of photocatalysis has been for remediation of volatile organic compounds in relatively high concentrations, low ppb indoor air applications appear very promising, with one commercial product and several pre-commercial prototypes showing good results.

There are several important and somewhat overlapping applications of photocatalysis in indoor air quality (IAQ): disinfection, removal of volatile organic compounds, and odor removal. Generally speaking, all of these destruction processes focus on compounds present in the parts per billion (ppb) concentration range and photocatalysis occurs at very low UV intensities (11, 12). Some of the sources of indoor air pollution, in addition to the pollution brought into buildings from outside air intakes, include home heating, tobacco smoke, building materials, household pets, new furnishings, damp carpets, musty closets, food preparation, cabinetry, pressed wood, home cleaning materials, personal hygiene products, hobby supplies, and humidifiers. These sources release small but palpable quantities of toxics such as benzene, ammonia, chloroform, formaldehyde, benzopyrene, trichlorethylene, carbon tetrachloride and other hydrocarbons.

The following are examples of product, prototype, and R&D activities related to IAQ applications of photocatalysis.

Universal Air Technology, Inc. (UAT), has a product line on the market, Sun-Air, consisting of stand-alone equipment that purifies and detoxifies air in residences and small offices using photocatalysis combined with filtration. Flow rates vary from 90 cubic feet per minute (cfm) to 350 cfm, cleaning between 225 and 875 square feet of space, depending on the number of required air changes. The product line integrates the photocatalysis into hybrid systems that include combinations of pre- and post-filtering and electrostatic precipitation. According to UAT, particles and gases eliminated include bacteria, viruses, mold, mildew, pollen, allergens, volatile organic compounds, organic odors, environmental tobacco smoke, pet dander, and dust particles. The technology employs a photocatalytic reactor coated with titanium dioxide-based proprietary catalysts, and low-energy UV lamps. Humidity control provides water vapor in the reactor which generates the hydroxyl radicals in the presence of the UV light and the catalyst. The hydroxyl radicals mineralize the contaminants. Initially, UAT's prototype reactors required excessive residence time (100s of minutes) to achieve 100% destruction. According to UAT, after six successive reactor design generations, the destruction is now achieved in about one-tenth of a minute. UAT has been involved with Florida Power & Light in a product demonstration.

United Technologies Research Center (UTRC) has developed prototypes for two photocatalytic IAQ applications. Working with Carrier Corporation, a division of United Technologies, UTRC has developed a photocatalytic module for Carrier HVAC equipment to provide IAQ control. Due to its low pressure drop, the module can be incorporated in existing HVAC units. A field prototype without photocatalysis will be deployed in 1999, and a photocatalytic prototype is scheduled for release in 2000. UTRC is now concentrating on establishing well-instrumented field demonstration sites, and has been talking to a number of electric utility consortia and an energy commission about support for these activities. Initial analyses by UTRC indicate favorable economics based on equipment and operating cost savings. UTRC has a second program with Hamilton Standard, another division of United Technologies, to develop a photocatalytic solution for commercial airlines. According to UTRC, improved air quality should lead to a substantial increase in customer satisfaction and the economics appear very favorable based on fuel savings (13). To support these programs, UTRC has developed sophisticated physics models of indoor air and is using these models in combination with detailed data from the EPA to develop system designs tailored to the requirements of different classes of air quality problems.

Lightstream Photocatalytic LLC (LPL) has completed the engineering and industrial design of a portable photocatalytic room air-cleaning unit capable of handling 300 cfm. The unit destroy volatile organic compounds, odors, and toxic contaminants. LPL has been working with EPRI to demonstrate a prototype commercial unit in a hospital environment. The company has also been seeking a partner with production engineering expertise and a distribution channel in order to launch the product. LPL is exploring additional applications of photocatalysis in fruit and vegetable ripening operations and in indoor and outdoor paints (14).

The China-America Technology Corporation (CTC), affiliated with the City College of New York, has an agreement with the Chinese Academy of Sciences to facilitate technology transfer from China. One of the product licenses available is for an indoor air cleaner based on photocatalysis. The catalyst is titanium with some noble metal and metal oxide additives. According to the CTC, one-hour destruction percentages, in a 43 cubic meter room, range from 75% for carbon monoxide to 99% for sulfur dioxide, with bacteria rate removal of 79%, and dust capture of over 95%. Capacity is 10 cubic meters per minute. Total power usage is 100 W.

The University of Missouri-Columbia has had an active IAQ program in collaboration with NREL. In this program, the feasibility of the total oxidation (mineralization) of bacterial cells to carbon dioxide by photocatalysis has been demonstrated. The process is self-cleaning (12). Several different reactor designs have been tested and a photocatalytic membrane reactor has been developed that functions as a self-cleaning, self-sterilizing filter for microbial pollution (11, 15). IAQ markers used included formaldehyde, acetaldehyde, and acetone in concentrations that varied from 2 to approximately 1,500 ppb. Note that

2 ppb is near the detection limit for carbonyl compounds. Very low UV intensities, e.g., 0.1 mW/square centimeter, achieved total destruction of formaldehyde. A review paper jointly written with NREL provides background information about the photocatalytic disinfection of air and water (16).

Michigan Technological University in Houghton, MI, has an active research and demonstration program in photocatalysis. One of its projects focuses on the photocatalytic oxidation of formaldehyde (which is an IAQ marker) in air. The experiment demonstrated complete destruction of 16.08 ppm of formaldehyde in just 1.74 seconds under light intensity of 1.9 mW/square centimeter for air with a relative humidity of 37.4%.

Volatile Organic Compounds (VOCs)

Working with its industrial partners, NREL has completed a number of demonstrations of photocatalytic cleanup of VOCs in gas streams. The program showed that photocatalysis is economically competitive for VOCs (nominal concentration of 500 ppm) for flow rates from 500 cfm to over 5,000 cfm (17). NREL has analyzed a number of applications (18, 19, 20):

- Working with NEPCCO (now part of Zentox), NREL has designed a 100 cfm reactor to treat the off-gases -- trichloroethylene, trichloroethane, and vinyl chloride -- from a Superfund Site air stripper

- NREL has achieved 95% destruction of VOCs from Army paint booths -- Methyl ethyl ketone, MIBK, toluene, n-butyl acetate, xylenes, and ethyl benzene -- in concentrations of several hundred parts per million in a photocatalytic reactor at a temperature of 150°C; similar work was done on paint booth emissions of E/M Corporation where ozone was added to the reaction chamber -- complete destruction was achieved in less than ten seconds

- Working with the semiconductor manufacturing consortium, SEMATECH, NREL researchers tested the efficacy of a variety of catalysts and reactor temperatures for the destruction of a mixture of isopropanol, acetone and methanol with a total concentration of 400 ppm; destruction rates of 95% appear possible

- NREL completed a pilot-scale study at McClelland Air Force Base of a solar light-based photocatalysis reactor applied to the destruction of chlorinated organic compounds from an air stripper; destruction rates exceeded 95% at 10 cfm with UV intensities at or greater than 1.5 mW per square centimeter, and at 20 cfm with intensities of 2 mW per square centimeter or more; the design of the reactor system was developed in collaboration with Industrial Solar Technology Corporation (IST); IST estimated that the capital cost of a 200 cfm system would be about $150,000 (21)

- In laboratory tests, photocatalysis exhibits very fast destruction rates of about 20 perchlorethylene molecules per photon for VOCs generated by dry cleaners

KSE Inc. has developed the AIR process (which is licensed to Trojan Technologies Inc. of Canada), a photocatalytic application for destruction of chlorinated hydrocarbons, alcohols, and other VOCs. A new proprietary catalytic absorbent is used and high concentrations of VOCs are treatable. The process has been successfully demonstrated for tetrachlorethylene emissions from a soil vapor extraction operation at a Loring Air Force Base Superfund Site. Over 99% destruction was achieved. Another field demonstration at Dover Air Force Base successfully destroyed dichloroethane from an air stripper (22, 23).

Zentox Corporation has developed a family of photocatalytic systems for the treatment of up to 500 ppm concentrations of VOCs. Vapor stream flow rates of up to 1500 cfm can be accommodated. Destruction rates for trichlorethylene can be as high as 90%, reducing as the relative humidity increases. Zentox also promotes the use of a hybrid photocatalysis and low-temperature plasma system for high removal rates of VOCs (24).

Aqueous Applications

Industrial Wastewater Streams

As mentioned above, aqueous applications present a more challenging environment for photocatalysis than gaseous atmospheres. However, two important benefits of photocatalytic treatment are that the destruction of the contaminants is done on-site with no secondary disposal requirements, and that it is cost effective for batch treatment in site clean-up projects, characteristics that are common to most AOTs. With the possible exception of drinking water disinfection, photocatalytic treatment of aqueous has tended to be project-based: a particular problem is identified, a treatability test is developed, and a custom-designed batch or continuous flow system solution is installed. Heterogeneous photocatalysis, using a titanium dioxide catalyst in an aqueous stream, has emerged as an important electrotechnology alternative and pilot plants have been built in Spain (25), Brazil (26), and the U.S. (27).

A number of factors constrain the treatability of contaminated water by photocatalysis including high UV absorbency by non target-species, high chemical oxygen demand (i.e., the total amount of oxidizable compounds in the water), pH, high alkalinity, suspended solids, presence of oil and grease, high levels of iron, and high chloride content. Some of these problems can be mitigated, at a cost, with pre-treatment processes. There can also be species present that reduce UV treatment efficiency. These can be categorized into UV interferences, hydroxyl scavengers, and suspended solids. Table 3-1 lists factors that negatively affect UV AOT treatment (4).

Table 3-1
Factors Affecting UV/Oxidation Treatment

Factors Affecting Treatment	Concentration of Concern
UV Interferences:	
Nitrate	>10 ppm
Nitrite	>10 ppm
Phosphate	>1%
Chloride ion	>1%
Chemical oxygen demand	>1,000 ppm
Ferrous ion	>50 ppm
Hydroxyl Scavengers	
Chloride ion	>1,000 ppm
NItrite	>10 ppm
Carbonates	>300 ppm
Sulphites	>target contaminant
Sulphides	>target contaminant
Precipitates	
Calcium	>50 ppm
Ferrous ion	>50 ppm
Magnesium	>1,000 ppm

It should also be noted that UV/titanium oxide photocatalysis, without the addition of an oxidant such as hydrogen peroxide, produces a very low quantum yield (about 4%) of hydroxyl radicals (6). For the destruction of methylene blue, UV/titanium dioxide's EEO is 15 - 50 times greater than a UV/hydrogen peroxide (non-catalytic) treatment. For the destruction of phenol, its EEO is 1.5 to 60 times greater than the same non-catalytic AOT process (6). However, in certain situations as noted elsewhere in this report, the UV/hydrogen peroxide AOT does not work well, and frequently, the operating and capital costs of the treatment process can be lowered significantly by the addition of photocatalysts such as titanium oxide (28).

In sunlight, titanium oxide can only utilize about 0.12% of the incident solar radiation energy (29). However, ferrioxalate has been shown to be a good absorber of solar radiation. It has a quantum efficiency of unity or more (equivalent to at least one hydroxyl radical per photon) and can utilize about 18% of incident solar radiation (29). Therefore, a ferrioxalate / hydrogen peroxide system could be about 120 times more efficient than titanium dioxide photocatalyst in using solar radiation.

Calgon Carbon is a leading manufacturer of AOT systems for groundwater, industrial water and process water. With the purchase Vulcan Peroxidation Systems Inc., Calgon Carbon added the Rayox®-F process to its product line. This is a photocatalytic application using UV and a Fenton-like catalyst. The addition of the catalyst enhances the treatment of certain aromatic and olefin compounds five-fold. In waters with a high background UV absorbency, Calgon Carbon has also developed a related catalyst that absorbs both UV and visible light from 200 nm to 500 nm. In one application, the addition of the catalyst to treat a BTEX mixture with high absorbency reduced the EEO from the 200 kWh per 1000 gallons per order of contaminant reduction for a UV / hydrogen treatment process to 5 kWh per 1000 gallons per order of reduction. In practice, a combination of the two processes provides the most economical solution.

Purifics Environmental Technologies Inc. (PETI) is a commercial supplier of continuous, automated photocatalytic wastewater treatment systems for flows from 4 to 2,000 liters per minute. The product line is named “Photo-Cat”. The systems are closed loop using a titanium dioxide slurry. Modular photocatalytic racks are connected in parallel or series depending on the concentration of the contaminants. The catalyst is maintained in a well-mixed state, and later separated from the purified water stream and recycled into the inlet stream. According to PETI, a broad range of pH levels, turbidity, pressure, temperature, types of contaminants, and water chemistry can be handled. Treatment times vary from 0.5 minutes to 20 minutes. Clean-up projects include organics in waste water at an NEC Electronics facility in California, a Superfund site in Texas, heavy water treatment at a nuclear facility, purification of water with hazardous contaminants for the Korean military, and the destruction of nitroaromic explosives, such as TNT, present in water for the U.S. Navy.

UV Technologies Inc. (UVT) has developed the UV-CATOX™ process which is a two-stage photocatalytic technology for the total destruction of organic contaminants in water. Both stages use an oxidant. The first stage uses high intensity, medium pressure mercury lamps and hydrogen peroxide plus recycled oxidant from the second stage. The second stage uses spectrally-modified low intensity, low-pressure mercury lamps and oxygen as the oxidant. According to UVT, the first stage reactor is capable of reducing contaminant concentrations by two orders of magnitude, e.g., from 10,000 ppm to 100 ppm, and the system is capable of economic treatment of industrial waste streams with more than 10,000 ppm concentrations of organics such as PCE, TCE, benzene, phenol, xylene, methanol, chlorobenzene, and MTBE. The system, which has been in development over the past six years, is currently classified as a bench-scale operation. Examples of successful test results at industrial sites are presented in Table 3-2.

Table 3-2
Industrial Waste Treatment Results for the UV-CATOX™ Process

Source of Wastewater	Characterization	Initial Contaminant Concentration	Energy Requirement (kWh/carbon order)
Textile Mill Sample #1	Sulfur and indigo dyes	740 ppm TOC	11.0
Textile Mill Sample #2	Fiber reactive dyes	100 ppm TOC	6.7
Specialty Chemical Manufacturer Sample	Mixed organics, principally formaldehyde and thiourea	11,925 ppm TOC	0.9
Environmental Consultant Sample	Mixed organics, principally toluene, tetrahydrofuran, and acetyl acetone	2,666 ppm COD	1.5

Zentox Corporation, with its acquisition of the NEPCCO Equipment Division of IT Environmental Services Inc., the assets of Photox Corporation, and a license to use photocatalytic oxidation technology developed by Photocatalytics Inc., has the capability to deliver photocatalytic solutions for contaminated water streams. Its flagship product, which carries the recommendation of Virginia Power Company, is ozone treatment of cooling tower water. As noted above, Zentox has already developed a photocatalytic decontamination system for VOCs (24). According to Zentox, its business objective is to develop a portfolio of electrotechnologies providing comprehensive treatment capability for groundwater, wastewater, process water, potable water, contaminated vapor streams and indoor air quality improvement.

Michigan Technological University (MTU) has completed photocatalytic treatment demonstrations for a number of different types of organic contaminants in water. Using solar radiation (average effective radiance: 0.1 mW / square centimeter) and a packed bed reactor, total mineralization of organic compounds was achieved as presented in Table 3-3 (10).

Table 3-3
Packed Bed Contact Time Required for Total Mineralization of Organic Compounds

Organic Compound Concentration (mg/l)	Rainy Solar UV (0.1 mW/cm^2), Packed Bed Contact Time (minutes)
TCE (8.81)	1.29
PCE (4.98)	0.95
p-DCB (2.35)	1.42
CTC (0.49)	42.8
2-PCB (3.58)	1.05
MEK (2.50)	27.3

At Tyndall Air Force Base, photocatalytic destruction of BTEX compounds using solar radiation in a packed bed was achieved with residence times less than three minutes, while the destruction of TCE and TCA at Sawyer Air Force Base using the same system was completed in under one minute. A semiconductor factory wastewater stream with TOC concentration at 2,500 ppb was photocatalytically treated to complete mineralization with solar radiation of 2.85 mW/ square centimeter in about 30 minutes, while the individual compounds acetone, methanol, and isopropanol required between 0.5 and 2 minutes to mineralize. The organics in computer chip rinse water with a TOC of about 750 ppb were destroyed in about one minute.

The MTU researchers also found that groundwater clean-up treatment presents some difficult challenges for photocatalysis because of the potential for excessive fouling and inhibition of the catalyst.

Sandia National Laboratory, working with a large computer chip manufacturer, completed photocatalytic treatability studies for process water contaminated with ethylene glycol. Various catalysts were used, with the most promising results coming from an advanced catalyst with gold and platinum added. Using 365 nm UV light, reactions rates were 3.7 times faster than rates achieved with titanium dioxide. Researchers estimate that an order of magnitude reduction in total organic carbon concentration could be achieved in 1,000 liters of water using about 11 kWh of electric energy.

Two Japanese companies, Ebara Corporation and Environmental Engineering Company, have developed photocatalytic processes using Fenton's reagent for difficult-to-treat organic compounds in water. Fifteen plants using these processes have been built (2).

Drinking Water Disinfection

The disinfection of drinking water using AOTs is a fully commercialized technology. For example, Calgon Carbon and Trojan Technologies Inc. of Canada have deployed numerous large UV/hydrogen peroxide systems that have been disinfecting drinking water economically and successfully for years. An average of about 100 UV water disinfection systems per year were installed in the period 1987 through 1996 (36). The efficacy of ozone for this application is well known, and was first practiced at the turn of the century in France. Both processes are adequate substitutes for chlorinating, the use of which may be impacted negatively by contemplated tighter regulation of the use of chlorine.

In Japan, the Kato Manufacturing Company (KMC) has recently spun out a new company, Photocatalytic Materials Inc. (PMI), which markets photocatalytic kitchenware. Glass jugs, tumblers, and swizzle sticks are coated with a see-through film of titanium dioxide. Tap-water is purified and rendered more tasty when the glassware is exposed to light or stirred with a swizzle-stick in sunlight or lamplight. According to the National Industrial Research Institute in Nagoya, Japan, alcohol in this glassware tastes mellower, and flowers last longer. The elegantly-designed glassware, which has a rainbow hue in light, is priced from 3,000 Yen for tumblers to 7,500 Yen for glass flasks, and swizzle sticks cost 1,800 - 2,000 Yen. KMC has indicated that they are working with a number of large Japanese companies such as Matsushita, Noritake, and Honda on advanced photocatalytic applications (30).

Other commercially-available photocatalytic applications in Japan include non-fogging mirrors, self-cleaning windows, and self-cleaning ceramic tiles.

Ultra-Pure Water

Michigan Technological University has designed an ultra-pure water plant for use in the semi-conductor industry using heterogeneous photocatalytic oxidation integrated with other unit operations. Ultrapure water has the following requirements: less than 5 ppb of total organic carbon, greater than 18.5 Mohm-centimeter ion content, less than 0.1 ppm of dissolved oxygen, less than 1 ppm of carbonates, and no particulate or bacterial matter. About 250 million gallons per day of ultrapure water are used by the semiconductor industry, the total cost of which is about $1.15 billion annually (40% of which is for energy consumption) (10).

Heavy Metals

Argonne National Laboratory has been investigating the ability of advanced photocatalysts to sequester and convert heavy metal ions from aqueous solutions to their less toxic, readily recoverable metallic forms, while simultaneously destroying toxic organic contaminants. Preliminary results indicate that lead and mercury ions can be removed using titanium dioxide colloids.

NREL has been investigating the possibility of using photoactivated ion-exchange resins to remove metals from water streams used in the pulping process of the pulp and paper industry. The metals cause scaling and decompose the bleach used in the pulping process.

Key Technical Challenges in the Development of Photocatalytic Processes

Except for drinking water purification, there is a distinct lack of replicated field performance data with which to verify the efficacy of photocatalysis applications.

For IAQ applications, photocatalysis appears to work well and shows considerable promise for the future. In laboratory testing, 100% destruction of a wide variety of contaminants has been demonstrated. There may be some open questions about the ability of current reactor designs to provide sufficient residence time to achieve full destruction of all targeted species in the field: generally, laboratories have instruments capable of measuring minute concentrations of compounds; the same cannot be said for residences and small offices, with the result that the performance of commercial products is hard to verify and the optimal timing for the replacement of critical parts is difficult to determine. There is also insufficient operating data available on catalyst life-time.

For VOC decontamination applications, there is little doubt that photocatalysis can achieve complete destruction. There are some concerns that, in the field, non-ideal conditions may lead to incomplete destruction and the creation of undesirable secondary contaminants. Most of the field demonstrations have been pilot tests of highly customized, often unique, systems. As yet, the ability to deliver a flexible, broadly-applicable high-performance system within a short-time frame does not exist. That is not to say, however, that VOC photocatalysis does not hold enormous promise for the future as more reference customers and field experience are accumulated.

For industrial wastewater applications, photocatalysis requires more development. As noted above, continuous high performance destruction is difficult to achieve because of low quantum yields, poor mass transfer, and scaling/fouling. It appears to have little advantage over UV/hydrogen peroxide technology in most situations. Nevertheless, there are a few demonstrated situations where UV/hydrogen peroxide has not performed well and where adding a photocatalyst to the system has accelerated the oxidation reactions to acceptable rates.

Drinking water disinfection is adequately handled by non-catalyst AOTs, with these applications being well-proven in dozens of large continuous installations.

As Professor David F. Ollis remarks in an excellent survey of the state of development of photocatalysis applications (31), a useful remediation treatment must be “general, robust, and cheap”. Photocatalysis has been demonstrated to be broadly applicable and a robust process. Good economics will depend on better quantum efficiency. Professor Ellis suggests that high opportunity paths to commercial processes involve process integration, feedstream conditioning, periodicity in illumination, and reaction integration. The key problem areas associated with photochemical oxidation are identified as catalyst deactiviation and regeneration for air remediation, catalyst selectivity versus undesired intermediates and final products for air remediation, and low quantum yields in both air and water streams (31).

4

COMPETITIVE BENEFITS AND ECONOMICS OF PHOTOCATALYSIS APPLICATIONS

Before discussing the specific benefits and economics of photocatalysis, there are a number of benefits that are common to all AOTs as follows (1):

- On-site contaminant destruction
- Compact, quiet equipment
- Can achieve non-detectable contaminant levels
- Can be combined with activated carbon or biological processes to reduce overall treatment costs
- Requires no phase transfer, eliminating the expense and liability of secondary handling
- Can be performed at ambient temperature and pressure
- Efficient for a wide range of contaminant types and concentrations
- Minimal maintenance and operating requirements
- Achieves complete mineralization of organics, if necessary, or forms biodegradable, non-toxic compounds

Indoor Air Quality Benefits and Economics

Photocatalytic air cleaning technology competes with a number of existing technologies, the most important of which are active carbon filtering, high efficiency particulate air (HEPA) filtering, air ozonation, chemical / biocidal treatment, high energy UV lighting, and electrostatic filtering. According to Universal Air Technology Inc. (32) , photocatalysis is a superior approach as presented by the company (somewhat promotionally) in Table 4-1.

Table 4-1
Comparative Benefits of Air Cleaning Technologies

Benefit	Photo-catalysis	Active Carbon Filter	HEPA Filter	Air Ozonation	Chemical/ Biocidal	High Energy UV	Electro-static Filter
Captures microorganisms	X	X	X				X
Destroys microorganisms	X			X	X	X	
Creates no hazardous waste products	X						
Generates no ozone	X	X	X		X		
Captures high molecular weight VOCs	X	X					
Captures low molecular weight VOCs	X						
Destroys high molecular weight VOCs	X			X		X	
Destroys low molecular weight VOCs	X						
Unlimited capacity	X			X		X	X
Eliminates organic odors	X	X		X		X	
Low pressure drop	X			X	X	X	X
Low maintenance cost	X			X			X
Low operating cost	X			X			X

While one can argue that some of the competitive claims in Table 4-1 are marginal or even somewhat biased, it presents a credible claim that all of the AOTs, i.e., photocatalysis, ozonation, and high energy UV light, rank high in benefits provided relative to the alternative technologies.

United Technologies Research Center completed several economic analyses of photocatalysis applications for indoor air quality. Building codes specify the number of required air changes in buildings in order to maintain a sufficient amount of fresh air for the occupants. The fresh air needs to be heated or cooled as it’s brought into the building, depending on the season. If a photocatalytic air purification system were installed, the number of air changes could be reduced. UTRC has calculated that a reduction in fresh air from 20 cfm to 5 cfm is feasible by adding photocatalytic air purification, which would in turn lead to a net reduction in heating, ventilating and air-conditioning costs of 20%, inclusive of the cost of the air purifier. In addition, the air purification system would eliminate odors and disinfect the air. The low operating costs are also cited as being important in residential applications and contrasted with HEPA filtration where the cost of the replacement filter can amount to as much as 50% of the initial cost of the air purification unit. There are of course a number of institutional and market barriers to this, which will be discussed in the marketing section below.

UTRC has also analyzed the economics of photocatalytic air cleaning in commercial aircraft. About 4% of fuel usage in an airplane is for environmental control systems. According to UTRC, installation of a photocatalytic system could reduce this fuel requirement by 50%. For a large national airline, this could translate into $25 million annual savings, in addition to increasing customer satisfaction. Again there are institutional and some practical barriers to the implementation of this scenario.

Destruction of Volatile Organic Compounds (VOCs) -- Benefits and Economics

The key competitors to photocatalytic treatment of VOCs are thermal incineration and carbon adsorption. Table 4-2 compares the benefits of the technologies.

Table 4-2
Comparison of Different VOC Treatment Processes

System Feature	Catalytic Oxidation	Thermal Incineration	Carbon Adsorption
Destroys contaminants	Yes	Yes	No
Ambient temperature	Yes	No	Yes
Byproduct issues	No	Yes	Yes
Process complexity	Low	High	High, regeneration required
Reactor size	Small	Small	Large
Energy requirement	Low	Higher	Higher
Total system cost	About the same	About the same	About the same

A number of economic analyses of VOC treatment have been published and a sampling of them follows.

NREL completed an engineering design and cost analysis of a 200 cfm VOC cleanup system for chlorinated hydrocarbons from an air-stripper operation for solar photocatalysis and compared it to the costs of two alternative treatment technologies (21). Table 4-3 presents their findings.

Table 4-3
Cost Comparison of VOC Cleanup Treatments

Cost Category	Solar Photocatalysis	Carbon Absorption	Thermal Oxidation
Capital Costs	$148,736	$121,241	$163,554
Annual Costs	$31,920	$32,811	$36,919
Levelized Cost*	$56,135	$25,549	$63,456
Levelized Cost/cfm	$281	$263	$318

** 10% discount rate, 10 year depreciation*

For this treatment situation, the results show that carbon absorption is the most economical approach, although all the total costs of all three approaches are similar. Note that UV light could be used to improve the quantum efficiency in the photocatalytic treatment, and the value of this improvement would need to be traded off against the capital and operating costs of the lamps.

In another study, NREL showed that solar photocatalysis of an air stream with 500 ppm of VOCs has superior cost performance at lower flow-rates and is cost-competitive with other technology options at higher flows, as shown in Figure 4-1 (33).

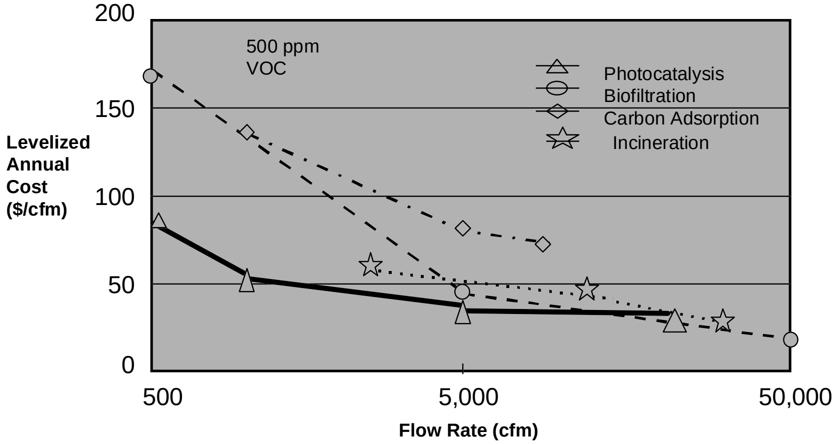


Figure 4-1
Cost of VOC Treatment vs. Flow-Rate

Citing an AIR system for cleaning 700 cfm of VOCs from 500 ppm down to 50 ppm at a Superfund Site, KSE claims project operating cost of $6,000 versus $355,000 for the alternate disposable carbon treatment of the same contaminants (23).

Another interesting economic analysis of off-gas treatment technologies was completed by the Los Alamos National Laboratory (34). They compared thermal, adsorption, and free radical technologies for VOC treatment. Free radical processes, in which an aggressive oxidant in the form of a free radical is generated, included photocatalytic/UV oxidation, ozone-enhanced oxidation, a silent discharge plasma, and a gas-phase corona reactor. A key conclusion of the analysis is that inlet air flow rate is the largest single determinant of system capital cost. However, as the duration of treatment increased, system operating cost gradually supersedes capital cost as the dominant cost parameter.

For low-flow rates (nominally 100 cfm) across a VOC concentration range of 50 ppm to 1,000 ppm, the first year cash flow requirement for short-term remedial projects was between $100,000 and $250,000 for adsorption and free radical processes versus an average of about $500,000 for thermal processes, with adsorption processes costing less than free radical processes at low ppm and vice versa at high ppm. All other variables being equal, for long-term remedial treatment, free radical costs were the lowest for all concentrations above about 225 ppm. For high flow rates (nominally 500 cfm), free radical was the best choice for all flow rates above 200 ppm for short term remediation projects (see Figure 4-2 below), while, for long-term remediation treatment, free radical and thermal processes were about equally good, and cost much less than adsorption processes for all concentrations about 50 ppm. Figure 4-2 provides a graphical depiction of some of these results.

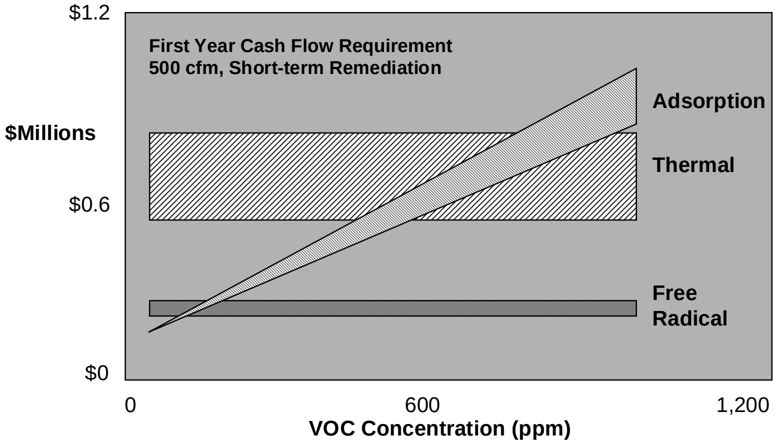


Figure 4-2
Cost Comparison of VOC Treatment Processes

Treatment of Water and Wastewater -- Benefits and Economics

Many of the qualitative benefits associated with photocatalytic treatment of gaseous streams are also be derived in aqueous treatments. In particular, the complete destruction of contaminants, on-site destruction with no need for secondary handling of contaminants or off-site disposal, high level of worker safety, the applicability to a broad range of species, low operating costs, and fast treatment times, e.g., less than ten seconds, are regularly cited as the most important benefits. While the efficacy of AOT applications has been successfully demonstrated for aqueous streams, except for special situations the use of photocatalysis is not widespread for the reasons noted earlier.

For water disinfection, UV radiation is a well-established solution, and does not require the addition of an oxidant or photocatalyst. Its key competitors are ozone, membranes, chlorine dioxide, and enhanced coagulation. Table 4-4 provides a comparison of the economics and characteristics of these technologies (35).

Table 4-4
Comparison of Water Disinfection Technologies

Characteristic	UV	Ozone	Membranes	Chlorine Dioxide	Enhanced Coagulation
Capital Cost ($000)	350*	1,250	5,000	100	2,400
Operational Cost ($/1000 gal)	<0.01*	0.085	0.35	>1.00	0.03
Effectiveness (# logs inactivation)	>4	2-3	>4	1-2	1-2
Secondary Treatment	None	Minor	Major	None	Major
Retrofitability	Good	Poor	Poor	Good	Good
Byproducts	None	Bromate, AOC	None	Chlorite, Chlorate	None
Footprint	Small	Large	Large	Small	Small

**Based on UV dose of 1 kW/MGD*

Wastewater treatment using AOTs is more challenging, and more expensive, than water disinfection. There are two commonly-used measures of the economics of these operations: cost in dollars per 1,000 U.S. gallons treated, and as mentioned previously, EEO (electric energy required per 1000 gallons per order of contaminant removal). The next paragraphs will provide examples of both for different treatment technologies and situations.

Activated carbon adsorption has been used for many years to cleanup wastewater. Table 4.5 presents a comparison of the operating costs of carbon wastewater treatments versus a UV AOT based on $ per 1,000 U.S. gallons treated (2,4).

Table 4-5
Operating Cost Comparison for UV/Peroxide vs. Activated Carbon

Contaminant Concentration (ppm)	AOT: UV/Peroxide	Poor Carbon Adsorbers*	Average Carbon Adsorber*	Good Carbon Adsorber*
0.1	\$0.5-\$2.50	>\$2.50	\$0.25-\$2.50	<\$0.25
1.0	\$1.50-\$4.00	>\$6.00	\$0.50-\$6.00	<\$0.50
10.0	\$2.00-\$6.00	>\$25.00	\$1.00-\$25.00	<\$1.00
Typical Contaminants	Aromatics, chloroalkenes, nitroaromatics, cyanides	Vinyl chloride, TCA, methylene chloride, 1,4-dioxane	Benzene, DCE, phenol, TCE, chloroform, TCA, DCA, carbon tetrachloride	Xylene, PCE, PCBs, pesticides

From Table 4-5, it can be seen that treatment costs for commonly occurring water contaminants can vary from \$0.25 to \$25.00 per 1,000 U.S. gallons. Rules of thumb for costs comparisons, based on Table 4-5, and the fact that UV/peroxide systems' capital costs are typically two to three times that of activated carbon (4) are as follows:

- UV/oxidation operating costs are less sensitive to inlet concentration of contaminants
- UV/oxidation operating costs are almost always less for contaminants which are poor carbon adsorbers
- For average carbon adsorbers, the economics must be analyzed on a situational basis
- For concentrations below 10 ppm, activated carbon is the most cost-effective treatment for good adsorbers
- Since the capital costs of UV/oxidation are more than for activated carbon treatment, longer-term projects may tend to favor UV/oxidation because the cumulative savings in operating costs begin to offset the higher capital costs

Reference (4) provides an excellent graphical depiction of the economic operating cost regions for activated carbon and UV/oxidation treatments.

A real-life example of the tradeoffs between the two treatment technologies was provided during a treatment project at Fort Ord Army Base in Monterey, California. A strategic alliance between Calgon Carbon Corporation and Solarchem Environmental Systems Inc. was commissioned to decontaminate water at the base. Three alternative treatments were considered: UV / Oxidation (Calgon Carbon's Rayox™ system), activated carbon, and a combination of Rayox and activated carbon. Table 4-6 compares the costs of these treatment options, showing that the combination offered the best economics, with a payback period of about 1.3 years (37).

Table 4-6
Project Economics of UV/Oxidant and Carbon Treatments

Economic Measure	Rayox™ Treatment	Activated Carbon Treatment	Combined Rayox™/ Activated Carbon Treatment
Relative Capital Cost	$1.07	$0.24	$1.00
Operating Cost ($/1,000 gallons)	$2.11	$2.20	$1.12
Annual Cost	$755,000	$787,000	$400,800

An interesting analysis of the economics of treating industrial wastewater streams with high concentrations of organic contaminants was provided by UV Technologies Inc. (38) for the first stage of its UV-CATOX process, which uses UV, hydrogen peroxide, and a photocatalyst. The analysis was completed for the same industrial streams presented earlier in Table 3-1. The following table, Table 4-7, summarizes the operating costs of the treatments (for one order of magnitude reduction of contaminant) which of course are situation dependent and are almost always much higher than water disinfection costs.

Table 4-7
Operating Costs for Industrial Strength Aqueous Waste Streams

Source of Material	Initial Contaminant Concentration	Electricity and Lamp Replacement Cost ($/1,000 gal)	Hydrogen Peroxide Cost ($/1,000 gal)	Total Operating Cost ($/1,000 gal)
Textile Mill Sample #1	740 ppm TOC	162	40	202
Textile Mill Sample #2	100 ppm TOC	13	5	18
Specialty Chemical Manufacturer Sample	11,925 ppm TOC	213	633	846
Environmental Sample	2,666 ppm COD	24	35	59

UV Technologies also developed an equation for the capital costs of UV-CATOX treatments as a function of lamp power requirements. For lamp power ranging from 15 kW to 400 kW, the estimated capital costs averaged $60,000 at low-power to $300,000 at high power, based on a linear log-log relationship.

The most systematic approach to economic analysis of AOT treatment of contaminated aqueous streams has been developed by Calgon Carbon. The cost of these types of treatments is primarily driven by the cost of the electricity that powers the lamps. The oxidant requirement is a secondary cost factor. The independent cost variable proposed by Calgon is the EEO, referred to earlier in this report. The EEO is the electrical energy required per 1,000 U.S. gallons treated per order of magnitude reduction in the concentration of contaminants in the stream.

The key system design variable is the UV dose required to achieve the required degree of decontamination and is defined as the lamp power multiplied by the total residence time per 1,000 U.S. gallons. Figure 2-2 presented the log-linear relationship between the UV dose in kWh per 1,000 gallons and contaminant concentration reduction for 1,4-dioxane. The slope of this curve is the EEO, and was equal to 6.1 for this example. The steeper the slope, the smaller the EEO, and the less expensive the costs of the treatment. Table 2-2 provides typical EEOs for various contaminants.

The EEO can be used as a figure-of-merit to compare different treatment options. The following are examples of its usefulness.

The EEO was used to compare the following AOTs: homogeneous UV/hydrogen peroxide, heterogeneous UV/titanium dioxide, and electron beam radiation treatment (6). Figure 4-3 is a plot of EEO versus input concentration for the bleaching of methylene blue, at different inlet concentrations. It is clear from the figure that the photocatalysis process is less efficient.

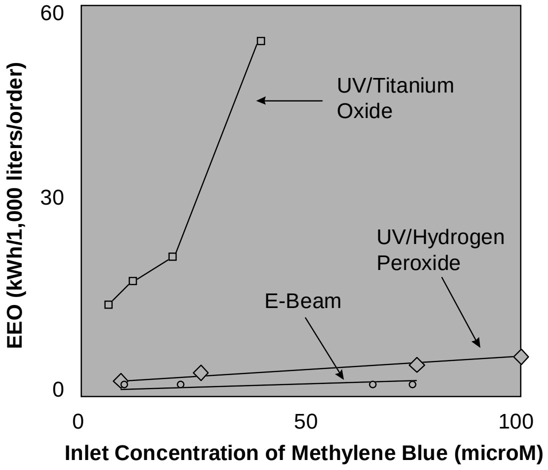


Figure 4-3
EEO Measures vs. Inlet Concentration

Figure 4-4 presents EEOs for the same three AOT treatment technologies for decontamination of phenol from an aqueous stream.

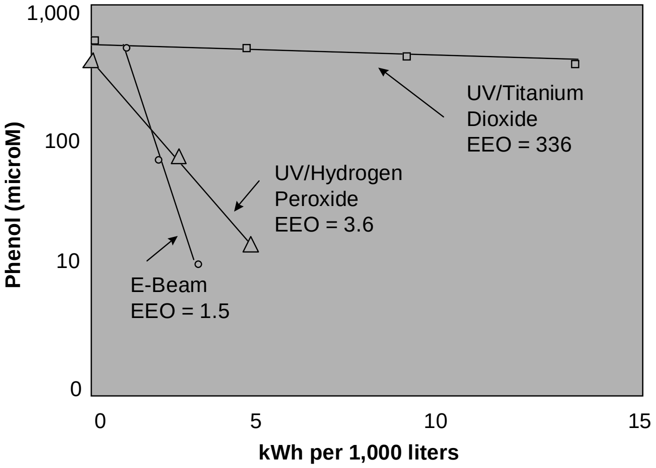


Figure 4-4
EEO Measures for the Treatment of Phenol

It can be seen from Figure 4-4 that photocatalysis for phenol destruction is about 100 times lower in efficiency compared to electron beam and UV/oxidation treatment. The primary reason for the low efficiency is the low quantum yield for the generation of hydroxyl radicals by titanium oxide particles. The yield is between 4% and 8% for slurries and even less for immobilized particles. In sharp contrast, the quantum yield of hydroxyl radicals for UV/hydrogen peroxide is about 100%.

For difficult-to-clean ground leachate water, the addition of a catalyst can improve the treatability and allow sunlight to be used in the photocatalysis. Table 4-8 compares the economics of three AOT applications for a leachate: UV/hydrogen peroxide, UV-visible light with a Fenton Reagent, and UV-visible light with a ferrioxalate catalyst and hydrogen peroxide (29).

Table 4-8
EEO for Destruction of Contaminants in Ground Leachate Water

Pollutant	EEO: UV, Hydrogen Peroxide	EEO: UV-Visible, Fenton	EEO: UV-Visible, Ferrioxalate, Hydrogen Peroxide
Toluene	20	9	1.6
Xylenes	23	10	2.5
MEK	54	29	5.7
Acetone	Not Available	108	58

The ferrioxalate is much more efficient that the other AOTs for the leachate mixture because ferrioxalate absorbs light up to 480 nm, resulting in more efficient use of lamp output, and the quantum yield from the iron ion is around 100%.

A final example of the economics of AOT is provided by the experience of Uniroyal (1). Uniroyal needed to treat N-nitrosodimethylamine (NDMA) in both wastewater and groundwater. The allowable levels of NDMA are very low because it is carcinogenic. Uniroyal's discharge criteria were 0.2 ppb in wastewater and 0.14 ppb in groundwater. The company investigated activated carbon, biological treatment, and ion-exchange resins, but none were capable of resolving the problem. However, NDMA absorbs strongly in the UV light range of 200 to 260 nm. Because of this, Uniroyal purchased a UV/oxidation system which they discovered routinely treated the water to concentrations well below discharge requirements, with an on-line availability of 98%

or better. Their electric bill for the nine-reactor unit was high at about $12,500 per month, but this was offset by lower maintenance costs (basically a changeout of UV lamps after about 3,000 hours of operation), and the elimination of secondary handling and disposal costs.

EEO is also useful in estimating the capital costs of a treatment system, since this cost is a function of system size, which is, in turn, a function of the UV power required to destroy the contaminants (4). If the EEO is known for a particular contaminant or group of contaminants, it can be used to calculate the UV power requirement in kW. Figure 4-5 provides the means to estimate capital costs without performing actual treatability tests (4).

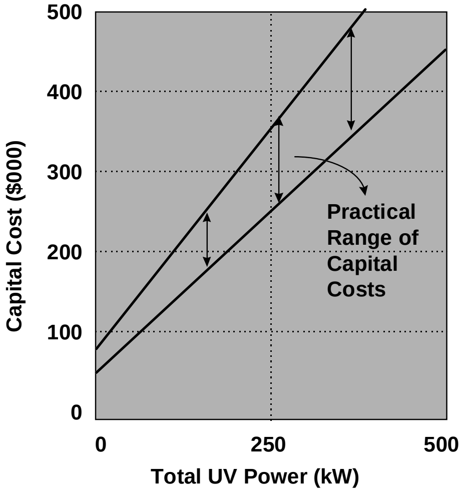


Figure 4-5
UV/Oxidation Capital Costs as a Function of UV Power

5

MARKET DRIVERS AND SIZE

Indoor Air Quality

Photocatalytic technology works well for IAQ applications. The size of this market is uncertain due to the lack of building codes and/or regulations detailing the allowable amounts of different contaminants. The existing building code merely mandates the number of air changes that are required, i.e., the amount of fresh air that must be injected as a function of time. The situation is further complicated by the fact that the concentrations of interest are in parts per billion, leading to difficulty and expense in monitoring whether the air quality actually would meet contaminant standards, if they existed. An American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) committee has been working on this problem for a number of years. The market drivers currently consist of what appear to be limited niches of severe IAQ, sometimes called “sick buildings”, specialized needs for people with health problems or allergies, hotels and motels seeking a competitive advantage, building energy managers looking for opportunities to reduce heating and cooling costs, and health-care and retirement home facilities concerned about the liabilities associated with air-borne diseases and infections.

The value proposition for the reduction of heating and cooling costs is very compelling. United Technologies Research Center (UTRC) has estimated that a 20% reduction in heating and cooling costs is possible if air purification equipment is used to reduce the number of fresh air changes necessary in a building. However, it is likely that there will be considerable resistance to this scenario from building operators, and from the HVAC industry itself looking at reduced capacity equipment sales, despite the fact that this sector is the logical supplier of the air purification equipment. The 1995 DOE building census estimates that the total heating and cooling energy costs in the commercial sector are about $95 billion annually. A 20% energy savings would therefore be valued at $19 billion annually. The total addressable commercial market is very large. For example, the health-care industry alone has about 100,000 buildings, the education sector has about 700,000 buildings, and the lodging industry has almost 160,000 facilities. Unfortunately, there is no strong universal market driver. The residential sector is in the same situation.

There are some market price data available for photocatalytic air cleaning equipment from Universal Air Technology (UAT). Note that one of the competitive technologies, HEPA filter units, sell in the hundreds of dollars range, with replacement filters costing up to 50% on the initial equipment cost, and requiring replacement about every year. UAT quotes a price of $2,000 for a 320 watt photocatalytic duct insert for a 1,500 cfm application. Fixed, low-profile wall-mounted 40 watt units for restrooms for odor control are priced at $500. UAT estimates maintenance costs as follows:

- Duct insert:
  - Replacement of the pre-filter every 4 - 6 months @ $30
  - Replacement bulbs every 5,000 hours of operation @ $10 /bulb for a total of $160
  - Replacement of the catalytic filter once per year @ $250
- Low-profile wall-mounted unit:
  - Replacement of pre-filter every six months @ $10
  - Replacement of bulbs every 5,000 hours of operation @ $10/bulb for a total of $20

Prototypes of air-cleaning units for commercial airplanes have been developed by UTRC as noted above. The fuel savings benefits are compelling, as is the expected increase in customer comfort and satisfaction. It was estimated by UTRC that a net fuel savings of about $25 million annually could accrue to a company the size of Delta airlines. However, the market barriers are substantial due to the need for the FAA to approve the new technology, and the need to modularize the units to fit within the tight space requirements of commercial airplane designs.

Volatile Organic Compounds (VOCs)

The market for VOC clean-up is driven by regulations. There are two types of applications: remediation projects (batch-type), and continuous processes to cleanup gaseous industrial streams. Most of the photocatalytic application demonstrations have performed well in these applications. There are thousands of sites or processes where the application could be installed economically, although there is a lot of competition in the market. A typical equipment sale might be in the range of $50,000 to $250,000 for a continuous application. A service business, using transportable equipment, can price its service contract to include a portion of the equipment depreciation together with typical operating costs of perhaps $30,000 to $100,000 on an annualized basis. Assuming that there are 2,000 to 4,000 projects per year, the total available equipment market is in the range of $100 million to $1 billion annually, and the services business could be in the range of $60 million to $400 million.

It was noted earlier, however, that each clean-up situation is different, and thus the clean-up system design must be customized for each project, based on a treatability test. The marketing and sales costs of each project will therefore be substantial.

The market for VOC clean-up is driven by regulations which change periodically, mostly by tightening the allowable discharges. It's unlikely that these regulations will be relaxed given the current social environment. Gradually, previously-created hazardous sites will be cleaned up, and these activities will provide an ongoing business opportunity for many years to come. It is likely that, for ongoing operations, many companies will be attempting to move towards a zero-discharge target, with significant recycling of scarce resources. This trend will increase the need for total destruction technologies such as photocatalysis.

Water Disinfection

The use of chloride dioxide may begin to be phased out as regulations are tightened. The alternative AOT-driven water disinfection plant might anywhere from $350,000 to $6,000,000.

In 1996, the total number of plant installations was about 190, representing an annual growth 15% growth rate over the previous decade. Figure 5-1 presents this market information. One of the leading providers of systems, Trojan Technologies of Canada, reported very strong customer demand in 1997, and grew its revenues by 44% during that year from Cn.$35.3 million to Cn.$51.2 million.

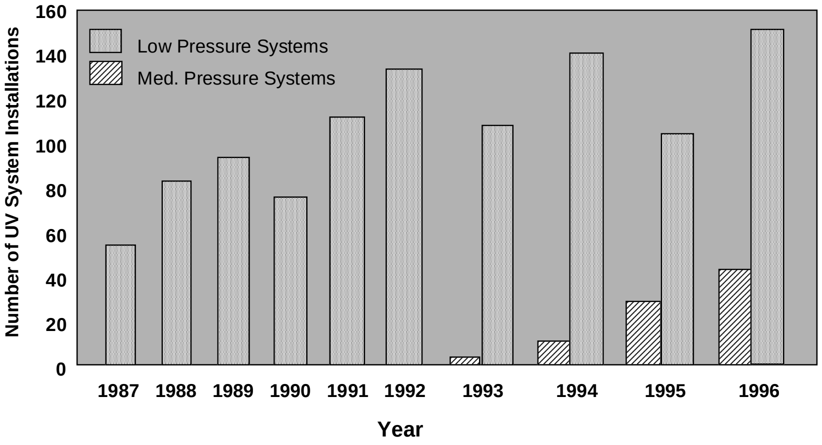


Figure 5-1
Sales of Water Disinfection Systems

If we assume that an average disinfection system sells for $1 million, the total size of the market today is probably about $200 million annually, growing at a double digit rate. This would suggest that Trojan Technologies has a significant share of the water disinfection market. The other key player is Calgon Carbon Corporation, with an annual revenue run rate of about $350 million in 1998, offering activated carbon-related and advanced oxidation products and services to municipalities and the industrial sector. Its applications include drinking water purification, wastewater treatment, sewage treatment, ground-water remediation, and emissions control. Calgon Carbon established an AOT business in 1996 with the acquisition of the Perox-Pure™ operations of Vulcan Peroxidation Systems Inc. and the equity of Solarchem Enterprises.

Wastewater Treatment

The market for contaminated water treatment is similar in its characteristics to the VOC clean-up market. AOTs have become a viable treatment alternative and their use is growing. However, photocatalytic AOTs are still in the development stage. The market is driven by environmental regulations. There are two main types of applications: remediation projects (batch processes), and continuous industrial effluent clean-up.

It has been estimated that there is the potential for about 1,000 - 1,500 projects per year (39). The capital cost per project varies from about $100,000 to $500,000, indicating a potential annual equipment market in the range of $100 million to $750 million.

Alternatively, the market can be sized as a service market: typical annual operating costs of wastewater remediation processes vary from $100,000 to $750,000, indicating a potential annual service market of $100 million to about $1,125 million.

According to Calgon, the growth in this market appears to be primarily in AOT applications (40).

Summary of Market Opportunity

The total potential market for photocatalysis applications is summarized in Table 5-1.

Table 5-1
Potential Markets for Photocatalysis Applications

Application	Market Size (Growth)	Market Drivers	Applicability of Photocatalysis
Indoor Air Quality (Buildings)	Market almost non-existent currently. Assuming that HVAC companies take responsibility for all aspects of conditioning indoor air, potential size is in the $billion annually (U.S. growth is flat, international market exhibits higher growth.	No strong universal market driver; potential for large energy savings, but code changes and new regulations will be needed	Good
Indoor Air Quality (Commercial Airplanes)	Market does not exist currently, and will be limited in size.	No strong driver; potential for significant fuel savings and increased customer satisfaction	Good
VOC Cleanup	Market size for equipment and service in the hundreds of millions annually; stable market	Market is driven by regulations, which are expected to tighten in the future	Good
Drinking Water Disinfection	In the hundreds of millions; growing rapidly	Market is driven by regulations, which are expected to tighten in the future	None; alternative AOT technologies work well
Waste Water Treatment	In the hundreds of millions; stable market	Market is driven by regulations, which are expected to tighten in the future	Potentially; further development needed

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KEY PLAYERS IN THE AOT MARKET

The AOT industry in the U.S. consists of one or two major players and a host of small, undercapitalized companies working on the development of advanced technologies. Since 1996, some consolidations have been consummated as companies strive to attain the critical mass necessary to develop the market. In addition, a substantial amount of research has been completed in the past decade in universities and the national laboratories, most notably at NREL. There is a strong interest world-wide in the development of AOTs. In particular, there are numerous ongoing industry/university/research institute research collaborations and product development efforts.

In indoor air quality, a number of companies have developed photocatalytic applications. Universal Air Technology, a small privately held company located in Florida, has launched photocatalytic products for the residential and small commercial market. A major NYSE company based in Connecticut, United Technologies, has progressed its development program to the prototype stage. Lightstream Photocatalytic, a small privately-held company located in California, has developed a 300 cfm prototype and is ready for market launch.

In the VOC area, Trojan Technologies Inc., a Canadian water disinfection company listed on the Toronto Exchange with projected annual revenues in excess of Cn.$60 million, recently purchased rights to KSE's photocatalytic AIR™ technology for VOC treatment in order to address the VOC market. Zentox, a privately-owned company, was formed to consolidate the AOT technologies of the NEPCCO division of IT Environmental Services Inc., Photox Corporation, and Photocatalytics, Inc.

In waste water applications, by far the most important player is Calgon Carbon, listed on the NYSE, with a projected revenue of over $300 million this year. Expecting the sales of its flagship products and services based on activated carbon to ease somewhat in the future, Calgon Carbon established an AOT business unit in 1996 with the purchase of the rights of Perox-Pure™ from Vulcan Peroxidation Systems Inc. for about $7.5 million, and the purchase of the stock of Solarchem Enterprises for about $11 million. Most of Calgon Carbon's AOT offerings to date are based on UV/hydrogen peroxide applications. As of this writing, Calgon Carbon is in final negotiations to be itself purchased by an unnamed acquirer.

U.S. Filter, with its acquisition of Zimpro Environmental Inc. now offers the Ultrox™ UV/ozone/hydrogen peroxide AOT for treating well-water and organics in aqueous streams. Purifics Environmental Technologies Inc. is a small privately-held Canadian company providing photocatalytic treatment of aqueous solutions. UV Technologies Inc., a small privately-held company, has developed the UV-CATOX system for photocatalysis of aqueous wastes, and Zentox offers photocatalytic treatment of aqueous streams to supplement its flagship AOT product, ozone treatment of cooling tower water.

In drinking water disinfection applications, Calgon Carbon and Trojan Technologies dominate the scene in terms of the application of AOTs.

Important photocatalytic knowledge bases and research capability also reside at NREL, North Carolina State University, the University of Missouri-Columbia, Michigan Technological University, Sandia National Laboratory, the University of Dayton Research Institute, and Arizona State University.

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BENEFITS OF PHOTOCATALYSIS FOR ELECTRIC UTILITIES

Increased marketplace acceptance of photocatalysis will have two main benefits for utilities. A direct benefit, in terms of revenues, is the increased use of electricity associated with the high-intensity UV lighting required for the process. Associated benefits include the demonstration of electricity's ability to provide highly controllable, flexible, and reliable process features, and the increased perception of the utility as innovative and progressive.

However, the potential to increase customer loyalty through the promotion of photocatalytic processes may be the most important benefit to utilities. The electricity market is being deregulated, providing customers with the option to choose their electricity supplier. The market is large but fairly flat, and a large number of new entrants are competing against utilities for their best customers. The cost of electricity is an important concern to these customers, but it's likely that the electricity prices will converge within a commodity market.

Therefore, in addition to price competitiveness, utilities are looking for other ways to differentiate themselves from their competitors and create superior value for their best customers. This has led to the development of competitive strategies that bundle the energy commodity with enhanced energy-related services which leverage the existing core competencies of the utility.

Utility customer representatives are working with their best customers in different industry and commercial sectors to better understand and help optimize their energy needs, and also to search for ways to apply electricity-based technologies, i.e. known as electrotechnologies, to solve some of their customers' product and process problems. Photocatalysis is an exciting new electrotechnology that has the potential to provide superior solutions for industrial customers' environmental problems, help municipalities improve the quality of drinking water, reduce liability in health-care facilities, and increase the comfort and safety of large commercial buildings. All of these customer segments are important sources of revenues and profits for utilities.

The utility wishing to leverage photocatalysis applications for its customers has a number of options, requiring progressively larger resource requirements. The utility can simply become informed about the technology and provide advice on suitable applications. It can, like Virginia Power has done in its “Positively Electric” series of technical briefs, assess the technology and applications providers, and provide its customers with documentation on successful applications and recommended suppliers. And finally, it can form strategic alliances with the “best-of-breed” suppliers to market and distribute the technology to its own and other utilities’ customers as a business development endeavor.

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