

Chemical Warfare Agent Decontamination Studies in the Plasma Decon Chamber

Hans W. Herrmann, Gary S. Selwyn, Ivars Henins, Jaeyoung Park, Mark Jeffery, and John M. Williams

Abstract—A “plasma decon chamber” has been developed at Los Alamos National Laboratory (LANL), Albuquerque, NM, to study the decontamination of chemical and biological warfare agents. This technology is targeted at sensitive electronic equipment for which there is currently no acceptable, nondestructive means of decontamination. Chemical reactivity is provided by a downstream flux of reactive radicals such as atomic oxygen and atomic hydrogen, produced in a capacitively coupled plasma. In addition, the decon chamber provides an environment that accelerates the evaporation of chemical agents from contaminated surfaces by vacuum, heat, and forced convection. Once evaporated, agents and agent byproducts are recirculated directly through the plasma, where they undergo further chemical breakdown. Preliminary studies on actual chemical agents were conducted at the U.S. Army Dugway Proving Ground, Dugway, UT. Exposures were conducted at a system pressure of 30 torr, exposure temperature of 70 °C, plasma-to-sample standoff distance of 10 cm, and 10% addition of oxygen or hydrogen to a helium balance. This exposure condition was based on optimization studies conducted at LANL on agent simulants. The agents studied were VX and soman (GD) nerve agents and sulfur mustard (HD) blister agent, as well as a thickened simulant. All agents were decontaminated off aluminum substrates to below the detection limit of $\sim 0.1\%$ of the initial contamination level of approximately 1 mg/cm^2 . For VX, this level of decontamination was achieved in 8–16 min of exposure, while only 2 min were required for the more volatile HD and GD. Evaporation and subsequent gas-phase chemical breakdown in the plasma appears to be the dominant decontamination mechanism for all of the agents. However, an observed difference in the decontamination process between oxygen and hydrogen indicates that chemical reactivity in the liquid phase also plays an important role.

Index Terms—Atmospheric-pressure, chemical warfare, decontamination, nonthermal, plasma, sterilization.

I. INTRODUCTION

THE threat of incidents involving chemical or biological warfare (CBW) agents has been growing in recent years. The U.S. military was forced to recognize its shortcomings in CBW readiness during the Gulf War, and our forces continue to face a real threat of CBW, particularly around the Persian Gulf and the Korean peninsula. The threat of a CBW attack on U.S. soil is also of major concern. The Tokyo subway nerve gas attack of 1995, the recent alleged activities of the Al-Qaida ter-

rorist network, and the recent rash of Anthrax in the mail have galvanized U.S. Government efforts to combat terrorism, particularly chemical terrorism and bioterrorism. Intensive efforts are underway to improve our capabilities in the areas of prevention, detection, modeling and prediction, personnel protection, therapeutics, and restoration and recovery. A critical part of restoration is decontamination (decon). Decon is the act of rendering an area (or volume in the case of a gas or a liquid) safe through removal or detoxification of a hazardous chemical or pathogen, preferably without significantly damaging or impairing the underlying area.

Ionized gases, or plasmas, can potentially satisfy many of the decon needs of the military as well as domestic emergency responders. Nonthermal plasmas, or partially ionized gases in which the electron temperature far exceeds the ion and background gas temperature, have particular appeal. The main advantage of using a nonthermal plasma for CBW decon is its ability to chemically activate a dry gas stream, where the reactive species population is governed by an applied electric-field strength rather than a gas temperature. This is possible because an oscillating electric field heats mainly the electrons rather than the heavier ions, which respond much more slowly. Due to the large difference in mass, thermal-energy transfer between energetic electrons and gas atoms and molecules is also greatly limited. However, these energetic electrons can transfer their energy effectively to excite and dissociate molecules, yielding reactive radicals such as oxygen atoms. As a result, it is possible to produce large quantities of highly reactive radicals while maintaining a background gas at or near room temperature in a plasma environment.

In addition to atomic oxygen (O), oxygen-containing plasmas also produce other reactive oxygen species (ROS) such as metastable oxygen (O_2^*), ozone (O_3), and oxygen ions (O_2^+). ROS produced inside a plasma readily oxidize many organic compounds, thus neutralizing chemical warfare agents and disrupting life functions of micro-organisms through interaction with cell membranes, enzymes, and nucleic acids [1]. Another benefit of plasma is its versatility in being able to produce many different chemically reactive species simply by changing feedgases. For instance, a feedgas containing hydrogen can be used to produce atomic hydrogen that can neutralize many chemical agents by reducing chemistry. The plasma also generates ultraviolet radiation that can destroy many biological agents as well as enhance chemical-reaction rates. Furthermore, if evaporated chemical agents pass directly through a plasma region, rapid chemical dissociation from electron and ion impact can detoxify the agents very effectively. An important benefit of plasma decontamination is that it

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provides this chemical destruction process without the need for caustic or hazardous solvents, which must be stored and then disposed of after using. Instead, plasma treatment offers a dry and potentially nondestructive means of decontamination.

The promising potential of plasmas for decon was clearly identified during the U.S. Military's Decon Front End Analysis (FEA) conducted at the U.S. Army Edgewood Chem/Bio Center, Aberdeen Proving Ground-Edgewood Area, Edgewood, MD, in December 1998. This FEA forms the backbone of the Joint Services Decon Master Plan [2]. An expert panel conducted an indepth analysis evaluating the ten-year potential for 19 different technology classes in several different functional areas: exterior equipment (field and fixed site); large area; sensitive equipment; interior equipment; and skin and personal equipment. Technologies were graded against 21 different criteria that were weighted by the military's user community.

Atmospheric-pressure plasma (APP) was deemed applicable in all functional areas except for immediate skin and personal equipment (i.e., within 2 min of an expected exposure), however, it was agreed that APP may prove useful in this area at a decon station. APPs ranked high in all other functional areas. However the areas where APP showed the greatest potential are in Sensitive Equipment and Interior decon. This is particularly important since there are not many promising technologies in these areas. The Plasma Decon Chamber, an extension of APP technology, was designed specifically for sensitive equipment. Sensitive equipment is defined as equipment that cannot be exposed to aqueous decontaminants and strong oxidizing or caustic solutions without destruction, degradation in performance, or significant disruption in use. To the military, this means electronic equipment such as avionics, communications, fire control and navigational equipment, and electro-optics, such as range finders and night-vision goggles.

At this point, there is *no acceptable method* of decontamination for sensitive equipment other than the extremely limited technique of thermal desorption. The competing technologies being considered in this functional area are: solvent wash; low-pressure plasmas; super-critical CO₂(SCCO₂); reactive gases and vapors; and reactive foams and gels. Solvent wash uses CFC replacement solvents to remove CBW agents. Clearly, this invariably contaminates the solvent in the process, thus requiring frequent replacement of the solvent and decontamination or acceptable disposal of the solvent. Furthermore, its effectiveness has not been fully demonstrated yet, particularly against BW agents. Low-pressure plasmas operating in the sub-torr range may have potential, but typically are not very penetrating and are much more limited in the type of materials that may be placed inside a vacuum and still maintain such low pressures. At sub-torr pressures, reactive species must rely on diffusion to penetrate into cavities and crevices, which are likely beyond the spread of the plasma. This severely restricts its usefulness for anything but smooth, vacuum-compatible objects having only external contamination. In contrast, pressure pulsing at pressures above 10 torr in the closed-loop Plasma Decon Chamber should allow convection driven by significant pressure gradients to augment the transport of reactive species, greatly enhancing penetration into cavities and crevices. SCCO₂ has shown promise for removal of CW

agents. However, this then requires secondary separation and neutralization in order to dispose of the agent without spreading it further. Also, the extreme pressure of the supercritical point of CO₂, at approximately 73 atmospheres, may greatly restrict the types of materials that can be decontaminated. Equipment containing polymers and which are hermetically sealed are most at risk to damage. Reactive gases and vapors, such as ozone, vapor hydrogen peroxide, and chlorine dioxide, tend to be relatively long lived, leaving hazardous residues and are relatively nonselective, corroding materials on the same time scale as decontamination. Reactive foams and gels may be of use in this functional area, but aqueous content and lingering residues may degrade performance of sensitive equipment. APPs offer the advantage of being a removal method as well as neutralization method, which is not harmful to most materials.

In Section II, we describe the origin and specifics of the Plasma Decon Chamber. In Section III, we describe the experimental method used and in Section IV, we present results obtained both during optimization studies on surrogates at LANL, as well as preliminary testing on actual agents at the U.S. Army Dugway Proving Ground, Dugway, UT. In Section V, we discuss the significance of the results and present ideas for future work before summing up in Section VI.

II. DESCRIPTION OF THE PLASMA DECON CHAMBER

The Plasma Decon Chamber [3] was developed as an extension of the atmospheric-pressure plasma jet (APPJ) technology [4]–[11] invented at LANL in 1995. The APPJ is a unique, nonthermal, high-pressure, uniform-glow, plasma discharge that produces a high-velocity, chemically reactive effluent gas stream. APPJ electron temperatures of ~ 2 eV ($\sim 20\,000$ °C) have been measured with gas temperatures of ~ 100 °C, clearly demonstrating the nonthermal nature of the discharge [9]. There are sufficient electrons in the distribution with energies exceeding the 5 eV necessary to dissociate O₂ to produce copious quantities of atomic oxygen. Previous studies have demonstrated that it is capable of producing O atom concentrations of up to 1×10^{16} atoms/cm³, or nearly 400 ppm [11]. At a typical effluent gas velocity of 10 m/s, this results in an O atom flux at 1×10^{19} atoms/cm²•s. This places an upper limit on the decon rate for VX of 3 mg/cm²•s assuming every O atom detoxifies one VX molecule and that oxidation by O atoms is the only decon mechanism.

The APPJ was previously demonstrated to decontaminate surrogates for anthrax, sulfur mustard and VX nerve agent [6], as well as actual VX. Testing on VX was conducted at the U.S. Army Edgewood Chem/Bio Center, Aberdeen Proving Ground-Edgewood Area, Edgewood, MD, in 1999. Cleavage of the phosphorus-sulfur bond in VX was demonstrated at a standoff distance of 0.5 cm, taking approximately 0.5 min at 240 °C and 2.5 min at 135 °C for each factor of ten reduction in contamination. Although the plasma-treatment method was capable of decontaminating VX, it was determined that significant improvement would be needed before the APPJ technology could be considered a practical decontamination technique for vehicle interiors. In particular, the configuration tested required copious consumption of helium (~ 50 standard

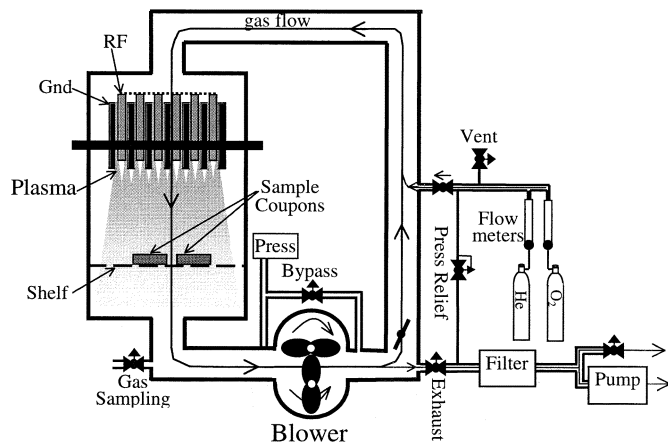


Fig. 1. Schematic of the Plasma Decon Chamber.

liters per minute (slpm)), had a limited standoff distance (< 1 cm), a relatively slow decon rate, and also might reaerosolize CBW agents, particularly at the higher exposure temperatures. The combination of these factors made a handheld APPJ unit limited in this application due to the logistics and operator effort that would be required.

To overcome these limitations, the APPJ concept was incorporated into a closed-loop recirculating system known as the Plasma Decon Chamber, and the focus was shifted to the decontamination of sensitive electronic and optical equipment, which could be placed inside a closed volume. Recirculation of the feedgas through a closed-loop system dramatically reduces helium consumption, as well as alleviating any concern over reaerosolization of agent. A closed system also allows employment of methods such as pressure reduction and/or pulsing. Reduced pressure increases the lifetime of reactive species, allowing greater standoff distances, while pressure pulsing allows them to penetrate more effectively into crevices and cavities. By using a chamber based approach to thoroughly clean an entire batch of equipment in an automated process, operator involvement is dramatically reduced and the overall decon rate is increased. We expect a process time of 20 min per batch would be adequate for most decon needs. It should be mentioned that since a chamber based approach does reduce the potential utility of this technology, we also continue to improve the complementary handheld decon jet approach in an attempt to overcome the previously mentioned limitations.

The experimental prototype Plasma Decon Chamber used in this study is depicted in Fig. 1. The cylindrical chamber consists of the plasma source on top and the sample chamber below. Plasma is formed in the top section by applying radio frequency (RF) power at 13.56 MHz to a stack of alternating RF and ground parallel-plate electrodes. The two outermost electrodes are grounded, resulting in one more ground electrode than RF electrodes. The number of RF electrodes can be varied from one, resulting in two plasma channels (one on each side of the RF electrode), to six, resulting in 12 plasma channels. Each plasma channel is 7.94 cm long in the direction of the gas flow and 6.35 cm wide. Since the mean free path between particle collisions increases as the pressure is reduced, the optimum gap spacing between electrodes also increases. This gap spacing,

which determines the plasma channel thickness, is set using glass spacers to 0.16 cm for high gas pressure (≥ 300 torr), or 0.40 cm for low gas pressure (< 300 torr).

Once powered, reactive species are formed in the plasma and are blown into the bottom part of the chamber, where contaminated samples are placed on an adjustable height shelf. The inner diameter of the lower chamber is 12.7 cm and the depth is 15.24 cm. However, the maximum standoff distance between the plasma and shelf is limited to about 10 cm to allow room for a thermocouple plug in the bottom of the chamber. A *K*-type thermocouple is mounted on a small piece of glass on the shelf to monitor exposure temperature. A 100-cfm (2832 lpm) Roots blower (Leybold RUVAC WS150) is used to recirculate the gas back to the top electrode section. The calculated plug-flow gas velocity in the sample chamber is 3.7 m/s. A low flow of fresh makeup gas is supplied to the system through rotameters and gas is exhausted to a rotary-vane roughing pump by way of an activated carbon filter, thus establishing a constant "feed and bleed" to replenish consumed gases and to expel reaction byproducts and other impurities. The exhaust valve is throttled in order to maintain the desired pressure in the chamber. A bypass valve allows a large fraction of the gas to bypass the chamber, thus giving some control over the gas-flow rate through the chamber. A gas sampling port at the outlet of the chamber is provided for diagnostic techniques such as sorbent-tube sampling or residual gas analysis.

For the testing conducted at Dugway Proving Ground, the Plasma Decon Chamber was configured with just one RF electrode opposed on either side by ground electrodes, resulting in two plasma channels. During optimization trials at LANL, it was determined that fewer channels were beneficial to the decon process, presumably since this minimized plasma volume and hence maximized plasma power density for a given exposure temperature. It is surmised that a higher power density leads to a higher electron temperature (typically $\sim 2\text{--}4$ eV), increasing the population of energetic electrons with greater than the 5 eV required to dissociate oxygen molecules into atomic oxygen. Fewer plasma channels also lead to more localized high-velocity flow in the center of the sample chamber, whereas the original 12-channel design was better represented by a plug-flow model. With only two plasma channels, the plug-flow gas velocity through the plasma is 96 m/s for 100 cfm of flow, a factor of 26 higher than it is for plug flow inside the sample chamber.

III. EXPERIMENTAL METHOD

Contaminated samples were prepared by spiking aluminum coupons with a dilute chemical agent and then allowing the methylene chloride solvent to evaporate between spikes, leaving a subtoxic film of essentially neat agent. Use of dilute agent allowed for more convenient handling, and allowed small quantities of agent to be applied as a resulting thin film. The coupons measured $2\text{ cm} \times 2\text{ cm} \times 0.64\text{ cm}$ and had a 1.27-cm diameter, 0.38-cm deep, cylindrical depression milled into them capable of holding $480\ \mu\text{l}$ of dilute agent. By waiting for the solvent to evaporate between spikes, the coupon could be spiked several times with $250\ \mu\text{l}$ of dilute agent to achieve the desired contamination level.

Once contaminated, two coupons were placed side by side inside the sample chamber on the center of the shelf and then the top electrode portion of the chamber was sealed to the lower sample chamber. In quick succession, the exhaust valve was opened to pump the system down to 10–15 torr, feedgases were introduced to bring the pressure back up to 30 torr, and the Roots blower was started with the bypass valve open. After waiting 1 min to allow the system to be purged of air, the RF was turned on to initiate plasma and the bypass valve was immediately shut to direct all gas flow through the chamber. After exposing the sample for a given period of time, the RF and the Roots blower were turned off, the exhaust valve was closed, the gas feed flow was stopped and the system was vented to atmosphere. Residual agent and byproducts were then immediately extracted by placing each coupon in a jar with 2 ml of methanol. The extractions were analyzed by gas chromatography/mass spectrometry (GC/MS).

An exposure temperature of 70 °C was selected to emphasize the relevance to sensitive equipment decontamination. Since there is no external heating other than from the plasma, the sample gradually warms up from room temperature once the exposure begins. To maintain as close as possible to a constant temperature throughout the exposure, a higher RF power was applied initially, followed by a programmed ramp down in RF power. An exposure temperature of 70 °C was obtained within the first 30 s from an initial setting of 600 W. This was followed by progressively decreasing ramp rate down to a final setting of 300 W over 8 min.

Separate exposures were done at higher pressure in order to draw gas samples through sorbent tubes since the sampling pump was unable to draw against 30 torr. These exposures were done at 600 torr and a sample shelf position approximately 2.5 cm from the electrode region. The sorbent tubes were subsequently thermally desorbed into a GC/MS for qualitative analysis of volatile compounds. However, no chemical agents, or their byproducts, were detected by this method. Apparently, the sampling efficiency was not high enough to obtain detectable levels upon desorption.

IV. RESULTS

A. VX

1) *VX Surrogate (Malathion)*: Prior to bringing the Plasma Decon Chamber to Dugway Proving Ground for actual agent testing, it was characterized and optimized using the commercially available pesticide, malathion. Malathion was chosen as a surrogate for VX due to its physical and chemical similarities to VX, but at a much lower toxicity. Coupons were prepared by spreading 6 mg of neat malathion over 1.27 cm² for a contamination level of 4.7 mg/cm².

Fig. 2 shows the effect of gas pressure on decon effectiveness as a function of standoff distance between the plasma and the contaminated coupon. At higher pressures (i.e., ≥ 300 torr), the rate of decontamination is severely degraded after a few cm. In comparison, the decon effectiveness remains relatively constant out to 7.5 cm at lower pressures (i.e., ≤ 100 torr).

The decon efficacy as a function of oxygen gas fraction in the feedgas at a total gas pressure of 100 torr is shown in Fig. 3.

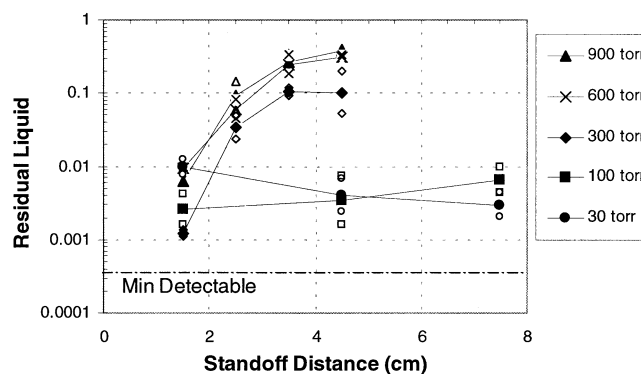


Fig. 2. Relative amount of residual malathion detected on aluminum coupons by GC/MS extraction as a function of standoff distance and pressure for: temperature = 70 °C; exposure time = 10 min; four plasma channels; O₂ fraction = 1% at ≥ 300 torr, 2% at 100 torr, and 4% at 30 torr. Solid symbols are average of duplicate data points shown in open symbols.

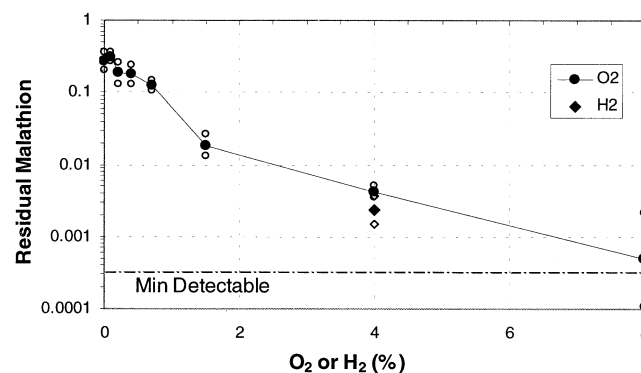


Fig. 3. Residual malathion remaining on aluminum coupon as a function of O₂ or H₂ addition: $T = 70$ °C, exposure time = 5 min, Press = 100 torr, $d = 4.5$ cm. Solid symbols are average of duplicate data points shown in open symbols.

The decon efficacy is seen to increase with oxygen concentration. One set of coupons was run with 4% hydrogen in place of oxygen, resulting in comparable removal of malathion.

Based on the above results, the following exposure conditions and constraints were selected for testing of actual chemical agents: Pressure = 30 torr, Gas Flow = 20 slpm helium with 10% oxygen or hydrogen addition (i.e., 2 slpm) and Standoff Distance = 10 cm. In addition, the RF power was programmed to maintain an exposure temperature of 70 °C \pm 3 °C based on the shelf mounted thermocouple reading. All subsequent exposures used these “standard” conditions.

Fig. 4 shows the results from the decontamination of malathion as a function of exposure time using the standard oxygen exposure conditions. After one minute, only 1% of the original malathion remains, while its dominant byproduct, malaoxon, builds up to 10% of the control concentration. With increasing exposure, however, the amount of malaoxon also decreases as its own decon rate begins to exceed its production rate from oxidation of malathion. After 3 min of exposure, the presence of malaoxon is no longer detectable in the sample extractions by the GC/MS. However, malathion remains at a level that is above the detectable limit of 0.05% even after 10 min of exposure. In addition a brown solid residue was observed to form on the coupon during the exposure to the plasma.

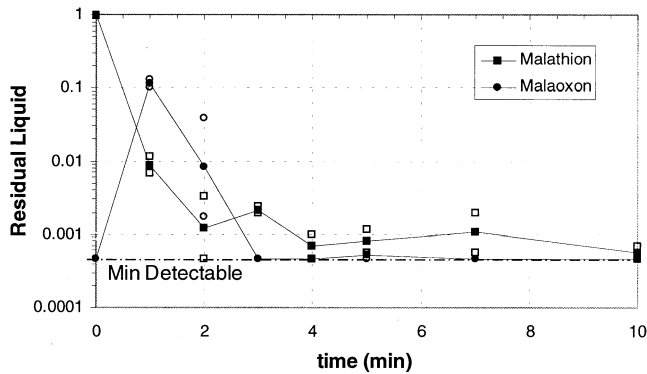


Fig. 4. Residual liquids remaining on a malathion contaminated aluminum coupon as a function of exposure time for the "standard conditions": $T = 70\text{ }^{\circ}\text{C}$, $d = 10\text{ cm}$, $\text{Press} = 30\text{ torr}$, $\text{O}_2 = 10\%$. Solid symbols are average of duplicate data points shown in open symbols.

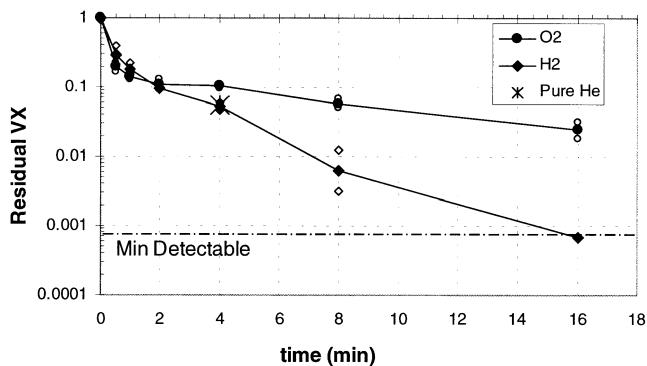


Fig. 5. Residual VX remaining on aluminum as a function of exposure time for the "standard conditions": $T = 70\text{ }^{\circ}\text{C}$, $d = 10\text{ cm}$, $\text{Press} = 30\text{ torr}$, O_2 , or $\text{H}_2 = 10\%$

2) *VX Nerve Agent*: The maximum concentration of VX dilute VX allowed by surety regulations is 1 mg/ml. Coupons were prepared by spiking 250 μl of dilute VX, at 5% below this limit, four times as described in Section III. The resulting coupons contained 0.95 mg of VX spread over 1.27 cm^2 for a contamination level of 0.75 mg/cm^2 .

The calibrated quantity of residual VX as a function of exposure time for both 10% oxygen and 10% hydrogen addition to helium is shown in Fig. 5. Clearly, hydrogen is more effective than oxygen, taking somewhere between 8 and 16 min to achieve nondetectable levels, corresponding to better than 99.9% decontamination. Although the plasma-containing oxygen appears to have a faster decon rate initially, the removal rate slows down significantly within 1 min and only reaches 98% removal after 16 min of exposure. Visual observation of contaminated coupons after oxygen exposure reveals a brown residue. As previously mentioned, a similar residue, and a corresponding decrease in the decon rate with time, was also observed for oxygen exposure of the VX simulant, malathion. In comparison, the exposures to the hydrogen containing plasmas also produced a brown residue, but in much smaller quantities. Furthermore, the brown residue disappeared with increasing exposure to the plasma with hydrogen feedgas. Complete removal of the brown residue was observed after 16 min of exposure.

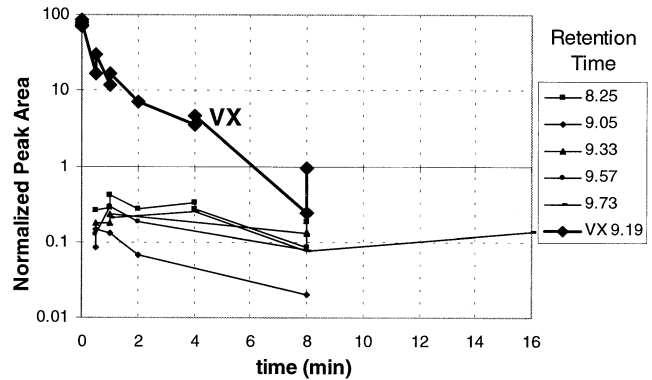


Fig. 6. Relative values of VX and byproduct peaks found at various GC/MS retention times (min) for H_2 exposure of Fig. 5.

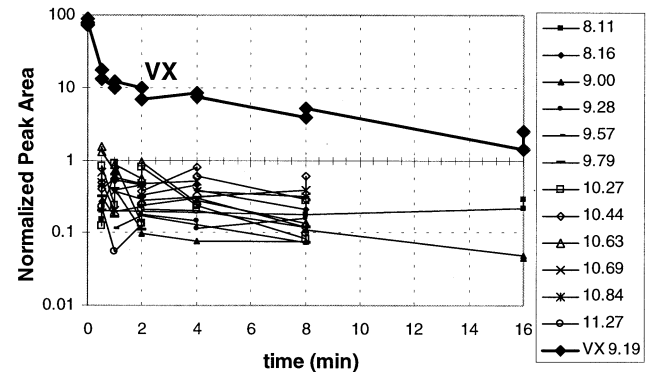


Fig. 7. Relative values of VX and byproduct peaks found at various GC/MS retention times (min) for O_2 exposure of Fig. 5.

The magnitude (as taken from the raw data with no calibration or background subtraction) of the various retention time peaks found in the GC/MS analysis representing the various VX byproducts, is shown in Figs. 6 and 7 as function of exposure time for H_2 and O_2 exposure, respectively. In contrast, the exposure to the plasma using pure helium resulted in no new byproducts, consistent with the inert nature of helium. It should be noted that the half dozen or so VX impurities that are found in the control samples (i.e., 0 min) are not plotted in Figs. 6 and 7. These impurities are found at below the 1% level in the control samples and decrease in absolute quantity with increasing exposure time. Since the VX "byproducts" plotted in Figs. 6 and 7 are also below the 1% level, some of them could conceivably be byproducts of impurities, but we will assume they are derived from VX until they can be positively identified. Unfortunately, due to the extremely small quantities of these byproducts, their mass spectra are unreliable, making positive identification difficult if not impossible (actual quantities are significantly smaller than Figs. 6 and 7 imply since background levels were not subtracted). However, the impurities and byproducts all appear to have fragmentation mass peaks in common with VX. Attempts to identify typical decontamination products [12]–[14] were unsuccessful.

B. Sulfur Mustard (HD) Blister Agent

1) *HD Simulant (Phenyl Half Mustard)*: The decon chamber was also tested on 2-chloro ethyl phenyl sulfide (CEPS), or phenyl half mustard, as a simulant for sulfur

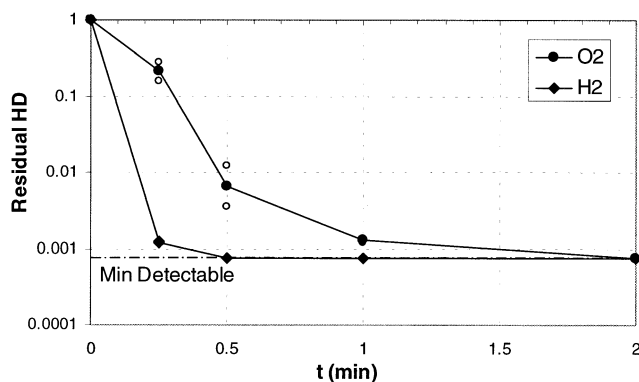


Fig. 8. Residual HD remaining on aluminum as a function of exposure time for the “standard conditions”: $T = 70\text{ }^{\circ}\text{C}$, $d = 10\text{ cm}$, Press = 30 torr, O₂, or H₂ = 10%. Solid symbols are the average of duplicate data points shown in open symbols.

mustard (HD). CEPS was easily decontaminated within a few minutes exposure to a He/O₂ plasma. A residual gas analyzer (RGA) was connected through a pressure reduction manifold to the gas-sampling port and the system was completely isolated (i.e., no feed and bleed). The RGA traces for CO₂ and H₂O increased, while O₂ decreased in quantities consistent with complete combustion of the simulant, C₈H₉ClS. There were also trace quantities of SO and SO₂ detected. However, no trace of the Cl was seen by this method. This oxidation process occurred on the same time scale as the decontamination process as determined by the GC/MS extractions.

2) *HD*: The maximum concentration of dilute HD allowed by surety regulations is 10 mg/ml. Coupons were prepared by spiking 250 μl of dilute HD (3.25% below this limit) and allowing the methylene chloride to evaporate, yielding 2.42 mg of HD spread over 1.27 cm² for a contamination level of 1.9 mg/cm². Since HD is relatively volatile, coupons were prepared in sets of eight, allowed to dry for only 8 min, and then sealed in a capped petri dish to prevent agent evaporation. All eight coupons were then used within an hour. Controls were taken from this set of eight at the start and at the end of the hour to ensure there was not significant evaporation of agent. The standard 1-min air purge was reduced to 30 s to minimize evaporation prior to plasma exposure. Controls were conducted to verify that significant evaporation did not occur during this period.

The quantity of residual HD as a function of exposure time for both 10% oxygen and 10% hydrogen addition to helium is shown in Fig. 8. Hydrogen appears to be more effective than oxygen, but both are extremely effective, resulting in >99.9% removal in under 2 min. No data was taken using a pure helium plasma. As for the GC/MS analysis of the residuals, numerous impurity peaks were detected in the control HD samples. With exposure to the plasma, many more GC/MS peaks were detected from chemical breakdown of the HD and these impurities. All of these impurities and byproducts decay away, apparently more quickly with H₂ addition than with O₂ addition.

C. Soman (GD) Nerve Agent

The maximum concentration of dilute GD allowed by surety regulations is 2 mg/ml. Coupons were prepared by spiking

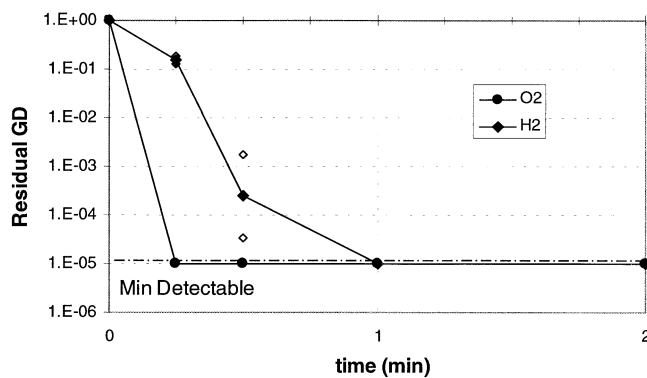


Fig. 9. Residual GD remaining on aluminum as a function of exposure time for the “standard conditions”: $T = 70\text{ }^{\circ}\text{C}$, $d = 10\text{ cm}$, Press = 30 torr, O₂, or H₂ = 10%. Solid symbols are average of duplicate data points shown in open symbols.

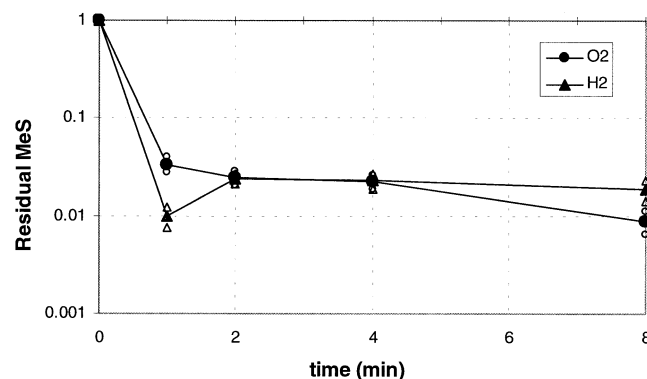


Fig. 10. Residual MeS remaining on aluminum as a function of exposure time for the “standard conditions”: $T = 70\text{ }^{\circ}\text{C}$, $d = 10\text{ cm}$, Press = 30 torr, O₂, or H₂ = 10%. Solid symbols are average of duplicate data points shown in open symbols.

250 μl of dilute GD (at the limit) four times, yielding 2.0 mg of GD spread over 1.27 cm² for a contamination level of 1.6 mg/cm². Precautions similar to those for HD were taken to minimize evaporation prior to plasma exposure.

The quantity of residual GD as a function of exposure time for both 10% oxygen and 10% hydrogen addition to helium is shown in Fig. 9. In this case, oxygen appears to be more effective than hydrogen, but again both are extremely effective resulting in >99.999% removal in under 2 min.

D. Thickened Methyl Salicylate

The chemical agent simulant methyl salicylate (MeS), or oil of wintergreen, was mixed with K125 thickener (Rohm and Haas) in the proportion of 96% MeS : 4% K125 by mass. The mix also contained a small amount of red dye useful in field exercises. The thickened simulant was then diluted to 10% by volume in methylene chloride and 25 μl was spiked onto a coupon, resulting in a contamination level of 2.0 $\mu\text{l}/\text{cm}^2$ after the solvent evaporated.

The quantity of residual MeS as a function of exposure time for both 10% oxygen and 10% hydrogen addition to helium is shown in Fig. 10. In both cases, the quantity of MeS is quickly reduced to the few percent level, then the decon process appears to saturate. For both gases, the red dye is still visible on the coupon surface even after 8 min of exposure time, although it

does appear to be somewhat reduced compared to the control samples. A white residue was seen on the coupons exposed to hydrogen plasma that appeared to increase in quantity with increasing exposure time. This residue was not observed for the oxygen plasma. However, this residue formation does not appear to correspond to any significant difference in the decon efficacy of hydrogen exposure as compared to oxygen as seen in Fig. 10.

E. Collateral Damage

As a preliminary test of collateral damage by exposure to a reactive plasma stream, a Sharp EL-233G handheld calculator was subjected to the decon process. The back cover was removed and the calculator was placed face down on the chamber's shelf to expose the internal circuitry directly to the gas flow. After 8 min of the standard exposure conditions with H₂ addition there were no visible effects to any surfaces and the calculator continued to function. After an additional 8 min of the standard exposure conditions with O₂ addition, there were obvious signs of etching of polymeric materials, turning shiny surfaces to a dull finish. However the calculator still continued to function without problem.

V. DISCUSSION

A. Decon Mechanisms

There are several significant chemical decontamination mechanisms apparent from these results, namely, reactive decontamination of agent while in the liquid phase on the contaminated surface producing nonvolatile (i.e., liquid or solid) or volatile byproducts and gas-phase reactive decontamination of agent (or capture by the filter) after it is evaporated from the surface. The dominant mechanism is determined by the relative volatility and reactivity of the agent in question. Malathion and VX have the lowest vapor pressures of the substances tested at 3×10^{-6} and 7×10^{-4} torr, respectively, at 25 °C, while HD and GD are much more volatile at 0.1 and 0.4 torr at 25 °C, respectively.

For the least volatile substance tested, malathion, chemical-surface decontamination is clearly dominant when oxygen is present in sufficient quantity, as illustrated by Fig. 3. The observed reduction in malathion without oxygen (i.e., evaporation) is only a small fraction compared to chemical breakdown of malathion with oxygen. For instance, the normalized residual malathion remaining on the aluminum coupon goes from 0.2 to 0.0006 in going from 0 to 8% oxygen, a greater than 300× improvement. From this, we deduce that reactive oxygen species (ROS) are reacting with the malathion. This is supported by the formation of malaaxon as illustrated in Fig. 4. Malaaxon differs from malathion only in the substitution of a sulfur atom for an oxygen atom. As to which ROS is dominant, we must look at production and lifetimes of the various species, namely, atomic oxygen, metastable oxygen, and ozone, and compare with the effective standoff distances which can be obtained from Fig. 2. This is done in the next section. Assuming for the moment that atomic oxygen is the dominant ROS, and that the chamber is producing an upper limit of $\sim 10^{19}$ O atoms/s, then the upper limit on the malathion decon rate is ~ 6 mg/s. The initial decon

rate taken from Fig. 4 is only about two orders of magnitude below this upper limit. Since the contaminated coupon surface is only about 1% of the cross section of the chamber, a very high percentage of O atoms striking the coupon must be reacting with the malathion to form malaaxon, demonstrating that malathion is very easily oxidized. A reducing environment produced by generation of atomic hydrogen also appears promising as the observed removal of malathion using 4% hydrogen shown in Fig. 3 is comparable to that of oxygen at the same concentration. For this reason hydrogen exposures were incorporated into the actual chemical warfare agent testing conducted at Dugway Proving Ground.

Unlike malathion, exposure of VX to a pure He plasma gives results similar to a plasma process consisting of 10% hydrogen and 90% helium, as shown in Fig. 5. Although VX is about 50 times more volatile than malathion at 70 °C, the evaporation rates when exposed to pure He discharges are of the same order of magnitude for the two substances. This implies VX is much more difficult to oxidize than malathion, allowing evaporation to be the dominant decon mechanism. However, there is sufficient reactivity in the liquid phase to note significant differences between oxygen and hydrogen exposures. There is a clear difference between an oxidizing and a reducing environment. This is evidenced by having only one of several GC/MS retention time peaks in common between the oxygen and hydrogen exposures plotted in Figs. 6 and 7. Although the byproducts have not been identified, they generally decrease with plasma exposure and thus should not result in any residual hazard.

A brown residue was observed to form in both malathion and VX experiments. This residue appears to correlate with a decreasing decon rate with time as the residue is forming, as seen in Figs. 4 and 5. This is most prevalent in the oxygen exposures. In the case of VX exposure to hydrogen, this brown residue is formed, but quickly goes away, resulting in a more continuous decon process to below the minimum detectable level. It is speculated that this residue shields small quantities of chemical agent from the reactive gas stream and inhibits the decon process. At this point, we do not know the property of this solid residue. As for possible GC/MS peaks related to the observed brown residue, we found that only two byproducts remain detectable in the GC/MS after 16 min of exposure in the case of oxygen. The new compound having a retention time of 8.11 min is quickly formed within the first 30 s of exposure and remains relatively flat out to 16 min, consistent with the formation of the brown residue. However, we suspect that the residue is a heavier, polymerized compound that is not passing through the GC column into the MS, and hence is not being detected.

For the more volatile chemicals, such as phenyl half mustard, HD and GD, evaporation and subsequent decontamination in the gas phase is likely to be the dominant decon mechanism. Once the agent is volatilized, it can be quickly neutralized as it passes through the plasma as nearly ten system volumes are circulated every second. This was quite evident with the HD simulant, which was seen to fully oxidize to CO₂ and H₂O on a time scale consistent with the decontamination process determined by GC/MS analysis of liquid extractions. Similar to the simulant result, HD and GD are likely readily combusted as they pass through the plasma. However, if evaporation were

the only decon mechanism, it would be expected that the decon rate would be independent of the gas composition. As seen in Figs. 8 and 9, H₂ is more effective for HD, and O₂ more effective for GD decontamination. From the GC/MS chromatograms for HD, there does appear to be chemical reactivity in the liquid phase producing nonvolatile byproducts, but the large number and quantities of impurities in the mustard solution used makes it extremely difficult to sort impurity byproducts from mustard byproducts. There does not appear to be significant nonvolatile byproducts for GD but the observation that the decon rate is dependent on gas composition indicates that there is reactivity. Most likely, GD byproducts are volatile and so are not detected in the liquid extractions taken for GC/MS analysis. Pure He plasma exposures are required to determine the degree of evaporation versus reactivity. It is unfortunate that these exposures were not conducted.

One of the more difficult challenges to any decon system is how well it performs against thickened agent. Thickeners are often added to chemical warfare agents, particularly the more volatile ones such as the G-agents, to make them more persistent. Since the object of this set of experiments was to see how the plasma performed in the presence of a thickener, agent simulant was used to avoid the unnecessary complications of using actual agents. As was the case with malathion and VX, it is speculated that a solid residue from the thickener or dye may be shielding MeS and inhibiting the decon process beyond 1 min of exposure. From these results, it appears that thickeners may present a challenge, but further investigation is needed before any definitive conclusions can be made in this regard.

B. Chemical Species Determination

Determining the dominant chemical species responsible for the observed reactivity can best be accomplished by comparing the effective standoff distances of Fig. 2 with calculated reactive species lifetimes. The effect of system pressure on atomic oxygen and hydrogen lifetimes are shown in the gas phase chemistry modeling results of Fig. 11. The calculated lifetimes for the singlet delta and singlet sigma metastable states of molecular oxygen [i.e., O₂(a) and O₂(b)] are also shown at 600 torr. These calculations were carried out assuming a gas temperature of 70 °C and initial species concentrations as given in the figure caption. These initial concentrations are reasonable estimates based on previous experimental measurements. Reaction rates were taken from exponential fits to the NIST Chemical Kinetics Database [15]. Greater details on the modeling technique and experimental measurements of reactive species can be found in [11].

For the purposes of this plot, the lifetime is simply defined as the time it takes for the initial concentration to decrease by a factor of (2.7). O atom lifetimes are plotted for 1% O₂ and 10% O₂ addition, whereas H atom lifetimes are independent of H₂ percentage. This is because the only significant loss mechanism for H atoms is through recombination: $H+H+M \rightarrow H_2+M$ where M is a third body and is assumed to be He. Hence, for a fixed initial concentration [H], the reaction rate depends solely on [He], which is inversely proportional to pressure. Oxygen atoms, on the other hand, have two significant loss

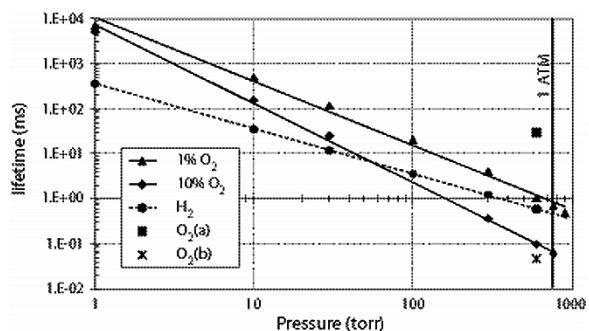


Fig. 11. Atomic O and H lifetimes as determined by gas phase chemistry modeling for 70 °C, and initial concentrations in 10^{15} cm^{-3} of [O] or [H] = 2.7, [O₃] = 2, [O₂(a)] = 2, and [O₂(b)] = 0.7.

mechanisms: recombination ($O+O+M \rightarrow O_2+M$) and ozone formation ($O+O_2+M \rightarrow O_3+M$). The latter loss mechanism is dependent on [O₂], which for a fixed percentage of addition, also varies inversely proportional to pressure.

The results of Fig. 2 clearly demonstrate that ozone can not be the species responsible for the chemical conversion of malathion because ozone concentration actually increases with standoff distance. This has been confirmed through direct measurement of ozone levels by UV absorption. This is because ozone is produced through the consumption of O atoms. Although ozone is lost through metastable quenching ($O_3+O_2(a/b) \rightarrow 2O_2+O$), this process produces atomic oxygen, which is quickly converted back to ozone resulting in little net loss of ozone. Therefore, atomic oxygen and ozone have inverse chemical concentrations; atomic oxygen decrease is balanced by ozone increase. Thus, one would expect an increasing decon efficacy with standoff distance if reaction with ozone were the dominant decon mechanism, but this is not the case.

Similarly, the dependence on standoff distance appears to be more consistent with O atom lifetimes than with the O₂ metastable lifetimes [11]. The calculated lifetime of the O₂(a) state at 600 torr is approximately 29 ms. At the plug-flow velocity of 3.7 m/s, the slowest possible flow in the system, these metastables would travel at least 10 cm before being reduced by a factor of e. This is clearly inconsistent with the ~0.5 cm it takes for the decon efficiency to drop by this same factor as seen for 600 torr in Fig. 2. The calculated lifetime of the O₂(b) state at 600 torr is approximately 0.05 ms. At the plug-flow velocity, these metastables would only travel about 0.02 cm before being reduced by a factor of e. Again, this is inconsistent with Fig. 2. Atomic oxygen, on the other hand, with a calculated lifetime of ~1 ms under these conditions travels at least 0.4 cm, consistent with the observation. Thus, atomic oxygen appears to be the most likely reactive species responsible for the observed chemical decontamination.

By decreasing the pressure to 30 torr, the O atom lifetime, and hence effective standoff distance, increases by a factor of 100, assuming all other parameters remain the same. However, at lower gas pressure, it is also desirable to use higher oxygen fractions to increase the initial O atom concentration. At the chosen standard-operating conditions of 30 torr and 10% oxygen, the model yields an O atom lifetime of 25 ms, consistent with the nearly flat decon efficacy shown in Fig. 2

between 1.5 and 7.5 cm. Under the same conditions, the H atom lifetime is about a factor of two less than for O atoms.

Development of a more useful size chamber will require standoff distances on the order of 0.5–1 m. This can be achieved through a combination of high gas flow (~ 10 m/s) and long O or H atom lifetime (~ 100 ms). Achieving a 100-ms O atom lifetime involves a tradeoff between gas pressure and added oxygen fraction but should be achievable at 10 torr and 20% O₂. A 100 ms, H-atom lifetime is slightly more difficult to achieve for the given conditions, requiring an operating pressure below 5 torr. Use of alternative process gas, such as NH₃, may also prove to be promising.

It should be noted that although this device may operate at reduced pressure, it is significantly different from low-pressure plasma devices that generally operate in the sub-torr range. The Plasma Decon Chamber operates in excess of 10 torr, where significant pressure gradients can be established to drive the flow of reactive species to where they are needed and the thermal capacity of the carrier gas is sufficient to thoroughly heat equipment surfaces internally and externally. Also, by working above the vapor pressure of water at room temperature, vacuum compatibility problems in treating equipment from the field are alleviated.

C. Evaporation of Agent

The exposures using plasma with pure helium feedgas were conducted to investigate the purely thermal effect on the agents. For example, the use of high-purity helium, combined with a very low air-leak rate, ensures a pure helium discharge does not produce a substantial amount of reactive radicals. This was clearly demonstrated by the lack of any byproduct in the GC/MS analysis when VX contaminated coupons were exposed to the pure helium plasma. However, these exposures do not necessarily represent a purely thermal effect. For example, in the case of malathion, evaporation should play only a minor role due to a very low vapor pressure of ~ 1 mtorr at 70 °C [16]. In comparison, evaporation should be much more rapid in the case of VX as the vapor pressure of VX is about 50 times greater than malathion at 70 °C [17]. However, comparing the pure helium plasma results of Figs. 3 and 5, it appears that the evaporation rates for the two compounds are of roughly the same order. One possibility that deserves mention is that metastable helium atoms, with a potential energy of 19.4 eV, can also deliver a considerable amount of energy to exposed agents and hence promote evaporation. UV radiation may also result in plasma-induced effects that are not purely thermal. In retrospect, it would have been preferable to have a purely thermal means of heating the feedgas to evaluate the baseline thermal effect.

However, it is noted that the object of this technology is not to decon equipment surfaces by purely chemical means. Evaporation of liquid agents from surfaces and subsequent destruction of these agents in the gas phase as they pass through the plasma discharge is an effective means for decontamination. By greatly reducing the feed and bleed rate, the agent loading of physical-filter media such as activated charcoal is significantly reduced. More importantly, plasmas still provide reactive gases to downstream surfaces for solid or thickened agents that do not evaporate readily. This is of particular importance

in the case of biological agents such as anthrax, which would require many days to be neutralized solely by the combination of vacuum and heat at temperatures below 70 °C [18]. Hence, this technology has significant advantages over infrared-heated, vacuum-based decon. The goal of Plasma Decon Chamber technology is to combine plasma, heat, vacuum, and forced convection (gas flow) into an effective decontamination method for all chemical and biological warfare agents.

D. Collateral Damage

Regarding collateral damage of sensitive equipment exposed to the reactive gas stream, it has been seen that exposure to He/H₂ plasma is gentler on materials, yet results in a comparable, or even more effective, decon process than He/O₂. This apparent lack of collateral damage using hydrogen plasmas is an encouraging sign for the potential use of this technology for the decon of sensitive equipment.

E. Future Work

This work was a initial investigation to explore the feasibility of using the Plasma Decon Chamber for decontamination of chemical and biowarfare agents. A few significant details have been missed during this initial phase of investigation. Baseline comparison of pure helium plasmas and thermal evaporation is needed to determine the relative importance of plasma-induced evaporation. In addition, gas sampling techniques must be improved to avoid the loss of information that occurred with the current sorbent-tube technique. Still, these initial results appear promising enough to warrant further investigation. For example, further agent work, using high-purity agent, is needed to understand the kinetics of chemical reactivity and to optimize exposure conditions. Also, residue formation needs to be understood and if possible avoided so as to not inhibit the decon process.

We believe that considerable improvements in the rate of decontamination can be achieved by future improvements to the design of the decon chamber and the use of new process gases. In particular, pressure pulsing must be incorporated and studied to determine if it promotes penetrative decontamination. Although our initial results have been highly promising, thorough material compatibility studies are also needed to ensure equipment will not be damaged by the decon process. At the same time, scaleup of the physical dimensions must be accomplished to be able to accommodate larger items. The next generation decon chamber should be approximately 1 m \times 1 m and 0.5-m high with the ability to flow gases in both vertical directions, possibly with multiple levels for plasma generation.

VI. CONCLUSION

An experimental prototype Plasma Decon Chamber has been developed and demonstrated at LANL to address the decontamination of sensitive materials and equipment that might result following a limited or large-scale chemical-weapon attack. The purpose of this study was to investigate a means of decontaminating highly valued equipment that would likely be damaged if treated by current decon methods. We have shown that a plasma may be used to generate highly reactive radicals, such as atomic oxygen or hydrogen, both of which are capable of selectively

neutralizing CBW agents without significantly damaging most materials. This decontamination chamber was characterized and optimized using CBW simulants at LANL. The same system was then used to decontaminate actual CBW agents in a collaborative program at the U.S. Army Dugway Proving Ground. At the selected "standard exposure" conditions, consisting of an exposure temperature of 70 °C, system pressure of 30 torr, and a plasma-to-sample standoff distance of 10 cm, decontamination levels of >99.9% were achieved in under 2 min for chemical agents HD and GD, and under 16 min for VX. Evaporation and subsequent chemical breakdown during recirculation through the plasma is believed to be the dominant decontamination process for these agents. Evidence for chemical decomposition on the aluminum-coupon surface demonstrates that this technology may prove effective in situations where vacuum and low temperature heat by themselves are not sufficient, particularly for decon of biological-warfare agents. The Plasma Decon Chamber combines heat, vacuum, forced convection, and reactivity for enhanced CBW decontamination of sensitive equipment.

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REFERENCES

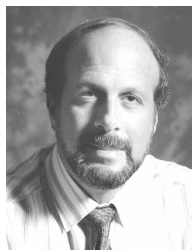
- [1] G. Irving, T. McMurray, and J. Herbold, "Non-medical dispersed biological weapons countermeasures," Tech. Rep. AL/OE-TR-1997-0081, U.S. Air Force Armstrong Lab., San Antonio, TX, 1997.
- [2] "Joint service chemical and biological science and technology base program in decontamination," CBIAC Product Number: CR-01-04, U.S. Dept. Defense, Chemical and Biological Defense Information Analysis Center (CBIAC), Edgewood, MD, Apr. 2001.
- [3] H. W. Herrmann and G. S. Selwyn, "Atmospheric-pressure plasma decontamination/sterilization chamber," U.S. Patent 6 228 330, May 8, 2001.
- [4] G. S. Selwyn, "Atmospheric-pressure plasma jet," U.S. Patent 5 961 772, Oct. 5, 1999.
- [5] A. Schütze, J. Y. Jeong, S. E. Babayan, J. Park, G. S. Selwyn, and R. F. Hicks, "The atmospheric-pressure plasma jet: A review and comparison to other plasma sources," *IEEE Trans. Plasma Sci.*, vol. 26, pp. 1685–1694, Dec. 1998.
- [6] H. W. Herrmann *et al.*, "Dry decontamination of chemical/biological warfare agents using an atmospheric pressure plasma jet," *Phys. Plasmas*, vol. 6, p. 2284, 1999.
- [7] J. Park, I. Henins, H. W. Herrmann, G. S. Selwyn, J. Y. Jeong, R. F. Hicks, D. Shim, and C. S. Chang, "An atmospheric pressure plasma source," *Appl. Phys. Lett.*, vol. 76, p. 288, 2000.
- [8] J. Park, I. Henins, H. W. Herrmann, and G. S. Selwyn, "Gas breakdown in an atmospheric pressure RF capacitive plasma source," *J. Appl. Phys.*, vol. 89, p. 15, 2001.

- [9] J. Park, I. Henins, H. W. Herrmann, G. S. Selwyn, and R. F. Hicks, "Discharge phenomena of an atmospheric pressure radio-frequency capacitive plasma source," *J. Appl. Phys.*, vol. 89, p. 20, 2001.
- [10] J. Park, I. Henins, H. W. Herrmann, and G. S. Selwyn, "Neutral Bremsstrahlung measurement in an atmospheric-pressure Radio-Frequency (RF) discharge," *Phys. Plasmas*, vol. 7, p. 3141, 2000.
- [11] J. Y. Jeong, J. Park, I. Henins, S. E. Babayan, V. J. Tu, G. S. Selwyn, G. Ding, and R. F. Hicks, "Reaction chemistry in the afterglow of an oxygen-helium, atmospheric-pressure plasma," *J. Phys. Chem. A*, vol. 104, p. 8027, 2000.
- [12] Y.-C. Yang, J. A. Baker, and J. R. Ward, "Decontamination of chemical warfare agents," *Chem Rev.*, vol. 92, p. 1729, 1992.
- [13] G. S. Groenewold, A. D. Appelhans, G. L. Gresham, and J. E. Olson, "Characterization of VX on concrete using ion trap secondary ionization mass spectrometry," *J. Amer. Soc. Mass Spectrom.*, vol. 11, p. 69, 2000.
- [14] G. S. Groenewold, A. D. Appelhans, G. L. Gresham, and J. E. Olson, "Analysis of VX on soil particles using ion trap secondary ion mass spectrometry," *Anal. Chem.*, vol. 71, p. 2318, 1999.
- [15] NIST chemical kinetics database, version 2Q98, 1998. Nat. Inst. Standards Technol., Gaithersburg, MD, [Online]. Available: <http://www.nist.gov/srd/nist17.htm>, NIST Standard Reference Database 17.
- [16] U.S. Dept. Agriculture. ([Online]. Available: <http://www.arsusda.gov/acsl/ppdb.html>) Agricultural research service pesticide properties database, 1995.
- [17] D. Fielder and A. B. Livesey, "Physical properties measurement in the selection of simulants," Tech. Rep. CRDEC-TR-007, Chem. Biol. Defense Inform. Anal. Center, U.S. Department of Defense, Washington, DC, Nov. 1988.
- [18] G. Molin, "Inactivation of bacillus spores in dry systems at low and high temperatures," *J. General Microbiol.*, vol. 101, p. 227, 1977.



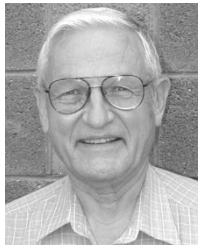
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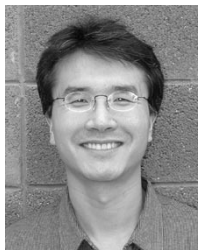
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