

Title:

**FIELD DEMONSTRATION AND COMMERCIALIZATION
OF SILENT DISCHARGE PLASMA AIR POLLUTANT
CONTROL TECHNOLOGY
(Paper for Proceedings)**

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Field Demonstration and Commercialization of Silent Discharge Plasma Hazardous Air Pollutant Control Technology

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Abstract

Silent electrical discharge plasma (dielectric barrier) reactors can decompose gas-phase pollutants by free-radical attack or electron-induced fragmentation. The radicals or electrons are produced by the large average volume nonthermal plasmas generated in the reactor. In the past decade, the barrier configuration has attracted attention for destroying toxic chemical agents for the military, removing harmful greenhouse gases (oxides of sulfur and nitrogen - SO_x and NO_x), and treating other environmentally-hazardous chemical compounds (hydrocarbons, chlorocarbons, and chlorofluorocarbons). At the Los Alamos National Laboratory (LANL), we have been studying the silent discharge plasma (SDP) for processing gaseous-based hazardous chemicals for approximately five years. The key objective is to convert hazardous or toxic chemicals into non-hazardous compounds or into materials which are more easily managed. The main applications have been for treating off-gases from thermal treatment units (e.g., incinerators, high-temperature packed bed reactors, arc melters; low-temperature thermal desorbers), and for abating hazardous air-pollutant emissions (e.g., industrial air emissions, vapors extracted from contaminated soil or groundwater).

In 1992, a collaborative agreement was negotiated with the Electric Power Research Institute (EPRI) to develop SDP technology for the treatment of industrial hazardous air emissions. Under that partnership, a small-scale, mobile unit was designed and constructed for industrially-relevant field demonstrations. In 1995, EPRI and Los Alamos jointly chose High Mesa Technologies LLC (HMT) as a commercialization partner for SDP air-pollution control technology. In addition to EPRI and HMT, Los Alamos is collaborating with the semiconductor-manufacturer consortium SEMATECH on evaluating SDP technology for industry-specific air emissions applications.

In this paper, we will summarize the basic principles of SDP processing, discuss illustrative applications of the technology, and present results from small-scale field tests that are relevant to our commercialization effort.

Introduction

Air Pollution Regulations and Motivation for New Technology

Large quantities of hazardous and/or toxic hydrocarbon and chlorinated-hydrocarbon air pollutants are emitted from a variety of sources nationwide, the bulk of emissions arising from industrial and commercial establishments. For 1990, total and point source VOC (volatile organic compound) emissions were estimated to be 1.4 billion pounds (636 million kg) from reporting facilities in the United States¹. The top six emitted VOCs, by mass in 1990, were toluene, methanol, acetone, xylenes, methyl ethyl ketone, and trichloroethane. Chlorinated hydrocarbons are not easily degraded by naturally-occurring microorganisms, so they persist in the environment, which makes them a more severe environmental threat.

The National Emission Standards for Hazardous Air Pollutants (NESHAPS) are the currently applicable regulations for hazardous air pollutants (HAPs)². In the past, the US Environmental Protection Agency (EPA) used criteria based on the risk posed to public health to establish emissions standards for HAPs. Up until 1990, emission standards existed for only seven specific compounds because of controversies over actual and perceived health risks. With the Clean Air Act Amendments of 1990 (CAAA 1990), a new approach targets 189 chemicals and groups of chemicals for more stringent emissions standards³. The 1990 CAA Amendments contain eight titles, three of which have a close relationship to our SDP air pollution control technology. Title III, Air Toxics, is directly concerned with the emission of HAPs and established standards for sources that emit any of the 189 listed chemicals. Title IV, Acid Rain, calls for the reduction of emissions of oxides of sulfur (SO₂) and oxides of nitrogen (NO_x). Title VI, Stratospheric Ozone, calls for phasing out the use of chemicals that contribute to ozone depletion (compounds such as some chlorinated VOCs).

The CAAA 1990 provisions require individual source categories to employ the most current or state-of-the-art methods and equipment to control hazardous chemical emissions. These are called Maximum Achievable Control Technology (MACT) standards. MACT standards require changes in equipment, processes, or operating procedures or the treatment of process, stack, or fugitive emissions to control air pollution. Immediately, CAAA 1990 was perceived to have severe economic impacts on industry, particularly small businesses. Technical and regulatory difficulties associated with current air-pollutant treatment methods, such as dilution/air-stripping, activated-carbon absorption, and incineration have prompted the search for alternative technologies. Drawbacks with current methods result in the generation of large secondary waste streams and increased costs.

As a representative of the major US electrical utilities, the Electric Power Research Institute (EPRI) has initiated programs that enable its utility members to assist their customers in producing less pollution and in meeting the CAAA 1990 standards. One area that looked promising for advanced air pollution control was nonthermal plasma (NTP) technology. In NTP, electrical energy is used to create active species (e.g., free radicals, electrons) that can degrade air toxics. EPRI and the Los Alamos National Laboratory (LANL) are collaborating on the development of a particular NTP technology for treating industrial air toxics, namely silent discharge plasma (SDP). Various aspects of this collaboration will be discussed in this paper.

Silent Discharge Plasma (SDP) Background

SDP Technical Overview

The SDP is a form of nonthermal plasma, which is easily created by a dielectric-ballasted electrical discharge.⁴ Nonthermal plasmas are characterized by conditions in which the various plasma species are not in thermal equilibrium - that is, electrons, ions, and neutral species have different temperatures, with the less massive electrons having the highest temperature (e.g., 1-10 eV). Gas-phase pollutants are decomposed by the free radicals or electrons generated by these plasmas. Nonthermal plasmas show promise for simultaneously treating different types of pollutants such as many VOCs, flue gases (SO_x and NO_x), and other hazardous chemicals.⁵

A dielectric-barrier electrical discharge is produced when one or both electrodes are covered with a dielectric. This arrangement provides a self-terminating discharge which is relatively independent of applied voltage waveshape. At gas pressures of order one atmosphere, gap spacings of order a few millimeters, and the application of alternating high voltage (e.g., 50 Hz to several kHz), a large number of "microdischarges", statistically spread in space and time over the electrode area, are created in the gas. Most evidence suggests that barrier discharges are generally described by a Townsend avalanche followed by a discharge streamer. The microdischarge streamers (cylindrical current filaments with typical radius of order 100 μm) are transient discharges (e.g., lasting only a few nanoseconds for oxygen or air), fed by ionization and detachment and then arrested when charge build-up on the dielectric reduces the electric field in the streamer to the point where electron attachment becomes dominant.

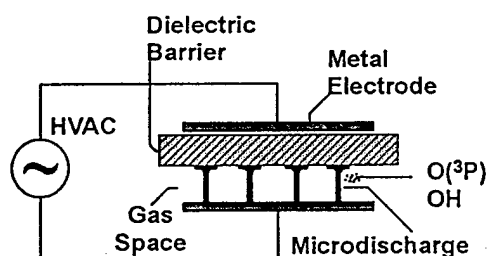
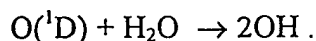
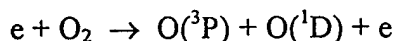


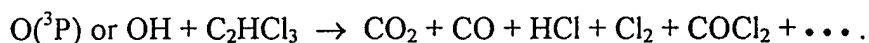
Fig. 1 Diagram of a single-dielectric-barrier discharge plasma reactor.

The barrier discharge configuration was first reported in 1857 by von Siemens⁶, was named the silent discharge by Warburg⁷ who investigated it around the turn of the century, and has been widely used for the generation of ozone. Figure 1 shows a single-barrier reactor schematic diagram. Corona discharges⁸ produce plasmas similar to barrier discharges but take advantage of their natural electric-field inhomogeneity to terminate the discharge, rather than charge buildup on a dielectric barrier.

In nonthermal plasmas, electrical energy is used to create large quantities of highly reactive free radicals (especially atomic oxygen O(³P) and hydroxyls OH) in a gaseous medium. For many compounds, the free radicals initiate the decomposition of the pollutants. At the relatively high plasma electron temperatures of an atmospheric-pressure barrier discharge, O-atoms and OH radicals are produced by reactions such as



Complex molecules, like many VOCs, will often undergo a series of reactions before the final products result. At high plasma electron temperatures, the decomposition of a gas-phase chlorocarbon like trichloroethylene (TCE) is dominated by free-radical reactions.⁹



Strongly electron-attaching molecules, like CCl_4 , are preferentially decomposed by dissociative attachment at low plasma electron temperatures, but direct electron-induced dissociation and radical attack dominate at high electron energies.^{10, 11} For CCl_4 , dissociative attachment is expected to be more advantageous than radical attack because Cl and ClO radicals resulting from O and OH reactions with CCl_4 drive circular kinetics which can reform it.

Fortunately, some commonly-formed hazardous byproducts (like phosgene COCl_2) are unstable and are quickly destroyed by reacting with liquid water or water vapor. In practice, a water-based scrubber can be easily employed to destroy phosgene and neutralize the acids which are an inevitable decomposition product of chlorinated hydrocarbons.

The key scaling parameter for decomposition is the plasma energy density, or the electrical energy per unit volume deposited in the treated gas.¹² This can also be expressed as the electrical power P deposited in the gas divided by the gas flow rate Q, or P/Q. We normally use units of J/liter or J/cm^3 for P/Q. In many cases, the removal of a pollutant approximately scales as an exponential function of P/Q, so the degree of removal of a given species is given by

$$-\log ([X]/[X]_0) = (P/Q)/\alpha ,$$

where $[X]_0$ and $[X]$ are the initial and post-treatment concentrations of species X, respectively and α is the characteristic energy density for one decade removal. With this scaling, to maintain a fixed energy density (and a corresponding fixed degree of removal), the power must be increased in proportion to the gas flow rate.

SDP Applications

Application of SDP to the destruction of organic compounds, although explored for several years, has become fairly common only in the last few years. Initial work on the destruction of nerve gases¹³ and flue gas^{14, 15} cleanup has expanded to many hydrocarbon and halocarbon compounds, generally with promising results. Near complete destruction of many hydrocarbons and chlorocarbons has been demonstrated. At Los Alamos, we have developed the silent discharge plasma process for treating hazardous organic wastes, particularly VOCs. Experiments at Los Alamos have been related to aliphatic hydrocarbons, chlorocarbons - e.g., TCE (trichloroethylene C_2HCl_3), TCA (trichloroethane $\text{C}_2\text{H}_3\text{Cl}_3$), PCE (tetrachloroethylene or perchloroethylene C_2Cl_4) and carbon tetrachloride (CCl_4), and CFCs (chloro-fluorocarbons) using silent discharges. Most experiments have used rectangular planar SDP cells (in both single-barrier and double-barrier configurations), although cylindrical reactors (using metal and dielectric tubes) have also been used for a few tests. For more details on this work, the reader is referred to the literature.^{9, 12, 16}

SDP chemical reactors can be used to treat stack-gas or flue-gas emissions (air streams) from incinerators or other primary treatment units, or industrial-process gas streams. Heterogeneous wastes (e.g., solvent-contaminated solids) can also be treated by applying heat to volatilize the solvents and then flushing with an inert carrier gas (e.g., Ar or N₂). Another potential application is the treatment of solvents or other volatile chemicals in soil or groundwater. In this case, the plasma processor is coupled to a soil vapor extractor that pumps vapors out of the soil through wells drilled in the ground.

At the time of the EPRI-LANL CRADA negotiations, EPRI commissioned the National Environmental Technology Applications Corporation (NETAC) to conduct a study to identify the size of potential US markets for industrial applications of SDP air pollution abatement technology.¹⁷ That study used the EPA Toxics Release Inventory (TRI) database to determine the amount of VOCs released by EPA region, focusing on the top six VOC emissions for 1990 (mentioned in the Air Pollution Regulations section above). The study identified nine industries as potential major markets for SDP technology: Wood Products (not furniture), Furniture & Fixtures, Paper & Allied Products, Chemicals & Allied Products, Rubber & Plastic Products, Fabricated Metal Products, Machinery & Computer Equipment, Electronic Equipment & Components, and Transportation Equipment. Pending further market studies, EPRI and LANL have considered these industry segments as preliminary targets for SDP air pollution control technology.

Anticipated Advantages of SDP Processing

SDP technology has shown strong potential for a high degree of hazardous compound cleanup and is expected to have these distinct advantages over conventional technologies:

- NTP treatment is not incineration;
- NTP operates at near-ambient pressures and temperatures;
- No fuel is added to the process, which minimizes secondary wastes;
- NTP can simultaneously remove hazardous organics and SO_x/NO_x effluents;
- NTP processing can be easily implemented in a closed-loop mode;
- Feedback and automation potential are inherent features of the process;
- No precious, poisonous, or proprietary metal compounds (e.g., catalysts) are used.

EPRI-LANL Collaboration

Background

In 1990, the Los Alamos National Laboratory (LANL) started work on the particular NTP called silent discharge plasma (SDP) technology. This was being developed in collaboration with Auburn University and the University of Illinois for the treatment of VOC and SO_x/NO_x emissions within US Department of Energy (DOE) facilities.¹⁸ Motivated by the need to assist utility customers with air pollution problems and the increased emphasis on the transfer of government-developed technology to the private sector, EPRI and LANL negotiated a Collaborative Research and Development Agreement (CRADA) to develop SDP technology for the treatment of industrial air toxics in 1992. The CRADA was approved in 1993 and, under that partnership, a

small-scale, mobile unit was designed and constructed for industrially-relevant field tests and technology demonstrations.

Mobile Field-Demonstration Unit

Figures 2a and 2b show a cross-section and floor plan of the EPRI-LANL mobile unit. Two stacks of SDP cells, each with ten modular, parallel-flow, flat-plate cells, placed in a containment tank, comprise the plasma processor. Each set of twenty cells is driven by an 18-kW rating sinusoidal-waveform power supply connected to a step-up transformer. Electrical power is measured by a combination of a voltage probe and a charge-measuring capacitor. Gas temperature, gas flow rate, and gas pressure are measured by thermocouples, flow meters, and pressure gauges. The electrical and gas-measuring instruments are interfaced to a computer-based data acquisition and analysis system. Gas sampling ports are located upstream of the plasma processor and downstream of the scrubber/neutralizer unit. A metal-bellows pump is placed in the inlet gas line to pump the gas stream through the plasma processor and scrubber/neutralizer. A back-up activated carbon filter is installed in the final exhaust output line to capture any pollutants (either unprocessed feed components or treatment byproducts) and to provide a safety feature in the event of an equipment processing failure.

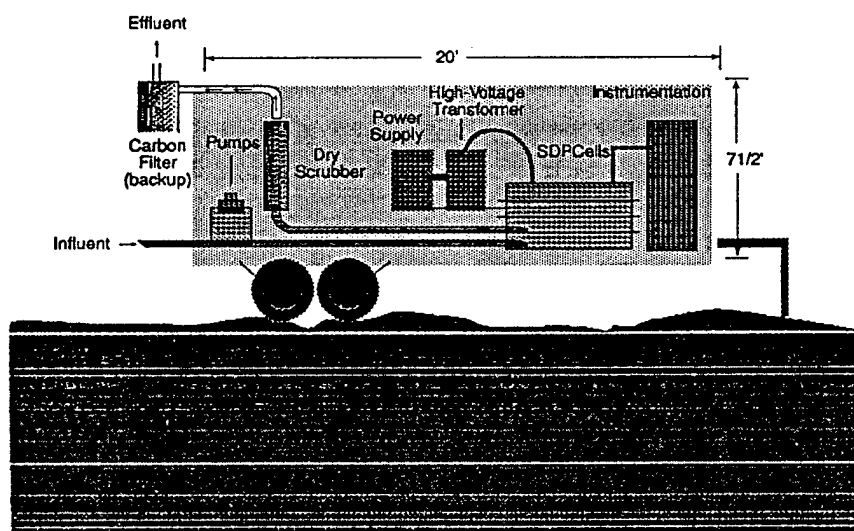


Fig. 2a: EPRI-LANL mobile silent discharge plasma processor.

Experience from Previous Field Test

The EPRI-LANL mobile SDP processor was patterned after a device that was tested at the DOE's Savannah River Site (SRS) in South Carolina at the time the EPRI-LANL CRADA was being negotiated and approved.¹⁹ It is instructive to examine the results of the SRS field demonstration because it provided valuable experience for future field tests and commercialization activities. This demonstration involved the treatment of solvents entrained in soil at an environmental remediation technology-testing site at SRS. In the field tests, an SDP ("cold plasma") processor was coupled to a soil vapor extraction (SVE) unit that pumped volatile

compounds out of the soil through wells drilled into the ground. The major soil and groundwater contaminants were TCE, TCA, and PCE.

Before going to the field, rigorous laboratory measurements were conducted to measure the destruction characteristics of the main compounds expected at SRS and to establish field operating parameters.

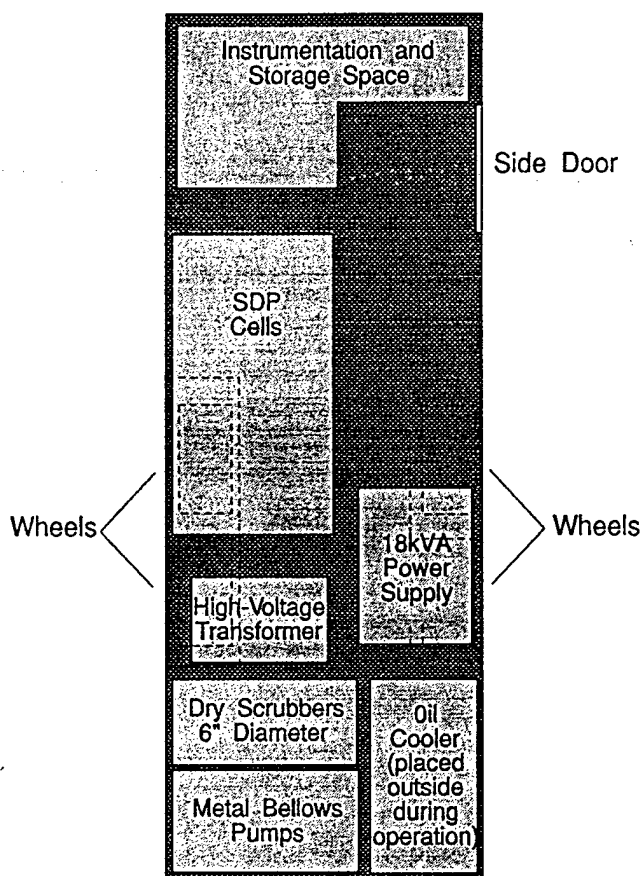


Fig. 2b: Layout view of EPRI-LANL mobile silent discharge plasma processor.

At the site, a series of treatment tests on the extracted air stream were carried out at total VOC concentrations in the range 700 ppm - 4000 ppm and flow rates of 30, 60, and 95 std liter/min. A field gas chromatograph (GC) was used for preliminary chemical analysis. Further analysis was performed on gas-phase samples collected in plastic bags using a GC equipped with both an FID (flame ionization detector) and an ECD (electron capture detector). A small fraction of samples was also analyzed with a gas chromatograph-mass spectrometer (GC/MS). Analytical samples were taken only for the plasma cell influent and effluent stream - the scrubber gaseous and liquid effluents were not sampled. The field tests demonstrated the same results as the laboratory tests in terms of ease of destruction: TCE was easiest to treat, PCE next easiest, and TCA was the most difficult. Removals of 99.999% were approached for TCE over a broad range of energy density (3.71 to 16.14 J/ cm³), concentrations, and flow rates. PCE

treatment achieved 99% to 99.9% removal over the whole range of test parameters. The best typical removal achieved for TCA was about 98% at 13.98 J/ cm³. Most of the data points for total VOC concentration ([PCE]+[TCA]+[TCE]) fell in a band from 99.326% to 99.966% removal. The mineralization of the VOCs was not complete and, as with other technologies (both thermal and nonthermal), byproduct PICs (products of incomplete combustion) also result from the gas treatment process. We have observed some of these in the laboratory and small byproduct peaks (probably each < 1 ppm) were observed in many of the field runs. But, in general, detailed calibrations of our instruments have not been available to quantify the concentrations of the PICs to high accuracy. At moderate energy density (6.6 J/ cm³), a few byproduct peaks above 1 ppm were observed with a GC/MS. The partitioning and absolute concentrations of these byproducts was not determined. The size of the peaks decreases with increasing plasma energy density and

the unstable byproducts are further decomposed in the scrubber/neutralizer. The results of the LANL SRS field tests, given in terms of the destruction and removal efficiency (DRE) are summarized in Table 1 below.

Table 1: DREs for LANL Cold-Plasma Reactor Tests at Savannah River Site.

| Flow Rate (std lit/min) | Energy Density (kJ/std lit) | TCE DRE (%) | PCE DRE (%) | TCA DRE (%) |
|----------------------------|-----------------------------------|----------------|----------------|----------------|
| 30 | 13.8 | 99.99 | 99.90 | 97.72 |
| 60 | 6.6 | 99.95 | 99.94 | 94.85 |
| 95 | 3.7 | 99.99 | 99.93 | 94.29 |
| 95 | 4.5 | 99.94 | 99.79 | 97.38 |

EPRI-HMT-LANL Collaboration for Technology Commercialization

A major objective of the EPRI-LANL collaboration was to identify an industrial partner to commercialize SDP technology. After an advertised search, that objective was met in 1995 with the choice of High Mesa Technologies (HMT) as the partner for technology commercialization. The agreement with HMT calls for demonstrating and scaling up the technology in stages. First, a longer-duration, small-scale field test using a pre-commercial prototype (at about 10 SCFM or 280 std lit/min) was conducted to provide more operational experience and engineering data to assess market potential and information for scale-up. If the results of the first test are encouraging, a larger commercial prototype with approximate capacity of 250 SCFM (7000 std lit/min) is to be designed, constructed, and tested. The third stage will then involve further scale up and the manufacturing and marketing of commercial units.

McClellan Air Force Base Field Tests

In cooperation with the US EPA and the California EPA, and under the overall supervision of CH2MHill, Inc., the US Air Force recruited several subcontractors to test innovative remediation technologies under industrial, real-life conditions. An SDP technology-demonstration proposed by HMT was chosen for a two-month campaign at a test site at McClellan Air Force Base in Sacramento, California.²⁰ This site had formerly been used as a disposal facility for a variety of solvents, volatile, and semi-volatile chemicals (perhaps more than 50 compounds are entrained in the ground). A partial list of contaminants at the McClellan test site includes TCE, 1,1,1-TCA, PCE, 1,1,1-dichloroethylene (1,1,1-DCE), benzene, toluene, ethylbenzene, xylenes, Freon 113 (a chloro-fluorocarbon), methylene chloride, vinyl chloride, and acetone. At the site, the compounds are vacuum extracted from the ground and a portion of the vapor-laden air stream is directed to the technologies to be tested, while the majority of the stream and the test-technology effluents are sent to an existing thermal-catalytic oxidation system. The air stream extracted from the ground presently contains total VOC concentrations of approximately 300 - 1000 ppmv.

Based upon information from the SRS field test and technical progress since then, LANL and HMT modified the EPRI-LANL mobile unit for more robust operation and about a three-fold increase in gas flow capacity (i.e., to 10 SCFM or 280 std liter/min). An illustration of the

upgraded mobile unit is shown in Figure 3. This unit incorporates two cold plasma processors, each one consisting of two banks of ten planar SDP cells in a containment tank. Each set of twenty cells is electrically driven by an 18-kW rating sinusoidal-waveform power supply connected through a tuning circuit to a high-voltage step up transformer. The gas flow is fed to the tanks in a parallel configuration. Each tank is usually operated at one-half the total gas flow (5 SCFM) with approximately 10 kW of plasma power. This gives an energy density in excess of 4 kJ/std lit. Gas-sampling ports are located before and after each tank. Heat is generated from the electrical power fed to the SDP cells and is removed with a heat exchanger which uses oil as a working fluid. Gas flows, temperature, pressures, and electrical power are monitored with sensors and the data is stored and analyzed using a computer-based data acquisition and control system.

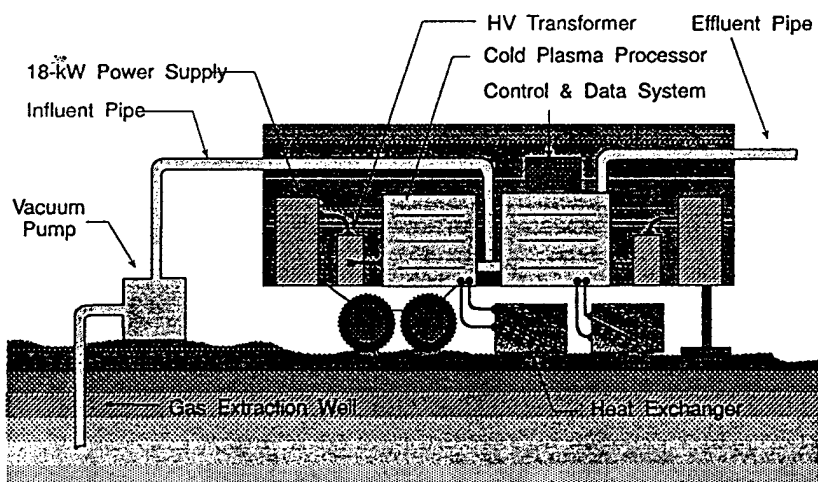


Fig. 3: Illustration of mobile SDP equipment for combined cold plasma-soil vapor extraction VOC treatment demonstration at McClellan AFB.

Before going to the McClellan site, laboratory tests were conducted at Los Alamos to determine the destruction efficiency, characterize the destruction products, and determine the plasma operating conditions for some of the major compounds expected in the field. This information was needed to specify the operating-parameter range for the field-demonstration equipment. Surrogate test mixtures contained TCE, TCA, PCE, DCB, toluene, and methylene chloride as principal components. The compound hardest to decompose was TCA. Unfortunately, it was also the one with the highest expected site concentration. Each species was also easier to treat in dry mixtures than in humid gas mixtures. Fortunately, the other two species with expected high site concentrations, TCE and PCE, showed greater than 1.5 and 1.0 decades DRE, respectively, at our selected 4 kJ/std lit field operating condition - even for 100% relative humidity.

At the McClellan site, HMT conducted a series of tests over a period of about two months, with technical assistance from LANL. During this time, the SDP system operated more than 400 hours with a maximum continuous operation time of four days. The system treated gas flows as high as 10.4 SCFM (295 std lit/min) and achieved a total DRE as high as 99.4%. Normally the air stream

extracted from the ground had a near-saturated relative humidity (i.e., about 100%). In some cases, the influent gas stream was dried with an in-line dehumidifier before being treated. In agreement with the pre-field laboratory tests, the dry streams achieved higher DREs. For some of the test runs, hydrogen gas, with a concentration approximately matching the total VOC concentration, was injected into the gas stream before the SDP units. This tended to increase the achieved DREs. Table 2 shows summary DRE results from the McClellan AFB site tests.

The test program included extensive analytical sampling and chemical analysis. VOCs, semi-volatile organic compounds, carbon dioxide, carbon monoxide, and oxygen were analyzed in both influent and effluent gas streams to evaluate the treatment effectiveness. The treated gas stream and residues generated from the SDP treatment process were also analyzed for dioxins, furans, hydrochloric acid, nitrogen dioxide, ozone, and phosgene. Hydrochloric acid is an inevitable product in the treatment of chlorinated hydrocarbons and significant amounts of liquid HCl were generated in these tests. This can be easily treated in a wet caustic scrubber/neutralizer attached to the SDP system. Approximately 59-65 ppmv of nitrogen dioxide and 58-59 ppmv of ozone were also detected in the effluent gas stream. Phosgene was not detected. Semivolatile compounds, principally naphthalene and 2-methylnaphthalene, were detected at combined concentrations ranging from 0.091 ppmv to 2.184 ppmv. Total polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF) emissions were extremely small - measured average emissions of 0.0657 ng/m³ for the combined tetra-, penta-, hexa-, and hepta-CDD congeners and 0.115 ng/m³ for the same CDF congeners.

Table 2: Summary results from SDP system tests at McClellan AFB.

| Sample Number | Operating Conditions | Gas Temperature (C) | Total Inlet VOCs (ppmv) | Gas Flow (SCFM) | Energy Density (J/std lit) | Total DRE (%) |
|---------------|----------------------------------|---------------------|-------------------------|-----------------|----------------------------|---------------|
| 1 | Wet gas/39 cells | 32 | 542 | 10.0 | 4162 | 93.5 |
| 2 | Wet gas/39 cells | 59 | 462 | 10.0 | 4193 | 88.1 |
| 3 | Wet gas/39 cells | 60 | 989 | 9.0 | 4680 | 92.5 |
| 4 | Wet gas/39 cells | 58 | 328 | 10.0 | 4185 | 95.6 |
| 5 | Wet gas/40 cells | 56 | 333 | 9.5 | 4416 | 90.0 |
| 6 | Wet gas/40 cells | 50 | 363 | 10.4 | 4068 | 90.0 |
| 7 | Wet gas/20 cells | 20 | 460 | 4.7 | 4494 | 97.7 |
| 8 | Wet gas/40 cells | 32 | 493 | 8.1 | 4716 | 92.4 |
| 9 | Wet gas/15 cells | 38 | 477 | 5.4 | 4034 | 93.0 |
| 10 | Wet gas/15 cells | 38 | 464 | 4.1 | 5075 | 92.5 |
| 11 | Wet gas/H ₂ /15 cells | 55 | 532 | 4.1 | 5189 | 92.5 |
| 12 | Dry gas/H ₂ /20 cells | 50 | 629 | 5.1 | 4083 | 99.4 |
| 13 | Dry gas/H ₂ /20 cells | 18 | 698 | 3.7 | 5734 | 98.5 |
| 14 | Wet gas/H ₂ /20 cells | 24 | 459 | 2.9 | 7396 | 96.7 |

The easiest compounds to remove were TCE, toluene, and PCE. The most difficult compounds to remove were methylene chloride, Freon 113, and 1,1,1-TCA. DREs for these three compounds were often below 90% without hydrogen addition or dehumidification.

A report incorporating the DRE test data, byproduct analysis data, and an economic analysis for projected operating costs is being written at the time of this conference. Based on the results of this field test, we are encouraged to continue scale-up and commercialization activities. Some practical engineering issues will need to be addressed but we consider these a normal part of making the transition from an emerging technology to a commercial reality.

Future Plans

Both the Savannah River and McClellan AFB tests have provided valuable data and experience for designing and constructing commercial-scale SDP treatment systems. In the near future we plan to conduct one additional test under the EPRI-LANL agreement. This is expected to be a small flow rate test on low-concentration VOCs that are extracted from a vacuum-sparger groundwater treatment facility at Tinker AFB in Oklahoma. A twenty-cell system from the EPRI-HMT-LANL mobile unit will be employed in an effort to evaluate the effectiveness of SDP technology for treating rather small VOC concentrations (e.g., a few ppmv). The particular compounds at the site are TCE, 1,2-DCE, PCE, toluene, xylene, and acetone.

LANL and HMT also plan to continue their collaborative work to design, construct and test a larger capacity system which will be tailored to a specific use or site. A goal for the next system is a gas-flow capacity of 250 SCFM (7000 std lit/min). However, this may vary depending on the compounds treated and the desired DRE because different compounds require different characteristic plasma energy densities. Market analyses are being carried out to determine the best market areas for the technology and plans are being formulated for manufacturing and marketing commercial units.

Summary

The Los Alamos National Laboratory (LANL) is developing and commercializing silent discharge plasma (SDP) air pollution control equipment in collaboration with the Electric Power Research Institute (EPRI) and High Mesa Technologies (HMT). The commercial technology is directed at the treatment of industrial hazardous air pollutants (HAPs), particularly volatile organic compounds (VOCs). At Los Alamos, the technology was originally developed for applications at US Department of Energy (DOE) and Department of Defense (DoD) installations. The results of laboratory and small-scale field tests have been encouraging. It is expected that SDP technology can remove multiple pollutants from air-emissions streams and provide advantages over conventional technologies.

A recent field test on the treatment of VOCs extracted from an environmental remediation site at McClellan Air Force Base has been described. The data and experience gained from this test will be used to evaluate the performance of the SDP processor for industrial emissions, provide benchmarking information for modeling and cost projections, and for advancing our scale-up and commercialization efforts.

References

1. 1990 Toxics Release Inventory Public Data Release, EPA 700-S-92-002, United States Environmental Protection Agency, Office of Pollution Prevention and Toxics (TS-779), Washington, DC (May 1992).
2. The NESHAPS provisions were created as part of the 1970 Amendments to the Clean Air Act (Public Law 91-604).
3. The Clean Air Act Amendments of 1990 were signed into law in November 1990 as Public Law 101-549. The Clean Air Act was originally passed in 1955 and has been modified several times since then. The CAAA 1990 provisions are the most stringent of any so far established.
4. Two excellent review papers on silent discharges and nonthermal plasma processing are: B. Eliasson and U. Kogelschatz, "Modeling and Applications of Silent Discharge Plasmas," *IEEE Trans. Plasma Sci.*, **19**, 309-322 (1991) and B. Eliasson and U. Kogelschatz, "Nonequilibrium Volume Plasma Chemical Processing," *IEEE Trans. Plasma Sci.*, **19**, 1063-1077 (1991).
5. An excellent collection of papers on nonthermal plasma technology for pollution control is: *Non-Thermal Plasma Techniques for Pollution Control*, NATO ASI Series G: Ecological Sciences, Vol. G34, Part A: Overview, Fundamentals and Supporting Technologies & Part B: Electron Beam and Electrical Discharge Processing, Springer-Verlag, edited by B.M. Penetrante and S.E. Schultheis (1993).
6. W. von Siemens, "Über die Elektrostatische Induktion und die Verzögerung des Stromes in Flaschendrahten", *Poggendorff's Ann. der Physik und Chemie* **102**, 66 (1857).
7. E. Warburg, "Über die Ozonisierung des Sauerstoffs durch Stille Elektrische Entladungen," *Ann. d. Phys.* **13**, 464-476 (1904).
8. J.-S. Chang, P.A. Lawless, and T. Yamamoto, "Corona Discharge Processing," *IEEE Trans. Plasma Sci.*, **19**, 1152-1166 (1991).
9. D. Evans, L.A. Rosocha, G.K. Anderson, J.J. Coogan and M.J. Kushner, "Plasma Remediation of Trichloroethylene in Silent Discharge Plasmas", *J. Appl. Phys.* **74**, 5378-5386 (1993).
10. D.G. Storch, M.B. Chang, M.J. Rood, and M.J. Kushner, "Modeling and Diagnostics of Dielectric Barrier Discharge Destruction of CCl_4 ," *Unpublished progress report to Los Alamos National Laboratory* (1991).
11. B.M. Penetrante, M.C. Hsiao, J.N. Bardsley, B.T. Merritt, G.E. Vogtlin, P.H. Wallman, A. Kuthi, C.P. Burkhardt, and J.R. Bayless, "Electron Beam and Pulsed Corona Processing of

- Carbon Tetrachloride in Atmospheric Pressure Gas Streams," *Physics Letters A*, **209**, 69-77 (1995).
12. L.A. Rosocha, G.K. Anderson, L.A. Bechtold, J.J. Coogan, H.G. Heck, M. Kang, W.H. McCulla, R.A. Tennant, and P.J. Wantuck, "Treatment of Hazardous Organic Wastes Using Silent Discharge Plasmas," *Non-Thermal Plasma Techniques for Pollution Control, NATO ASI Series G: Ecological Sciences, Vol. G34*, Part B, pp. 281-306, Springer-Verlag, edited by B.M. Penetrante and S.E. Schultheis (1993).
 13. E.J. Clothiaux, J.A. Koropchack, and R.R. Moore, "Decomposition of an Organophosphorus Material in a Silent Electrical Discharge," *Plasma Chemistry and Plasma Processing*, **4**, 15-20 (1984).
 14. M.B. Chang, J.H. Balbach, M.J. Rood, and M.J. Kushner, "Removal of SO₂ from Gas Streams Using a Dielectric Barrier Discharge and Combined Plasma Photolysis," *J. Appl. Phys.* **69**, 4409-4417 (1991).
 15. I. Sardja and S.K. Dhali, "Plasma Oxidation of SO₂," *Appl. Phys. Lett.* **56**, 21-23 (1990).
 16. L.A. Rosocha and J.J. Coogan, "Processing of Pollutants in Dielectric-Barrier Plasma Reactors," *Proceedings of 12th International Symposium on Plasma Chemistry (ISPC-12)*, pp. 665-670, University of Minnesota, edited by J.V. Heberlein, D.W. Ernie, and J.T. Roberts (1995).
 17. "Identification of Potential Markets for the Silent Discharge Plasma Reactor Process," National Environmental Technology Applications Corporation, Pittsburgh, PA, (January 1993).
 18. W.H. McCulla, L.A. Rosocha, W.C. Neely, E.J. Clothiaux, M.J. Kushner, and M.J. Rood, "Treatment of Hazardous Organic Wastes Using Wet Air Plasma Oxidation," *Proceedings of 1st INEL Workshop on Plasma Applications to Waste Treatment*, Idaho Falls, ID (January 1991).
 19. L.A. Rosocha, "Cold Plasma Destruction of Savannah River Off-Gas VOCs," United States Department of Energy, Office of Environmental Management Technology Development, *Technical Task Plan TTP AL121109* (December 1991).
 20. In response to Request for Proposal (RFP) No. 116462.36.WP.02 from CH2MHill (July 1995); and "Demonstration Work Plan, Environmental Management of Offgas Technology," McClellan AFB Contract No. F04699-93-D-0017, CH2MHill (August 1995).