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The literature on NTP de-NOx has been reviewed, laboratory measurements and modeling studies on NTP-initiated NOx removal have been carried out, adsorber performance for NOx removal aimed at hybrid systems have also been done, and scaling and optimization relationships and algorithms have been developed. We have completed cost analyses and economic assessments for various NTP reactor systems compared to conventional selective catalytic reduction (SCR) - wet scrubber technology and find that NTP technology is cost-competitive for jet-engine exhaust de-NOx. We are now at the point where initial design options for NTP reactor systems for a field-pilot demo on CMTC excaust at Tinker AFB (currently scheduled for September, 1999) have been completed.

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**Los Alamos**
NATIONAL LABORATORY

# Development of Non-Thermal Plasma Reactor Technology for Control of Atmospheric Emissions: Interim Technical Report for SERDP Project CP-1038 (1998)


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# Development of Non-Thermal Plasma Reactor Technology for Control of Atmospheric Emissions

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## Abstract

Incentives for implementing new pollution-control technologies for oxides of nitrogen ($NO_x$) and hazardous air pollutants (HAPs), including volatile organic compounds (VOCs), are both regulatory and economic. Of immediate concern, given considerable regulatory pressure, e.g., the promulgation of a NESHAPS (National Emissions Standard for Hazardous Air Pollutants) for $NO_x$ emissions in CY 2000, new de-$NO_x$ technologies are necessarily being explored. This project is currently emphasizing evaluations of non-thermal plasma (NTP) technologies for treating jet-engine exhaust and other hazardous air pollutants. This report will summarize our technical progress for calendar year 1998; considerable further details of our work are contained in the reports and papers cited in the Appendix.

The literature on NTP de-$NO_x$ has been reviewed, laboratory measurements and modeling studies on NTP-initiated $NO_x$ removal have been carried out, adsorber performance for $NO_x$ removal aimed at hybrid systems have also been done, and scaling and optimization relationships and algorithms have been developed. We have completed cost analyses and economic assessments for various NTP reactor systems compared to conventional selective catalytic reduction (SCR) - wet scrubber technology and find that NTP technology is cost-competitive for jet-engine exhaust de-$NO_x$. We are now at the point where initial design options for NTP reactor systems for a field-pilot demonstration on Cruise Missile Test Cell (CMTC) exhaust at Tinker Air Force Base (currently scheduled for September 1999) have been completed. The field-pilot demonstration is necessary to provide further data and operating experience to more fully evaluate economic and performance projections for NTP de-$NO_x$ technology and to design larger systems with confidence.

## Project Background

Because of a greater emphasis on environmental issues, increasing regulations, and increased scrutiny by regulators, there is a growing need to control the emission of oxides of nitrogen ($NO_x$) and hazardous air pollutants (HAPs) - including volatile organic compounds (VOCs) - at DoD installations. These emissions are frequently episodic (e.g., JETCs - jet engine test cells; painting, stripping and cleaning operations) are variable, with toxic gas loadings spanning a large concentration range from parts-per-million (ppm) to parts-per-thousand (ppt). Optimal existing technologies for high destruction-efficiency $NO_x$ and HAP/VOC control suffer from significant drawbacks. Our overall project objective is to evaluate and develop an emerging technology, namely non-thermal plasma (NTP) reactor technology for DoD air emissions control applications.

Incentives for implementing new pollution-control technologies are both regulatory and economic. Given considerable regulatory pressure, e.g., the promulgation of a NESHAPS (National Emissions Standard for Hazardous Air Pollutants) for $NO_x$ emissions in CY 2000, new de-$NO_x$ technologies are necessarily being explored. This project is currently evaluating non-thermal plasma (NTP) technologies for treating jet-engine exhaust and other hazardous air pollutants, with a first priority on $NO_x$ removal.

## Objective

Our overall project objective is to evaluate and develop new technology, namely non-thermal plasma (NTP) reactor technology for DoD air emissions control applications. A key goal is to provide a basis for selecting the most appropriate NTP technology for DoD applications by evaluating the performance of prototype and pilot-scale NTP reactors (corona, dielectric barrier, electron beam) for $NO_x$ abatement as a primary focus, as well as HAP and specialized VOC control (should other technologies prove inadequate or emissions standards become more stringent), and to assist in the commercialization of the technology. This will be accomplished by (1) developing a predictive, reactor simulation model for use in prototype development and scale-up; (2) by experimental verification of the modeling results; and (3) formulation of engineering scaling and optimization criteria and the use of these in the demonstration of scaleable laboratory-pilot and field-pilot reactors. The development of an efficient, reductive-mode $NO_x$ processor is a key goal. A comparison with conventional technologies (relative costs and benefits) will also be carried out.

## Technical Approach

To meet our technical objectives, we have planned a four-year effort starting with technology assessment and laboratory evaluation tests, progressing through laboratory-pilot equipment optimization and scaling, and culminating in the development of NTP technology selection criteria, based upon field-pilot testing. In the first year a comparative assessment of electric-discharge driven and electron-beam driven NTP reactors will be performed, reaction kinetic models will be developed, and experiments for issue resolution will be designed. In the second year reactor scaling criteria and optimization models will be developed and scaling studies will be initiated with laboratory-pilot apparatus. In the third year reactor scale-up, optimization, and system engineering will be completed to the point of starting the design of a field-pilot unit. The fourth year will concentrate on constructing and testing a field-pilot unit at a selected DoD site and providing criteria for selecting the most appropriate NTP technology for DoD applications. The field-pilot reactor is meant to approach a practical scale device (flow rate in the $Nm^3/hr$ range). In a practical application, for example, one would use several of these reactors in parallel to treat the exhaust gases from an emissions source.

The comparative assessment work has built upon a 1995 NIST workshop on NTP applications to air pollution control and considerable progress made in the field since then. NIST will also assist in plasma chemistry model development and laboratory measurements of reaction-chemistry relevant parameters (e.g., role of water-cluster reactions). Reactor performance measurements will be carried out using GC/MS (gas chromatography/mass spectrometry), TDL (tunable diode laser) and LIF (laser induced fluorescence) probes, with ARL taking the lead on optical/laser measurements. ARL will also carry out CFD (computational fluid dynamics) calculations to predict and optimize fluid flow patterns and treatment residence times. Los Alamos will focus on electric discharge physics, electrical drive circuit engineering and optimization, and the design and construction of laboratory test, pilot, and scaled-up reactors. McMaster University will be contracted to ARL to assist in reactor evaluations and testing, economic assessments, and pilot-unit design. Earlier SERDP work, EQ (Environmental Quality) work, and the NIST and McMaster University collaborations feed into this project.

## Project Accomplishments

### Overview

Below, we will summarize our technical progress for calendar year 1998; considerable further details of our work are contained in the reports and papers cited in the Appendix.

In overview summary: The literature on NTP de-$NO_x$ has been reviewed, laboratory measurements and modeling studies on NTP-initiated $NO_x$ removal have been carried out, adsorber performance for NOx removal in hybrid systems have also been done, and scaling and optimization relationships and algorithms have been developed. We have completed cost analyses and economic assessments for various NTP reactor systems compared to conventional selective catalytic reduction (SCR) - wet scrubber technology and find that NTP technology is cost-competitive for jet-engine exhaust de-$NO_x$. We are now at the point where initial design options for NTP reactor systems for a field-pilot demonstration on Cruise Missile Test Cell (CMTC) exhaust at Tinker Air Force Base (currently scheduled for September 1999) have been completed. The field-pilot demonstration is necessary to provide further data and operating experience to more fully evaluate economic and performance projections for NTP de-$NO_x$ technology and to design larger systems with confidence.

In the finer summary that follows below, we will describe some specific aspects of our 1998 accomplishments in various categories or types of work associated with the project.

**Computational Fluid Dynamics (CFD) and Chemical-Kinetics/Reaction Modeling:**
During 1998, the CFD code has been further adapted to the de-$NO_x$ problem in electric-discharge reactors. In the last quarter of FY98, the CFD code has been set up with 26 species and 60+ reaction mechanisms. The code has been set up for calculations of the performance of the ARL NTP reactor and has been de-bugged for the use of a multitude of plasma-streamer sites (in contrast to the 5 sites previously used). In addition, the code has been refined to calculate the energy

deposited in the plasma, as required for benchmarking. The following specific work in support of the reaction modeling program was carried out:

1. An NO-in-air system has been modeled with the full set of positive ion chemistry to validate the electron concentrations used in the above modeling calculations.
2. The rate constants for the important electron-molecule reactions in the air system have been compiled from the literature, and plots of the rate constants as a function of reduced electric field E/N were prepared, from which Arrhenius-type rate expressions can be derived.
3. Some limited work on the effect of including electron-positive ion recombination processes has been carried out.
4. A study and associated technical report "Reactions of Oxides of Nitrogen ($NO_x$) Leading to the Formation of Nitric Acid ($HNO_3$) in Non-Thermal Plasmas (NTPs): White paper for SERDP Project CP-1038" was completed detailing the reaction pathways for converting $NO_x$ to nitric acid in NTP reactors.

**Experiments**

Dielectric barrier and pulsed corona reactor experiments have been carried out and experimental electron-beam data from other sources evaluated. During the last quarter of FY98, the ARL NTP reactor was operated with a variety of gases to check out performance (plasma stability, operating parameter ranges) and to survey emission spectra in $N_2$, air, methane, and propene (a compound representative of diesel-engine emissions). The system was also interfaced with a mass spectrometer for product analysis. At LANL, preliminary data has been acquired on de-NO using an extremely fast-pulsed electric-discharge NTP reactor. The data appear promising for creating high reduced electric field (E/N) bulk-volume NTPs. Additionally, a special activated carbon has been tested for both NO and $NO_2$ adsorption and thermal regeneration, for potential future use in a hybrid NTP-adsorber system.

At McMaster University, experiments on the removal of $NO_x$ in simulated stationary jet-engine exhaust wre carried out using a large bench-scale corona radical shower (CRS) reactor and a CRS reactor in combination with a catalyzer, both systems incorporating ammonia ($HN_3$) injection. In these experiments, optima for acid-gas ($NO_x$ and $SO_2$) removal were determined in terms of the ammonia to acid gas molar ratio, the applied voltage and the injected (that forming additional reactive species) gas velocity. Both the removal of NO and $SO_2$ increase with increasing applied voltage (plasma specific energy) and decreasing initial NO concentration. High concentrations of methane ($CH_4$) have a negative effect on NO removal, where part of the NO is converted only to $NO_2$ but not to desirable, collectable ammonium nitrate ($NH_4NO_3$) aerosol particles. The effects of a catalyzer following the CRS reactor are significant with respect to acid-gas removal using ammonia injection, even at room temperature. However, these effects are not significant with methane injection. A conference paper and technical report have been written on these experiments ("Acid Gas Removal Characteristics of Corona Radical Shower System for Treatment of Stationary Engine Flue Gas" and "Development of Scaling Algorithms and Economic Evaluation for Non-Thermal Plasma Reactors - Adsorbant/Catalyzer Hybrid System for Control of $NO_x$ Released During Army and Related U.S. Department of Defense (DoD) Operations").

**Scaling and Optimization Relationships and Algorithms**

To design and build NTP reactors that are optimized for particular DoD 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. The report "First Report on Non-Thermal Plasma Reactor Scaling Criteria and Optimization Models" was completed and is intended to serve as an overview of the subject of reactor scaling and optimization and discusses the basic decomposition chemistry of nitric oxide (NO) and two representative VOCs, trichloroethylene and carbon tetrachloride, 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 NTP reactors can be combined or ganged to achieve higher capacity, was also be briefly discussed in this report and in an additional report "Feasibility Analysis Report for Hybrid Non-Thermal Plasma Reactors".

This last report was intended to provide a preliminary summary analysis of a few representative hybrid systems (combinations of different NTP reactor types or architectures), as a means of introducing the hybrid or staged-system concept. It presented qualitative, rather than quantitative, analyses of hybrid reactors. That is, primarily discussing relative advantages and/or disadvantages of example systems. Additional project work will be required to present more quantitative data for hybrids. Three representative hybrid systems were discussed: a serial-mode NTP-absorber architecture, a regenerative-mode (or 'trap and treat') architecture, and a dual-NTP-mode reactor system (namely, the use of an auxiliary reactor to inject active species into a main NTP reactor).

A companion report, which deals with further aspects on the development of reactor-scaling algorithms and discusses a test-case hybrid-reactor system, was completed at the end of FY97 under a subcontract managed by our Army Research Laboratory (ARL) team member Dr. Andrzej Miziolek. That project report is entitled "Development of Scaling and Economic-Evaluation Algorithms for Non-Thermal Plasma Reactors for Control of $NO_x$ Emissions," and was produced by M. Matsuoka, S.J. Kim, P.C. Looy, and Prof. J.S. Chang of McMaster University (October 27, 1997).

**Economic Evaluations**

In August 1998, the results of initial economic analyses of NTP flue-gas processing were completed and documented as a technical note to the SERDP Program Office, in partial fulfillment of some post-IPR(In-Progress Review) feedback on the need for economic feasibility analysis: "Notes on Economics of Non-Thermal Plasma Processes for Jet-Engine Emissions Control". In November 1998, a more-detailed technical white-paper report on NTP de-$NO_x$ economic assessments was completed ("Cost Analysis and Economic Assessment of Proposed Electric-Discharge Non-Thermal Plasma Processes for $NO_x$ Removal in Jet-Engine Exhaust: White paper for SERDP Project CP-1038"). In that report, we analyzed the costs of example NTP technologies for jet-engine emissions control. In some cases, these analyses have shown lower exhaust-gas treatment costs for NTP systems compared to a baseline standard de-$NO_x$ technology (like SCR combined with wet scrubbing). Therefore, the main conclusion was that NTP de-$NO_x$ can be cost competitive and that completing this project's work through the small field-pilot demonstration phase should proceed to provide further data and operating experience to more fully evaluate economic and performance projections for NTP de-$NO_x$ technology.

A companion report, which deals with further aspects of NTP de-$NO_x$ system performance and economics (especially for a particular hybrid system), was completed at the end of October by the McMaster University team under a subcontract managed by our Army Research Laboratory (ARL) team member Dr. Andrzej Miziolek. That project report is entitled "Development of Scaling Algorithms and Economic Evaluation for Non-Thermal Plasma Reactors - Adsorbant/Catalyzer Hybrid System for Control of $NO_x$ Released During Army and Related U.S. Department of Defense (DoD) Operations."

**Preparations for Field-Pilot Testing:**
Agreements for field testing of NTP de-$NO_x$ equipment are in the process of being finalized with Tinker AFB (under a memo of understanding - MOU), with a demonstration target of September 1999. It is anticipated that the field-pilot tests will use CMTC jet-engine exhaust for the field-pilot tests. Additionally, we have initiated exploration of technical and field-demonstration collaborations with two additional industrial partners, both with commercial prototype equipment experience relevant to de-$NO_x$.

In November 1998, a technical white-paper report on initial designs for field-pilot test equipment was completed ("Initial Designs of Electric-Discharge Non-Thermal Plasma Field-Pilot Demonstration Units for $NO_x$ Removal In Jet-Engine Exhaust: White paper for SERDP Project CP-1038"). The field-pilot demonstration is necessary to provide further data and operating experience to more fully evaluate economic and performance projections for NTP de-$NO_x$ technology and to design larger systems with confidence. This report discussed the exhaust stream to be addressed, the test setup, the candidate reactor systems, and projected operating parameters and specifications for the field-pilot units. Because the cost and logistics of using an electron-beam NTP reactor are, respectively, too high and too complicated for this project, we have limited our candidate systems to those based on electric-discharge-driven NTP reactors (which previous economic analyses have shown to be more cost effective). From the design options presented, a further downselection will take place before final designs are completed.

## Appendix

### SERDP Project CP-1038 Reports, Publications, and Papers for 1998

**Peer-Reviewed Journals or Papers**

1. "Advanced Oxidation and Reduction Processes in the Gas Phase Using Non-Thermal Plasmas," L.A. Rosocha and R.A. Korzekwa, *Los Alamos National Laboratory manuscript LA-UR-98-968 submitted to Journal of Advanced Oxidation Technologies*, accepted for publication after revisions (August 1998).

**Technical Reports**

1. "First Report on Non-Thermal Plasma Reactor Scaling Criteria and Optimization Models," L.A. Rosocha and R.A. Korzekwa, *Los Alamos National Laboratory Report LA-UR-98-125* (January 1998).
2. "Feasibility Analysis Report for Hybrid Non-Thermal Plasma Reactors," L.A. Rosocha, *Los Alamos National Laboratory Report LA-UR-98-206* (January 1998).
3. "Reactions of Oxides of Nitrogen ($NO_x$) Leading to the Formation of Nitric Acid ($HNO_3$) in Non-Thermal Plasmas," L.A. Rosocha, A.W. Miziolek, M.J. Nusca, J.-S. Chang, and J.T. Herron, *Los Alamos National Laboratory Report LA-UR-98-3598* (August 1998).
4. "Notes on Economics of Non-Thermal Plasma Processes for Jet-Engine Emissions Control," L.A. Rosocha, S.J. Kim, and J.-S. Chang (August 1998).
5. "Cost Analysis and Economic Assessment of Proposed Electric-Discharge Non-Thermal Plasma Processes for $NO_x$ Removal in Jet-Engine Exhaust: White paper for SERDP Project CP-1038," L.A. Rosocha, J.-S. Chang, K. Urashima, and A.W. Miziolek, *Los Alamos National Laboratory Report LA-UR-98-4926* (October 1998).
6. "Development of Scaling Algorithms and Economic Evaluation for Non-Thermal Plasma Reactors - Adsorbant/Catalyzer Hybrid System for Control of $NO_x$ Released During Army and Related U.S. Department of Defense (DoD) Operations." K. Urashima, S.J. Kim, and J.S. Chang, McMaster University Report Under Contract No. DAAL01-98-P-0741, A. Miziolek, Army Research Laboratory, Contract Monitor (October 1998).
7. "Initial Designs of Electric-Discharge Non-Thermal Plasma Field-Pilot Demonstration Units for NOx Removal In Jet-Engine Exhaust: White Paper for SERDP Project CP-1038," L.A. Rosocha, J.-S. Chang, and A.W. Miziolek, *Los Alamos National Laboratory Report LA-UR-98-5345* (November 1998).

**Conference/Symposium Proceedings Papers**

1. "Nonthermal Plasmas as Gas-Phase Advanced Oxidation Processes", L.A. Rosocha, *Proceedings of Second International Symposium on Non-Thermal Plasma Technology for Pollution Control,* Catholic University of Brasilia Press; edited by J.-S. Chang and J.L. Ferreira, pp. 1-6 (1998).
2. "Experimental and CFD Studies of Non-Thermal Plasmas for $NO_x$ Control," M.J. Nusca, P.A. Sagear, and A.W. Miziolek, *Proceedings of Second International Symposium on Non-Thermal Plasma Technology for Pollution Control,* Catholic University of Brasilia Press; edited by J.-S. Chang and J.L. Ferreira, pp. 23-26 (1998).

3. "Acid Gas Removal Characteristics of Corona Radical Shower System for Treatment of Stationary Engine Flue Gas," T. Nomura, S.J. Kim, T. Ito, A. Miziolek, L.A. Rosocha, and J.S. Chang, *Proceedings of HAKONE VI, International Symposium on High Pressure, Low Temperature Plasma Chemistry* (September 1998).
4. "SUENTP Code Simulation of Scaleup and Economic Evaluation of Non-Thermal Plasma Technology for Exhaust Gas Emission Control of Coal Fired Power Plants," S.J. Kim and J.-S. Chang, *to be published in Proceedings of International Conference on Electrostatic Precipitators* (September 1998).
5. "Factors and Uncertainties That Impact Economic Assessments of Non-Thermal Plasma Based Devices to Control $NO_x$ Generated from Jet Engine and Cruise Missile Test Facilities," L.A. Rosocha, S.J. Kim, K. Urashima, J.-S. Chang, A.W. Miziolek, M.J. Nusca, R.G. Daniel, and J.T. Herron, LA-UR-98-5474, *submitted to Asia-Pacific Workshop on Water and Air Treatment by Advanced Oxidation Technologies: Innovative and Commercial Applications* (December 1998).