

Title:	Silent Discharge Plasma Technology for the Treatment of Air Toxics and Other Applications
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FINAL ABSTRACT

CRADA TITLE: Silent Discharge Plasma Technology for the Treatment of Air Toxics and Other Applications

CRADA Number: LA95C10267

Under this CRADA, the Los Alamos National Laboratory (LANL) and High Mesa Technologies, Inc. (HMT) carried out a joint project on the development of the silent discharge plasma (SDP) technology for the treatment of hazardous air pollutants and other hazardous or toxic chemicals. The project had two major components: a technology-demonstration part and a scale-up and commercialization part. In the first part, a small-scale, mobile SDP plasma processor, which was being developed under a CRADA with the Electric Power Research Institute (EPRI) was the mobile equipment was modified for higher capacity service and employed for an innovative remediation technologies demonstration on soil-vapor extraction off-gases at the McClellan Air Force Base near Sacramento, CA. The performance of the SDP system for the variety of volatile organic compounds (VOCs) encountered at the McClellan site was sufficiently promising to encourage further scale-up and commercialization of the technology. During the second part of the project HMT and LANL worked together to formulate a scale-up strategy and a commercialization/manufacturing plan, and to design a prototype scaled-up SDP unit. HMT and LANL are now in the final stages of completing a licensing agreement for the technology and HMT is in the process of raising funds to engineer and manufacture commercial prototype SDP equipment focused on stack-gas emissions control and environmental remediation. HMT, in collaboration with another Northern New Mexico business, Coyote Aerospace, has also successful in receiving a Phase I Small Business Innovative Research (SBIR) award from the Army Research Office to develop, design, and construct a small non-thermal plasma reactor for laboratory studies ("Non-Thermal Plasma Reactor for Control of Fugitive Emissions of Toxic Gases").

SILENT DISCHARGE PLASMA TECHNOLOGY FOR THE TREATMENT OF AIR TOXICS AND OTHER APPLICATIONS

Final Report

CRADA No. LA95C10267

A. Parties

The subject project is a relationship between the Los Alamos National Laboratory (LANL), P.O. Box 1663, Los Alamos, NM 87545 and

High Mesa Technologies, Inc. (HMT)
1441 Paseo de Peralta
Santa Fe, NM 87501

B. Project Scope

A silent discharge plasma (SDP) arises from an electrical discharge in a gas, carried out when one or more discharge electrodes are covered with a dielectric. The SDP generates highly reactive chemical species (e.g., free radicals) that can decompose entrained pollutants to benign or more-easily managed compounds. The process was researched and developed to the pre-commercial level (a small-scale mobile SDP demonstration unit) at Los Alamos under various DOE projects and a CRADA with the Electric Power Research Institute (EPRI). Also, as part of the EPRI-LANL CRADA, HMT was chosen as a partner for commercializing the SDP technology.

This HMT-LANL project was directed at demonstrating the commercial applicability of SDP technology for treating hazardous chemical compounds in industrial air emissions or compounds which can migrate to the air from contaminated soil or groundwater. The main purpose of the HMT-LANL CRADA was to mature the silent discharge plasma (SDP) technology to a state feasible for transfer to the commercialization partner (HMT) by further developing the technology and performing a demonstration representative of industrial air-toxics abatement. To that end, the key objectives of the project were to: 1) identify and select compounds or processes which are good technical-performance matches for the technology and that have application in identified industrial sectors; 2) upgrade the EPRI-LANL mobile unit for robust, higher capacity service (300 liter/min, 10 SCFM) and test it at a selected site; and 3) scale-up and demonstrate an SDP unit in a field-test representative of full-scale industrial service.

The original target technical performance goals for a commercial SDP prototype were: four decades removal (99.99%) of non-chlorinated volatile organic compounds (VOCs) at 250 SCFM (7,000 liter/min) gas flow rate and 1 - 1000 ppm concentrations and two decades removal (99%) of chlorinated VOCs at gas flow rates > 500 SCFM (14,000 liter/min) and similar concentrations.

A survey of compounds potentially relevant to the SDP process was conducted and several hydrocarbon and chlorocarbon VOCs were identified as candidates for testing as industrially-representative compounds. Through HMT's California affiliate ENV America, Inc., an arrangement to field-test the upgraded SDP unit was negotiated as part of a project on the demonstration of innovative environmental remediation technologies at the McClellan Air Force Base near Sacramento, CA. There, the plasma unit was tested on soil-vapor extraction (SVE) off-gases containing a variety of chlorinated and non-chlorinated VOCs (perhaps fifty species). The performance of the SDP system for the simultaneous removal of the large variety of compounds encountered at the McClellan site was sufficiently promising to encourage further scale-up and commercialization of the technology. During the second part of the project HMT and LANL worked together to formulate a scale-up strategy and commercialization-manufacturing plan, and to design a prototype scaled-up SDP unit.

The first part of the project, selection of relevant compounds and testing the upgraded unit at a selected site (the McClellan innovative remediation demonstration), was completed on time within the schedule negotiated with the base and the contractors responsible for coordination of site testing. The second part of the project, scale-up and commercialization, was extended six months to enable a more focused market strategy and commercialization plan to be formulated. Under the extension, HMT's basic idea was to focus on a market segment employing compact, smaller-capacity SDP units for "point-of-use" applications (e.g., semiconductor manufacturing facilities). The prototype unit to be designed and tested under the modified CRADA was specified to have a processing capacity of 50-250 SCFM, rather than 250 SCFM.

A baseline scale-up design has been completed but the industrial partner must finish raising funds for commercial prototype engineering and manufacturing. HMT and LANL are now finalizing a licensing agreement for the technology. HMT is in the process of raising funds to engineer and manufacture commercial prototype SDP equipment focused on stack-gas emissions control and environmental remediation. The 50-250 SCFM prototype would be built and tested as part of the post-licensing efforts, after the closure of this CRADA.

Under the CRADA, Los Alamos was responsible for carrying out the major technical tasks required for upgrading and preparing the EPRI-LANL mobile unit for the McClellan demonstration, assisting in field-testing the plasma-processing equipment, and consulting on the design of a larger scaled-up unit (50 - 250 SCFM nominal capacity). HMT's major technical tasks focused on providing an interface between the site demonstration-management contractor and managing the SDP demonstration in the field. HMT also had the lead responsibility for developing a marketing strategy, scale-up plan, and commercialization plan for the technology.

The CRADA called for the following major deliverables: 1) brief reports on the status and results of laboratory tests on a gas mixture designed to simulate the effluent stream to be encountered at the McClellan site (LANL); 2) periodic reports describing the field-test status and performance results (LANL); 3) reports on marketing strategy, scale-up plans, and commercialization plans (HMT); 4) A field-test report for the McClellan demonstration (HMT); 5) A final CRADA report, namely this document (LANL/HMT). The LANL deliverables were satisfied in terms of regular communications with HMT/ENV, written progress reports, a technical publication

(placed in the Appendix) describing the SDP process and summarizing the McClellan site testing, and this document - the Final CRADA Report. The HMT deliverables were satisfied in terms of test-report input information to McClellan AFB and the site contractor who coordinated the innovative technology demonstrations (CH2MHill) and a marketing and business plan for the LANL Industrial Partnership Office (IPO). A major HMT deliverable for the second part of the project, building and testing a 50-250 SCFM commercial prototype, has not been completed. HMT envisions completing this under post-CRADA work, once sufficient financing is obtained and the company's technical infrastructure is arranged.

C. Technical

In this section, we will present technical accomplishments associated with the two major parts of the CRADA project: 1) choice of compounds matched to SDP technology, upgrade of the EPRI-LANL mobile plasma processor and subsequent testing at McClellan AFB; 2) scale-up to commercially-relevant capacity and the design of a commercial-prototype SDP processor.

C1. Compound Identification and Field Demonstration

A survey of chemical compounds was carried out to identify compounds that were both a potential match for SDP treatment and representative of industrial pollution control and/or environmental remediation needs. A microcosm of such compounds was identified at McClellan AFB, which has sought new technologies to assist in remediating vadose-zone sites that are contaminated with VOCs. Example compounds at the site are trichloroethylene (TCE, C_2HCl_3), perchloroethylene (PCE, C_2Cl_4), 1,1,1, trichloroethane (TCA, $C_2H_3Cl_3$), xylenes, acetone, toluene, chlorocarbons, and semi-volatile organic compounds (SVOCs).

At these sites, SVE systems are used to pull VOCs from the soil using wells and vacuum pumps. SDP technology, in the form of an upgraded EPRI-LANL mobile plasma processor, was demonstrated at McClellan AFB, Site S, Operable Unit D, as part of its innovative technology demonstration program. The program is a partnership among the U.S. Air Force, McClellan AFB, the U.S. Environmental Protection Agency (EPA), the California Environmental Protection Agency (Cal-EPA), and the Environmental Process Improvement Center. The SDP demonstration was carried out from November 2, 1995 to January 12, 1996. HMT/ENV arranged for the transport of the equipment from Los Alamos to Sacramento and back.

To meet the McClellan demonstration requirements of a 10 SCFM gas flow and sufficient plasma energy density to decompose the target compounds, the EPRI-LANL unit would require modification. Based upon information gained at an earlier field test at the U.S. DOE Savannah River Site and technical progress since that test, LANL and HMT modified the EPRI-LANL mobile SDP processor for more robust field operation, unattended operation, and a three-fold increase in gas-flow treatment capacity. This required adding two additional banks of SDP cells and one additional power supply to the unit. Before going to the McClellan site, laboratory tests on surrogate pollutant-air mixtures were conducted at Los Alamos to gather data that would provide guidance for the field-demonstration operating parameters. At the site, a portion of the SVE wells were employed for this demonstration and the extracted vapor from these wells was sent through the SDP system. Influent and effluent samples were collected for analysis to

determine the destruction efficiency and byproduct concentrations. The analysis was not the responsibility of HMT/ENV, but was contracted to other organizations.

For a more complete discussion of the McClellan demonstration, technical details concerning SDP technology and its applications, and a history of the development of the LANL SDP process, the reader is referred to the document in Appendix A: "Field Demonstration and Commercialization of Silent Discharge Plasma Air Pollutant Control Technology," LA-UR-96-1846 (and to the other documents referenced in Section E of this report).

During the field tests it was shown that the best results for destruction and removal efficiency (DRE) could be obtained with the addition of small amounts of hydrogen gas (concentration comparable to the pollutant concentrations). The table below summarizes the average DRE values obtained, running the system with added hydrogen.

Compound	Average Inlet Concentration (ppm)	Average Outlet Concentration (ppm)	Average DRE (%)
TCE	82.7	0.29	99.6
PCE	76.3	0.35	99.5
1,1,1-TCA	157.0	7.3	95.4
Xylenes	16.3	0.09	99.4
Acetone	115.6	2.46	97.9
SVOCs	0.4744	0.0056	> 99.9
TNMOCs*	5515.0	168.0	97.0

* TNMOCs are total non-methane organic compounds; this DRE is essentially the overall DRE for all the compounds in the treated air stream.

The overall DRE goal for the demonstration was 95% so, under hydrogen-additive conditions, this goal was exceeded. Drying the air stream (i.e., dehumidification also resulted in better performance). Without dehumidification and hydrogen addition, the individual DREs for some of the more difficult-to-remove compounds (e.g., TCA) were often below 90%.

C2. Scale-Up and Commercialization

To design and build SDP reactors that are optimized for particular applications, one must understand the basic decomposition chemistry of the target compound(s) and how the decomposition of a particular chemical species depends on the air-emissions stream parameters and the reactor operating parameters. This section is intended to serve as a summary of the subject of reactor scaling and optimization, as applied to this CRADA. It will discuss basic reactor scaling relationships and the connection between the basic plasma chemistry, the target species properties, and the reactor operating parameters (in particular, the operating plasma energy density). System architecture, that is how SDP (or other non-thermal plasma) reactors can be combined or ganged to achieve higher capacity, will also be briefly discussed.

C2.1 Decomposition-Scaling Relationships

In many non-thermal plasma devices (of which SDP is representative), a key process parameter governing the decomposition of a pollutant is the specific energy (plasma energy density) deposited in the gas. Experiments with various reactors have shown that the degree of removal of a particular contaminant depends on the applied plasma energy density \bar{E} and a characteristic energy-density parameter β (which is related to the target compound), the carrier gas, and the reduced electric field E/N for the reactor.

The pollutant decomposition can be ideally expressed as

$$[X] = [X]_0 \exp(-\bar{E}/\beta),$$

where $[X]_0$ is the initial pollutant concentration, $[X]$ is the resulting concentration, \bar{E} is the applied specific energy (or plasma power divided by gas flow rate, P/Q), and β is the e-fold energy density.

Supplying one β to the reactor reduces the concentration by $1/e$, 2β by $1/e^2$, and so on. In this ideal case, when $-\ln([X]/[X]_0)$ is plotted versus \bar{E} , a straight line of slope $1/\beta$ results. For real cases, the plot is not necessarily a straight line, so such a slope-determined β -value is only an approximation. In some cases, the removal function can additionally depend on the initial pollutant concentration.

C2.2 Reactor Scaling Concepts

The specific energy can also be expressed as

$$\bar{E} = P/Q = \bar{P} \tau_r,$$

where P and Q are the plasma power and gas flow rate, respectively, \bar{P} is the power density (power per unit volume) and τ_r is the residence time of a unit volume of gas in the active portion of the reactor.

To increase the removal fraction $[X]/[X]_0$ for a given gas mixture, the specific energy \bar{E} must be increased. \bar{E} can be increased by either increasing \bar{P} or τ_r (or, equivalently, decreasing the flow rate Q for a given cell volume). Assume the reactor volume is kept fixed. Therefore, to increase the removal fraction at a fixed flow rate, one can directly increase the power to the reactor. To increase the removal fraction at a fixed power, one can decrease the gas flow rate.

For a given reactor, the power and gas flow cannot be arbitrarily increased. Limits such as gas-flow impedance or heat conduction out of the reactor may limit the practical size of the reactor in terms of how much gas flow or deposited power can be achieved.

Additionally, the power density \bar{P} depends on the particular type of reactor being employed. Typically-achieved power densities for SDP reactors are quite high (order 1 W/cm³), compared to other electric-discharge plasma reactors, like pulsed corona (< 15 mW/cm³).

C2.3 Reactor Architectures

In the context of this report, architecture refers to the manner in which an SDP reactor, or combination of reactors and other equipment is configured to treat an emissions stream. At present, we assume that we will mainly deal with end-of-pipe emissions treatment (right before discharge to the air). The simplest end-of-pipe architecture is to employ an SDP reactor (or array) as a stand-alone emissions control device. Two basic reactor scaling architectures are discussed below: simply increasing the size of a single reactor (monolithic scaling) and parallel or ganged connection of smaller reactors (modular scaling).

C2.3a Monolithic Scaling

To increase the capacity of an NTP reactor, we need to increase the gas flow rate. At a fixed removal fraction, the power must be increased in proportion to the flow rate. That is, if we scale up the flow by a factor N_s , the power must be scaled up by the same factor to keep the energy density fixed ($N_s P / N_s Q = P/Q$). This represents monolithic scaling, where we simply increase the physical size of the reactor while proportionally increasing the gas flow rate and plasma power.

C2.3b Modular Scaling

Alternatively, the total gas flow and total plasma power can be divided among several reactor modules that are connected in parallel. The power to each reactor is then P/N_s , while the gas flow rate is Q/N_s (which keeps a constant energy density $P/N_s / Q/N_s = P/Q$). This represents modular scaling, whereby a reactor module of desirable properties is replicated many times, is quite attractive. Such modularization scaling of silent discharge cells has been previously demonstrated for the industrial-scale synthesis of ozone, where municipal water treatment plants frequently require the on-site generation of thousands of kilograms per day.

The modular approach has been employed at Los Alamos for scaling up both laboratory-size and small, field-pilot-scale units. Typically, rectangular electrode-area, dielectric-barrier (silent discharge) reactors have been employed for VOC treatment tests. However, for systems requiring the treatment of higher temperature (e.g., > 100 C) emissions streams, cylindrical reactor cells may be more robust and practical in an engineering sense.

C2.4 Baseline Scale-Up Design for 50-250 SCFM Unit

One of the project deliverables was a design for a 50-250 SCFM commercial-prototype SDP unit. This section will summarize such a design, based upon matching the system design to the decomposition-energy requirements of two representative chemical surrogates: a hydrocarbon with a β -value of 50 J/liter and a chlorocarbon with a β -value of 1000 J/liter.

The plasma power requirement for each of these cases is obtained from the product of degree of removal (number of β -values, n) and gas-flow rate (Q): $n \beta Q$. The actual power supply output requirement depends on the power supply-to-plasma coupling efficiency (ratio of plasma power

to power supply output rating). Typically, this value is about 80-85%. As a conservative example, we will take a coupling value of 80%. Another factor to consider is the power-handling capability of the SDP cells (determined by heat removal and mechanical stress). Here, we assume that the power-handling capability of individual SDP cells is 1 kW. The table below gives the plasma power requirements, the nominal power supply output, and the number of SDP cells for 50 and 250 SCFM units, in the example hydrocarbon and chlorocarbon cases, assuming a 3β degree of removal (i.e., ~ 95% DRE). The power supply output (rounded-up value) and number of cells are in parentheses.

Q / \bar{E}	$3\beta = 150 \text{ J/liter}$	$3\beta = 3 \text{ kJ/liter}$
50 SCFM	3.5 kW (5 kW, 5 cells)	70.8 kW (89 kW, 89 cells)
250 SCFM	17.7 kW (22 kW, 22 cells)	354.0 kW (443 kW, 443 cells)

Recently, LANL has achieved a power supply coupling efficiency of nearly 90%. Therefore it should be possible to lower the nominal power supply ratings somewhat. If the power handling capability of individual cells can be further increased, fewer cells would be required. Additional engineering in terms of dielectric materials and cell-cooling methods are required to achieve significant increases in power-handling capability, while maintaining a compact cell size.

A generalized electrical circuit schematic diagram for the SDP system (including power supply and control and data acquisition system) is shown in Figure 1. A commercial variable frequency (100 Hz to 2000 Hz) sinusoidal-waveform power supply (or a specially-constructed power supply) can be used to drive the plasma cells. Using a step-up transformer, high voltage is applied to the plasma cells to achieve an electrical discharge in the gas. An electrical matching circuit is also employed to maximize the efficiency of power coupling into the plasma. The details of this circuit are not presented here because they are proprietary to EPRI-LANL-HMT agreements. The deposited plasma energy density (determined from the electrical power and the gas flow) is monitored and controlled by the computer-based system, the details of which are also confidential.

Gas temperature, gas flow rate, and gas pressure are measured by thermocouples, flow meters, and pressure gauges. The gas-measuring instruments are also 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. A gas-flow schematic diagram is given in Figure 2.

A drawing which represents the general plasma-cell arrangement for the stackable modules designed for the 50-250 SCFM plasma processor is shown in Figure 3. This modular-cell arrangement was developed as part of an earlier DOE-sponsored soil-vapor-extraction off-gas treatment demonstration at the Savannah River Site and refined for better power-handling capability and compactness under other LANL projects (e.g., a CRADA with the semiconductor consortium SEMATECH). Both the process gas flow and electrical power are individually fed to each cell (i.e., they are connected in parallel). The metal plates sandwiched between the dielectric plates serve two functions - an electrode and heat sink. A dielectric cooling fluid is circulated through voids in the plates and through a heat exchanger to extract heat from the cells. The modular arrangement is very useful in scaling up the plasma processor capacity - one can simply combine many cells in a stack and/or replicate stacks of cells to achieve higher throughput. The usually-employed dielectric material is Pyrex glass. The gas-gap spacing and active cell area are typically 3 - 4 mm and 1650 cm², respectively. Ten or more cells could easily be employed in a single stack. As with the electrical-drive circuits, construction details of these cells is proprietary information.

It is envisioned that a 50-250 SCFM system could be designed either as a mobile unit (perhaps carried in a 40-foot semi-trailer) or a ground-based system. A 5-kW system would certainly be more manageable in terms of weight and space than a 443-kW system. It is possible that the exact system would need to be tailored for the particular site and waste stream requirements.

C.3 Outstanding Technical Issues

There are some outstanding technical issues to resolve relative to this CRADA. The 10-SCFM McClellan demonstration equipment was prepared as fielded as planned. However, the resolution of some engineering issues associated with the development of robust, commercial equipment remains. Examples components requiring additional engineering are: mass-produced SDP cells; advanced, robust dielectric materials; and highly-efficient power supplies. It is expected that such engineering can be carried out after the LANL-HMT licensing agreement is in place.

D. Partner Contributions

The major contributions of the industrial partner, HMT, to this CRADA were:

- Identified representative chemical compounds to serve as a performance-benchmarking basis for evaluating and commercializing SDP technology.
- In partnership with its California affiliate ENV America, HMT conducted a scoping study to identify a site at which to carry out a field demonstration of the technology; negotiated with site representatives to establish a working partnership and contract for the field test.
- With assistance from Los Alamos, transported the upgraded EPRI-LANL equipment to McClellan AFB and carried out field tests during the eleven week period November 2, 1995 through January 12, 1996.
- Provided market-survey data concerning potential commercial markets for the technology. Worked with Los Alamos and contacts from Northern New Mexico businesses on marketing and commercialization strategies and plans.

All of HMT's deliverables have been met, with the exception of designing, constructing, and testing a scaled-up 250 SCFM commercial prototype; and the completion of a detailed manufacturing plan. HMT has not been able to raise sufficient funds to complete these deliverables within the duration of the CRADA. However, the LANL Principal Investigator is satisfied with the Participant's performance and in-kind contributions to the CRADA and is encouraged that HMT and LANL are finalizing a licensing agreement for the technology. With the license in place, HMT should have a better chance of raising the capital necessary for constructing a scaled-up commercial prototype and establishing a means for manufacturing commercial units.

No subject inventions were created during this CRADA project. However, the performance of this CRADA project did, in some cases, augment background intellectual property (BIP) other than inventions pertaining to the technology. The licensing of such intellectual property is the subject of agreements separate from this CRADA.

E. Documents/Reference List

a) CRADA reports and other topic/periodic reports connected to the project:

1. L.A. Rosocha, J.J. Coogan, R.A. Korzekwa, D.A. Secker, R.F. Riemers, P.G. Herrmann, P.J. Chase, M.P. Gross, and M.R. Jones, "Field Demonstration and Commercialization of Silent Discharge Plasma Air Pollutant Control Technology", *Proceedings of 2nd International EPRI/NSF Symposium on Environmental Applications of Advanced Oxidation Technologies*, (San Francisco, CA, Feb. 28 - Mar. 1, 1996), Electric Power Research Institute, Section 5, pp. 107-121 (September 1997).
2. L.A. Rosocha, "Non-Thermal Plasma Session Overview," *Proceedings of 2nd International EPRI/NSF Symposium on Environmental Applications of Advanced Oxidation Technologies*, (San Francisco, CA, Feb. 28 - Mar. 1, 1996), Electric Power Research Institute, Section 3, pp. 13-2 (July 1997).
3. L.A. Rosocha, R.A. Korzekwa, D.A. Secker, J.J. Coogan, and M.R. Jones, "Industrial Air Toxics Treatment Demonstration (Using Silent Discharge Plasma), Final Report for CRADA LA93C10100, Los Alamos Report LA-CRADA-97-007 (September 30, 1996).
4. "Silent Discharge Plasma Technology Demonstration at Site S, Operable Unit D, McClellan Air Force Base California", *ENV America Draft Report, ENV Project No. CHM-02-F001*, Prepared for: CH2M Hill, Inc., Project Reference No. 116462.36SD.02 (Feb. 28, 1996)
5. "Silent Discharge Plasma Technology, Technical Memorandum, Environmental Management of Offgas Technology, Site S, Operable Unit D," Delivery Order 7036, McClellan Air Force Base, California.
6. "Nonthermal Plasma Destruction of Vapor Phase Compounds," McClellan AFB internet document, http://www.mcclellan.af.mil/EM/TECH/sd_nonth.htm.
7. Regular Quarterly Reports submitted to LANL Industrial Partnership Office.

b) Patent/copyright activity

There has been no patent/copyright activity pertaining to this CRADA, nor is any expected in the future.

c) Subject inventions

There are no subject inventions for this CRADA.

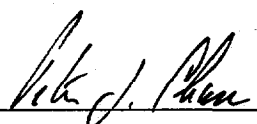
d) Licensing status of Background Intellectual Property (BIP)

With EPRI's concurrence (necessary because of agreements under initial EPRI-LANL CRADA for developing SDP technology), the BIP pertaining to this CRADA (and other BIP refined or augmented from experience gained under this CRADA) has become part of a licensing agreement with the jointly-chosen, third-party commercialization partner HMT. LANL and HMT are finalizing the terms of that agreement.

F. Acknowledgment

Participant's signature on the final report indicates the following:

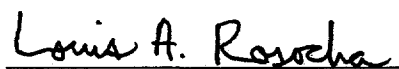
- 1) The Participant has reviewed the final report and concurs with the statements made therein;
- 2) The Participant agrees that any modifications or changes from the initial proposal were discussed and agreed to during the term of the project;
- 3) The Participant certifies that all reports either completed or in process are listed and all subject inventions and the associated intellectual property protection measures attributable to the project have been disclosed or are included on a list attached to this report;
- 4) The Participant certifies that proprietary information has been returned or destroyed by LANL.



Peter J. Chase
Industrial Participant, HMT

6/10/98

Date



Louis A. Rosocha
Principal Investigator, LANL

6/10/98

Date

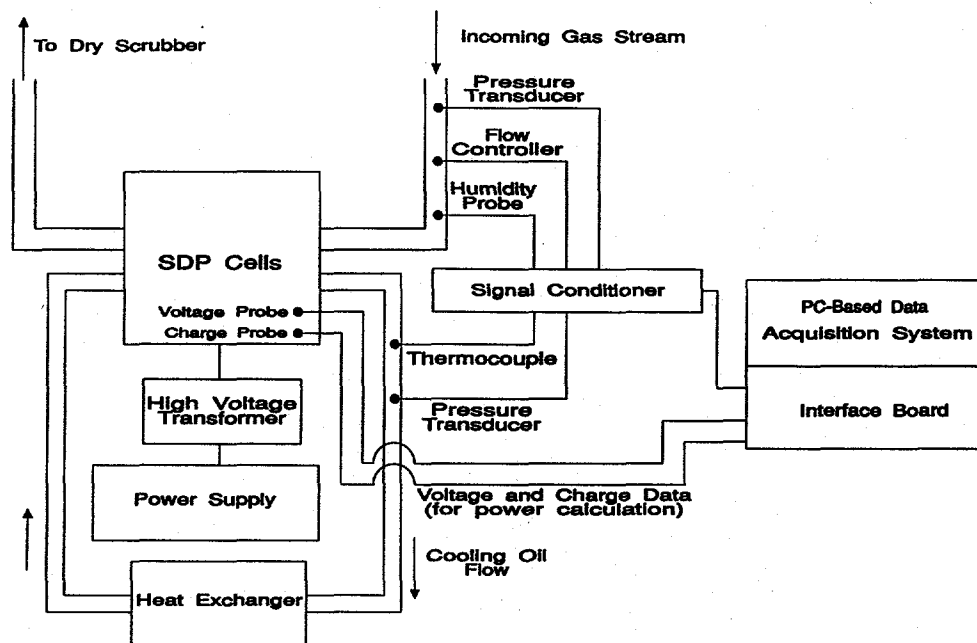


Figure 1: Electrical schematic diagram for power supply and control & data acquisition system for the baseline-design 50-250 SCFM SDP Processor.

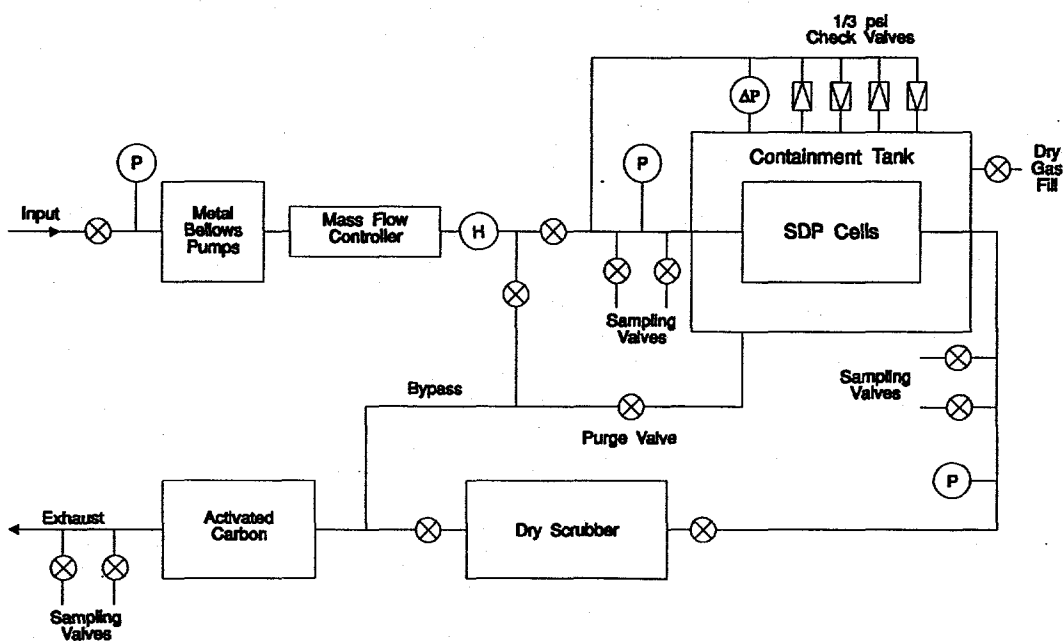


Figure 2: Gas-flow schematic diagram for 50-250 SCFM SDP processor. More than one containment tank and power supply might be required for this capacity (for simplicity, only one tank is shown in the illustration).

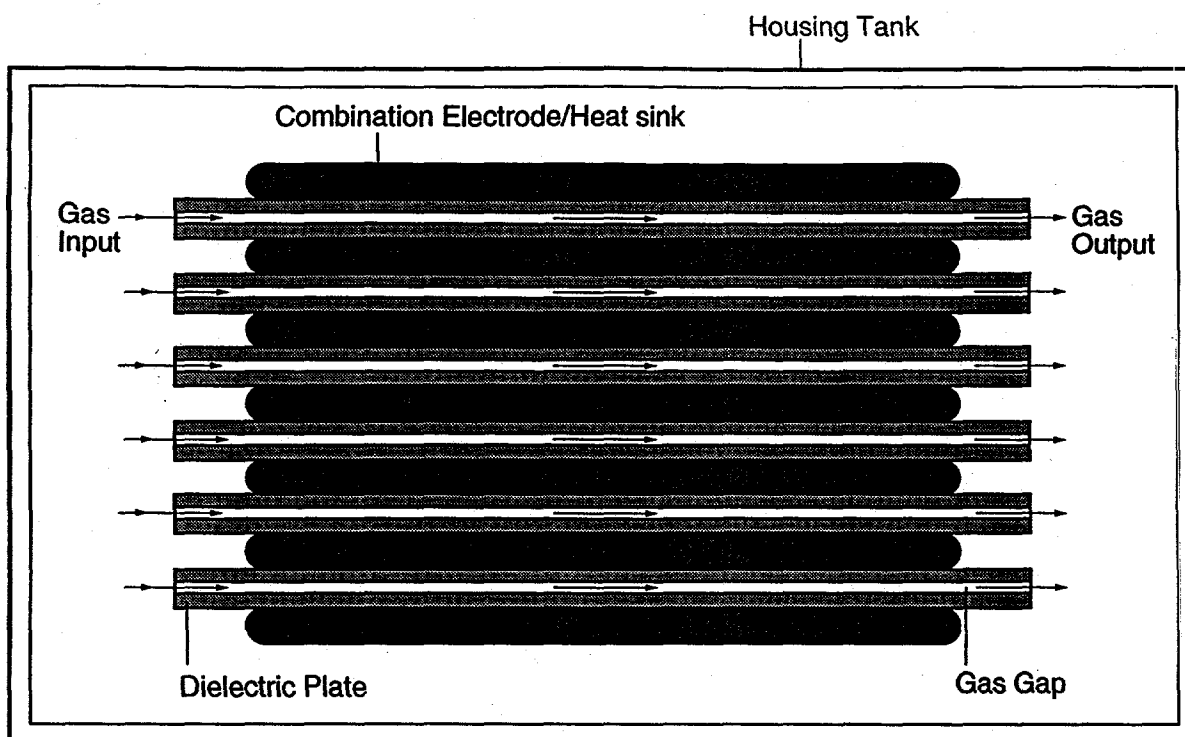


Figure 3: Illustration of a six-cell example of a modular SDP-cell array (top view) and its housing tank. The cells are combined in parallel for both gas flow and electrical-power feed. The housing tank is filled with an inert gas such as nitrogen or argon. Details such as the electrical hookups and gas-feed manifolds are omitted here for simplicity of illustration.

Attachment: Los Alamos National Laboratory report LA-UR-96-1846

L.A. Rosocha, J.J. Coogan, R.A. Korzekwa, D.A. Secker, R.F. Riemers, P.G. Herrmann, P.J. Chase, M.P. Gross, and M.R. Jones, "Field Demonstration and Commercialization of Silent Discharge Plasma Air Pollutant Control Technology", *Proceedings of 2nd International EPRI/NSF Symposium on Environmental Applications of Advanced Oxidation Technologies*, (San Francisco, CA, Feb. 28 - Mar. 1, 1996), Electric Power Research Institute, Section 5, pp. 107-121 (September 1997).

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 chloro-fluorocarbons). 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.

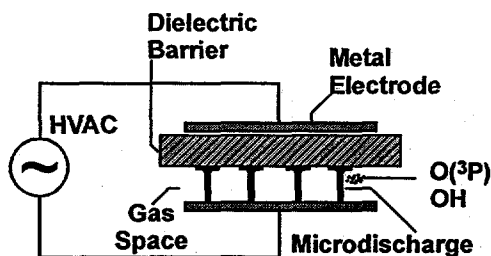
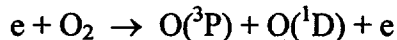


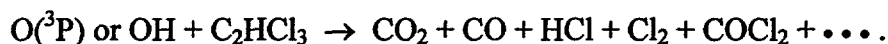
Fig. 1 Diagram of a single-dielectric-barrier discharge plasma reactor.

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.

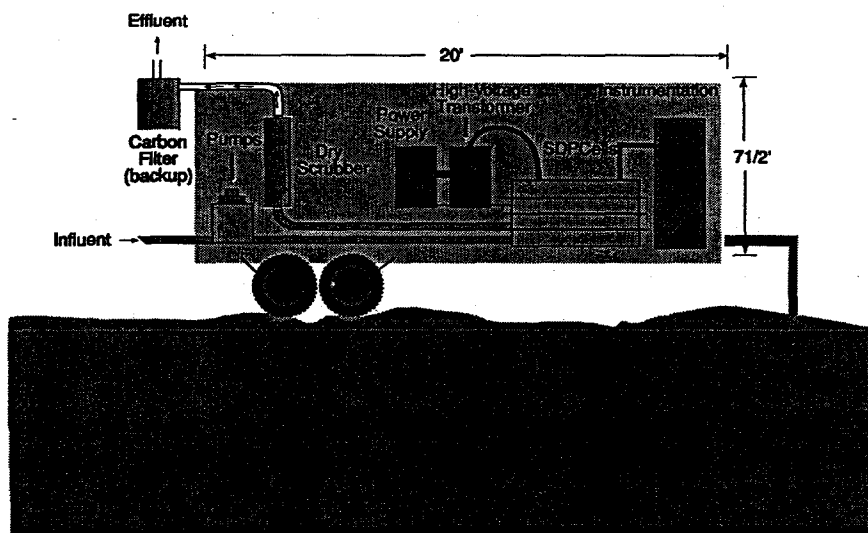


Fig.2a: EPRI-LANL mobile silent discharge plasma processor.

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.

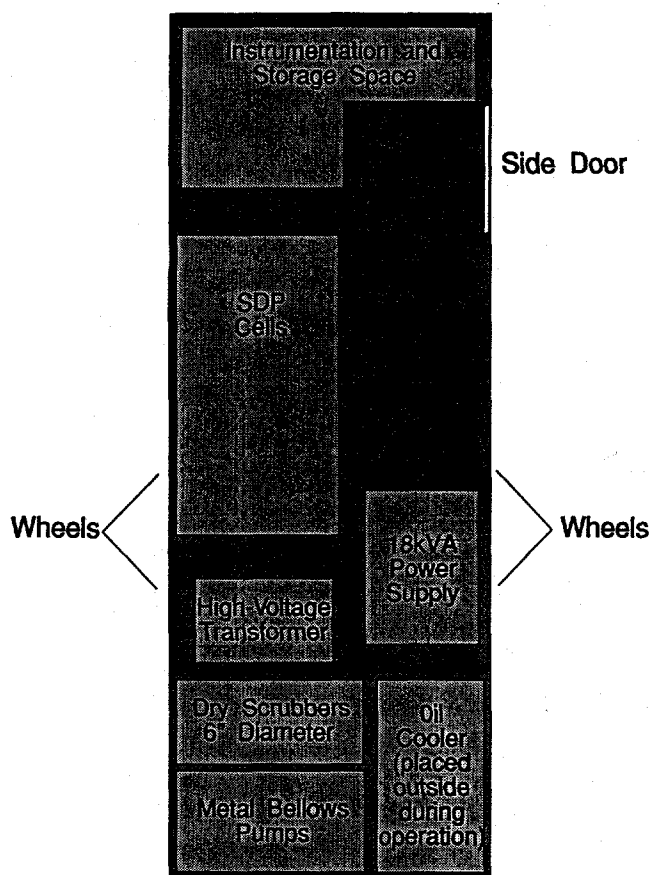


Fig.2b: Layout view of EPRI-LANL mobile silent discharge plasma processor.

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/cm^3), 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/cm^3 . Most of the data points for total VOC concentration ($[\text{PCE}] + [\text{TCA}] + [\text{TCE}]$) 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 $< 1 \text{ ppm}$) 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/cm^3), 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.

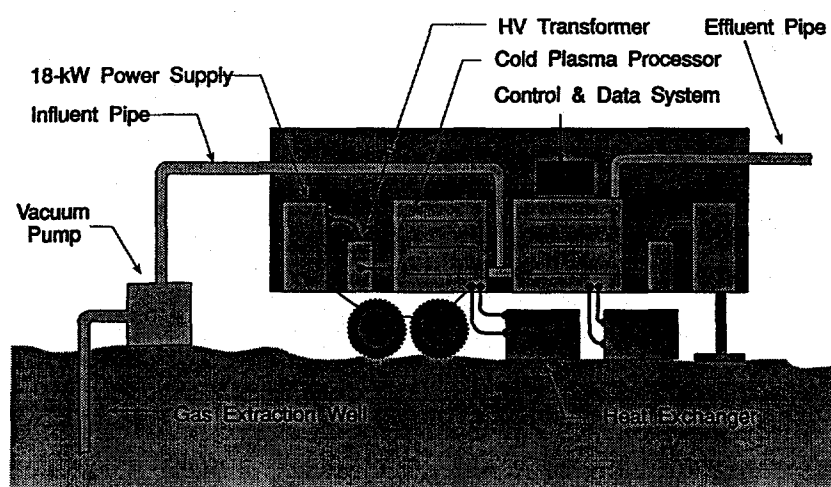


Fig. 3: Illustration of mobile SDP equipment for combined cold plasma-soil vapor extraction VOC treatment demonstration at McClellan AFB.

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).