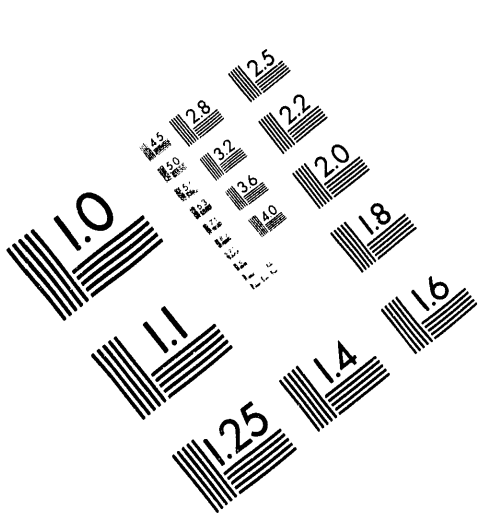

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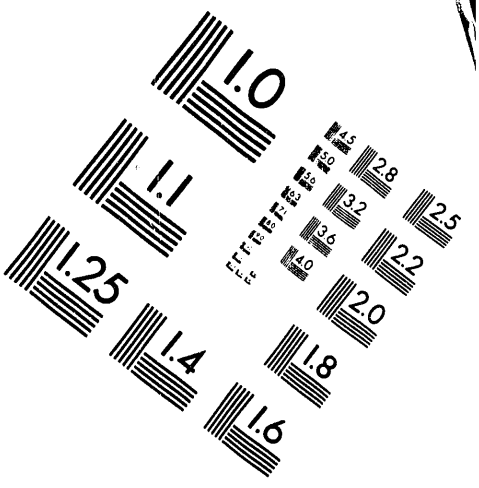

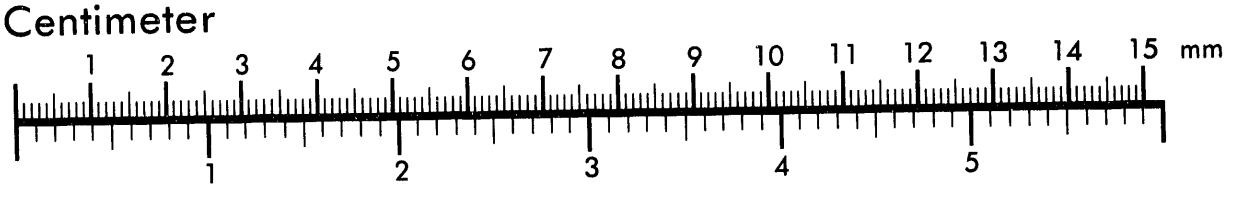

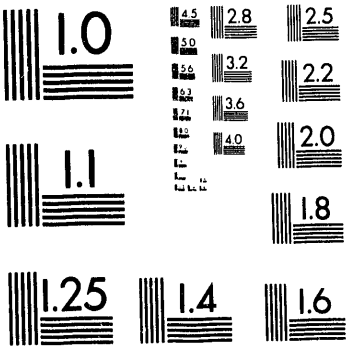

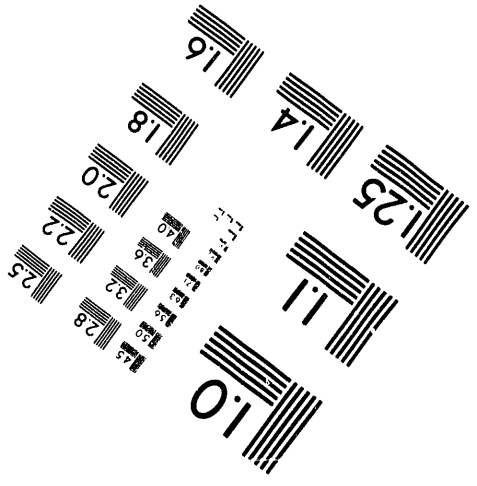

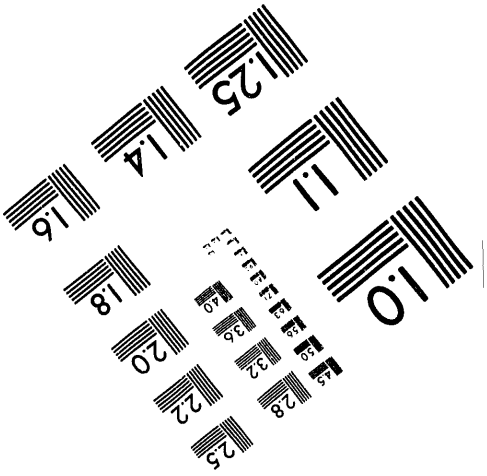

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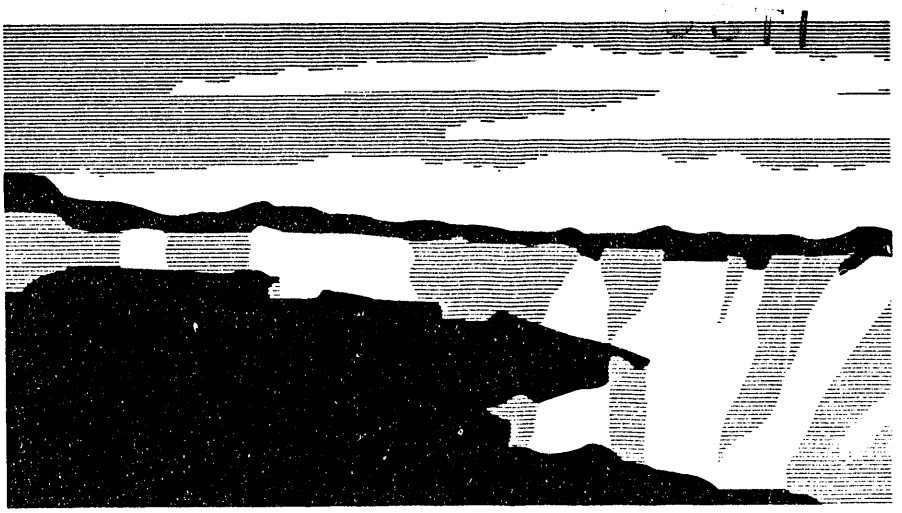

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SCALING OF SILENT ELECTRICAL DISCHARGE REACTORS FOR HAZARDOUS ORGANICS DESTRUCTION

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Silent electrical discharges are used to produce highly reactive free radicals that destroy hazardous compounds entrained in gaseous effluents at ambient gas temperatures and pressures. We have carried out destruction experiments at Los Alamos on a range of volatile organic compounds (VOCs), including trichloroethylene (TCE), carbon tetrachloride, perchloroethylene (PCE), and chlorofluorocarbons (CFCs). We have measured a "nine-factor", the amount of energy required to reduce the VOC concentration by a factor of ten. For practical reactor power densities, the "nine-factor" can be used to predict the destruction and removal efficiency (DRE) in terms of gas flow rate and the number of reactor modules. We propose a modular, stackable architecture for scaling up the reactor throughput.

INTRODUCTION

The silent discharge plasma produces energetic electrons (typical energies of 1-10 eV), which in turn generate copious quantities of highly reactive free radicals **[1]**. Within the transient, electrical microdischarges electrons are selectively heated, resulting in an efficient transfer of electrical energy to desirable chemical reactions at near-ambient temperatures and pressures. Although the volume of the microdischarges is quite small, an extremely large number of them are statistically spread out in space and time, resulting in a large effective processing volume ideally suited for high throughout chemical processing **[2]**. The free radicals, primarily atomic oxygen $O(^3P)$ and hydroxyl OH, oxidize organic compounds to nonhazardous, easily managed compounds such as H_2O, CO_2, and HCl. The potential of nonthermal plasma processes (dielectric barrier, corona, pulsed corona, etc.) is being pursued through a variety of international research efforts directed at flue gases **[3-6]** and hazardous organics **[1,7-10]**.

The prototype SDP laboratory at Los Alamos has been used to demonstrate cold plasma destruction of compounds directly applicable to various off-gas waste streams (e.g., gas flows up to 60 std lit/min, TCE/PCE concentrations as large as 2,000 ppm). This silent discharge plasma is produced by electrical discharges in gases, where one or both of the reactor electrodes are covered by a dielectric layer (we use glass). The geometry is usually planar (using metal and dielectric plates) or cylindrical (using metal and dielectric tubes). A typical planar cell has approximate dimensions of 71-cm length, 18-cm width, and 2.5-mm gap, giving a mean discharge area of 1236 cm^2 and an active discharge volume of 310 cm^3. Figures 1 and 2 illustrate the planar cell design. Both single or double dielectric barrier has been employed.

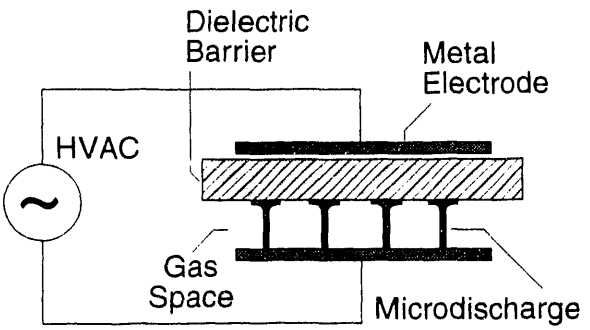

Figure 1: Schematic diagram of planar dielectric-barrier configuration for producing silent electrical discharges.

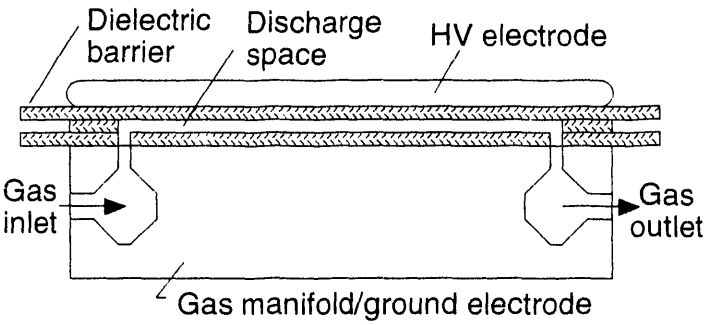

Figure 2: Representative double-barrier, planar SDP cell used in Los Alamos experiments.

Our principal electrical power supply is a series inverter which switches charged capacitors through a high-quality pulse transformer by means of high-power thyristors. This unit presently supplies nearly 4 kW of power at voltage pulse repetition frequencies up to 4.5 kHz. The electrical power deposited into the discharge plasma is both calculated and measured. The calculations use a well-known power formula for dielectric barrier discharges developed by Manley **[11]**. To analyze effluents and determine the mass balances, gas flow meters and controllers, a combustion gas analyzer (CGA), a gas chromatograph (GC), an infrared (IR) spectrophotometer, an ultraviolet absorption spectrometer, a humidity meter, a scale, and various specific gas monitors are used. The GC is equipped with both a flame ionization detector (FID) and electron capture detector (ECD).

Destruction rates for sample wastes containing both TCE and CCl_4 in an Ar/O_2 carrier gas have been treated under both wet and dry conditions. Ar/O_2 carriers were used in our initial experiments to simplify reaction conditions (e.g., to avoid dealing with nitrogen compounds); since these earlier tests, we have typically employed air as a carrier gas. Wet mixtures were prepared by passing the gas through a bubbler prior to entering the SDP reactor. The experimental results are summarized in Figure 3.

SCALING STUDIES

To scale SDP reactors, the fractional removal must be related to the plasma energy density. A figure of merit for removal is essentially determined by the energy delivered to the plasma per hazardous molecule removed from the gas stream. This can be expressed as follows:

$$\chi = \frac{<\overline{E}>}{\Delta[X]} = \frac{<P>/Q}{\Delta[X]} \quad , \tag{1}$$

where χ is the removal figure of merit, <E> is the average plasma energy density (average power <P>, divided by gas flow rate Q), and Δ[X] is the hazardous compound concentration that is removed. A convenient unit for the figure of merit is the number of kilowatt-hours required to remove a kilogram of hazardous compound (i.e., kW-hr/kg). From the data presented previously, the removal figures of merit are determined to be approximately 12 kW-hr/kg for 90% removal of TCE, 84 kW-hr/kg for >> 99% removal of TCE (650 - 1,000 ppm to ~100 ppb) and 270 kW-hr/kg for 90% removal of CCl_4. In terms of G-values (molecule/100 eV), the 90% TCE removal point is equivalent to G = 1.79 for the 650 ppm case.

These values generally agree with modeling results which suggest a radical chain reaction process for dry gases. For wet gases where destruction is dominated by OH, the waste removal can be described with relatively good accuracy by an exponential form:

$$[X] = [X]_0 \cdot \exp(-\frac{<\overline{E}>}{\beta}) \quad , \tag{2}$$

where $[X]_0$ is the initial waste concentration and β is the exponential-folding factor.

It is instructive to express the β parameter in base ten units, where it represents the amount of energy required to destroy the contaminant level by a factor of 10. We have named this factor the 9-factor, since if three 9's destruction (i.e., 0.999 or 99.9% destroyed) is required, three times the 9-factor must be applied to the waste stream. This factor has the units of J/lit (or J/cm^3). Preliminary values of the 9-factor for TCE are: 25.3 J/lit (0.0253 J/cm^3) dry, and 75 J/lit (0.075 J/cm^3) wet. The advantage of this parameter is that it is a single value and, unlike kW-hr/kg, is valid regardless of the initial concentration of waste. The two factors are essentially equivalent and are related by the following equation:

$$\chi = \frac{\beta}{[X]_0} \cdot \exp(\frac{<\overline{E}>}{\beta}) \quad . \tag{3}$$

Using the 9-factor, scaling calculations are simplified. For example, the removal of TCE under wet conditions can be scaled as shown in Figure 4, a plot of degree of destruction versus gas flow rate for one, two, and four cells.

The scalability of SDP reactors and associated power supplies is influenced by the desired gas flow rate and the concentration of hazardous compounds to be treated. Mechanical and thermal constraints must also be considered because the thin dielectric materials (few-mm glass or ceramic) cannot be made arbitrarily large in area without risk of mechanical failure. Also, a single large module is probably not desirable from the point of view of servicing or single-point failure modes.

Therefore, the preferred approach at present is modularization. This approach has proven to be quite successful for SDP reactors used in the commercial ozone generation industry, where gas flows of thousands of kilograms per day are routinely handled. Currently, we are considering scalable modules consisting of combinations of several smaller modules. This design will quickly enable a scale up of gas flow rates by factors of 10 to 100. For more corrosive compounds double barriers can be used so that there is no contact between the corrosive gas mixture and any metal surface.

It is anticipated that most practical waste streams (like machining oils) will have various degrees of inhomogeneity. Therefore, some feedback in the process loop may be highly desirable. The SDP units that we build employ variable-frequency power supplies, so fluctuations in the influent composition can be accommodated, provided feedback is available through continuous-emissions monitoring. This allows better treatment efficiency and cleaner effluent streams.

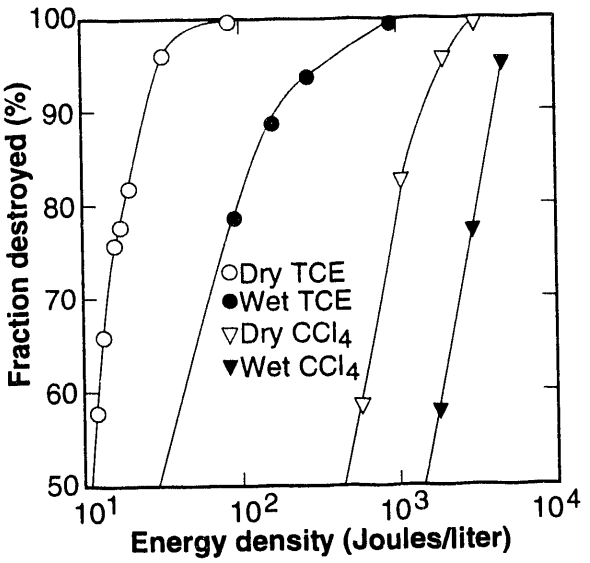

Figure 3: Summary showing measured TCE and CCl_4 destruction as a function of deposited electrical energy, for both dry and humid mixes.

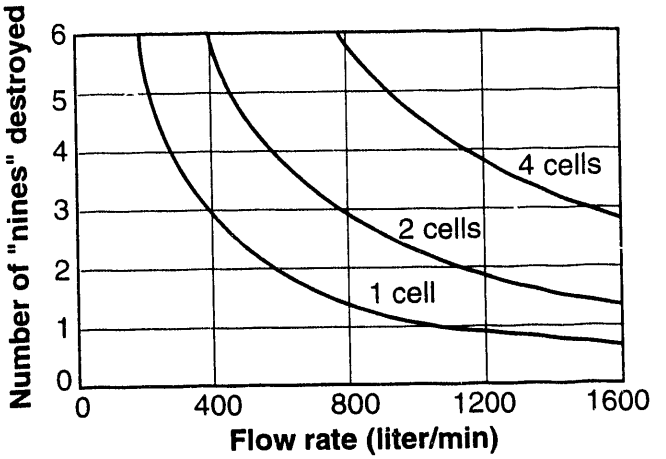

Figure 4: Scaling plot for the destruction of TCE under humid conditions. The number of nines destroyed is plotted versus flow rate.

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