ESTCP
Cost and Performance Report

(CP-9506)

Photocatalytic Destruction of Nitrate Esters in Air

July 2000

ESTCP
ENVIRONMENTAL SECURITY TECHNOLOGY CERTIFICATION PROGRAM

**ENVIRONMENTAL SECURITY
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U.S. Department of Defense

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LIST OF ACRONYMS

acfm	Actual cubic feet per minute
AOT	Advanced oxidation technology
AIA	Ambient impact analysis
CEM	Continuous Emission Monitor
DoD	Department of Defense
DRE	Destruction removal efficiency
ECAM	Environmental Cost Analysis Methodology
EDB	Extruded double-base
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
EUAC	Equivalent uniform annual cash flow
FAD	Forced air dryer
FSEC	Florida Solar Energy Center
HPLC	High-pressure liquid chromatography
IHD	Naval Surface Warfare Center, Indian Head Division
LPML	Low-pressure mercury lamps
MDE	Maryland Department of the Environment
MILCON	Military construction
MPML	Medium-pressure mercury lamp
NG	Nitroglycerin
NIOSH	National Institute for Occupational Safety and Health
NOx	Oxides of nitrogen
OAQPS	Office of Air Quality Planning and Standards
OSHA	Occupational Safety and Health Administration
PCU	Pollution control unit
PDC	Power distribution center
PDU	Process development unit
ppbv	Parts per billion by volume
PPCU	Photocatalytic pollution control unit
ppmv	Parts per million by volume
RAAP	Radford Army Ammunition Plant

SCC	System control center
scfm	Standard cubic feet per minute
SES	Southeastern Engineering Sales, Inc
TAP	Toxic Air Pollutants
TCE	Trichloroethylene
TiO2	Titanium dioxide
TWA	Time weighted average
UV	Ultraviolet
VOC	Volatile organic compound

ACKNOWLEDGMENTS

Appendix A contains a list of contacts for this demonstration.

Technical material contained in this report has been approved for public release.

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1.0   EXECUTIVE SUMMARY

Extruded double-base (EDB) propellant rocket motors are used to propel conventional munitions from a variety of tri-service platforms. Nitroglycerin (NG) emissions are generated during propellant annealing operations from the EDB rocket-motor manufacturing plant at the Naval Surface Warfare Center, Indian Head Division (IHD). Conventional technologies have been deemed unacceptable for controlling NG emissions due to the inherent hazards associated with the explosive-laden vapors. The objective of this Environmental Security Technology Certification Program (ESTCP) demonstration was to show that air-phase photocatalytic oxidation is a viable treatment technology for the destruction of NG air emissions.

Photocatalytic oxidation is a low-temperature, destructive process that uses ultraviolet (UV) light and a titanium dioxide (TiO_2) semiconductor photocatalyst to generate highly reactive species for destruction of organic molecules. In the case of NG, the reaction products are H_2O, CO_2, and NOx. A full-scale (650-scfm) photocatalytic pollution control unit (PPCU) was designed and built by the University of Central Florida's Florida Solar Energy Center (FSEC) for demonstration under this ESTCP project. The PPCU consisted of two modules, each containing 32 low-pressure mercury lamps (LPMLs), connected in parallel. The PPCU was designed to remove 10 ppmv of NG in air at a destruction removal efficiency (DRE) of 99.5%. The PPCU was installed at the IHD's annealing oven and tested using a combination of simulated and actual production operations. The demonstration consisted of 200 hours of testing and three trials totaling 250 hours of operation between July and October 1998.

Photocatalytic oxidation worked but the performance objectives were not met. At the design flow rate of 650 scfm, the PPCU was unable to remove 10 ppmv NG from an air stream that also contained lesser amounts of inert plasticizers. When challenged with low NG inlet concentrations (0.7 ppmv or less) and operated at half the design flow rate (324 scfm), the PPCU was able to maintain a DRE of 96% or greater.

Trojan Technologies, Inc., FSEC's industrial partner for the fabrication of the 650-scfm PPCU, provided an equipment cost estimate of $368,000 ($608,000 installed). The total annual operating cost was estimated to be $935,000 per year. This is equivalent to $3 per pound of propellant annealed or $14,652 per pound of NG destroyed. Approximately 95% of the operating cost was directly related to replacing the catalyst cartridge, which would be necessary at the beginning of each annealing oven cycle due to catalyst fouling.

The high operating cost for photocatalytic oxidation at the performance level observed during the demonstration compared to estimates of $49-70 per pound of NG destroyed by alternative technologies of carbon absorption or incineration, which have safety concerns. However, it is unlikely that the operating cost of photocatalytic oxidation could be reduced to a comparable low level by increasing the catalyst cartridge life.

The advantages of air-phase photocatalytic oxidation are very appealing, and the 650-scfm PPCU had many desirable features such as a modular design, low pressure drop, uniform catalyst illumination, and sanitary stainless steel construction. The unit was easy to operate, and had no problems operating intermittently. Excluding catalyst replacement, no maintenance was required on the PPCU during this demonstration. However, the technology will not be cost-competitive until

an effective solution to the catalyst fouling problem is developed. Then the high capital cost would be less important.

In its current configuration, photocatalytic oxidation is not an economical solution to the Navy's problem. It did not meet the performance requirements for use in the IHD annealing oven facility. The technology has potential applications only assuming the unit can be optimized and the catalyst life can be extended. A water scrubber/aqueous phase photocatalytic oxidation system has been selected over air-phase photocatalytic oxidation for use in the new P-149 annealing oven military construction (MILCON) facility at IHD.

2.0   TECHNOLOGY DESCRIPTION

2.1   BACKGROUND

In the early 1990s, IHD was faced with the requirement to reduce the emissions of NG from its production processes, and began investigating potential solutions to the challenge. One of the advanced oxidation technologies (AOTs) of interest to the Navy and Army for the treatment of air streams contaminated with nitrate esters was UV oxidation. The use of a photocatalyst in UV oxidation processes was being researched as a method to reduce operating costs by providing in situ oxidants. At that time, the majority of research in photocatalytic oxidation was in the aqueous phase. The challenge faced was to develop an air-phase AOT process to destroy the NG stack emissions.

IHD funded FSEC, which resulted in a viability demonstration of air phase photocatalysis and the development of a 5-scfm process development unit (PDU). The majority of this work focused on the Army's triple-base manufacturing process, specifically the NG in air emissions from the forced air dryer (FAD).

The approach for the ESTCP project in 1995 was to validate a scaled-up 50-scfm PDU at FSEC, and then to build a 650-scfm full-scale PPCU system for demonstration at two DoD sites. Additional details regarding the 50-scfm PDU can be found in the ESTCP demonstration plan [1]. The first full-scale demonstration was conducted at IHD, focusing on the annealing oven process. A subsequent demonstration was also planned at the Radford Army Ammunition Plant (RAAP). The project considered two full-scale designs:

(1)   Zentox Corporation had developed a prototype photocatalytic oxidation reactor and was prepared to test it at IHD. The Zentox reactor sacrifices uniform catalyst illumination to increase the catalytic surface area, achieve a small foot print, and provide for easy catalyst access.

(2)   A new "baffleless" FSEC design. The FSEC reactor is configured to provided uniform catalyst illumination.

Live tests were conducted at IHD during the summer of 1997, and both reactors performed comparably achieving 97-98 % DRE's. The two designs had many similarities and each excelled in different areas. The Zentox test results were presented at the Eighth International Symposium on Chemical Oxidation [2]. The FSEC results may be found in the FSEC final report [3]. The decision was made to complete the project using the new FSEC reactor design.

2.2   THEORY

Photocatalytic oxidation of organic molecules is a heterogeneous process that uses UV light and a titanium dioxide (TiO_2) semiconductor photocatalysts to generate highly reactive species in situ. These highly reactive species oxidize the organic molecules that adsorb onto the TiO_2 catalyst surface. The nature of the photochemical and photophysical events that occur at the surface is quite complicated although it is clear that, before photooxidation can occur, the target contaminant must adsorb onto the surface of the catalyst. The theory as it relates to the destruction of NG is detailed in the FSEC final report [3]. A detailed description of photocatalytic oxidation of organic compounds

has been prepared by Serpone [4]. Any compound (e.g. water) that absorbs the UV radiation or prevents the target contaminant from contacting the catalyst will result in decreased performance. Relatively small changes in waste stream composition can result in dramatic changes in performance.

The process by which organic contaminants are destroyed via heterogeneous photocatalysis can be described in seven steps, which occur simultaneously:

- Catalyst photoactivation
- Generation of active radicals on the surface of the photocatalyst
- Diffusion of the organic compounds through the bulk medium to the catalyst surface
- Adsorption of the compounds onto the catalyst surface
- Reaction of the compounds with reactive radicals
- Desorption of the reaction products from the catalyst surface
- Diffusion of the reaction products into the bulk media.

Although it seems to differ for each compound, there is a point at which increasing the irradiance by moving the light closer to the catalyst reduces the efficiency of the reactor.

It is generally believed that the hydroxyl radical, oOH, is the major oxidizing species involved in the oxidation of organic contaminants. Hydroxyl radicals rapidly attack virtually every organic contaminant, and in the presence of oxygen this initiates a complex cascade of oxidative reactions leading toward complete oxidation and mineralization to CO_2, H_2O, and N2 [5]. As the number of contaminants in the influent stream increases, the probability of or mineralization decreases, although not required for a successful application of photocatalytic oxidation. However, he effects of the reaction products on the reaction rate and effluent composition must be evaluated. According to Raissi et. al. [3], the mass transfer to and from the catalyst surface limits the process efficiency. A detailed treatment of adsorption and desorption in photocatalytic oxidation is presented by Pichat and Herrmann [6].

2.3   ADVANTAGES

There are many potential advantages of a photocatalytic oxidation system over other possible choices for treating airborne NG emissions are shown in the following list. The advantages that were not realized during this demonstration are marked with an asterisk.

- It destroys the pollutants and produces minimal by products.
- It achieves high efficiencies for dilute streams (95% plus).
- It is flameless and operates at relatively low temperatures (30-55℃).
- It can selectively destroy NG in mixed streams (e.g. acetone, ethanol, NG).*
- It creates oxidants in situ so there are no additional chemicals required.
- Electricity is the only required input.*
- Operating costs are low.*
- The pressure drop through the unit is low.
- It is easy to operate and maintain.
- It can be operated intermittently.

2.4   ALTERNATIVE TECHNOLOGIES

A review of the remaining treatment alternatives for vapor phase NG yielded four possibilities [7]. These four technologies are thermal treatment (direct flame or incineration), absorption (scrubbing), biofiltration, and adsorption (activated carbon). The recommended abatement technologies for the IHD annealing oven were incineration or water scrubbing (absorption) in combination with activated carbon (adsorption) treatment of the wastewater.

Although incineration is a proven technology for the destruction of VOCs, there are safety concerns pertaining to the incineration of explosive compounds [8]. Incineration is generally applied to heavily laden VOC steams, and typically achieves a 99% DRE. Although there are many different incinerator designs, they can be broadly classified as thermal systems and catalytic systems. Catalytic systems employ a bed of noble metal catalyst that increases the reaction rate and enables conversion at lower reaction temperatures (150 to 500 °C) than in a thermal incinerator. In general, a tradeoff exists between the higher operating cost of thermal incinerators and the higher capital cost of catalytic incinerators [9]. Heat recovery can be employed to improve the economics and lower the operating costs. Catalytic incinerators are not tolerant of wide variations in the inlet composition although much more so than photocatalytic oxidation units. Fouling is an issue. Catalysts used in incinerators are more expensive than the TiO_2 used in photocatalytic oxidation systems.

In 1998, a catalytic solvent vapor incinerator was installed at IHD's Nitramine Propellant Mixing facility. This system is capable of handling air streams with as much as 10 ppmv of NG. The total direct cost for the incinerator was $1.2 million. It is expected to come online in FY 00. No operating data were available at the time of this report.

Water scrubbers are typically inexpensive but only remove, and not destroy, the NG. They would require a large amount of water, and would require treatment of both the wastewater and the spent carbon. The DRE is 55% to 95% depending on the solubility of the compound being removed. Pressure drops through these systems tend to be high. Water scrubbers can operate intermittently, but startup and shutdown tend to be complex. These systems have relatively high maintenance requirements and can require significant operator interface while running. Water systems must be designed to prevent the NG from condensing, collecting, and, most importantly, freezing. Two variations of water scrubbing are: (1) adding chemicals to the water (either acid or caustic) or (2) recycling the water through an aqueous phase photocatalytic system. Both approaches eliminate the carbon and reduce the water consumption. The use of an aqueous phase photocatalytic oxidation system increases the capital equipment cost but eliminates the chemical handling and wastewater issues.

Biofiltration is an inexpensive and safe process applicable to many large-scale dilute VOC problems. It is effective at treating nitrogen-containing compounds and has been proven to handle explosive material such as acrylonitrile. The only costs are for the disposal of excess, inert biomass and the electricity for the pump. Typically, DREs are 90%. These systems suffer from all of the challenges facing a water-scrubbing system in addition to those related to maintaining a microbial community. They are not tolerant of large changes in inlet concentrations and are not suitable for intermittent operation.

Direct treatment of the annealing oven effluent using carbon adsorption was not recommended due to the danger of condensation and accumulation of NG in the system beds. Due to the incompatibility of NG with activated carbon and the potential to collect large quantities of NG inside the treatment vessel, the U.S. Army, the U.S. Navy and, as far as is known, the entire explosive community has discounted carbon adsorption as a viable treatment alternative for vapor phase NG [10]. However, carbon adsorption is being successfully used in a production setting at the Schering Corp. of Miami Lakes, Florida to treat NG emissions from its pharmaceutical manufacturing process. According to the 1997 toxic release inventory their system had a 95% DRE [11].

3.0   DEMONSTRATION DESIGN

3.1   PERFORMANCE OBJECTIVES

The objective of the 650-scfm PPCU demonstration was to demonstrate that photocatalytic oxidation is a viable treatment technology for the reduction of NG air emissions generated from propellant processing operations. A full-scale prototype was designed and tested at the existing IHD annealing oven facility. The 650 scfm PPCU design parameters were developed from the requirements for the new P-149 annealing oven military construction (MILCON) project at NSWC, IHD which are similar to the existing ovens. The PPCU would be considered acceptable if it could reduce in a safe and economical manner the NG concentration of the annealing oven exhaust, containing a maximum NG concentration of 10 ppmv and minor amounts of inert plasticizers, by 99% when flowing at 650 scfm. The answers to the following questions were sought in the attempt to validate this technology:

•   What is the maximum sustainable DRE?
•   How do inert plasticizers found in typical EDB propellant affect performance?
•   How long do catalyst cartridges last before breakthrough occurs?
•   How much NOx is generated during treatment? Will this technology require NOx treatment?
•   Can the PPCU be operated intermittently?
•   Is the PPCU easy to maintain?
•   Is the PPCU an economically feasible solution to the Navy's problem of NG emissions?

3.2   DEMONSTRATION SITE/FACILITY BACKGROUND & CHARACTERISTICS

IHD has the capability to manufacture a vast array of propellant and explosive products, many of which contain NG as a major ingredient. IHD has the potential to emit NG vapors from over 90 different sources in 82 buildings. The solventless extrusion process used to manufacture EDB rocket motors accounts for a large number of these sites. The initial steps in the manufacture of EDB rocket motors are completed at RAAP. The propellant is delivered to IHD in the form of thin, 0.09-inch-thick by 4-inch-wide sheet stock strips that are rolled into 15-inch-diameter "carpet rolls". Extrusion and machining to final form at IHD produces rocket motor grains from 0.3 to 12 inches in diameter. During the extrusion process, stress concentrations are induced in the grains, which are relieved in annealing ovens. Finally, end inhibitors are applied.

Of all the 90 NG emitting sources, IHD has determined that the annealing ovens used in the manufacture of EDB rocket motors are the worst. IHD is presently in violation of the Code of Maryland Regulations 26.11.15: "Toxic Air Pollutants (TAPs)." The 1998 MDE Toxic Air Pollutant Screening Level Database states that the 8-hour screening level for NG is 4.6 µg/m3. IHD has been unable to demonstrate compliance with the TAPs regulation for NG emissions since the first ambient impact analysis (AIA) was reported to MDE in 1991. Under the supervision of MDE, IHD has been aggressively pursuing compliance with state regulations since 1992. MDE recognizes that the inherent danger of NG prevents the use of off-the-shelf pollution control equipment. This safety concern has been instrumental in the MDE's decision not to take regulatory action against the facility to date. Until compliance can be demonstrated, MDE will no longer approve any "Permits to Construct" or registration updates that include NG emissions.

The solventless extrusion production plant is the only Navy facility of this type and is classified as mission critical. Many of the items produced in this facility support triservice DoD requirements and foreign military sales. There are currently two annealing oven facilities at IHD, Buildings 579 and 871, which will both be replaced once the new MILCON annealing oven project is complete. Buildings 579 and 871 are located approximately 800 feet and 50 feet, respectively, from the fence line. Their proximity to the fence line is a significant factor in IHD's inability to comply with the state regulations. Building 871, pictured in Figure 1, consists of 20 ovens.

Figure 1. Annealing Oven Facility at Building 871.

IHD has been designated as a mobilization production facility for the Mk 90 propellant grain and the Mk 22 rocket motor by the Army Industrial Operations Command. IHD is currently permitted to process annually more than 6 million pounds of double-base propellant, and did not require any additional permits or approvals for this demonstration.

3.3   PHYSICAL SETUP AND OPERATION

To ensure that the full-scale unit would be industrially robust and commercially available, FSEC subcontracted the fabrication of the unit to Trojan Technologies, Inc., a Canadian company that manufactures UV water treatment systems and was interested in developing a commercial presence in the air-phase photocatalytic oxidation market.

The PPCU was installed at the existing IHD annealing oven facility located at building 871. Figure 2 shows the layout of the equipment. The PPCU was installed on a temporary 12 by 16-foot plywood platform. A temporary 50-foot polypropylene duct system was installed to connect the unit to the annealing oven. In a permanent installation, a metal duct would be required.
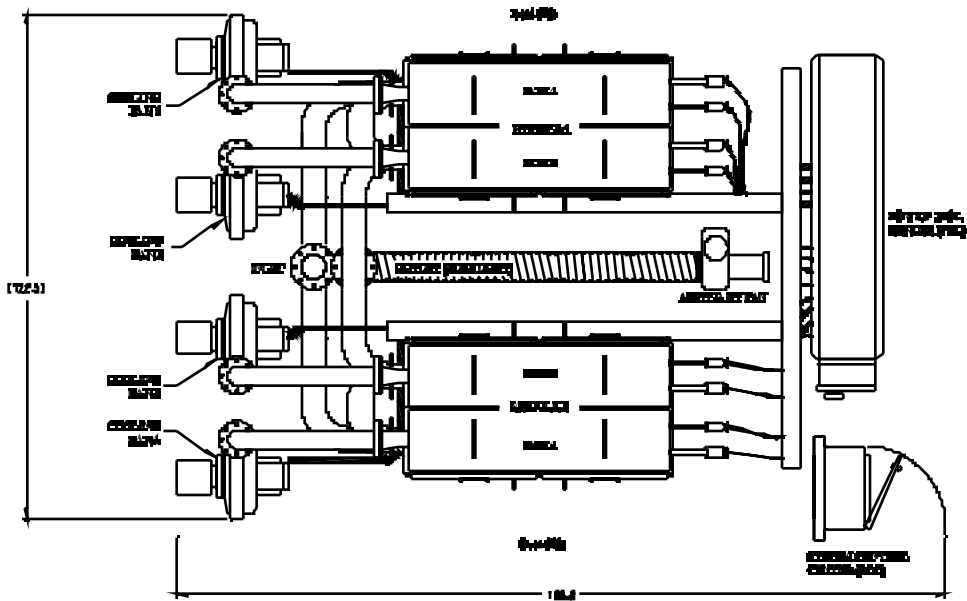
Figure 2. Equipment Layout.

FSEC designed the 650 scfm PPCU to remove 99.5% of the NG released from an annealing oven having a flow rate of 650 scfm and containing a maximum concentration of 10 ppmv NG. The PPCU was designed to be easy to install, operate, control, and maintain. Adding the PPCU had no effect on the annealing process. The PPCU, pictured in Figure 3, was composed of two stand-alone modules, an integrated thermal management system, a power distribution center (PDC), a system control center (SCC) and four external cooling fans. The PPCU modules were made of 316 stainless steel welded construction. The modules were connected in parallel via external 6-inch-diameter piping located on the ends of the unit. The control system for the PPCU was based on the Trojan Technologies UV 3000 water treatment system. All the electrical components were standard off-the-shelf items. The PPCU operated off a single 208-volt, three-phase power input that was fed to the PDC. The total electrical power requirement was 19 kVA. The PDC also housed the communication board that controlled and monitored the lamps. All communications to and from the PDC originated from the SCC via an RS 422 serial link. The operator controlled the system by interfacing the SCC via local or remote terminals. Local operator interface was accomplished via a menu-driven workstation that included a LCD display and two keyboards. The system was password protected and was fitted with a meter to record the cumulative hours of operation.

Each module of the PPCU was made up of two banks of low-pressure mercury lamps (LPMLs), and each bank contained 16 LPMLs. The total number of LPMLs in the unit was 64. The LPMLs emit essentially monochromatic light having a wavelength of 253.7 nm. Lamps were accessed via the top of each module through a non-contact air-cooling compartment. The electrical connections for each lamp were housed in this compartment. The lamp ballasts were located opposite the entrance and were housed in aluminum ballast boxes. The cooling compartment was separated from the contaminated fluid by an outer quartz sleeve, which resembled a large test tube and enclosed the lamps. The sleeves were made of type 214 clear fused quartz circular tubing and were rated for 89% UV transmission.

Figure 3. 650-scfm PPCU (Inlet Manifold Removed).

The PPCU used ambient air to cool the lamps. Thermocouple sensors measured the exhaust cooling air temperature and automatically began the airflow when the temperature reached the desired set point. The cooling air was directed into each quartz sleeve via a quartz dip tube, which extended to the middle of each lamp. Cooling air was supplied by four 1-hp cooling fans (one per bank, as shown in Figure 3) to a manifold located in the cooling compartment, and was distributed to each lamp via plastic tubing. The length of each tube was sized to promote uniform air flow. The air exited via the annulus created by the lamps and the protective quartz sleeve, and then through vents located in the side of the cooling air compartment.

The catalyst was deposited on the inner surface of a cylindrical cotton fabric support. These catalyst cartridges, or socks, had a nominal catalyst loading of 1.8 mg/cm^2. The catalyst used in the PPCU was Uniti 908, manufactured by Kemira, Inc. The catalyst loading varied by less than 10% along stocking length. The socks were placed around the outer quartz sleeve so that the TiO_2 catalyst received a uniform irradiance. The illuminated surface area per sock was 5,252 cm^2 per sock. The separation distance between the lamp, and the catalyst surface, which is critical for optimal destruction, was fixed by the geometry of the unit.

The catalyst socks were secured to the unit with plastic cable ties. Plastic ties were selected over metal clamps to eliminate metal pinch points. The top of the catalyst cartridge attached to a bulkhead, through the center of which passed the LPMLs and quartz sleeves. The bulkhead forced the gas to pass through the illuminated catalyst cartridge. Contaminated gas was prevented from entering the cooling compartment by two O-ring seals on the outside of the quartz tubes. The bottom of each sock was attached to a nipple at the bottom of the bank. The contaminated air was distributed to each sock via a plenum located beneath the banks. The plenum was fitted with Teflon drain plugs to allow for cleaning. Access to the catalyst cartridges was provided by side access doors

Figure 4. Interior of 650-scfm PPCU Module (Lights "On" and No "Socks").

as shown in Figure 4. Each door housed a neoprene gasket, which sealed the unit, and contained a view port to enable visual inspection of the unit during operation.
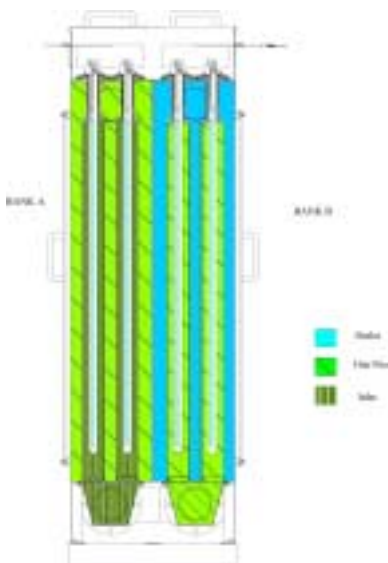
Figure 5. Cross Section of 650-scfm PPCU.

The PPCU could be operated in either a forced flow or an induced flow configuration. The cross-section of one module is shown in Figure 5. As the contaminated flow entered the externally located inlet manifold, it split, and half was directed to each module. Once the flow reached a module, it entered a plenum at the bottom of the first bank or "Bank A." The contaminated gas split into 16 streams as it flowed up and out of the plenum. The contaminated gas is indicated as "Inlet" in Figure 5. The contaminated gas traveled into the irradiated annulus between the outer quartz sleeve and the catalyst support or sock. The gas was forced through the catalyst cartridge, ensuring intimate contact between the contaminant and the activated catalyst. The largest portion of the NG

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was removed in this first stage. The partially treated gas recombined in Bank A and exited via a 6-inch-diameter exit port located above the entrance port near the top of the unit. The gas flowed to the inlet of the second bank or Bank B via external conduit. The partially treated gas is labeled as "One Pass" in Figure 5. Because the banks of each module were identical, the contaminated air flowed into the bottom plenum and through Bank B in the same manner as previously described. The exhaust from Bank B of each module was combined into one stack and emitted into the atmosphere.

Maintenance for the PPCU was easily accomplished and could be performed by the existing work force. Handling the quartz sleeves, LPMLs, and catalyst cartridges required the use of gloves to prevent contamination from body oils that could damage these items. The most complicated part of the PPCU was the control system. If a problem arose on the control panel that could not be identified by the in-house electronic technicians, a modem allowed the manufacturer to troubleshoot the system remotely.

The pressure drop through the PPCU was measured to be less than 1 inch water gauge. With an auxiliary fan, a maximum flow rate of 498 acfm was achieved. The PPCU and the external piping were insulated with 1 inch of fiberglass insulation to prevent NG from condensing on the interior walls.

Operating the PPCU required one day of hands-on training to learn the menu commands.

3.4   SAMPLING AND MONITORING PROCEDURES

The data collected to evaluate the performance of the PPCU were inlet NG concentration, outlet NG concentration, flow rate, ambient conditions, and oven temperature. Outlet NOx concentration and cooling air exit temperature measurements were also made.

Inlet and outlet gas samples were taken simultaneously. Simultaneous sampling minimized errors associated with changing NG concentrations and allowed for direct comparison of inlet and outlet samples. The Occupational Safety and Health Administration (OSHA) Method 43 with minor modifications was followed for sample collection [1] [12]. NG sample ports were located close to the inlet and outlet of the PPCU in the vertical sections of duct. Sample tubes were located on the centerline and sized to ensure sampling was isokinetic. The ports were positioned to ensure there was eight pipe diameters of straight pipe before the sample port and two after them. Standard sorbent tubes as described in the method were used to collect the outlet samples and larger custom sorbent tubes were used to collect the inlet samples. Samples were initially taken at 30-minute intervals, but this was increased to 60 minutes after the first test.

A pitot tube was used to determine the flow rate into the PPCU in the long portion of ductwork connecting the stack and the inlet manifold. Differential pressure readings were taken with each set of NG samples. An oil-filled manometer was initially used to measure differential pressure, but it was eventually replaced with a more stable Magnehelic gauge.

Ambient conditions were monitored by an automated weather system located approximately one-half mile from the test site. The oven temperature and annealing time were collected by the oven control system.

NOx measurements were taken from the exhaust stack of the auxiliary blower with a pre-calibrated API Model 200A Chemiluminescent NOx analyzer with a range of 50 to 1,000 ppbv. The air sample was diluted with ultra-pure air. Adjusting the dilution gas flow rate regulated the dilution rate. The flow rates of the dilution gas and the sample were measured using rotameters. A baseline was taken half an hour prior to loading the oven with propellant. Flow rate and NOx readings were manually recorded every 15 minutes throughout each test.

The lamp cooling exit air was measured using thermocouples mounted on the PPCU. These thermocouples were also used to control the cooling fans. Temperature measurements were manually recorded with each set of NG samples.

The total residual NG on the socks was estimated from three 4-in^2 samples taken along the length (top, middle and bottom) of the used socks. However, this original method to estimate the amount of residual NG remaining on the socks was flawed due to the wrong assumption that the residual NG was uniformly dispersed on the surface of the sock. Analyses were made during the second test on whole socks to provide more accurate estimations of residual NG (see section 4.5).

3.5   ANALYTICAL PROCEDURES

The concentration of NG entering and exiting the PPCU was measured using OSHA Method 43, which employs high-pressure liquid chromatography (HPLC) using either a thermal energy detector or an UV detector. A similar HPLC procedure also was used to evaluate the residual NG on the socks. Samples were soaked in acetonitrile for 24 hours, and then the extract was analyzed using IHD lab procedure 3330.6, "Analytical Method for the Determination of Nitrate Esters in Wastewater." The limit of detection for this method is 0.00025 mg NG per in^2 of sock.

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4.0   PERFORMANCE ASSESSMENT

4.1   TEST MATRIX

Propellant formulations were selected to ensure that the PPCU influent contained all of the volatile ingredients that are regularly emitted during an annealing operation at IHD. A selective destruction test was not included in the demonstration because the EDB manufacturing process is solventless. The test matrix, shown in Table 1, was designed to increase the challenge to the PPCU as the testing progressed. The original demonstration plan [1] included a repeat of the first test using only one module. The remaining tests were to be completed using the appropriate number of modules based on the results of the first two tests. However, all single module tests were cancelled after reviewing the data from Test One.

Originally, all the tests were to be conducted using sheet stock propellant. The tests were arranged so the inert plasticizer content of the propellant went up as the NG content decreased. Test One was designed to generate the maximum NG vapor and test the upper design limits of the 650 PPCU. Test One was conducted using sheet stock propellant. Laboratory testing conducted prior to the demonstration indicated that the photocatalytic destruction rate of NG is significantly inhibited in the presence of diethylphthalate, an inert plasticizer used in double-base propellant [3]. Poor performance during Test One necessitated evaluation in the subsequent tests of the performance of the unit at the lower end of the design envelope. Actual production rocket motor billets were used for the subsequent tests to reduce the NG concentration of the PPCU influent.

Mk 22 rocket motor units were used for Test Two. These had a significantly lower surface area than the sheet stock, they were made of N5 propellant, which has the lowest NG content of the proposed propellants, and the annealing temperature was low. The only drawback to using the Mk 22 was that it had the highest inert plasticizer content of the three propellants used in the demonstration.

Table 1. Test Matrix for 650-scfm PPCU.

Test No.	Propellant	Oven charge form	Oven temp. (ºF)	Flow rate (scfm)	Duration (hr)	No. of modules	Predicted DRE (%)
1	HEN12	Sheet stock	165	416	10	2	100
2	N5	Grain sheet stock	143	324	22	2	100
3	AA6	Grain sheet stock	150	325	168	2	100

4.2   TEST ONE

The first test was designed to mimic the laboratory tests as closely as possible and test the upper design limits of the 650 PPCU. The inert plasticizer content was minimized and NG content was maximized. This was accomplished by operating the annealing oven at the maximum allowable temperature, using sheet stock propellant to maximize the exposed propellant surface area and selecting HEN 12 propellant. HEN 12 propellant has the highest NG content and lowest inert plasticizer of any propellant currently used in production at IHD. The data are summarized in Table 2. The PPCU was unable to maintain a 99% DRE throughout the test. The DRE declined

throughout the test to a final value of only 6%. The scatter in the data is large; however, the performance trend is downward. No inert plasticizer was detected entering the unit, however tests at FSEC on a used sock revealed inert plasticizer on the catalytic sock.

The three most likely causes of the poor performance in Test One are: (1) poor lamp cooling due to high ambient temperatures, which would reduce the output of the UV lamps; (2) contaminant overloading; (3) non-uniform contaminant deposition, which would preclude optimum performance; and (4) inert plasticizer loading. The photograph in Figure 6 shows that the contaminants were preferentially distributed to the socks farthest from the inlet. FSEC believed that the inert plasticizer, di-n-propyladipate, was also responsible for a performance reduction. They estimated that 21 mg of inert plasticizer was retained on the used sock they analyzed.

Table 2. Test One Data.

Sample Number	Sample Start Time	Stack Temp • F	Flow Rate acfm	NG DRE %	NG Inlet Concentration ppmv	NG Outlet Concentration ppmv	NOx Outlet Concentration ppmv
1001	7/24/98 9:16	156	496	100%	2.206	0.000	8.223
1002	7/24/98 9:45	160	498	99%	3.913	0.027	16.262
1003	7/24/98 10:29	162	487	76%	4.783	1.146	10.288
1004	7/24/98 11:01	157	491	67%	5.820	1.894	30.866
1005	7/24/98 11:40	163	491	27%	6.534	4.766	24.937
1006	7/24/98 12:32	165	497	51%	8.352	4.053	16.898
1007	7/24/98 13:00	165	483	56%	8.478	3.725	12.257
1008	7/24/98 13:33	163	471	75%	8.536	2.112	9.272
1009	7/24/98 14:05	166	469	67%	9.950	3.290	7.889
1010	7/24/98 14:30	166	472	58%	10.620	4.483	7.176
1011	7/24/98 15:00	166	478	41%	10.348	6.125	5.467
1012	7/24/98 15:30	166	478	37%	9.994	6.249	4.825
1013	7/24/98 16:00	165	483	10%	8.223	7.399	4.439
1014	7/24/98 16:27	165	489	44%	9.306	5.206	2.600
1015	7/24/98 17:00	165	489	57%	8.491	3.643	2.248
1016	7/24/98 17:34	164	494	36%	10.854	6.959	2.333
1017	7/24/98 18:07	164	497	35%	10.584	6.896	2.333
1018	7/24/98 18:45	164	497	6%	9.964	9.372	2.294
	Average (Starting at Sample 1007)	165	483	43%	9.612	5.455	5.261
	Max	166	497	75%	10.854	9.372	12.257
	Min	163	469	6%	8.223	2.112	2.248
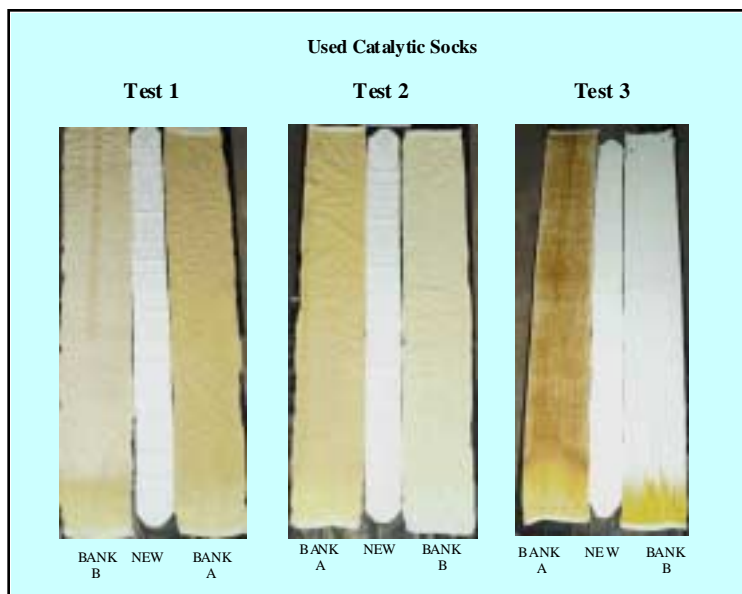
Figure 6. Interior of Used Catalytic Socks.

The mass balance in Table 3 accounts for nearly all of the NG. The masses of each stream are estimates and were calculated by splitting the test into two sections. The first section or transient section was composed of samples 1001 through 1006, and the second, or steady state, section was composed of the remainder of the samples.

Table 3. Test One NG Mass Balance.

Estimates	NG		Percent of Inlet
	Mgs	**Moles**	
Total NG into unit	589,603	2.597	100.00
Total NG out	308,026	1.357	52.24
Equivalent NG as NOx out	246,478	1.086	42
Residual NG on all socks	17,408–9,661	0.077–0.043	2.95–1.64

4.3   TEST TWO

The second test was conducted with a reduced inlet feed concentration of 0.7 ppmv NG, and was scheduled to last 10 hours while operating at a reduced oven temperature. The lamp temperature was measured to be about 59 °C (138 °F). The data are presented in Table 4. The performance of the PPCU during Test Two was dramatically improved. The average NG DRE for this test was 96%. The plasticizer was detected in the inlet, and it was completely removed from the PPCU effluent. The NOx levels generated during this test were slightly higher than the maximum possible stoichiometric values. On average, the values were in line with the expected emission rates. At the 10-hour mark, the light emanating from Bank B was not dark green as it was during Test One. This was taken to indicate an improvement in performance, and the test was continued for the remainder of the annealing cycle. No additional samples were taken until the final 3 hours of operation. The final data point was not used in the analysis because it is obviously erroneous.

In every case the outlet concentration was below the maximum allowable NG emission limit calculated by the IHD environmental office. This test showed that for low inlet concentrations, photocatalytic oxidation is an effective technology to abate NG emissions. It also indicates that a properly sized and optimized PPCU could be used to mitigate the NG emissions from an annealing oven.

The residual NG in the socks at the completion of the Test Two was not substantially lower than the values measured for the Test One. Sock samples were taken from the ends and the middle of each bank in an effort to determine whether NG was being preferentially delivered to the socks farthest from the inlet. All the socks appeared to contain similar amounts of NG. No significant difference was detected between the socks in Bank A and those in Bank B.

Table 4. Test Two Data.

Sample Number	Sample Start Time	Stack Temp (°F)	Flow Rate acfm	NG DRE %	Inlet NG Concentration ppmv	Outlet NG Concentration ppmv	Nox Outlet Concentration ppmv	Inlet DEP Concentration ppmv	DEP DRE %
2001	8/18/98 17:08	121	376	100%	0.070	0.000	0.120	0.000	-
2002	8/18/98 18:09	136	367	91%	0.208	0.019	0.749	0.034	100%
2003	8/18/98 19:26	140	369	90%	0.256	0.025	1.814	0.071	100%
2004	8/18/98 20:00	141	369	91%	0.437	0.039	2.320	0.082	100%
2005	8/18/98 21:14	143	369	80%	0.471	0.094	1.323	0.088	100%
2006	8/18/98 22:06	144	369	100%	0.599	0.000	1.218	0.117	99%
2007	8/18/98 22:59	144	373	90%	0.731	0.077	1.494	0.155	100%
2008	8/19/98 0:03	143	355	100%	0.712	0.000	2.660	0.141	99%
2009	8/19/98 0:59	144	355	100%	0.559	0.000	2.239	0.150	100%
2010	8/19/98 2:01	144	362	91%	0.785	0.067	2.226	0.163	99%
2011	8/19/98 2:47	144	355	99%	0.907	0.009	1.874	0.203	98%
2012	8/19/98 14:03	147	355	100%	0.935	0.000	NA	0.192	100%
2013	8/19/98 14:43	148	362	100%	0.924	0.000	1.774	0.179	100%
2014	8/19/98 15:33	147	362	52%	0.920	0.440	1.667	0.181	52%
	Average (Starting at Sample 2005) Neglecting 2014	144	362	96%	0.7359	0.0	1.85	0.1543	100%
	Max	148	373	100%	0.9348	0.1	2.66	0.2028	100%
	Min	143	355	80%	0.4713	0.0	1.22	0.0822	98%

The mass balance for Test Two accounted for 92% of the NG and is presented below in Table 5.

Table 5. Test Two NG Mass Balance.

Estimates	NG		Percent of Inlet
	Mgs	Moles	
Total NG into unit	83,696	0.369	100.00
Total NG out	3,312	0.015	3.96
Equivalent NG as NOx out	66,354	0.292	79.28
Residual NG on all socks	12,478–6,925	0.055–0.031	14.8–8.3

4.4   TEST THREE

The final test was designed to test the performance of the unit during a week-long annealing cycle with an increased NG inlet concentration. The oven was charged with two carts of Mk 93 rocket motor grains, which contained AA6 propellant and had a NG content of 39% by weight. The ambient temperature was slightly above 10 °C (50 °F) during this test, so no extraordinary measures were taken to lower the lamp cooling air temperature. One new lamp was installed in the unit. This lamp had a thermocouple bonded to the lamp at its midpoint in an effort to more accurately monitor the temperature. The lamp temperature during the test was measured to be 60 °C (140 °F). NG samples were taken every hour for the first 10 hours. Thereafter, sampling occurred only two times per day. The test extended through a weekend, and no samples were collected during this period.

The data from Test Three are presented in Table 6 and the NG mass balance is presented in Table 7. No NG could be detected entering the unit during the first 23 hours. This was very perplexing because the NG concentration was expected to be higher than during Test Two. The AA6 propellant had an increased NG content, the Mk 93 grains had a surface area equivalent to the Mk 22s, and the annealing oven set point was increased by 10 degrees. NG was detected entering the unit later in the test. These data were used to calculate the average performance starting at sample 3010. The average DRE was 94% taken over the last 146 hours.

The mass balance for the same time period shows that even when NG was being detected, the PPCU was unexplainably producing an excess of NOx. At the onset of the test, the NOx emissions were greater than expected and declined as the performance declined. The NOx values were determined by averaging the NOx reading taken at the start and end of the NG sampling. The maximum NOx emission should have been three times the NG inlet concentration based on stoichiometry. There were no other nitrogen-containing compounds in the waste stream except the stabilizer. It is unlikely that the stabilizer, 2-nitrodiphenylamine, has any appreciable effect on NOx emissions because of its low concentration and its extremely low vapor pressure.

Table 6. Test Three Data.

Sample Number	Sample Start Time	Stack Temp °F	Flow Rate acfm	NG DRE %	Inlet NG Concentration ppmv	Outlet NG Concentration ppmv	Outlet Nox Concentration ppmv
3001	10/22/98 11:03	123	358	-	ND	ND	0.042
3002	10/22/98 12:00	140	366	-	ND	ND	2.264
3004	10/22/98 13:37	144	368	-	ND	ND	6.211
3005	10/22/98 14:03	145	371	-	ND	ND	7.232
3006	10/22/98 14:58	146	368	-	ND	ND	8.967
3007	10/22/98 15:57	146	368	-	ND	ND	6.769
3008	10/22/98 17:05	147	368	77%	0.062	0.016	7.549
3009	10/22/98 17:38	147	375	-	ND	0.003	8.044
3010	10/22/98 18:36	147	368	-	ND	0.001	8.639
3011	10/23/98 9:33	151	369	98%	0.748	0.017	11.516
3012	10/23/98 12:19	152	376	97%	0.820	0.022	11.036
3013	10/26/98 13:09	154	371	91%	0.836	0.079	13.664
3014	10/26/98 20:37	150	373	86%	0.499	0.070	9.502
3015	10/27/98 13:01	150	373	100%	0.530	ND	8.309
3016	10/27/98 20:45	148	369	78%	0.301	0.066	6.944
3017	10/28/98 14:57	151	372	100%	0.467	ND	8.538
3018	10/29/98 11:09	124	368	100%	0.204	ND	4.491
	Average (starting at sample 3011)	147	371	94%	0.55	0.051	9.250
	Max	154	376	100%	0.84	0.079	13.664
	Min	124	368	78%	0.20	0.017	4.491

Table 7. Test Three NG Mass Balance.

Estimates	NG		Percent of Inlet
	Mgs	Moles	
Total NG into unit	491,408	2.165	100
Total NG out	4,688	0.021	1
Equivalent NG as NOx out	2,634,993	11.608	536
Residual NG on all socks	1,791	0.008	0

4.5   INSPECTION OF CATALYST SOCKS

At the conclusion of the tests, socks were sampled from the middle position of each bank and tested for residual NG. NG was detected on every sock. No difference was measured between the socks in the first bank, "Bank A," and the socks in the second bank, "Bank B." The socks from both banks were discolored at the conclusion of the test (see Figure 6 on page 17). The socks in Bank B were lighter in color than those of Bank A. A pleat caused the dark streak on the sock taken from Bank B by preventing illumination. A similar effect was also seen on the lower portion of each sock, corresponding to the entrance region where there is no lamp. This illustrates that the change in color was a photocatalytic effect rather than due to filtration.

Inspection of the catalyst socks at the completion of the Test Three resulted in several important observations. There were stains on the outside of the socks, which had never been seen before. Although the outsides of the socks were stained, the interiors of the socks were uniform in color. Perhaps more importantly, the socks in Bank B of each module were not as discolored as in the previous two tests. In fact, the socks in Bank B looked reusable as shown in Figure 6. Two socks were sampled from each module for residual NG measurements. The socks were taken from opposite ends of the same bank. The residual NG measurements for Bank A showed a per sock concentration of 52 and 9 mg. The high concentration occurred at the end of the unit farthest from the inlet. Bank B showed no difference between the positions, and each sock contained 26 mg of NG.

There was a distinct color difference between the Bank A socks of Tests One and Two, which were exposed to UV light for a short time, and those of Test Three, which were exposed to the UV light for 168 hours. In the first two tests, the color was yellow, whereas in the last test the color was dark brown. In the first two tests, the dark discoloration corresponded to reduced performance but, in Test Three, the performance did not seem to decrease. It is thought that the dark coloration was due to degradation of the socks. The socks, although still intact, had suffered mechanical degradation. Upon removal, the socks were very dusty and could be easily torn by hand. The combination of mechanical degradation and discoloration indicated that the socks could not be used continuously for one year. Furthermore, to be sure that the contaminants are destroyed, it is recommended that the socks be replaced after each run.

The non-uniform deposition of contaminants is clearly illustrated in the photographs in Figures 7 and 8 of the used socks from Test Three. The stains located on the outside of the socks indicated the area on which contaminants were concentrated. Since the stains were not uniformly distributed along the length of the socks, it seems reasonable to conclude that the NG was not uniformly distributed along the length of the socks. Figure 8 also clearly shows that the first 4 inches of the socks are a different color than the remainder of the sock. This area corresponded to the portion of the sock in which no lamp extended and indicated an area of less photocatalytic activity.
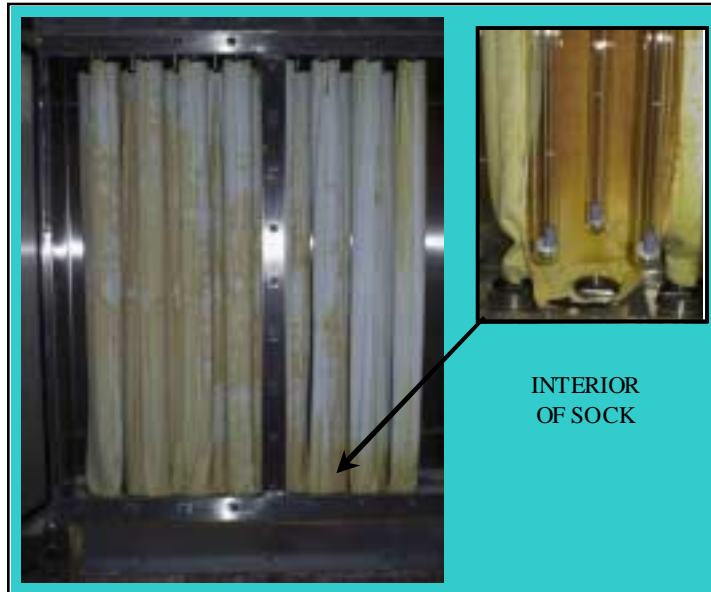
INTERIOR
OF SOCK

Figure 7. Used Catalyst Socks in Bank A after Test Three.

Figure 8. Used Catalytic Socks in Bank B after Test Three.

While independently analyzing socks from the first test, FSEC reported a discrepancy between the data gathered by IHD using the sampling method and their data gathered using a complete extraction technique. FSEC reported a value of 65 mg per sock compared to the IHD estimated residual NG value of 275 mg per sock.

A study was conducted during the Test Two to investigate this discrepancy. In the study, three used socks were tested using the sampling method. The remainders of the three socks were then subjected to a complete extraction. The estimated residual NG content obtained following the sampling method was compared to the actual residual NG content on the entire sock. The study confirmed that the sampling method overestimated the residual NG by an average of 55%. All the values gathered using the sampling method were corrected by reducing them by 55% to bring them closer to the actual values. The residual NG concentration is presented as a range from the corrected to the uncorrected values. The samples taken for Test Three were subjected to a complete extraction and no range is reported.

4.6   CLEANING CYCLE

To investigate the feasibility of cleaning the socks of residual NG and other hard-to-oxidize species, two experiments were conducted at the completion of Tests One and Two. After the socks required for analysis were removed and replaced with the corresponding socks from the other module, the PPCU was allowed to operate under a no-load condition. With the PPCU and the auxiliary fan on and the oven stack cap removed, ambient air was passed through the PPCU without going through the oven. The unit was allowed to operate overnight and the times varied from 16 to 20 hours. At the completion of the UV cleaning cycle, two socks were removed from one module and analyzed for residual NG. In the case of Test One, the residual NG was reduced to approximately 8 to 10 mg per sock after 20 hours of UV cleaning. The cleaning cycle after Test Two reduced the estimated NG per sock from 109 to 9 mg. NG sampling was not conducted during the sock cleaning runs, so it is not known whether the NG was destroyed or merely desorbed into the air stream.

4.7   PERFORMANCE CONCLUSIONS

The performance of all three tests is summarized in Table 8. Averages values were calculated for the first two tests neglecting the first 3 hours of operation. This time period was selected because the NG concentrations began to level off at that point and it is generally believed that rocket motor grains reach temperature equilibrium in that time. For Test Three, an average was calculated neglecting the first 22 hours of operation. Problems were encountered during this final test, and a steady stream of NG was not detected entering the PPCU until 22 hours had elapsed.

Table 8. Performance Summary.

Test No.	Duration (h:min)	Oven Temp. (°F)	Flow rate (scfm)	DRE (%)	Inlet NG conc. (ppmv)	Inlet plasticizer conc. (ppmv)	Outlet NOx conc. (ppmv)	Estimated residual NG (g)
1	9:44	165	414	43	9.6	ND	5.3	17.4-9.6
2	22:40	144	322	96	0.74	0.15	1.8	12.5-6.9
3	168:26	147	328	94	0.55	NT	9.25	1.8

The performance objectives were not met. It was concluded that the PPCU was not capable of removing 9.6 ppmv of NG from a heated air stream flowing at 416 scfm. The PPCU was able to

achieve DREs of 96% or better when treating a NG-contaminated air stream containing 0.74 ppmv of NG and flowing at 360 scfm. The poor performance during high flow rate and high NG conditions might have been due to increased lamp temperature and/or reduced reaction sites caused by non-uniform contaminant deposition and deposition of inert plasticizer co-contaminants. Optimization and/or additional cells could produce a PPCU capable of treating the NG effluent from the annealing oven. However, the data gathered were inadequate to determine the precise cause of the lower than expected performance or to predict the number of additional cells required for an optimized full-scale system.

In terms of operation and maintenance, the PPCU performed exactly as anticipated. No equipment failures were experienced during the demonstration. One lamp change was performed, in minutes. Changing one bank of cartridges took one-half man-hour although the operation was slightly dusty and required the use of a dust mask. Additionally, gloves were required to prevent contamination of the quartz sleeve and the catalyst socks by body oils, which could reduce performance. Removing used catalyst socks was a little faster. Care was exercised because the socks were contaminated with low levels of NG.

At the completion of each test the catalyst socks had to be replaced, which substantially increased the projected operating cost. One 30-gallon trash bag full of waste was generated per test. The socks were burned at the IHD thermal treatment facility because they were contaminated with NG.

Due to the poor performance at IHD, the second demonstration at RAAP was cancelled. However, a preliminary hazards analysis of the 650-scfm PPCU was conducted during the IHD demonstration by personnel from RAAP. The report may be found in Appendix D of the ESTCP final report [14].

5.0   COST ASSESSMENT

At its present level of performance, air-phase photocatalytic oxidation is uneconomic compared to alternative technologies. The following cost analysis shows the potential of photocatalytic oxidation and provides some measure of the future improvements needed to compete with other air treatment technologies. The estimates are equivalent to a Level I cost estimate as defined in the Environmental Cost Analysis Methodology (ECAM) Handbook[13].

The total cost of this demonstration project was $1.9 million. Table 9 breaks out each task and its associated cost. Additional monies were contributed by the U.S. Army Corps of Engineers, Construction Engineering Research Laboratory ($440,000) and IHD ($80,000) to perform a hazards analysis of the 650 PPCU and to complete the project documentation. The total cost of the 650 PPCU was $511,000. This does not include $200,000 that Trojan Technologies, Inc., discounted from the fabrication cost.

Table 9. Project Funding Summary.

Task	Cost ($1,000)	
	Subtotal	**Total**
Process development (50-scfm PPCU)		852
CEM development and testing		100
Down-select (IHD)		140
Fabrication of 650 PPCU		511
PPCU design (FSEC)	268	
Fabrication (FSEC/Trojan Technologies)	191	
Spare catalyst socks (FSEC)	17	
Documentation (FSEC/Trojan Technologies)	35	
650 PPCU demonstration		378
Demo plan	63	
Installation	55	
Testing	200	
Analysis/report	60	
Grand total		1981

In an effort to generate a useful technology comparison, six different cost estimates are shown in Table 10. The first three are for the PPCU and are intended to illustrate the cost of the current design and the potential for improvement. The last three are for incineration and carbon adsorption. The useful lifetime of each system was considered to be 10 years. Full details of each cost estimate may be found in Appendix K of the ESTCP Final Report [14].

All the estimates are based on the design requirements for annealing oven MILCON project as described in the demonstration plan [1]. The annealing oven is assumed to operate 351 days a year, 24 hours per day. This is equivalent to 260 annealing oven cycles processing 342,000 pounds of propellant annually. The cost to treat NOx was not included in the estimate. Photocatalytic oxidation and incineration both produce NOx, the latter producing the greatest amount. Prior to the demonstration it was determined that if stoichiometric amounts of NOx were produced from the treatment of NG, no NOx treatment would be required. If NOx treatment were required, the cost for implementation would increase.

Table 10. Cost Comparison for NG Treatments.

Technology	Total capital cost ($K)	Total annual operating cost ($K)	Annual energy cost ($K)	Annual maintenance cost ($K)	Annual labor costs ($K)	Cost per pound of NG removed ($)
PPCU	608	934.9	6.8	9	851.9	14,652
PPCU (Monthly catalyst replacement)	608	149.3	6.8	9	66.3	2,340
PPCU (if it worked as designed)	608	114.5	6.8	9	31.5	58
Catalytic incinerator	53.1	139.3	45.8	32.5	54.1	70
Thermal incinerator	39.9	132.9	41.8	31.3	54.1	68
Carbon adsorber	32.1	96.1	1.5	6.3	83.6	49

All technologies were considered "add-on" devices. Actual estimates from equipment vendors were used to estimate the capital costs. (The first three entries of Table 10 used the Trojan Technologies, Inc. price estimate for a 650-scfm PPCU production unit, which would be lower than for the prototype fabricated unit.) The EPA's Office of Air Quality Planning and Standards (OAQPS) Control Cost Manual [9] was used to generate a +/- 30% estimate of installation and operating costs. The labor rates used for the estimates were actual FY 99 stabilized rates. It is recommended to estimate unspecified material costs as 100% of the labor rate [9]. This analysis used one-quarter of the stabilized rate as this reflects the approximate portion that goes towards labor. No salvage value was assumed at the end of the equipment's useful life.

The cost analysis used the equivalent uniform annual cash flow (EUAC) method to facilitate comparisons between the technologies. This method is recommended when comparing systems that have different economic lives [9]. The total annual operating cost or EUAC includes a capital recovery cost, which was calculated using a pre-tax marginal rate of 7%. Because this differs from the recommended ECAM approach, the individual components and the total annual operating costs are shown in Table 10. The difference between the total annual operating cost and the sum of the annual maintenance, annual operational, and annual energy costs is the capital recovery cost.

The total capital cost of the PPCU is nearly six times greater than the other technologies. The first entry in Table 10 is the PPCU with performance equivalent to that of Test Two. It requires that the catalyst socks be changed after every annealing cycle. Using these conditions, it costs over $14,500 per pound of NG destroyed to operate this technology. The drivers for this unacceptably high cost are the cost of catalyst socks, the labor to change the socks, and the low performance of the unit.

The second scenario assumes the catalytic socks and/or the performance of the unit could be improved so that only monthly catalyst change-out would be necessary. For the same performance, the cost per pound of NG destroyed would decrease to $2,300 or 44 cents per pound of propellant processed. This would be a significant improvement that may be attainable through optimization. However, the annealing ovens can emit as much as 0.23 pounds of NG per hour, and the PPCU was not effective under those conditions.

The third scenario illustrates what happens to the cost if the PPCU could perform as planned. In this case, the PPCU would achieve a 99% DRE and the catalyst cartridge would be changed yearly. The

cost to remove NG would be a competitive $58 per pound of NG removed. However, even if the PPCU were optimized, catalyst fouling would likely prevent achieving this level of performance.

The purpose of this estimation exercise was to demonstrate the economic potential of photocatalytic oxidation. The annual energy costs and the annual maintenance costs for photocatalytic oxidation are among the lowest listed in the table. Because of the limited possible configurations for photocatalytic oxidation system, it is expected that all equally sized systems would have similar costs.

The fourth and fifth entries in Table 5-II are incinerators. Southeastern Engineering Sales, Inc. (SES) provided the equipment costs, which are significantly lower than for photocatalytic oxidation. Neither of the systems included a heat recovery system. Adding this feature would reduce the fuel consumption and more than double the capital equipment cost according to SES. The annual energy costs of both of these systems are similar and nearly an order of magnitude greater than the PPCU. The thermal incinerator has a DRE of 99%, while the catalytic incinerator has a DRE of 98%. Both systems have been sized to treat a 650-scfm air stream containing 12 ppmv of NG.

Finally, carbon adsorption technology was estimated. The economics of this approach are appealing. The capital cost was supplied by the TIGG Corporation. This system is composed of two carbon vessels, each capable of holding 1500 pounds of carbon and a blower. Two vessels are used to provide continuous operation during carbon replacement. Carbon removal is estimated to occur 14 times per year. However, it is important to recall that this technology has been deemed unsafe for vapor phase NG applications. Additional engineering and extensive safety testing would be required before it could be implemented in an explosive facility.

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6.0   IMPLEMENTATION ISSUES

6.1   PERFORMANCE OBSERVATIONS

Two hundred hours of testing and over 250 hours of operation showed that photocatalytic oxidation works, but not at an acceptable performance level. The PPCU could not effectively treat 10 ppmv of NG and lesser amounts of inert plasticizers in a waste stream flowing at 650 scfm. However, he PPCU was able to maintain DREs of 96% or greater when challenged with low NG inlet concentrations (0.7 ppmv or less) and operated at half the design flow rate (324 scfm). This was below expectations and did not meet the performance requirements for use in the MILCON project. Photocatalysis is not an economical solution to the Navy's problem in its current configuration. The technology has potential applications assuming the unit can be optimized and the catalyst life can be extended.

A water scrubber/aqueous phase photocatalytic oxidation system has been selected over air phase photocatalytic oxidation for use in the new MILCON facility at Indian Head. The proposed system consists of 18 individual scrubbers (each equipped with a heating and air handling unit), a central holding tank, a water chiller, an acid distillation column, and two aqueous phase photocatalytic oxidation systems. NG will be scrubbed out of the stack gas using acidic water. The water will be collected in the holding tank and distributed to the individual systems so that cool, clean water is recycled through the scrubber. Excess nitric acid, produced by the photocatalytic reaction, will be removed using the distillation column. The design is not finalized so operating data and costs are not available. However, the total direct cost is not expected to exceed $2.5 million.

The effect of inert plasticizers on the destruction of NG was not determined. No inert plasticizer could be detected during the first test although it was detected on the used socks. During the second test (reduced NG loading), plasticizer was detected and the unit performed acceptably.

When the unit was performing acceptably, the NOx gases were generated at or above stoichiometric levels. However, the increase in NOx shown in the mass balance obtained for Test Three was puzzling. Maximum NOx emissions should be expected.

The operation and maintenance of the unit excluding catalyst replacement were very low and in line with predictions. The unit was easy to operate and had no problems operating intermittently. No maintenance was required on the PPCU during this demonstration. Based on the results of Test Two, it is clear that a system containing more modules would be able to remove the NG. The data collected during the demonstration were inadequate to predict the required number modules. More testing would be required to develop this correlation.

The PPCU did not achieve the theoretical DRE predictions. Modeling predicted performance based on optimum lamp operating conditions and uniform distribution of contaminants in each cell, which did not appear to have occurred during the demonstration. IHD believes that an improved lamp cooling system and better flow distribution would increase the performance of the unit but the magnitude of the improvements is unknown. FSEC believes that its new "decoupled" cartridge design could achieve the required performance increase necessary to meet Navy needs. The enhanced cartridge is described in the FSEC final report [2] and on the FSEC web site, http://www.fsec.ucf.edu/Env/DETOX/Reactor_new.htm.

FSEC states that inert plasticizers that do not readily desorb from the catalyst eliminate the decoupling effect [2]. Thus, it seems unlikely that this enhancement alone would solve the Navy's problem. The answer seems to be more catalytic surface area or a more active catalyst or both.

The problem with adding additional surface area to the PPCU is that it requires additional modules. The housings of the modules are expensive and adding them rapidly increases the capital cost and, more significantly, the foot print. Zentox Corporation believes that the only solution is to ensure, by using a large catalytic surface area, that the catalyst surface never becomes overwhelmed. The Zentox reactor has many features that seem to solve the problems encountered with the PPCU. The cooling design is simple and effective, the catalyst is deposited on corrugated fiberglass panels that contain a very large catalytic surface area, the reactor is designed to provide uniform through flow, and it accomplishes all of this with a small foot print. Based on the demonstration results, Zentox Corporation indicated that it could provide a system capable of removing 98% of the NG from a waste stream containing 12 ppmv for $400,000. This cost estimate is provided in Appendix K of the ESTCP final report [14].

6.2   COST OBSERVATIONS

The problems with photocatalytic oxidation are low performance, high capital cost, and catalyst fouling. Improving performance by adding more cells would increase both capital and operating costs. New catalyst socks would still be required prior to each annealing cycle. Therefore, until some method can be devised to keep the catalyst surface clean, this technology will struggle to compete. If an effective solution to the catalyst fouling could be developed, then the high capital cost would not be such a burden.

Photocatalytic oxidation also seems to be limited to dilute concentrations and low flows. The technology does not become more cost-effective as contaminant concentration increases, unlike conventional treatment technologies such as incineration. The range of usefulness varies depending on the contaminant. FSEC has stated that for moderate activity organic compounds, full photocatalytic oxidation is possible if the total concentration of organics times the reactor throughput is less than or equal to 100 ppmv scfm. The limiting factor is the need to illuminate the surface of the catalyst. As the mass of contaminants increases, so does the size and complexity of the reactor.

6.3   OTHER SIGNIFICANT OBSERVATIONS

Currently, there is no way to predict how the catalyst will react to small changes in waste stream composition. Catalyst fouling must be avoided for this technology to be economical. The limitations that feed stream composition imposes on the flexibility of the process must be evaluated prior to installation.

It was suspected that the use of cotton as a substrate for the catalyst is partially responsible for the limited catalyst life. Although using a material such as fiberglass would not improved the performance of the unit, it would eliminate the mechanical degradation which occurred in Test Three. In that case, a cleaning cycle, which was demonstrated effective, could be employed to possibly extend the catalyst life.

Used catalyst socks generated unexpected hazardous waste. NG was detected in every used sock that was sampled, indicating that used catalyst socks might need to be disposed of as hazardous waste. During the demonstration the used socks were burned at the IHD thermal treatment point as if they were rags contaminated with propellant. No attempt was made to determine the maximum level of NG contamination acceptable for landfill disposal. It was clear, even in light of the problems encountered during the sock analysis that NG was being destroyed in significant quantities and not merely being collected on the catalyst socks.

Most of the limited number of vendors of photocatalytic oxidation technology are small companies that are unable to absorb the cost of testing. Even if the testing is provided at no cost up front, current pricing seems to indicate that it is recouped in the sale price.

6.4   REGULATORY AND OTHER ISSUES

Maryland Department of the Environment (MDE) continues to receive yearly reports of IHD NG emissions and efforts to abate them. Besides MDE, there has been no interaction with any other regulators.

6.5   LESSONS LEARNED

1.   The importance of fully characterizing the waste stream to be treated cannot be stressed enough. If a thorough and complete characterization had been performed prior to beginning the design, perhaps more time could have been spent evaluating the effects of inert plasticizers on the destruction of NG to achieve higher performance during the demonstration.

2.   Seemingly insignificant contaminants can have a tremendous effect on performance and economics. A contaminant (as is the case for ethanol) could have a synergistic effect on the destruction of the target compound and removing it could decrease reactor performance.

3.   If possible, conduct the demonstration on the actual waste stream that is going to be treated at the facility where it is going to be installed. The challenges that had to be overcome were not completely understood until testing the PPCU began on actual annealing oven emissions. A large portion of time and funding was expended developing, planning, and performing small-scale tests at FSEC using ethanol, acetone, and NG.

4.   Photocatalytic oxidation reactor designs should include LPMLs, which were found to be the best type of lamp. They are small, they last a long time without a significant reduction in output, and they do not generate a lot of heat. They have a relatively high electrical-to-photon conversion efficiency, nearly double that of a black light, although the relative output of a LPML is reduced by approximately 50% above 75 °C (167 °F). They are inexpensive and readily available in standard sizes. Although the energy density of medium-pressure mercury lamps (MPMLs) is very appealing, they are too hot and too intense. Photocatalytic activity is adversely affected by high intensity. Also, the relative output of MPMLs drops off significantly during the first month.

6.6   SCALEUP

Additional testing would be required to be able to predict the cost of scaling the FSEC design to meet the need of the new Navy MILCON annealing oven. The reduced performance that occurred as a result of poor lamp cooling and non-uniform contaminant distribution might be overcome through design optimization. The reduced performance that occurred as a result of inert plasticizer can only be addressed by increasing the number of modules. Currently, the only way to implement this technology on a large scale would be to build and test a full-scale prototype.

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