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Solving Widespread Low-Concentration VOC Air Pollution Problems: Gas-Phase Photocatalytic Oxidation Answers the Needs of Many Small Businesses

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ABSTRACT

Many small businesses are facing new regulations under the 1990 Amendments to the Clean Air Act. Regulators, as well as the businesses themselves, face new challenges to control small point-source air pollution emissions. An individual business—such as a dry cleaner, auto repair shop, bakery, coffee roaster, photo print shop, or chemical company—may be an insignificant source of air pollution, but collectively, the industry becomes a noticeable source. Often the businesses are not equipped to respond to new regulatory requirements because of limited resources, experience, and expertise. Also, existing control strategies may be inappropriate for these businesses, having been developed for major industries with high volumes, high pollutant concentrations, and substantial corporate resources.

Gas-phase photocatalytic oxidation (PCO) is an option for eliminating low-concentration, low-flow-rate emissions of volatile organic compounds (VOCs) from small business point sources. The advantages PCO has over other treatment techniques are presented in this paper. This paper also describes how PCO can be applied to specific air pollution problems. We present our methodology for identifying pollution problems for which PCO is applicable and for reaching the technology's potential end users. PCO is compared to other gas-phase VOC control technologies.

INTRODUCTION AND OPERATING CHARACTERISTICS

NREL researchers are working to establish a commercial industry for photocatalytic oxidation (PCO) treatment techniques. The use of ultraviolet (UV) light in conjunction with a semiconductor photocatalyst (commonly titanium dioxide, TiO_2) breaks down toxic organic chemicals into nontoxic or easily treatable compounds such as carbon dioxide, water, and simple mineral acids. The process can use electric lamps or sunlight. PCO offers many advantages as an option for pollutant destruction:

- Achieves high destruction efficiency
- Operates at ambient or near-ambient temperature and pressure
- Uses a safe nontoxic catalyst
- Creates no nitrogen oxides (NO_x)
- Requires no auxiliary fuel
- Requires no hydrocarbon source of hydrogen for treating chlorinated pollutants
- Treats very low, but often harmful, concentrations of pollutants effectively
- Employs a modular design
- Eliminates—rather than transfers—toxicity of pollutant

NREL is currently conducting research on various aspects of PCO. Through NREL's program, researchers are:

- Analyzing chemical processes, products, and intermediates
- Researching the reactivity of photoactive catalysts
- Evaluating the treatability of organic and inorganic pollutants
- Developing engineering design and scale-up models

PCO has a wide variety of potential applications. The application closest to commercialization is gas-phase destruction of volatile organic compounds (VOCs). Gas-phase processes can be applied to airborne emissions (air pollutants) and to gaseous pollutants generated from remediation techniques, such as soil vapor extraction and air stripping.

In the following sections we describe the technical characteristics of PCO and introduce the current regulatory mandates in the United States that make PCO attractive in many small and newly regulated business operations.

PCO uses UV light, a catalyst, and the oxygen in air to completely mineralize VOCs in air. Organic pollutants are converted to carbon dioxide, water, and simple mineral acids (if chlorinated VOCs are treated). The process can be applied to a variety of problems, including vent streams from buildings and industrial processes, or the remediation of VOC-contaminated water and soil. To treat contaminated water or soil, the VOCs are first removed by air stripping or soil vapor extraction, and the resulting off gas is treated in the PCO unit. At its simplest, a PCO treatment system consists of a photoreactor, instrumentation, and a blower. When used to treat chlorinated compounds such as trichloroethylene, a scrubber is added to remove acid gas products like hydrochloric acid (HCl) and chlorine. A generic lamp-based system design is presented in Figure 1.

Destruction efficiencies in excess of 99% are possible in the PCO system. This level of destruction equals the level achievable in conventional thermal and thermal catalytic incinerators; however, because the PCO process relies on light energy rather than thermal energy, the process occurs at ambient temperatures and pressures. This translates into lower construction and operating costs. The low-temperature operation also allows plastics to be used for most components. Not only does this decrease weight and cost, but corrosion from acid gas products is minimized. Unlike thermal catalysts, the PCO photocatalyst, titanium dioxide, is an inexpensive semiconductor powder and is not susceptible to acid attack. However, like any catalyst, fouling or poisoning is possible if the operating conditions are not carefully controlled. Ultraviolet light is supplied by fluorescent blacklights, similar to those found in tanning salons. In some applications, sunlight can be used as the light source, further reducing operating costs.

The PCO process has been extensively tested in the laboratory and is currently transitioning to pilot and commercial applications. The compounds susceptible to PCO treatment include chlorinated solvents, alcohols, ketones, and amines. Fuel components, aromatics, and chlorinated aromatics can also be treated, although in some instances additives or higher temperatures (ca. 100°C) are required to achieve complete contaminant destruction.

Compared to other available technologies, PCO is well suited for treating chlorinated compounds, particularly chlorinated ethylenes such as trichloroethylene and perchloroethylene. These compounds degrade rapidly in PCO systems but are difficult to treat by other means because they do not burn or adsorb well and are toxic to most microorganisms. Aliphatic hydrocarbons, on the other hand, are easily incinerated, adsorbed, or biodegraded, but are only moderately reactive in the PCO system.

A recent analysis by NREL and IT Corporation[1] suggests that PCO is best suited for low concentration (1000 ppm or less) waste streams. This is partially a result of the strong dependence of PCO cost on VOC concentration and partially a result of the suitability of product recovery technologies (such as condensation) for high-concentration waste streams. In addition, the advantages of PCO are most apparent on low- to moderate-volume streams (<20,000 cfm) where the modular nature of PCO offers the advantage of system flexibility. The modular nature, much like carbon canisters, is a key advantage when treating smaller-flow-rate streams. However, this same attribute prevents PCO from benefitting from economies of scale. Given that surveyed users expect 80% of their expenditures for VOC control systems to be for low-flow-rate streams (<5000 cfm)[2], PCO systems could operate successfully in applications where small, individual systems are needed.

COMPARISONS OF PCO TO OTHER TECHNOLOGIES—COSTS

The estimated cost and performance for the PCO technology are based on laboratory data, pilot-scale tests, and engineering estimates. Although these data are inherently less accurate than information from commercially operating systems, they are sufficient to identify the following trends pertaining to the relative merits of the PCO technology.

When compared to the other technologies such as incineration, PCO generally has similar capital costs. The major benefit of PCO arises from its lower operating costs. Largely because of these low operating costs, when levelized annual costs are examined, the PCO process is projected to have cost advantages over the other destructive technologies. As depicted in Figure 2, the cost advantage of PCO is most apparent on low-flow-rate streams.

The cost projections in reference 1 followed the methodology of previous air pollution control reports published by the American Institute of Chemical Engineers. This format limited the cost projections to systems of 250 scfm or greater. Yet the PCO technology is well suited to treat lower-flow-rate streams as well. A low-flow-rate PCO unit would consist of one or a few fluorescent lamps, replaceable catalyst supports, and some air handling connections. Depending on the application, a blower, packed bed scrubber, or monitoring sensors could be added. In production, such a system could cost as low as a few hundred to a few thousand dollars and would be ideal for handling fugitive emissions and other small sources.

In larger PCO systems, electrical consumption can account for more than 50% of the operating cost. One way to reduce this power cost is to collect UV light from sunlight. Of course, solar PCO systems must deal with limited system availability due to weather and nightfall. These restraints make solar units best suited for applications where daylight operation is sufficient, averaged emission levels are more important than temporal levels, and electricity is expensive or not available. A good example of an application favorable to solar is a site with emissions during an 8-to-5 work shift and regulatory requirements based on total annual emissions. Such applications are not uncommon, particularly with small air pollution sources, such as dry cleaners, auto repair shops, bakeries, or coffee roasters. Other possible solar applications include remote sites, storage tank vents, or potentially explosive waste streams.

One promising application for a solar system is the regeneration of a carbon bed or other adsorbent[5,6]. In this application, the adsorbent does the 24-hour VOC removal work, and the solar system is used to purge and destroy the contaminants during daylight hours. By minimizing the required capacity of both units, a combined system could be less expensive than either process used individually.

REGULATORY DRIVERS

Regulatory Mandates

The need for new, more efficient VOC treatment technologies is highlighted by the 1990 amendments to the Clean Air Act (CAA), which drastically increase the number and types of businesses that will be subject to its regulatory requirements. The new Air Toxics section (Title III) mandates much stricter regulation of chemical (mostly VOC) emissions, making it the single most important new CAA program for industry[3]. Title III is structured to regulate Hazardous Air Pollutants by industry category and subcategory. The Environmental Protection Agency (EPA) published an initial list of categories for major and area sources in 1992 (57 Fed. Reg. 31576, July 16, 1992). These are the industries and businesses that will be subjected to regulation. A schedule of development of standards for each industry was published December 3, 1993 (58 Fed. Reg. 63941). In addition to those sources designated as major (more than 25 tons per year of emissions), "area sources" are also included in these regulations. Area sources refer to small sources that are numerous and, taken together, form a significant source of air pollution. In general, states will probably implement these programs and have the authority to promulgate more stringent requirements.

Many small businesses will be regulated for the first time under the CAA. These businesses typically lack expertise and staff to comply with new environmental regulations. Small profit margins make it imperative for these businesses to find and implement low-cost, effective, low-maintenance air pollution control measures if they have to reduce emissions.

Regulatory Decision Making

The process of deciding upon control technology should include an examination of the complete range of control options. The technology chosen should minimize costs, ensure flexibility, and be fully compliant with applicable standards[4]. The MACT (Maximum Achievable Control Technology) regulations, which have been promulgated thus far under Title III, describe control technology requirements to varying degrees but include equivalency provisions. Therefore, if the MACT regulations state that carbon adsorption is required, the operator has the opportunity to select another technology if certain equivalency guides are meet. It may behoove the industry to explore additional technologies and consider not only economic but liability issues. Table 1 illustrates the process a small business can follow to determine its action plan under air pollution control regulations.

In addition to the regulatory specifications found in the Federal Register, other sources of information are available. Often, instructional documents are available, including internal EPA policy, guidance manuals, technical documentation, and penalty policies. The EPA has developed software, available free of charge, specifically to evaluate control options for hazardous air pollutants (HAP-PRO). Thus far, both carbon adsorption and thermal/catalytic expert systems (decision tree) have been written and are available from the Control Technology Center HOTLINE (919) 541-0800.

Small businesses have available to them technical and environmental compliance assistance from states, as required in the Clean Air Act. Each state air quality office has a Small Business Assistance Program available to assist small business. As an example of the decisions operators must consider for meeting these new regulations, a scenario specific to one industry has been prepared (Figure 3).

It is of utmost importance to remember that the federal regulations may not be the final requirement. As stated above, states have the authority to enact more stringent criteria. Businesses should also contact their trade associations for information and help in complying with these regulations. Often they can provide additional contacts and guidance documentation.

Interaction with Government

Many types of environmental legislation and regulations are technology specific. If regulators are not familiar with a new control or pollution prevention technology, it may be excluded from regulations and laws as an approved strategy. If agency personnel are involved from the early stages of technology field testing and commercialization, an interactive relationship can develop that assists both regulators and engineers. The regulators learn about the developing technology and become familiar with its applications and advantages. Regulators are also often familiar with the regulated community and can provide advice to researchers on how to develop the technology to be most effective with its projected application. Regulators may also provide a forum for contacting new potential end users and can provide information about other applicable technologies and their strengths and weaknesses.

Experienced staff members at regulatory agencies often have extensive technical knowledge about industrial processes and emissions. They can provide practical advice about real-world applications for new environmental technologies. For new regulations and control measures under development, interaction with regulatory agencies is critical. Regulators need to know what kind of control technology is available and businesses need to be aware of regulatory developments that may affect commercialization and use of their new technology. Working together, regulators and the private sector can develop regulations that take advantage of new technology and that effectively protect human health and the environment.

New regulations are often developed through a negotiated process called regulatory negotiations, or reg neg. This is a potential arena for effective interactions between government and businesses. In addition, federal agencies, such as EPA, Department of Energy, and Department of Defense, have selected several major industrial categories as "industries of the future" (or a similar name). These industries have been identified as critical for national interests such as competitiveness, energy consumption, or environmental challenges. These selected industries are likely to receive increased attention from the relevant agency, including allocation of resources to assist in solving environmental problems.

CONCLUSIONS

PCO of hazardous air pollutants is an emerging process for air pollution control that is particularly effective in the ranges of low concentration and moderate to low volumetric flow rates. It has many unusually favorable intrinsic characteristics, such as high destruction efficiency in a single pass, ambient or near-ambient temperature and pressure operations, no nitrogen oxide (NO_x) formation, very low, but harmful, concentrations of pollutants can be effectively treated, and toxicity of pollutant is completely eliminated. These characteristics make the technology publicly acceptable as a control measure, as well as environmentally advantageous. PCO's relatively low cost and modular, self-contained design potential make it potentially useful to small and newly regulated businesses with limited financial and technical resources.

The development and commercialization of the technology is being conducted through governmentsponsored research at national laboratories in partnership with American businesses. This effective technology—capable of solving many of today's challenging air pollution problems—will meet the needs of many of today's regulated industries and reduce air pollution to protect public health.

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7. Federal Register, Vol. 58, No. 182, 49354, September 22, 1993.

Table 1. How a small business can determine its action plan to comply with air pollution control regulations.

Begin by assessing the regulatory requirements:

- Determine source definition and industry category (Federal Register, Vol. 57, 31576)
- Quantify actual emissions and compare with threshold definitions for major source category and area source category
- If you meet source definition and threshold level, determine date of regulation (Federal Register, Vol. 58, 63941.

Thoroughly examine the requirements of your project:

- Are there nuisance as well as regulatory drivers?
- Is your source applicable as defined by the requirements?
- What future plans do you have including expansion? Will this trigger new regulations as you exceed the regulatory threshold?

Characterize your emissions in terms of flow rate, concentration, heat content, and humidity. Include possible upsets and peak conditions.

Finally evaluate the control options available; the first look should include maintenance and good practice changes.

Include in this assessment hidden charges such as monitoring, performance testing, permitting costs, and disposal of wastes generated.

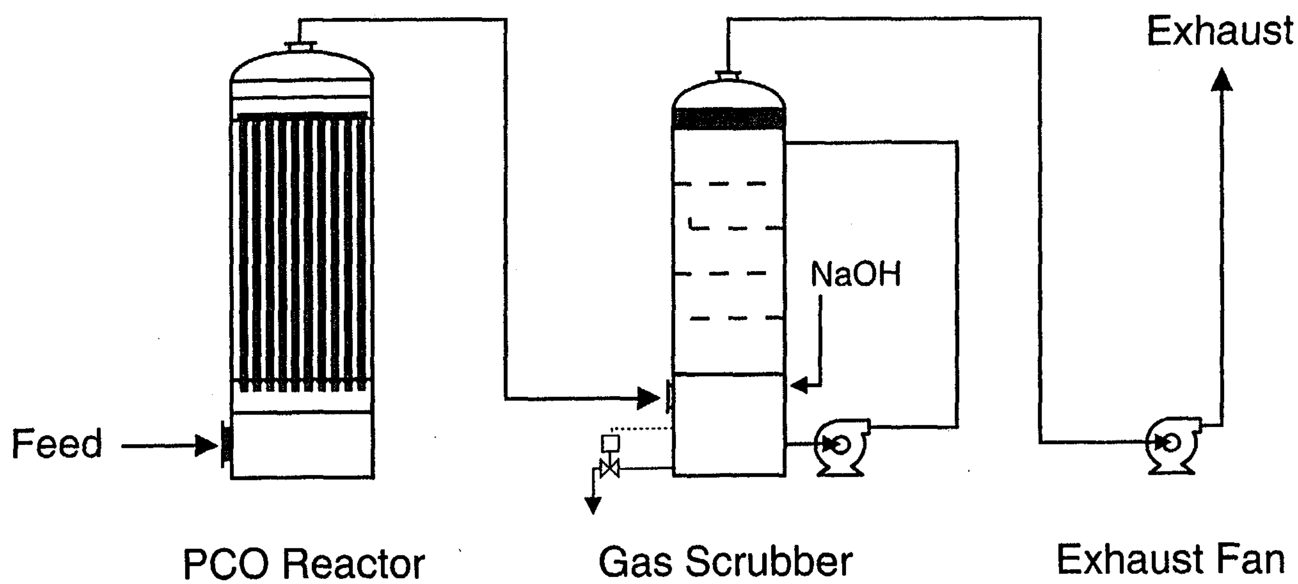

Figure 1. Lamp-based photocatalytic oxidation process flow diagram.

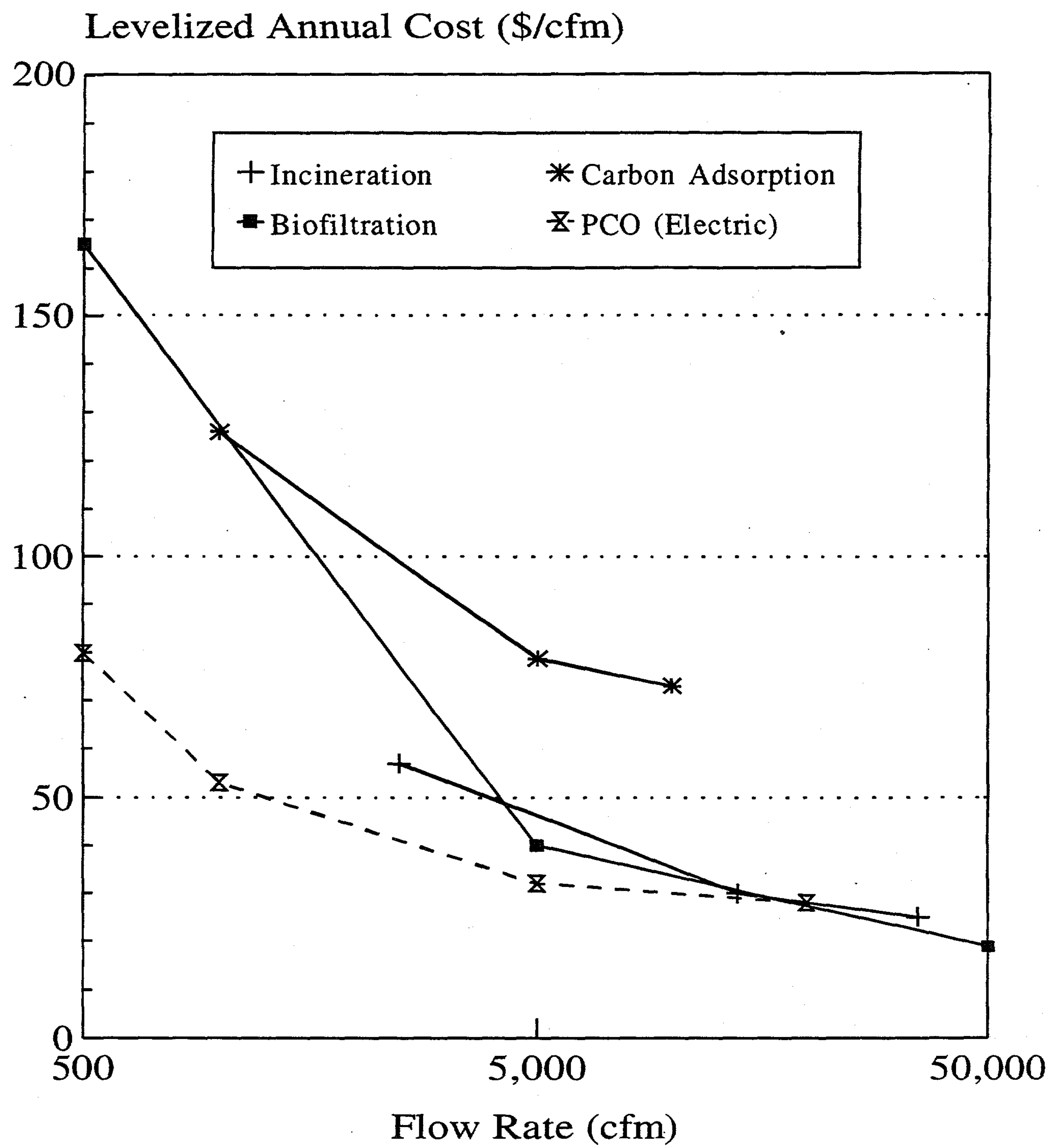

Figure 2. Annual treatment cost vs. flow rate.

Commercial Dry Cleaning Operation (SIC 7216)[7]
1. Ascertain your perchloroethylene (PERC) solvent usage in terms of gallons per year. The EPA is using solvent usage as a surrogate for the potential to emit limits.
2. Determine what type of dry cleaning equipment you use: Dry-to-Dry only, Transfer only, Both.
3. From the results of 1 and 2 your operation will be considered either: Small Area Source, Large Area Source, Major Source. Let's assume you are considered a **Major Source**.
4. The MACT standards are specific for your operation:
For Process Vents: Install Refrigerated Condensers (or equivalent); if you already have Carbon Adsorption, this may remain as your control technology.
For Fugitive Emissions (clothing transfer operations, equipment leaks, solvent exposure): Transfer Machines (if part of the operation) must be contained inside a room enclosure and Carbon Adsorption (or equivalent) used at room vent.
The MACT regulations for Dry Cleaning Facilities (Federal Register Vol. 58, No. 182, 49354) have specific steps which must be taken so that the EPA may determine whether equipment a dry cleaner proposes to use is equivalent to that required by the regulation. These include diagrams, destruction comparison information, and accuracy explanations.

Figure 3. An example of the decision-making process for complying with environmental regulations.