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Title: **COST EFFECTIVENESS OF SILENT DISCHARGE PLASMA FOR POINT-OF-USE VOC EMISSIONS CONTROL IN SEMICONDUCTOR FABRICATION**

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Cost Effectiveness of Silent Discharge Plasma for Point-of-Use VOC Emissions Control in Semiconductor Fabrication

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Summary

Extensive research into the treatment and control of Volatile Organic Compounds (VOCs) from semiconductor industry manufacturing processes has identified the need for alternatives to existing combustion devices. Specifically, semiconductor manufacturing design is moving toward exploiting effective, small-scale, abatement control technologies for specific point-of-use (POU) waste streams associated with a particular component or manufacturing tool. Proponents of POU control argue that replacing a single large emissions control system with smaller, distributed systems designed for very specific waste streams will increase manufacturing flexibility, minimize waste generation, and reduce environmental impact.

The Silent Discharge Plasma (SDP) developed at Los Alamos National Laboratory is a nonthermal plasma technology created by a dielectric-ballasted electrical discharge. Influent gas-phase pollutants are destroyed in the reactor by the free radicals or electrons generated by the plasma. Reaction rates normally associated with extremely high temperatures -- 10,000 to 100,000 °K -- are maintained while the actual gas temperature remains near ambient.

This paper examines the potential for SDP to be used in niche circumstances for POU control of VOC exhaust streams specific to the semiconductor industry. A sensitivity analysis is presented, showing how SDP cost of ownership is affected by changes in the major operational parameters of exhaust flow rate, target compound, destruction removal efficiency (DRE), and electrical duty cycle.

The results of cost analysis show that SDP performance and cost effectiveness are flow rate- and compound-specific; costs for treatment of exhaust streams containing methanol and acetone are prohibitive at the high flow rates (3000-4000 scfm) associated with solvent bench emissions. However, the SDP technology may be a cost effective alternative for treating POU exhaust gases generated by lithography tools because of the lower flow rates (100-500 scfm) associated with individual lithography tool exhaust output, and because the target exhaust compounds (i.e., HMDS, PGMEA) are particularly conducive to destruction via SDP. We conclude that the Silent Discharge Plasma is a viable, cost effective technology under high-concentration, low-flow rate regimes, and for target compounds that have been empirically shown to be conducive to destruction via free radical chemistry.

Introduction

The current approach to air pollution control for the semiconductor industry combines all exhausts from process tools, cleaning tools, and fume hoods into a single large stream. Typically, exhaust gases are piped to a concentrator wheel where the organic constituents are combined prior to being fed to a regenerative thermal oxidizer (RTO). Concentration of the exhaust stream enhances the performance and cost effectiveness of the RTO by increasing the thermal capacity of the feed stream, thereby decreasing reliance on an external fuel source.

The advantage of RTO is that it is a well-understood and thoroughly tested technology that can handle the high air flow rates associated with the combined exhaust streams generated in manufacturing. The disadvantages of RTO are high operating and maintenance (O&M) costs, decreased flexibility, and fouling of the equipment by particular exhaust stream constituents. O&M costs are relatively high because RTO is labor- and utility-intensive. Fouling of the system by exhaust gas constituents, primarily hexamethyldisilazane (HMDS) increases maintenance, leading to an increase in downtime and expense. The lack of flexibility inherent in a single, large air emissions system is significant within the semiconductor industry because products change rapidly and have a relatively short commercial life.

To increase manufacturing flexibility, reduce operating expenses, and provide a higher level of pollution control the industry is exploring the point-of-use (POU) pollution control philosophy. In a POU environment, smaller distributed pollution control systems are integrated into individual tools, replacing the centralized air emissions system currently in use. Whereas current plenum exhaust is high flow, low concentration, and extremely variable, POU exhaust is low flow, higher concentration, and specific to the particular tool.

The SDP technology is well-suited to fit the needs of POU emissions control for the several reasons. First, the technology is capable of oxidizing a wide range of intractable exhaust compounds at ambient temperatures and pressures and at high destruction removal efficiencies (DREs). Second, the electrical power levels required for destruction of target compounds can be finely tuned and adjusted in order to optimize operating expenses. In addition, the SDP equipment can cycle on and off to take advantage of the transient nature of exhaust gas release. Third, the SDP system has a small footprint relative to other VOC abatement technologies. Fourth, HMDS is readily destroyed by SDP at low concentrations without reducing removal rates for other target compounds.

SDP Technical Description

A nonthermal plasma made up of nearly equal numbers of positive ions and electrons is generated by introducing electrical discharges into a gas stream. *Nonthermal* discharge means that the various species in the plasma are at very different temperatures. Nonthermal is used to differentiate these sources from *thermal* plasmas in which all particles, electrons, ions, and non-charged species are at the same temperature.

With SDP and all other nonthermal plasmas, the lightest particles—the electrons—are heated to very high temperatures (in air discharges typical electron temperatures are 3eV and are approximately equal to 30,000 °K) while the bulk gas remains at ambient temperature. This means that a nonthermal or *cold* plasma is able to access very energetic chemistry without heating the bulk of the gas. For example, the plasma used to etch wafers is nonthermal; it uses the chemical energy of atomic fluorine to selectively remove silicon.

SDP treatment is an advanced oxidation process that relies on free radical chemistry at ambient temperatures and pressures to oxidize gas phase contaminants. Within the SDP, myriad micro-arcs similar to tiny lightning bolts and each lasting only a few nanoseconds produce energetic electrons. The high temperature electrons efficiently dissociate oxygen and water to produce large concentrations of free radicals. In the presence of water vapor, the primary radicals are OH and O; these radicals attack the organic contaminants, breaking carbon and halogen bonds and reducing the gaseous waste stream to CO_2, H_2O, and HCl.

The desired chemistry is very similar to thermal oxidation, except that the radicals are produced by electronic dissociation of water and oxygen, not by thermal dissociation. Usually this nonthermal regime is accessed at low pressures where collisions are less likely and electrons have a much longer mean free path. As pressure increases, so do collision rates and the transfer of energy from one species to the other. Atmospheric cold plasmas must interrupt the collisions before equilibrium is reached.

SDP exploits the interaction of the discharge with the dielectric surface to produce a homogeneous distribution of self-terminating pulses (microdischarges) even when the high voltage is applied slowly (typically 1-5 kHz). The electrical microdischarges occur across parallel glass plates in the reactor (see **Figure 1**). Typically, a reactor will contain a "stack" of 10-20 of these glass plates.

Coogan, et al, 1993 [1], have designated what they call a "nine-factor" in terms of the amount of additional energy required to reduce a particular VOC effluent concentration by a factor of ten. Use of the 9-factor -- units are in Joules/liter -- simplifies scaling calculations. If, for example, a given contaminant has a 9-factor of 250 J/liter, this means that it requires that much plasma energy density to destroy 90% of the contaminant. To increase the DRE from 90% to 99%, an additional 250 J/liter would need to be added to the

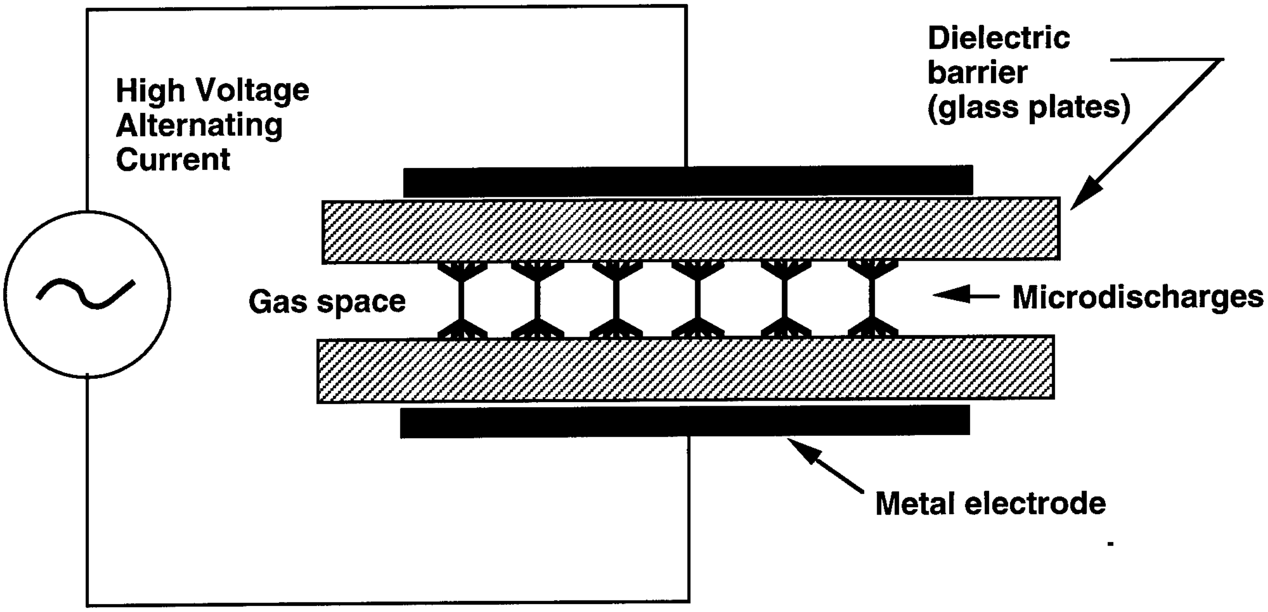


Figure 1. Side view schematic of planar dielectric barrier configuration for producing silent electrical discharges (from Coogan, et al., 1993).

energy requirement of the system. The 9-factor is proportional to the power-to-flow ratio P/Q, such that given the 9-factor, or energy density in Joules/liter, one can calculate the power requirement for a particular flow rate, or adjust the flow rate to meet a particular power requirement [1].

Energy density requirements vary greatly depending on the specific compound(s) to be treated. For instance, acetone has a relatively high energy density requirement of 1100 J/liter, whereas methanol requires an energy density of approximately 800 J/liter. Destruction of isopropanol (IPA) requires an energy density of about 200 J/liter; PGMEA and EEP are readily destroyed at less than 50 J/liter [2]. A typical target P/Q for the removal of chlorinated hydrocarbons is likely to be in the range from 200 - 500 J/liter for 90% removal of Total VOC.

The effect of power vs. flow rate on DRE can be observed in **Figure 2**. For example, to remove 90% of a given contaminant at a flow rate of 12.5 scfm requires only 2.5 kW, whereas 90% removal at 50 scfm requires about 12 kW, regardless of influent concentration. Because power and flow rate increase at an essentially linear rate, and capital cost is predominantly the cost of the power supply, the capital cost structure is also linear in regard to flow rate. Therefore, other operational parameters remaining constant, the capital cost of a 500 cfm system is generally about five times as expensive as a 100 cfm system. For this reason, SDP is most cost efficient at low flow rates and high concentrations.

Summary of Test Results

Bench Tests with VOCs From Solvent Cleaning Operations

The destruction removal efficiency of IPA/methanol/acetone at 133 ppmv (combined mixture 400 ppmv) in dry and humid air (approximately 45% relative humidity

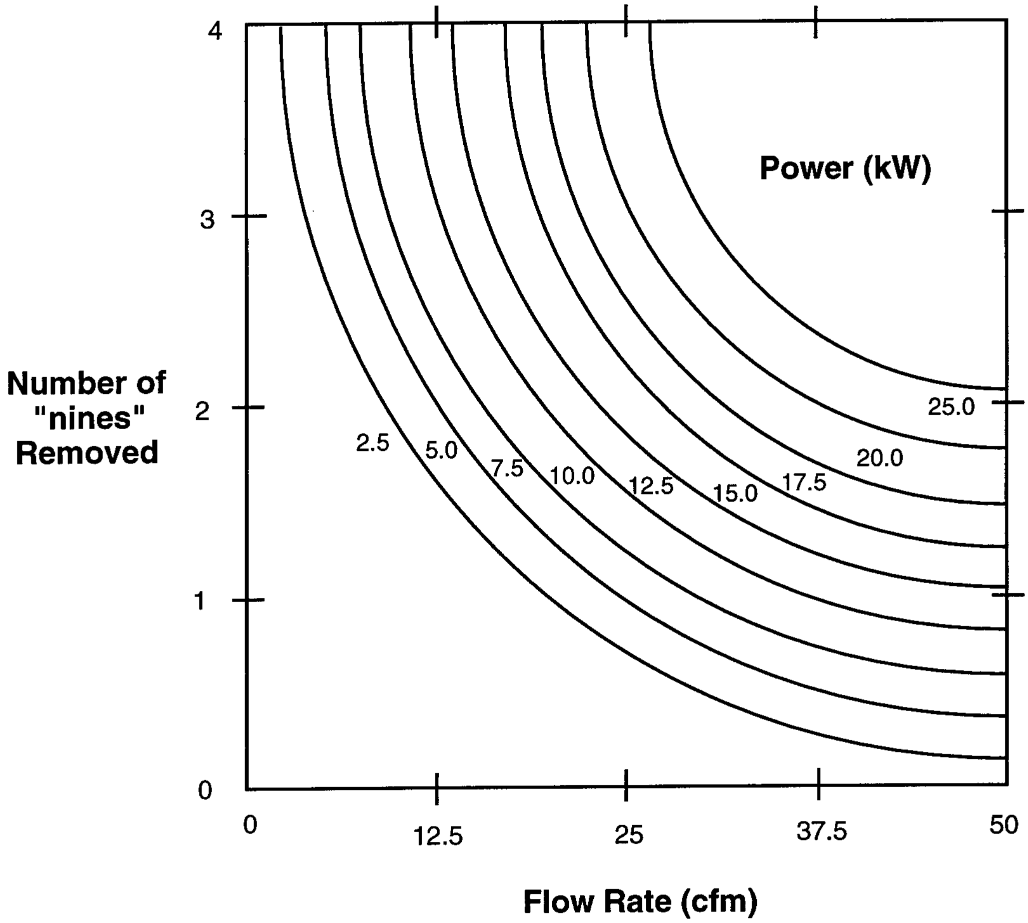


Figure 2. Relationship among flow rate, removal rate, and power requirement for Silent Discharge Plasma (from Coogan, et al., 1993).

at room temperature) was measured using gas chromatography. For the three-compound mix, the measured nine-factors were 200 J/liter for IPA, 800 J/liter for methanol, and 1100 J/liter for acetone. That is, 90% removal of IPA requires 200 J/liter, 90% removal of methanol requires 800 J/liter, and 90% removal of acetone requires 1100 J/liter. The same removal efficiencies were measured with single compound mixtures.

Small amounts of acetone are generated during the destruction of IPA (similar to photocatalytic systems). The destruction of total organic compounds, measured using a flame ionization detector (FID), was dominated by the power required for the acetone. Because acetone is produced during the oxidation of IPA, 1250 J/liter is required to destroy 90% of the organic compounds from this mix of VOCs. Therefore, a 500 scfm air stream would require approximately 300 kW of electrical power—a very large system. A system removing only IPA (a nine-factor of 200 J/liter) would require only 50 kW [2].

Bench Tests with Lithotrack VOCs

Simulated air streams containing HMDS were combined with EEP and PGMEA at 10–20 ppmv in humid (~ 45% relative humidity) air and treated in the lab-scale SDP reactor. Tests of EEP in both dry and humid air showed better than 90% destruction at 40 joules/liter. A nine-factor of 40 J/liter means that 90% removal of a 15,000 slpm (500 scfm) air stream would require approximately 12 kW of electrical power, less than 30 times the cost of a similar flow system removing room temperature acetone.

Tests were then continued to evaluate the effect of HMDS and its principle byproduct, silicon dioxide (SiO_2), on SDP cell performance. The laboratory system treated 3,000 standard liters of air contaminated with 50 ppmv of HMDS. A flow of 10 slpm of the air/HMDS mixture combined with a 2 slpm flow of air saturated with water at 35°C (the resulting 12 slpm stream contained 42 ppmv of HMDS at 20°C and 40% relative humidity) was fed through an SDP cell for 4.2 hours. $SiO_2$was produced without reducing SDP efficiency. The hexamethyldisilazane was destroyed with a 95% destruction efficiency measured at 1.4 kJ/liter. This yields a nine-factor close to 1 kJ/liter. Tentatively identified byproduct compounds include trimethylsilanol, pentamethyldisiloxane, and diethoxydimethylsilane (the combined concentrations of these compounds is < 0.5 ppmv). A second test with a more complex air/water/PGMEA and HMDS mixture produced similar results to the individual tests: removal was consistently unaffected by the presence of HMDS [2].

Cost of Ownership

Based on the pilot test data, cost of ownership (COO) estimates for the SDP technology show annual operating expenses (including amortized capital and installation costs, maintenance, and utilities) are $8.3K for a single 250 scfm lithotrack tool. POU SDP system costs are $33.3K per 1000 scfm as compared to about $22K per 1000 scfm for a typical end-of-pipe (EOP) concentrator/thermal abatement system. These cost details have been researched and published in the Los Alamos National Laboratory report "Silent Discharge Plasma Cost of Ownership Model for Point-of-Use VOC Emissions Control" (Cummings, 1997 [3]). Although replacing existing EOP systems with SDP is not recommended, SDP could easily be installed in niche circumstances for POU control of VOCs from lithotrack tools.

SDP shows optimal performance under a high concentration, low flow regime. It is not particularly sensitive to influent exhaust stream concentration, but is sensitive to flow rate, specific exhaust compound(s), and the target DRE. Cost of ownership calculations depend upon these latter three parameters. This results in both advantages and disadvantages to the system. If the target compounds are favorable to destruction via SDP such as those emitted by lithography tool exhaust (i.e., PGMEA, HMDS), and if flow rates are relatively low (i.e., ranging from approximately 100-500 scfm), then the cost of ownership is competitive. If, on the other hand, target compounds are unfavorable to SDP treatment such as those emitted by solvent benches (i.e., acetone), then cost of ownership becomes relatively high, particularly at the high flow rates (3000-4000 scfm) associated with solvent bench exhaust output. Cost is also dependent on the specific target DRE. Increasing DRE from 90% to 99.9% or greater is achievable, but operating costs increase accordingly.

The most expensive capital component for an SDP system is the power supply -- approximately $1.00 per watt for power supplies ranging in design from 15 - 100 kW [3]. The cells and support equipment are made from simple, inexpensive materials and are minor components of capital cost. Total annual costs and unit costs are dependent upon values given for the important parameters of flow rate, energy density requirement for a particular compound, desired DRE, and exhaust stream duty cycle.

Because of the dynamic influence of these parameters on cost, a sensitivity analysis is presented showing their relationship to the cost of ownership. For this analysis we assume a flow rate of 250 scfm, an energy density of 50 J/liter for destruction of PGMEA, a destruction removal efficiency of 99%, and an electrical duty cycle of 25%.

These are assumed to be typical values for lithotrack tool emissions. Figures 3 - 6 illustrate the cost of ownership in terms of both total annual cost and unit cost in $/1000 scfm as a function of flow rate, energy density requirement, target DRE, and duty cycle, respectively, for treatment of PGMEA from lithography tool exhaust output. Data points shown for flow rate are based on actual flows from coaters at four different U.S. chip fabrication plants (Bowie, 1996 [4]).

Sensitivity Analysis

The four major parameters that influence SDP cost of ownership are flow rate, energy density (i.e., power requirement), target effluent concentration (DRE), and duty cycle (the percentage of time that the exhaust output is actually being emitted). All of these affect to some degree the cost of the SDP system.

The unit cost of the power supply decreases as the size of the power supply increases. This is significant because it results in some economy of scale for the SDP systems. The unit cost for a single lithotrack tool is $33,300 per 1,000 scfm; but if we wanted to treat the combined flow from 10 lithography tools using a larger SDP system, a 2500 scfm flow rate would require 118 kW of power instead of only 12 kW for the 250 scfm flow rate. The power supply unit cost decreases by half at this level of electrical power (> 100 kW ==> $0.75/W; < 15kW ==> $1.50/W), so the total unit cost for the larger SDP system would decrease to approximately $23,700. In addition, the annual cost for a system designed to treat 2500 scfm is less than 10 SDP units designed to treat 250 scfm -- $59,000 as opposed to 10x the annual cost ($8,400) of the smaller systems = $84,000.

Figure 3 illustrates the relationship between cost and flow rate. As shown, the total annual cost rises with the increase in flow rate; however, the unit cost stays constant due to the linear dependence of cost on flow rate.

Figure 4 illustrates the relationship between cost and energy density requirement. The energy density required is empirically derived from the specific compound(s) of interest in the exhaust stream. The energy density is a function of power, so an increase in the energy requirement means a necessary increase in the power supply at a fixed flow rate, and hence, a concomitant increase in capital and utilities costs. Looking at the slope of the two cost curves, it is evident that unit cost is particularly dependent on the compound of interest.

Figure 5 shows how cost increases as a function of destruction removal efficiency. Each "nine" increases the power required to maintain the the energy density for greater percentage destruction of a given compound. We can observe that the unit cost doubles from $16,700 to $33,300 per 1,000 scfm when the target DRE is increased from 90% to 99%.

Figure 6 shows that cost increases with an increase in duty cycle, but it is evident from the shallow slope of the cost curves that neither annual nor unit cost is as strongly affected by changes in the duty cycle as with the other parameters above. This is because duty cycle does not affect the design specs for the power supply, so capital cost is independent of the duty cycle. The change in cost as duty cycle increases reflects an increase in electrical utility cost requirements.

Figure 3. SDP sensitivity to flow rate

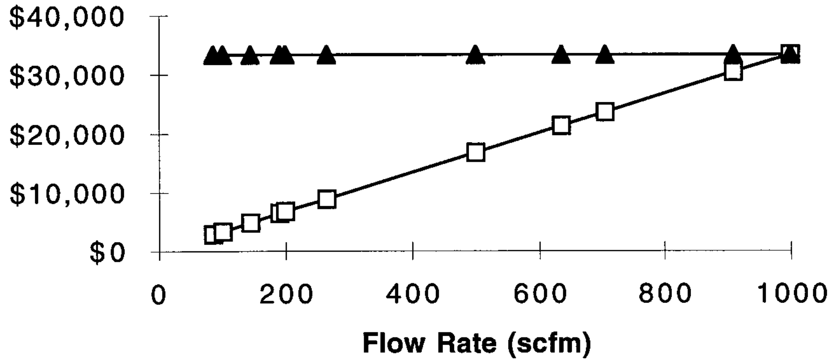


Figure 4. SDP sensitivity to energy density

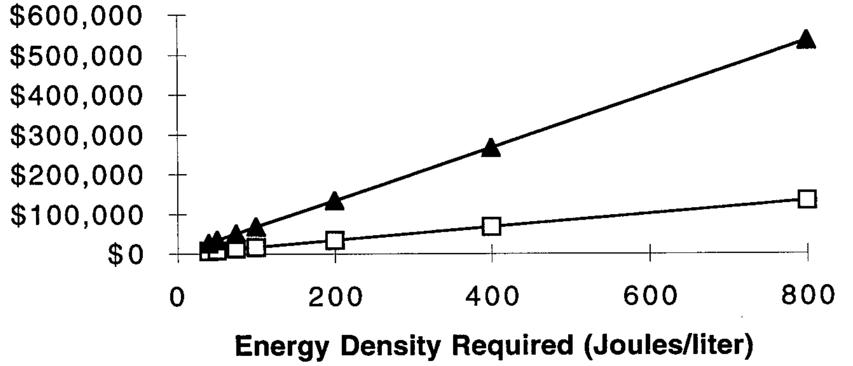


Figure 5. SDP sensitivity to target DRE

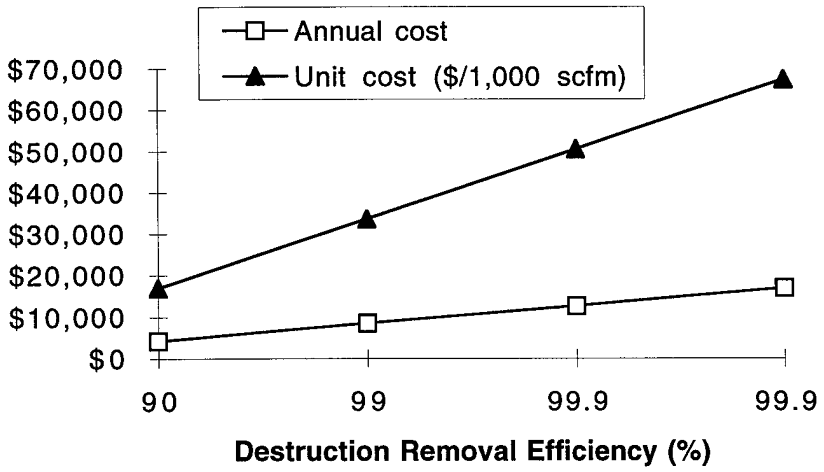
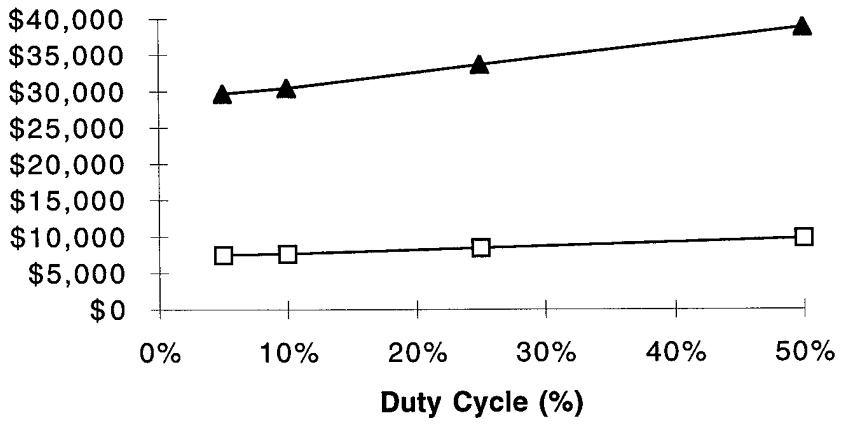


Figure 6. SDP sensitivity to duty cycle



Figures 3 - 6. Sensitivity of annual and unit costs to major performance metrics for the Silent Discharge Plasma [data from Cummings, 1997.]

Conclusions

Silent Discharge Plasma (SDP):

- is an innovative technology for destroying VOCs by directing the exhaust gas stream through an electrically created low-temperature plasma
- destroys VOCs at near ambient temperature and pressure
- can be engineered to attain very high destruction removal efficiencies
- effectively treated PGMEA and HMDS in tests on lithography tool exhaust streams without fouling at typical influent concentrations
- costs are independent of VOC concentration, but highly dependent on the specific target compound, desired DRE, and inlet exhaust flow rate
- is not recommended as a replacement for conventional end-of-pipe treatment systems, but shows promise in niche circumstances as a cost effective alternative for POU emissions control

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