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MARITIME EVALUATION OF AEROSOL FIRE KNOCK DOWN TOOLS

PART 2: TOXICITY AND CORROSION POTENTIAL

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1 Introduction

Full-scale live fire tests were conducted at the University of Waterloo (UW) Fire Research Laboratory in collaboration with Defence R&D Canada, Atlantic Research Center, Royal Canadian Navy (RCN) personnel from the Director of Maritime Ship Support and the Canadian Forces Naval Engineering School. The tests were designed to study possible impacts such as toxic gas generation, aerosol deposition or corrosion of equipment due to deployment of handheld aerosol extinguishers in a naval application. The experimental data contained in this report will be used by the RCN for determining the relative merits of handheld aerosol extinguishers as potential fire knockdown devices onboard naval warships and to better understand the potential hazards that pyrotechnically generated aerosol agent devices may present when used or accidentally discharged within a naval vessel.

A total of 26 live fire suppression tests and 6 cold discharge (agent only) tests, instrumented for gas analysis, were conducted in the UW modified shipping container burn facility. The facility has a volume of 20 m^3 to represent a small marine machinery space. The fuel loads for the suppression tests were designed and characterized to provide a steady heat release rate and a fully developed fire environment at the onset of aerosol agent suppression, allowing comparison among the various repeatable tests.

The aerosol units tested were the StatX First Responder® with a single unit rated for use in fire compartments of no more than 20 m^3 and the DSPA 5-4 Manual Firefighter® with a single unit rated for use in fire compartments of no more than 18 m^3. These are shown in Figure 1-1 a) and 1-1 b) respectively.

a) StatX First Responder®   b) DSPA Manual Firefighter ®

Figure 1-1: StatX and DSPA 5-4 extinguishing units used in testing

The aerosol units were supplied by each manufacturer together with design criteria, operating instructions, drawings and technical data. The respective company representatives delivered the aerosol units to UW and provided training and technical support in their use to ensure proper and repeatable activation per manufacturers' instructions. UW maintained a collaborative relationship with both industrial partners throughout the testing [1].

This report summarizes work focused towards the assessment of possible toxicological effects that might be encountered through the use of aerosol agents for fire suppression, as well as post suppression impacts such as corrosion or residue due to deposition of aerosol agents on sensitive electronics or common shipboard materials. A companion report and MASc thesis focus on the suppression efficacy, safe storage and incendiary potential of the units based largely on results from an earlier series of tests [1, 2] that are extended in this work.

1.1 Background Issues

Some key issues surrounding the use of aerosol extinguishing agents were identified in the previous work [1, 2]. These are briefly discussed here in order to put the present test plan and results into perspective.

1.1.1 Toxicity and Exposure Thresholds

There is potentially cause for concern over toxic gas evolution arising from the use of aerosol agents for fire suppression even though they are often described as environmentally friendly fire extinguishing agents [3, 4, 5]. Emission of gases and particulates from the units is particularly important, especially in the context of the relatively confined spaces encountered in marine or naval applications. Even if such extinguishing agents are only utilized in normally unoccupied spaces, there is still the potential for human exposure either due to improper confinement of a compartment following suppression or through accidental release of the unit into an occupied space.

The particulate aerosol, which is the main suppression agent generated from handheld units, is produced via thermal decomposition of a solid, aerosol forming compound or compounds in the presence of a hydrocarbon binding agent. While the exact composition of the aerosol generation materials in most units is proprietary, pyrotechnic aerosol extinguishing systems often involve base compounds such as potassium nitrate (KNO_3) mixed with an organic oxidizer and binding agent. Upon activation, the base materials react to generate fluid aerosols in proximity of the units which then condense into solid particles. These can be comprised of compounds such as potassium carbonate (K_2CO_3) and potassium bicarbonate ($KHCO_3$), as well as ammonium bicarbonate (NH_4HCO_3). Gases such as CO_2, N_2, and H_2O are generated via the activation reactions and mix with ambient air; however, due to the combination of reactions taking place and the temperatures involved, there is also the potential for the production of other species such as oxides of nitrogen (NO_x or NO and NO_2), hydrogen cyanide (HCN), ammonia (NH_3) and carbon monoxide (CO) as well depending on the nature of the base compounds and details of the reaction and decomposition processes [6]. For example, Chattaway et al. found that certain KNO_3 based pyrotechnic aerosols produce NO concentrations between 300-600 ppm [7] and CO concentrations between 350-3000 ppm [8]. Pyro-aerosols have also been shown to produce trace amounts of hydrogen cyanide (HCN) between 10-15 ppm [8], possibly also with formation of NO in the presence of unburned hydrocarbons and combustion radicals. In terms of human impact, the presence of even low concentrations of CO and NO_x and the ultra-fine potassium salt aerosols may lead to irritation or interference with the function of human mucus membranes [8]. By way of setting benchmark concentration values for later comparison with measurements, summarized below are some of the existing exposure thresholds and guidelines for NO_x, HCN, NH_3, CO and CO_2 exposure as outlined in occupational health and safety literature.

Toxicological concentration thresholds for nitrogen oxides (NO_x) are generally specified with respect to measured values of NO_2, since better data exists with respect to toxicology of NO_2 than for NO and NO_2 is also often used as an indicator for the presence of nitrogen oxides (NO_x). In addition, NO_2 is five times more acutely toxic than NO [9]. That said, it should be noted that there is little consistent evidence of long term health effects with exposure to NO_2 and there is still significant uncertainty in human exposure-response data for both acute (< 3 hour) and long term exposure [10]. According to the World Health Organization (WHO), sub-chronic or acute exposures to concentrations of NO_2 of as little as 2 ppm can have some physiological impacts particularly in the case of children between the ages of 5 and 12, and asthmatic adults [10]. As such, the levels of exposure proposed in the WHO guidelines are 0.1 ppm for continuous 1-hour exposures and 0.02 ppm for long term exposures [10]. In contrast in the USA, the Occupational Safety and Health Administration (OSHA) has set a higher 15-minute exposure limit of 5 ppm for NO_2 in workplace air, with an IDLH of 20 ppm [11, 12]. Both OSHA and United States National Institute for Occupational Safety and Health (NIOSH) indicate a permissible exposure limit of 25 ppm NO averaged over an 8-hour work shift, with an Immediate Danger to Life or Health (IDLH) limit of 100 ppm [11, 13, 14]. Other published levels suggest ten minute exposure levels for NO_2 of 5 ppm, while exposure to several hundred ppm over the course of minutes is purported to cause deep lung irritation potentially leading to pulmonary edema or fluid buildup in lungs, which can also lead to death [9]. Although not as pertinent to this work, the United States Environmental Protection Agency (EPA) has established that the average concentration of NO_2 in ambient air in a calendar year should not exceed 0.053 ppm for outdoor exposures [15]. These values can be used as benchmark levels against which to compare the NO and NO_x concentrations presented in this report, provided that note is taken of the overall lack of sound toxicological data for nitrogen oxides and consequent uncertainty in potential threshold and exposure values [11].

Compounds such as hydrogen cyanide, HCN, are thought to arise during aerosol generation possibly through secondary reactions of NO in the presence of unburned hydrocarbons and various combustion radicals. HCN is particularly worrisome since it is generally considered to be around 30 times more toxic than CO and is toxic to humans if inhaled even at the relatively low concentrations and for the short exposure durations listed in Table 1-1 [16]. As with exposure to NO_x, exposure to HCN for even short periods of time can lead to severe health complications so concentration thresholds for HCN exposure are generally specified with respect to a time of exposure. Current OSHA guidelines stipulate that an 8 hour time weighted average level of 10 ppm of HCN is permissible [17]. In contrast, the NIOSH indicates a lower threshold of 4.7 ppm as the 15 minute time weighted average exposure threshold. After ten minutes of exposure to concentrations of only 181 ppm, however, HCN gas can potentially induce pulmonary edema with subsequent failure of the respiratory organs [17]. At the IDLH of 270 ppm, death is almost instantaneous after a few inhalations of HCN [17]. While the literature reviewed on pyrotechnically generated aerosols does not report measured HCN concentrations that exceed acute toxicity levels, the health dangers associated with HCN exposure should dictate a high standard of care and vigilance in understanding the potential for generation of HCN. As such, measurements of HCN concentration were attempted during several of the fire and agent only test scenarios conducted in this work.

Table 1-1 Time to death following hydrogen cyanide inhalation in humans [16]

Dose		**Time to Death**
mg/m3	**ppm**	
150	135	30 min
200	180	10 min
300	270	Immediate

In addition to the generation of NO_x and HCN during aerosol production, there is also some potential for formation of other nitrogen containing compounds such as ammonia (NH_3) due possibly to the decomposition of ammonium bicarbonate (NH_4HCO_3) to ammonia (NH_3), water (H_2O) and carbon dioxide (CO_2) when it reaches temperatures higher than 36°C. Concentration thresholds listed for human exposure to NH_3 again differ depending on organization. Current OSHA guidelines indicate permissible exposure levels of 50 ppm for 8-hour time weighted average exposure to NH_3 [18]. In contrast, NIOSH and the American Conference of Governmental Industrial Hygienists (ACGIH) indicate a permissible threshold of 35 ppm for 15-minute exposure but a lower value of 25 ppm as the 8-hour time weighted average exposure limit [18, 19]. These sources also suggest IDLH limits of 300 ppm [18, 19]. Although no direct references to concentrations of NH_3 formed during aerosol generation were found in the literature, due to the potential for formation of NH_3, concentration measurements were attempted during several of the fire and agent only test scenarios conducted in this work.

Carbon dioxide (CO_2) and other common exhaust gases are produced from the aerosol units during the combustion process involved in the primary stages of aerosol generation. Depending on conditions in which the oxidation reactions take place, both CO_2 and carbon monoxide (CO) can be produced. CO is a clear, colourless and poisonous gas for which toxicological concentration thresholds are again generally specified with respect to time weighted exposure values, but do vary considerably depending on organization. For example, the levels of exposure proposed in the

WHO guidelines are approximately 90 ppm for 15 minute average exposures and less than 10 ppm for 8 hour time weighted average exposures [20]. In contrast in the USA, the OSHA has set a higher 8-hour weighted average exposure limit of 50 ppm for CO in workplace air, with a ceiling level of 100 ppm [21]. NIOSH suggest 8-hour exposure levels for CO of 35 ppm with ceiling levels of 200 ppm and an IDLH of 1,200 ppm [22]; while exposure to 2000-5000 ppm is purported to cause death in minutes. The National Research Council in the United States (NRC) set Emergency Exposure Guidance Levels (EEGLs) for CO based on exposure time as: 10-minute EEGL: 1,500 ppm, 30-minute EEGL: 800 ppm, 60-minute EEGL: 400 ppm, and 24-hour EEGL: 50 ppm with a lethal concentration threshold for humans of 5000 ppm for 5 min [23], although values are adapted depending on other details of the exposure situation [24]. CO levels produced from pyrotechnically generated aerosol units will vary widely based on the solid tablet composition and thus details of the aerosol oxidation reactions. Kopylov et al. [8] studied the CO production from five different pyrotechnic aerosol combinations, using samples of about 1 kg in initial mass. The study revealed that the concentrations of CO from the different aerosol generation compounds varied between 572 and 4000 mg/m^3 which, based on the molecular weight for CO of 28 g/mol, equates to a concentration range of approximately 464 to 3243 ppm [8]. The range of CO concentrations observed in the experiments in ref [8] highlights how dependent the production of CO is on the initial pyrotechnic tablet composition and reaction conditions, but also that the potential for CO production during aerosol activation should not be overlooked in a naval application. Based on this potential, the Royal Navy Institute of Naval Medicine has approved pyrotechnic aerosols for use in unmanned compartments only, stating that personnel must be able to vacate the scene within two minutes, i.e. before CO levels become prohibitive [25]. To further investigate this issue, CO and CO_2 concentrations were assessed during both agent only and fire suppression scenarios.

Based on the above information, there is sufficient variability in the public literature on the toxicity of pyrotechnically generated aerosol systems to warrant a more stringent, thorough, and independent toxicology study prior to procurement or use by the RCN. Preliminary investigation into some of these issues forms one important aspect of the present work.

1.1.2 Heat and Flame Ejection

The thermal decomposition and combustion of solid pyrotechnic fuel tablets is known to generate significant heat and flames, as well as rapidly expanding hot gases and liquid aerosol materials a short period of time after initiation of aerosol generation [6]. The combustion temperature of a KNO_3 based solid tablet is between 1200-2100^{o}C [26]. While an effective fire suppression agent is being produced in conjunction with the generation of any heat and flames, suppression systems based on pyrotechnically generated aerosols can eject flames and hot gases up to 1 m from the canisters and render the metal surfaces of those canisters red hot [7], thus potentially posing significant thermal hazards. These impacts were discussed in depth in a companion report [1] and thesis [2] and, except in relation to the nature of gases produced, are not dealt with further in the present report.

1.1.3 Corrosion Potential

Pyrotechnically generated aerosol fire suppression agents produce a buoyant mixture of micron-sized liquid and particulate aerosols carried in a gaseous medium that consists of a range of decomposition and oxidation products of aerosol forming compounds. For effective suppression, this mixture should be well dispersed throughout the compartment and therefore, the liquid and particulate aerosols and gases may come into contact with surfaces and equipment. In modern naval applications, even machinery spaces contain thousands of electronic devices that are critical for platform systems management and control, and therefore, survivability of a vessel. As a result, any adverse impacts due to deposition of liquid or particulate aerosol compounds onto surfaces are of interest, as is potential corrosion due to contact of the aerosol compounds with sensitive surfaces, electronic equipment or other devices.

Deposition of aerosol residue onto electronics and samples of various metal and polymer materials commonly used in electronics has been evaluated to some degree, but not in sufficient depth to fully appreciate any possible long term effects [7, 27]. In a fully developed fire scenario, exposure of equipment to heat, flames and hot toxic gases produced from the burning fuels certainly has the potential to cause damage. Suppressing the fire by the quickest means will minimize the damage due to the fire, but with aerosol agents, there may be the potential for corrosion or deposition of residue from the extinguishing agent itself. Further, in the case of accidental discharge of fitted aerosol systems, or activation of fitted aerosol systems for very small fires in large compartments, the resultant residue may be of considerable concern. As a result, it was decided to further investigate issues such as particle deposition and the potential corrosive by-products arising from the aerosol agents in this work since these impacts may not be considered acceptable trade-offs, particularly when there are several candidate suppression systems for a given application.

Technical white papers outlining tests on some pyrotechnic aerosol extinguishers note that after the fire is suppressed most of the suppression agent can be exhausted in the same manner as smoke, but results also indicate that a slight film may be left on surfaces [28, 29]. Manufacturers recommend removing any aerosol residue deposited on equipment and electronics using a damp cloth, vacuum or compressed air. In the case of large compartments with thousands of sensitive electronic devices, however, this process could prove expensive and time consuming and it would be extremely difficult to ensure that all surfaces had been cleaned. Some manufacturers postulate that aerosol agents are non-corrosive, citing studies conducted in the early 1990s [29]. These report that aerosol agents were found to be non-corrosive to electrical and structural materials, although the included references could not be found and therefore were not reviewed as part of this work. Jacobson et al. [27] conducted a corrosion study on the GreenSol aerosol material and found that the agent was non-corrosive against 12 common metal and polymer materials; however, the composition of the agent was not provided and unfortunately, the composition of the aerosol has been demonstrated to make a significant difference on potential corrosive impacts. For example, pyrotechnically generated aerosols based on perchlorates of nitrogen produce potassium chloride, which is known to be corrosive to aluminium and certain grades of steel [7]. In other units, potassium nitrate, KNO_3, is thermally decomposed with a resultant powder residue comprised mainly of potassium carbonate. Potassium carbonate particles may not lead to corrosion of most metals and alloys [30], but when dissolved in water it results in a medium to strong basic solution [31]. There could also be other as yet unidentified corrosive agents present and known substances such as potassium carbonate may react with those [31], leading to the potential for corrosion of some materials. Due to the potential for significant consequences of corrosion in the context of large marine compartments containing thousands of critical electronic devices, the second main focus of the present work was to undertake preliminary studies into the deposition and possible corrosivity of aerosols on electronic devices and firefighter personal protective equipment (PPE) to gain a better understanding of post suppression impacts of agent use for naval applications.

Based on the above review, it was decided to focus the present assessment on the measurement of concentrations of various gases, as well as evaluation of powder deposition and post suppression damage that occurred during a series of controlled agent only discharge and fire suppression tests conducted in a fixed volume test compartment using the two different handheld aerosol units described above.

The next Chapter outlines the fire tests and agent only scenarios used in the present work, followed by more detailed descriptions of the burn compartment set up, instrumentation and methods in Chapter 3, with results and discussion in Chapters 4 through 7. Chapter 8 contains conclusions and some recommendations for future investigation into handheld aerosol extinguishing units in the context of the present study.

2 Fire Test Description

Reference conditions for the tests were set via a series of characterization tests which used an unobstructed diesel fire (diesel characterization fire) with no suppression and the door of the compartment held in three positions: fully open, open to 0.3m and fully closed. Initial fire and agent only tests were conducted in conjunction with a set of well controlled suppression efficacy tests that have been reported in detail elsewhere [1, 2]. The two handheld aerosol units were employed against four different instrumented fire scenarios (unobstructed diesel, obstructed engine enclosure fire, obstructed bilge fire and softwood crib fire) and also deployed in an aerosol agent only scenario. In the initial diesel characterization fires, unobstructed diesel, obstructed engine enclosure and softwood crib fires, the door was held open (with a set 0.3m opening) after discharge of the aerosol agent, while the door was closed immediately after discharge during the obstructed bilge fire and agent only tests.

A second round of testing was conducted for comparison and enhancement of these initial results. In the second round tests, the compartment door was closed after discharge of the agent and was held shut for the 10-15 minute duration of the test for all of the fire and agent only scenarios.

Key details of all of the fire loads and scenarios investigated are outlined in Section 2.1 below. The initial fire suppression tests are also described in further detail in [1] and [2].

2.1 Suppression Test Fires and Programme

The test programme involved the fire loads outlined in Table 2-1 and the scenarios described in Table 2-2. Each test listed in Table 2-1 was conducted several times for both aerosol units.

Table 2-1: Fire loads used in aerosol testing

Fire	Type	Fuel	Fire Size, MW
A	0.82 m^2 with 10 ℓ of diesel over a 105 ℓ water base	Diesel	0.9
B	Softwood crib	Spruce	0.12
C	0.1 m^2 tray with 0.2 ℓ methanol	Methanol	0.03
D	Butane lighter	Butane	0.0005

The characterization tests used an unobstructed diesel fire, Fire A, as noted above. The first fire scenario was the same open diesel pool fire using Fire A, where the fire was allowed to reach a steady state burning rate before the unit was deployed. The second fire scenario consisted of an obstructed fuel fire, again based on Fire A, where a 1.4 m x 1.3 m x 0.46 m steel structure was suspended 0.4m over the floor to simulate an engine enclosure. The third scenario, again involving Fire A as the base fire, involved activation of the extinguishers and then placing them into a pan of water 0.3m deep to simulate the units falling into a watery bilge. The final fire scenario was a wood crib fire, using Fire B and designed to simulate a general 'Class A' fire in a shipboard compartment. As a reference case, the units were also discharged into the test compartment when no fire was present (agent only). Once the agent was activated in the agent only tests, the compartment door was sealed for the duration of the experiment.

In all tests, gas concentration data were gathered using a Novatech P-695 measurement system, capable of detecting unburned hydrocarbons (UHC), nitric oxide (NO), nitrous oxides (NO_x), oxygen (O_2), carbon monoxide (CO) and carbon dioxide (CO_2). In addition, a Gastec STR-800 hand pump system with pre-calibrated gas absorption tubes was employed during some tests to measure NO and NO_2, as well as additional compounds such as hydrogen cyanide (HCN) and ammonia (NH_3). Since there is not a well-defined standard test procedure for gas analysis during full scale fire experiments, a variant of the ASTM E-800-5 standard test method was adopted for gas concentration sampling and measurement in the present work [32].

Table 2-2: Aerosol suppression test programme

Test No.	Fire Suppression Test Scenarios
	Characterization Fires: 0.82 m^2 tray unobstructed diesel pool fire with no suppression Gas concentration measurements and exposure of material coupons (chrome plated aluminum, chrome plated nickel and chrome plated steel and copper)
1	Fire A: 0.82 m^2 tray as unobstructed diesel pool fire Gas concentration measurements and exposure of material coupons (chrome plated aluminum, chrome plated nickel and chrome plated steel and copper, copper beryllium, high tensile and mild steel, circuit board and CD disc).
2	Fire A: 0.82 m^2 tray as an obstructed diesel pool fire under engine enclosure mock-up Gas concentration measurements
3	Fire A: 0.82 m^2 tray as obstructed diesel pool fire under engine enclosure mock-up; activate extinguisher, slide into fuel pan to simulate units falling into a watery bilge Gas concentration measurements
4	Fire B: 4 softwood cribs near back wall of test room as unobstructed Class B fire with Fire C as an ignition source – 1 methanol ignition fire Gas concentration measurements
5	Fire D: Agent Only: Activate unit in burn room with no fire Gas concentration measurements and exposure of material coupons (chrome plated aluminum, chrome plated nickel and chrome plated steel and copper, copper beryllium, high tensile and mild steel, Nomex, open computer tower, circuit board and CD disc).

Aerosol residue and its potential corrosive effects were investigated by exposing coupons of various materials and electronic components during agent only tests, as well as unobstructed diesel pool fires with and without aerosol suppression as listed in Table 2-2 above.

More details of the fire test compartment set up, instrumentation and methodology follow in Chapter 3.

3 Compartment Setup and Testing Methods

The overall experimental approach adopted in this work follows sections of the IMO MSC Circular 1007 Machinery Space Test Protocol [33]. The Circular provides guidelines for testing aerosol extinguishing systems against machinery space fires as defined by the International Convention for Safety of Life at Sea (SOLAS). The protocol as written, however, is more applicable to testing of larger scale fitted aerosol extinguishing systems than to handheld aerosol extinguishers appropriate for use in the smaller spaces of interest in this work. Hence, for the present research this protocol was reviewed and those portions deemed most applicable to the required RCN handheld aerosol extinguisher evaluation were incorporated into the experimental plan. Further the experimental plan was held consistent with that used for related research into other aspects of aerosol extinguishing units [1, 2].

The burn compartment used in the aerosol testing was the University of Waterloo modified 6.1m (20ft) shipping container. It was configured for tests as shown in Figure 3-1 and Figure 3-2 below and described in detail in [1]. This burn compartment closely mimics the specifications set by the ISO 9705 room fire test environment [34].

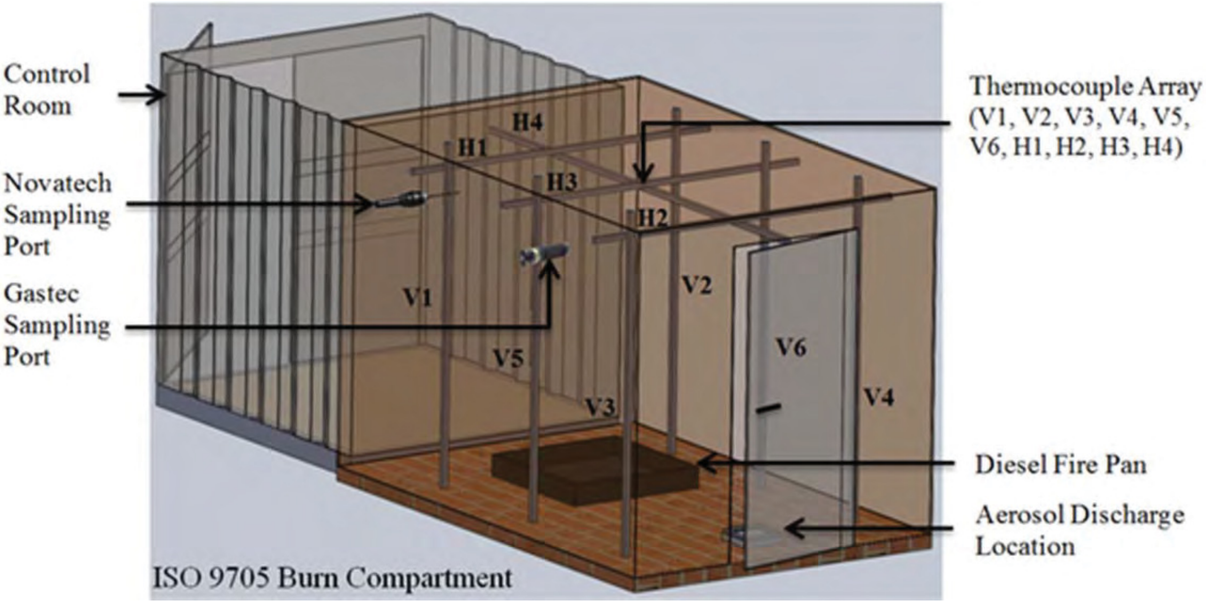

Figure 3-1: UW shipping container burn room configured for diesel suppression in the machinery space

As shown in Figure 3-1, the UW shipping container facility is comprised of two sections, the burn room and the control room. The control room holds all of the electrical equipment to support testing, including the field point data logger used for data acquisition and electrical cabling used for powering the instrumentation. The burn room measures 2.4m wide x 3.6m long x 2.4m tall, for a total volume of 20.74 m^3. At one end is a door measuring 0.91m wide x 1.75m tall which provides ventilation to the compartment. The compartment walls and ceiling are made of 2mm thick Corten steel, insulated with a 25.4mm layer of Fibrefrax Durablanket insulation and clad with 1.25mm (18 gauge) aluminum sheeting. The floor is finished with fire brick [35].

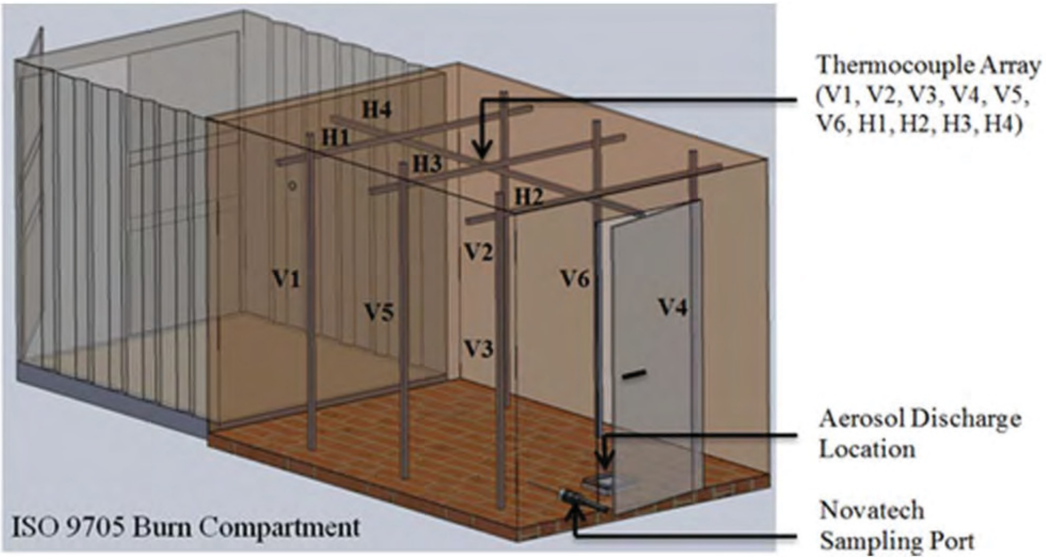

Figure 3-2: UW shipping container burn room configured for agent only test

Gas samples were withdrawn from two gas sampling ports positioned approximately 2 m above the floor and 1 m apart on the same side of the burn compartment, as shown in Figure 3-1. The Novatech samples were withdrawn from the location closest to the back of the compartment via a 6m long heated PTFE coated line with an internal graphite filter that prevented particulates from entering the sampling cell. Samples for the Gastec unit were withdrawn via a hand pump from a port approximately 1 m away and closer to the door of the compartment (Figure 3-1). Both gas sampling ports were positioned high in the compartment for all of the fire characterization and aerosol fire suppression tests.

During the first set of agent only tests, gas samples were withdrawn at a location near the floor of the compartment to measure gas concentrations generated very close to the discharge ports of each aerosol unit, as shown in Figure 3-2. In later agent only tests, samples were withdrawn from high in the compartment (Figure 3-1) in order to directly compare data to measurements obtained during fire characterization and suppression tests.

As per the locations above, gases in this study were sampled in regions where the highest concentrations were expected to occur rather than attempting to capture gas samples that might provide either averaged or integrated values of concentration in the compartment. This is because gas concentration measurements are highly dependent on details of the compartment and the fire geometry, location of sampling probe and ventilation conditions in a given experiment. Thus, gas samples withdrawn at the highest ports in the compartment during both suppression and agent only tests provide concentration data representative of those gas concentrations that would be found in the upper layer of a compartment during accidental aerosol discharge or during fire development and subsequent suppression using an aerosol agent. On the other hand, in the aerosol only tests for which the data were sampled close to the discharge of the aerosol unit, measured gas concentrations are indicative of 'worst case', localized gas concentrations that would be seen in gases issuing directly from the unit during activation and discharge. In either case, it must be cautioned that gas concentrations at other locations within the compartment may be significantly different than those reported in the present work. Instead results presented here are anticipated to represent values close to the maximum concentrations of gases that could accumulate in a compartment and migrate to other areas on a vessel, albeit they would dilute due to significant mixing as they travelled downstream of the sampling location and out of a compartment opening.

3.1 Gas Analysis Instrumentation and Test Methods

3.1.1 Novatech Gas Sampling System

A Novatech P695 gas sampling and analysis system was directly connected to the heated gas sampling line shown in Figure 3-1 and was used to measure concentrations of NO, NO_x, CO, CO_2, O_2 and UHC with built-in analyzers [36]. These included a TML 41H system for measuring NO and NO_x and thus deducing concentrations of NO_2, Servomex 4900C gas analysers for measuring O_2, CO_2 and CO and a Baseline 8800H unit for measuring total unburnt hydrocarbons (UHC). Each analyzer was calibrated before every test to ensure consistent 'zero' and 'span' values. During each experiment, the sampling train continuously collected gases at a flow rate of 1.8 L/min and data was output at 1125 millisecond (0.89 Hz) intervals, providing pseudo-time-resolved measurements of concentration at the chosen sampling locations [1].

For nitrogen-based compounds, gas samples entered the TML detection cell where the amount of NO was first determined by exposing the sample to ozone and measuring the resulting chemiluminescence signal. The NO_2 in the sample was also converted to NO and the combined concentration was reported as total NO_x [36]. Concentrations of NO_2 were then estimated as the difference between the measured concentrations of NO and NO_x. Oxygen concentrations were determined using paramagnetic sensor technology, while CO and CO_2 concentrations were measured, respectively, via gas filter correlation and single wavelength IR photometric methods. Finally, total UHC were determined using flame ionization detection. In all cases, voltage outputs from the detectors, linearly related to concentration, were sent to a National Instruments Compact Field Point distributed data logging system that allowed remote placement of the analogue to digital (A/D) signal conversion hardware. A conventional Ethernet protocol was used to communicate with multiple A/D units and to transfer the digitized signals back to a central computer located in the burn facility control room.

The report focuses on the time evolution of measured concentrations of nitrogen-based compounds during each of the fire and agent only scenarios outlined in Chapter 2, with CO, CO_2 and/or O_2 results included as appropriate to provide a reference to the state of the fire with time.

3.1.2 Novatech Sample Lag Time

There is an inherent time lag in response of the Novatech system to a change in concentration due to the length of sample lines used in the experiments and the inherent time response of each sensor in the unit. Since it is important to account for this delay in response during analysis and interpretation of measured gas concentrations, a test was undertaken to quantify the detection lag in the present results. A gas of known concentration of NO was injected at 1.8 L/min directly into the sampling line with no fiberglass filter present and the output from the detector was recorded by the data logger over time. Results are plotted in Figure 3-3 where the lag in response is clearly evident. Based on the data, the combined lag due to length of the sampling line, sampling flow rate and the purge and response time for the detector cell was approximately 38 seconds. This lag time is strongly influenced by the presence and condition of the filters in the sampling line; as far as possible, any time lag in system response is taken into account and the time axes for the data have been appropriately corrected to better facilitate interpretation of the results in the following sections.

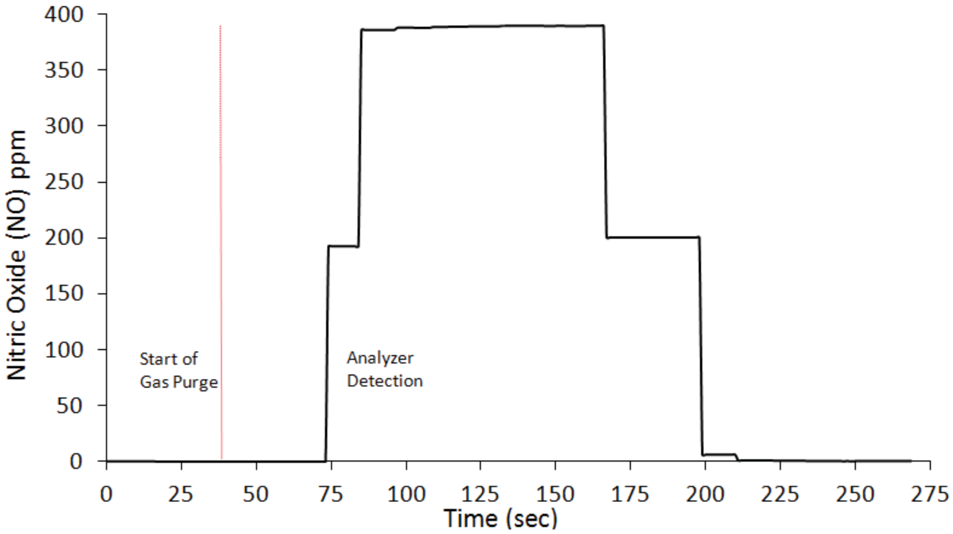

Figure 3-3- Determination of lag time for NO gas analysis system

3.1.3 Gastec Sampling System

The sampling probe from a Gastec STR-800 hand pump system with pre-calibrated gas absorption tubes was directly inserted into the test container and used to measure concentrations of NO and NO_2, as well as to investigate concentrations of additional compounds such as hydrogen cyanide (HCN) and ammonia (NH_3) at specific times during both agent only and fire suppression tests. In addition to the new information they provided with respect to the fire environment, these results were used as cross checks on the NO and NO_2 measurements obtained using the Novatech system (Section 3.1.1).

3.2 Powder Characterization

Samples of the raw aerosol tablet were collected from each unit before discharge and samples of the aerosol powder generated during suppression were collected after both agent only and fire suppression tests. All were stored in electrostatic bags and later characterized using a Bruker "D8" Focus X-ray Diffractometer to better understand the nature of the aerosol generation reactions, as well as the composition of the particulate aerosol powder generated from each unit [37]. In the Bruker unit, the characteristic crystalline lattice structure of the aerosol powder was determined based on diffraction patterns generated when an X-ray beam generated from a cobalt source was passed through the powder sample. The recorded diffraction patterns were analyzed using the XRD Commander with Diffrac-EVA software. Intensities and areas of the measured peaks were compared to patterns of compounds contained in the existing database to identify the composition of the powder under test [38, 39].

3.3 Corrosion Analysis Test Methods

The potential for aerosol powder deposition and corrosion during suppression was investigated by exposing material coupons and electronic components to the aerosols generated during agent only tests, as well as during unobstructed diesel pool fires with and without aerosol suppression. Functioning electronic circuit boards were placed within the compartment and subjected to the aerosol during selected tests. After testing, they were inserted into a working computer on a regular basis to determine any effects of aerosol powder residue on their longer term operation. An open computer tower was exposed and tested in a similar fashion. Individual material coupons were also exposed to aerosol agent. These included chrome plated aluminum, chrome plated nickel and chrome plated steel, copper and copper beryllium, high tensile and mild steels, CD discs and Nomex fabric. Coupons were photographed and examined using an optical microscope before exposure to the agent, and immediately after exposure were stored in electrostatic bags in order to preserve any residue that had deposited on the surfaces during the fire suppression. The materials were examined visually and under an optical microscope on an approximately weekly basis over several months to monitor any post-suppression effects on the samples. More detail on the samples tested and methods used are contained in Chapter 6.

In this work, testing and assessment of impacts that might accrue through use of aerosol fire suppression agents were conducted using the compartment set up, instrumentation and test methods described in this Chapter for each of the fire scenarios and the aerosol only tests described in Chapter 2. Results of the testing for NO_x, CO, O_2, HCN and NH_3 are presented in Chapter 4 with powder characterization studies discussed in Chapter 5. Chapter 6 focusses on the results of the corrosion analysis study, with conclusions and recommendations in Chapter 7.

4 Formation of NO_x, HCN and NH_3 during Aerosol Discharge and Suppression

Measured concentrations of nitrogen oxides (NO_x), HCN and NH_3 for diesel characterization fires, for each of the four fire scenarios outlined in Section 2.1 and for the agent only tests are outlined and discussed in this Chapter. In addition to using the Novatech to measure NO, NO_2 and NO_x, the Gastec sampling system was used to cross check measured values of NO and NO_2 during some tests, as well as to probe for the presence of NH_3 in the hot layer during the diesel fires. Only representative results from all measurements are presented below. The significant data compiled throughout the course of this project is contained in the raw data files which will be forwarded with the final copy of the report on flash drive.

4.1 Diesel Fire Characterization Test Results

To establish baseline concentration levels due to the diesel fires used in the aerosol suppression tests, gas concentrations measurements were made during 3 diesel characterization fires. In one, the door was held fully open throughout the test; in another, the door was open to 0.3m throughout; and in the final, the door was fully open then closed at approximately 3 minutes after ignition. Representative values of measured concentrations of NO, NO_2 and NO_x are plotted with respect to time in Figure 4-1 with measured concentrations of O_2 in the hot layer plotted on the right hand axis, for the test with the door held open throughout the experiment. In Figure 4-2, the same parameters are plotted for the test in which the door was closed after a hot layer had been established within the compartment. The Figures are formatted to indicate concentrations of NO and NO_2, with the sum of the two values providing the level of NO_x shown on the plot.

It can be seen from Figure 4-1 that after ignition[1], the concentration of NO increased gradually to levels of approximately 30 ppm as the fire reached steady burning. As peak concentrations of NO were reached, small concentrations of NO_2 were also measured (less than 5 ppm). Gastec samples withdrawn from the upper layer at 138 seconds into this test indicated concentrations of NO of approximately 22.5 ppm and of NO_2 of below 5 ppm respectively, confirming the results of the Novatech P695 measurements shown in Figure 4-1. No measurable concentrations of NH_3 were detected in additional Gastec samples withdrawn at 240 seconds into the test.

For the two diesel characterization fires in which the door was held open at 0.3m through the test (not plotted here) and for those in which the door was initially held open and then fully closed at 3 minutes into the test (Figure 4-2), concentrations of NO grew more slowly, but in a similar fashion after ignition, to those seen for the test with the fully open door (Figure 4-1). Slightly higher peak values of NO, between 30 and 35 ppm, were measured, most probably due to the containment of hot combustion gases within the test compartment. After the door was closed (Figure 4-2), NO levels gradually decayed throughout the 10 minute duration of the test. This was due to leakage from, and mixing within, the compartment as well as confinement and extinguishment of the fire.

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[1] The initial response of the NO_x analyzer and delay in sensor response has been taken into account in all graphs so that the x-axis on all plots has been shifted to start at the time of ignition unless otherwise specified.

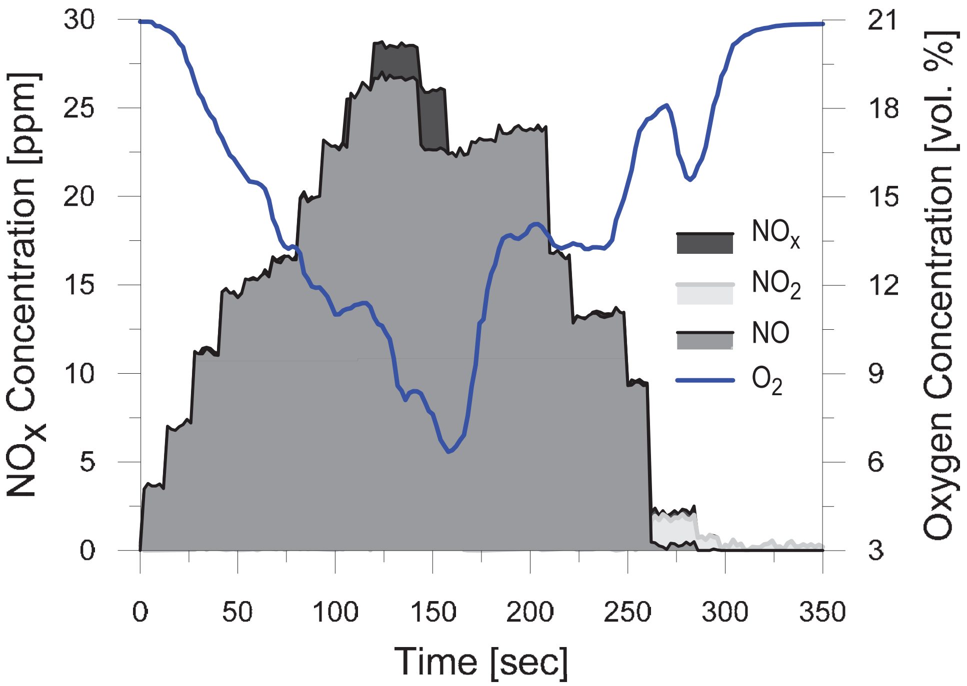

Figure 4-1: NO_x concentrations during a diesel fire characterization burn with door fully open

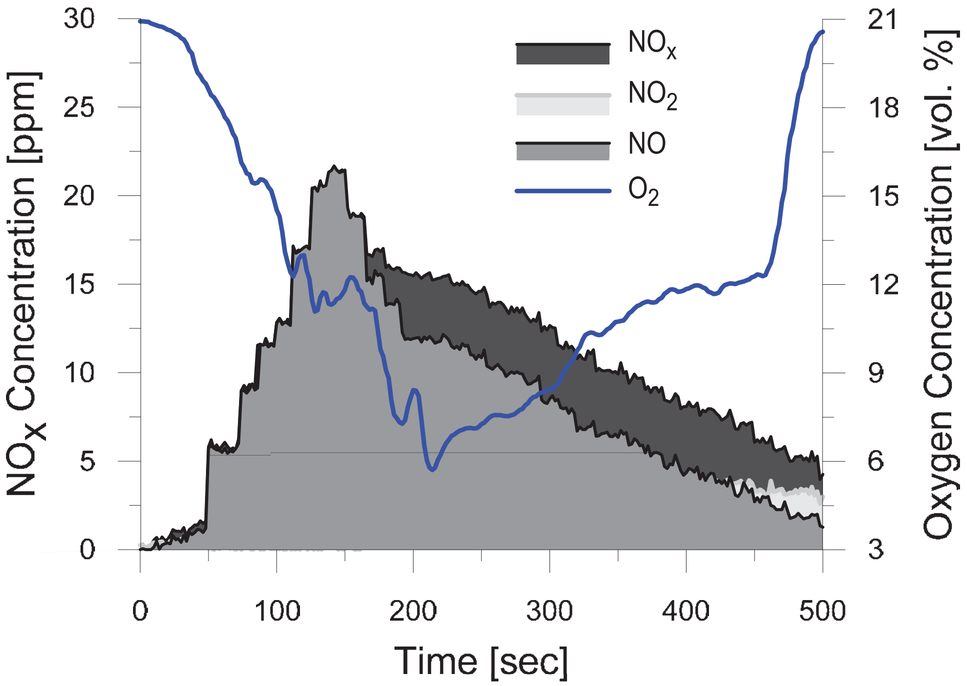

Figure 4-2: NO_x concentrations during a diesel fire characterization burn with door initially open then closed after development of hot layer

In these tests, concentrations of NO_2 remained below 5 ppm throughout the test, as they did for the case with the door fully open, but the NO_2 persisted from the time that NO levels reached peak concentrations through decay of the fire to the end of the test. Again, Gastec samples confirmed the order of magnitude of NO and NO_2 concentrations measured by the Novatech system, and indicated that there was no measurable concentration of NH_3 in the upper layer gases. In all diesel characterization tests, combined levels of NO and NO_2 (i.e. total NO_x) remained below 40 ppm for the full duration of the fire scenario.

4.2 Discussion of Diesel Fire Characterization Test Results

Both NO and NO_2 contribute to the total NO_x produced during the diesel characterization fires. As expected based on literature relating to the combustion of diesel fuel, measured concentrations of NO are 3-10 times higher than those for NO_2 [40]. Measured concentrations of NO remain well below threshold values suggested in the OSHA guidelines [11, 13, 14] across the 3 minute period of open diesel burn. Average NO_2 concentrations in the hot gases are similarly well below threshold levels established by OSHA [11, 12] and barely exceed one hour average exposure levels proposed by WHO [10]. Additional NO or NO_2 generated as a result of the activation of the aerosol and its interaction with hot gases in the compartment however, might exacerbate this situation during aerosol suppression of compartment fires. Therefore, NO_x concentration data measured during the various aerosol suppression scenarios are presented and discussed in the following sections.

4.3 Results for Unobstructed Diesel Burn with StatX Suppression

Concentrations of NO, NO_2 and NO_x were measured during four different unobstructed diesel burns with StatX aerosol agent suppression. Measured concentrations of nitrogen oxides are plotted on the left hand axis against time for the case with a 0.3m open door in Figure 4-3 and in Figure 4-4 for a representative case in which the door was closed immediately after agent was discharged into the compartment. In both plots, measured O_2 concentrations are plotted against the right hand axis to indicate the state of the fire in the compartment. In the latter test, after a fully developed fire was established within the compartment (hot layer temperatures of 900K), an aerosol unit was discharged and the compartment door was immediately closed and kept sealed for 10-15 minutes. This was to compare results against 10 and 15 minute short term exposure limits for NO_x [9, 11, 12, 13, 14]. To supplement the information on NO_x evolution, measurements of NH_3 and HCN concentration were made using the Gastec sampling system in some of the tests.

For the StatX diesel fire suppression test shown in Figure 4-3 in which the door was held open at 0.3m, NO levels increased after ignition of the diesel pool and reached values typical of those measured during the diesel characterization fire discussed in Section 4.1. Shortly after activation of the StatX aerosol unit (approximately 120 seconds), measured concentrations of NO increased sharply to values exceeding 250 ppm, then decreased back to ambient levels after the fire was suppressed. As concentrations of NO decreased, measured concentrations of NO_2 (163 seconds) increased to peak values of approximately 50 ppm, and subsequently decreased back to ambient levels as well (248 seconds). High values of NO_x were sustained for only a very short period of time because the compartment door was held partially open during the test, allowing the hot upper layer gases to quickly mix with ambient air and to escape from the compartment after suppression of the fire.

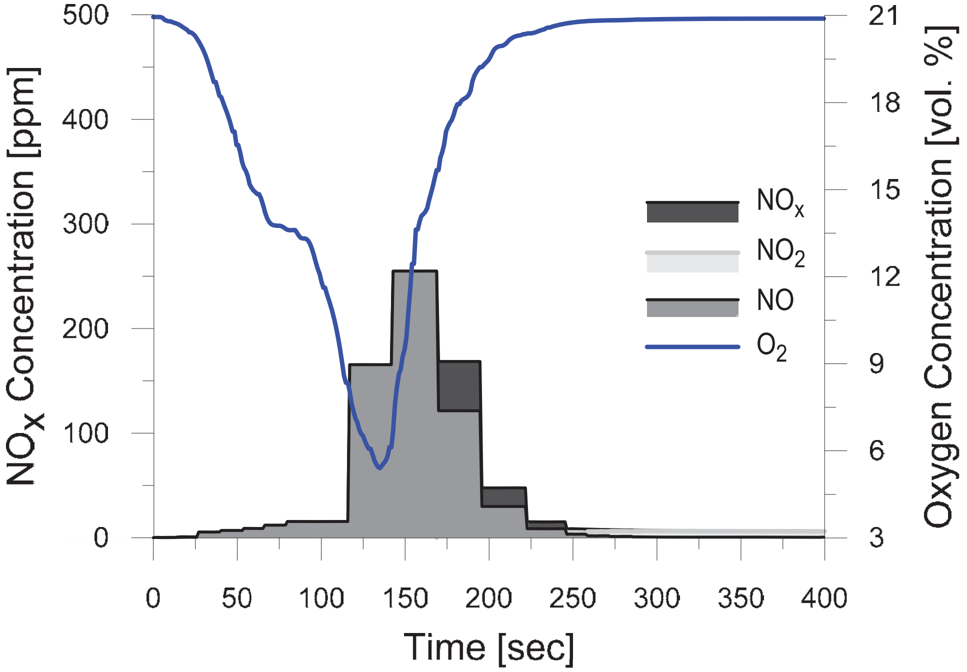

Figure 4-3: Measured NO_x concentrations during diesel burn, Stat X suppression, door open

Measured NO_x concentrations from a StatX suppression test in which the door was closed immediately after activation of the aerosol unit are plotted against time in Figure 4-4.

As with all other tests, measured concentrations of NO and NO_2 before activation of the unit (135 seconds) were consistent with those measured during the diesel characterization fires discussed in Section 4.2. After discharge of the aerosol unit, concentrations of NO reached peak values of around 300 ppm and since the compartment door was closed, they decayed slowly, likely due to leakage from the compartment over the 10-15 minute duration of the test. At the same time NO_2 concentrations increased to sustained values that were lower than NO concentrations, ranging between 65 and 75 ppm in this test and 65 to 100 ppm across all the StatX diesel fire suppression tests that were conducted. The high concentrations of NO_x in the upper gas layer, above 300 ppm, were confirmed through data from two more recent tests, which suggested that even higher concentrations of NO might be seen for short periods under some circumstances.

Concentrations of NO and NO_2 were also measured using the Gastec sampling system. A gas sample withdrawn at 284 seconds into the test indicated that the concentrations of both gases were close to 200 ppm, as demarcated by the right edge of the thick black tape on the upper (NO) and

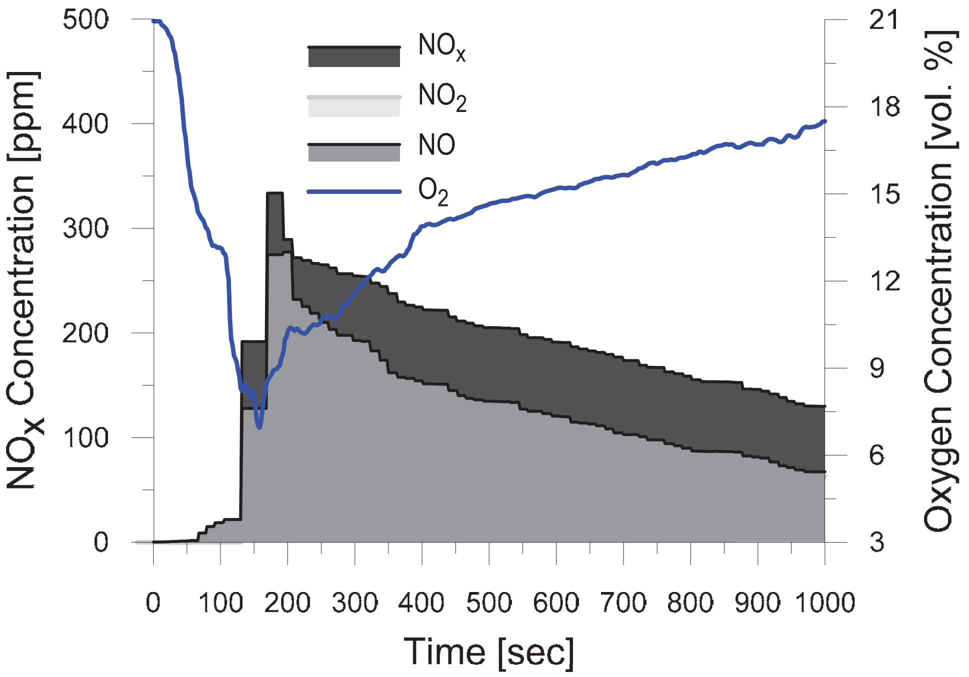

Figure 4-4: Measured NO_x concentrations during diesel burn, Stat X suppression, door closed

lower (NO_2) sampling tubes shown in Figure 4-5. While these confirm combined NO_x concentrations of between 350 and 400 ppm, the NO_2 concentrations determined using the Novatech and Gastec sampling systems do differ significantly. Possible explanations include sensitivity of the Gastec tubes and sampling system to interference from secondary species and soot in the gas stream [41], differences in gas sampling location and thus residence times and temperatures in the hot gas layer, differences in sampling methodology between the two systems, error in reading and marking the gas sampling tubes, and errors inherent in the methods by which the Novatech system deduces the concentration of NO_2 [36]. Nonetheless, the order of magnitude of the combined results suggests consistency across the measured concentration of total NO_x.

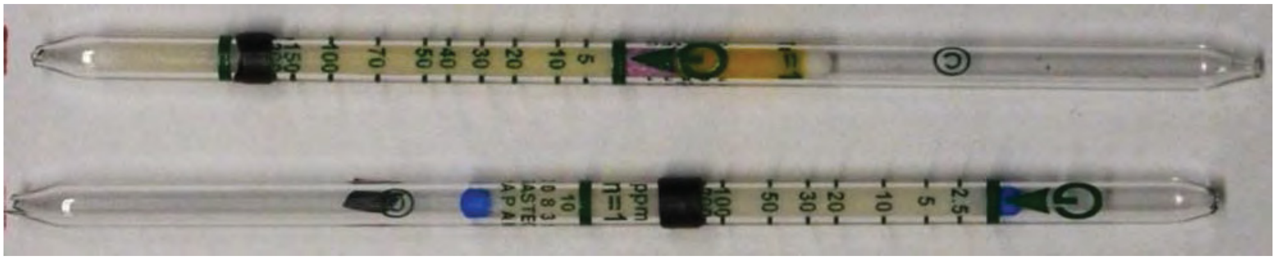

Figure 4-5: NO and NO_2 concentrations measured using Gastec tubes during suppression of a diesel fire using a StatX aerosol (284 seconds) [2,3]

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[2] There can potentially be high errors involved in concentration measurements using the colourimetric tube method. This note applies equally to all Gastec measurements contained in the present report.

In addition to the NO_x measurements presented above, additional Gastec samples were withdrawn at times of 444 seconds and 564 seconds respectively, to determine whether any HCN or NH_3 was present in the hot layer gases after discharge of the aerosol unit. It can be seen from Figure 4-6 that no measurable concentration of HCN was seen in this test, as was consistent with other comparable tests. In contrast, an NH_3 concentration of approximately 105 ppm was measured, as indicated by the left edge of the yellow tape on the sampling tube in Figure 4-7. This concentration is consistent with NH_3 concentrations of between 60 and 90 ppm that were measured in other tests during agent discharge into a closed compartment.

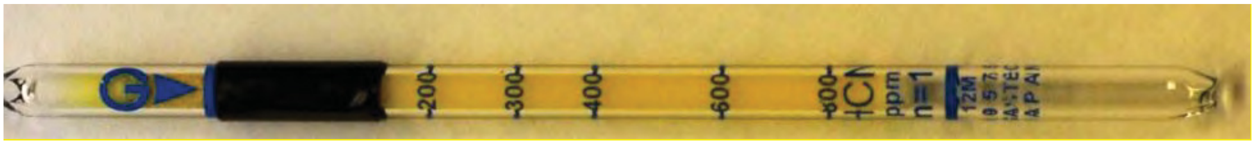

Figure 4-6: HCN concentration measured using a Gastec tube during suppression of a diesel fire using a StatX aerosol unit inside the UW Burn Room (444 seconds)[4]

Figure 4-7: NH_3 concentration measured using a Gastec tube during suppression of a diesel fire using a StatX aerosol unit inside the UW Burn Room (564 seconds)[5]

4.4 Results for Unobstructed Diesel Burn with DSPA Suppression

Concentrations of NO, NO_2 and NO_x were measured during four different unobstructed diesel burns with DSPA aerosol agent suppression. Measured concentrations of nitrogen oxides are plotted (left axis) against time for one case with a 0.3m open door in Figure 4-8 and in Figure 4-9 for a scenario in which the door was closed and sealed immediately after agent was discharged into the compartment. In both plots, measured O_2 concentrations are plotted against the right hand axis to indicate the state of the fire in the compartment. Additional measurements of NH_3 and HCN concentration were made using the Gastec sampling system.

For the test shown in Figure 4-8 in which the door is held 0.3m open, NO and NO_2 levels first increased to values typical of those observed during the diesel characterization fire discussed in Section 4.1. Upon activation of the aerosol unit (110 seconds), concentrations of NO and NO_x seen in the upper hot gases increased sharply to very high values, reaching levels near 400 – 500 ppm

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[3] The pre-calibrated sampling tubes had threshold limits of 200 ppm for NO and NO_2; concentrations in Figure 4-5 were very near that threshold.

[4] The pre-calibrated sampling tube had a threshold limit of 800 ppm for HCN.

[5] The pre-calibrated sampling tube had a threshold limit of 800 ppm for NH_3.

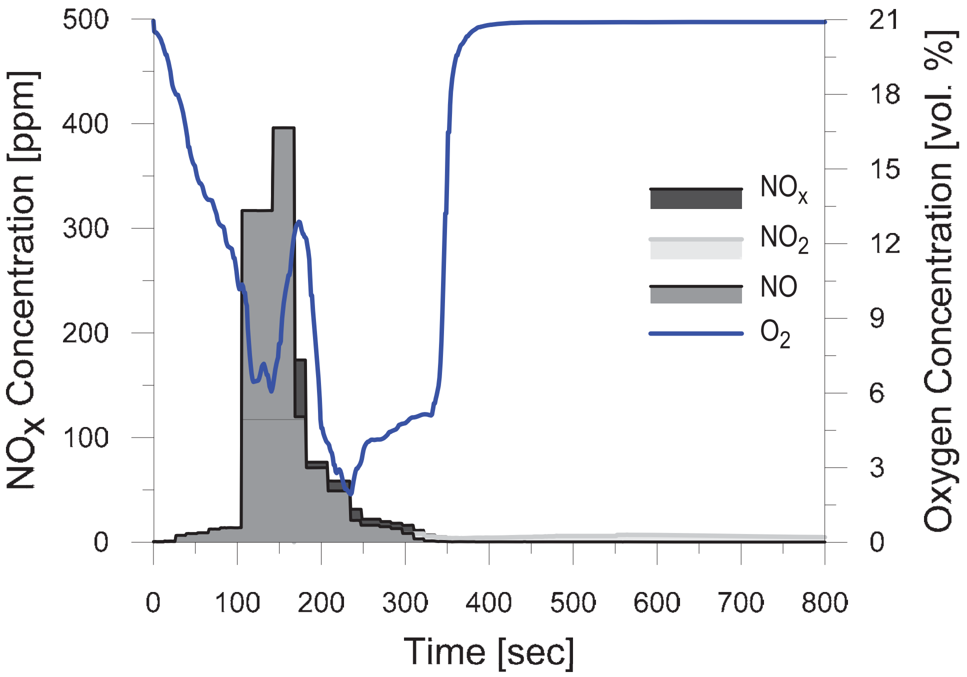

Figure 4-8: Measured NO_x concentrations during diesel burn using DSPA suppression, door open 0.3m

but unfortunately capped out at the saturation limit of the detection system (i.e. peak concentrations exceeded the detection limit of 500 ppm). After the fire was suppressed, the levels decreased back to ambient concentrations due to mixing with air and ventilation through the door opening. Levels of NO_2 rose after discharge of the agent and appeared to reach values of between 50 and 100 ppm as the concentration of NO decreased; however, measured NO_2 values in this test are suspect since they are determined by the Novatech system as the difference between measured values of NO and the NO_x. Once the NO and NO_x values decreased well below saturation, more representative values of NO_2 were again measured. The concentrations of nitrogen oxides cannot quantitatively be determined during time periods over which the detector was saturated; however, it is fair to say that relatively high concentrations of both NO and NO_2 were present in the upper layers of the burn compartment for a period of time after discharge of the agent during this test, even with the 0.3m door opening.

Subsequent to the test above, the same test was repeated except the compartment door was closed immediately after discharge of the agent. This scenario was intended to generate a 'worst' case scenario in which any gases generated due to interactions of the agent with the pre-existing hot fire gases would be trapped in the upper hot gas layers. In this case (not shown here), the detectors saturated (500 ppm) almost immediately upon activation of the DSPA unit and remained saturated until the end of the 10 minute test since there was minimal ventilation and mixing with the compartment door closed. To better determine the peak concentrations of gases which could accrue from aerosol suppression using the DSPA unit, the Novatech NO and NO_x detectors were modified and recalibrated to allow detection of NO_x concentrations as high as 1800 ppm. Results from one of several repeat tests conducted using the recalibrated detector on a diesel fire suppression test with the door closed immediately after activation of the DSPA aerosol unit is plotted against time in Figure 4-9.

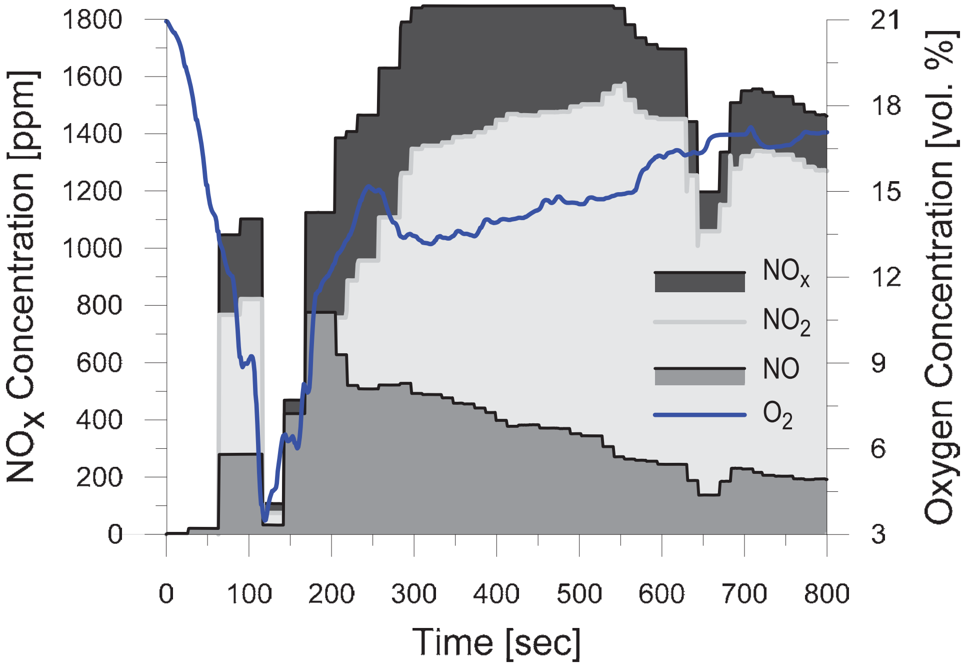

Figure 4-9: Measured NO_x concentrations during diesel burn using DSPA suppression, door closed

As with all previous tests, measured concentrations of NO and NO_2 before activation of the unit were initially consistent with those measured during the diesel characterization fires discussed in Section 4.2 following which there appeared to be a significant build-up of nitrous oxides locally at the position of the sampling probe just before the door was opened and the unit activated[6]. After activation of the aerosol unit (131 seconds), the compartment door was closed and concentrations of both NO and NO_x increased again sharply to very high values. Concentrations of NO appeared to peak at values of around 775 to 800 ppm before decreasing again. As the NO concentration decreases, concentrations of NO_2 increased to high levels possibly due to a shift in equilibrium between production of NO and NO_2 as the compartment cooled with the suppression of the fire. Despite the increased detector range, measured concentrations of NO_x exceeded the new saturation limit of the detection system; therefore, NO_2 concentrations were quantitatively suspect through much of the test. Because the door was closed, concentrations of all species remained high through the duration of the 10 min test.

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[6] During repeat tests peak concentrations of all nitrogen oxides varied substantially due to variations in ventilation and temperature within the fire compartment during and after agent discharge.

Concentrations of NO and NO_2 were also measured using the Gastec sampling system. A gas sample withdrawn at 295 seconds into the test indicated that the concentrations of both gases were very high; the absorbent in the sampling tubes saturated almost immediately during withdrawal of the hot gases indicating concentrations of both NO and NO_2 well over the 200 ppm threshold of the tubes and consistent with the high levels illustrated in Figure 4-9.

Additional Gastec samples were withdrawn at times of 447 seconds and 586 seconds into the test, respectively, to determine whether any HCN or NH_3 was present in the hot layer gases after discharge of the aerosol unit. While no measurable concentration of HCN was observed, NH_3 concentrations of approximately 500 ppm were registered on the adsorbent as marked by the left edge of the yellow tape on the sampling tube in Figure 4-10. Similar values of NH_3 concentration were confirmed during Gastec sampling at approximately the same times in other tests as well.

Figure 4-10: NH_3 concentration measured using a Gastec tube during suppression of a diesel fire with a DSPA 5-4 aerosol unit (630 seconds)

4.5 Summary and Discussion of Open Diesel Fire Agent Suppression Results

Comparison of measured gas concentrations during StatX and DSPA 5-4 activation and aerosol suppression of open diesel fires in the present compartment, Figure 4-3 through Figure 4-7, and Figure 4-8 through Figure 4-10 respectively, suggest that, during and immediately after activation of both variants of aerosol extinguisher, NO and NO_2 are produced at levels exceeding those expected due only to the fire.

Independent of suppression unit employed, peak measured concentrations of NO in the hot gases in the upper layer of the fire compartment surpassed the IDLH limit for occupational exposure set by OSHA [11, 13, 14]; however, it would be expected that high concentrations would be seen only locally and for only a short period of time after activation of the aerosol units.

During the DSPA suppression tests discussed here, the reported values of NO_2 concentration were not quantitatively reliable due to saturation of the Novatech NO_X detector; no similar problems were identified in the StatX results, although uncharacteristically high concentrations of NO_x were seen in one test. In any case, for both units, measured NO_2 concentrations quickly rose to values that far exceeded the 1-hour continuous exposure limit proposed by WHO [10], as well as the various OSHA IDLH and OSHA 15-minute exposure thresholds [11, 12].

For both units as well, concentrations of NH_3 deduced using Gastec sampling were well above the published exposure threshold values [18, 19].

Caution is required in interpreting all of these results, as it must be realized that the concentrations contained herein are measured by a sampling probe located at a single point, which is immersed directly in the hot gas layer of the fire. As such, the probe will pick up changes in concentration due to both variations in the behaviour of fire as it is suppressed and those directly resulting from discharge of the aerosol agent. Concentrations in other locations within the compartment may also be considerably different than those presented here. Further, the 'worst' case tests in which the highest concentrations were measured were conducted with the door closed immediately after activation of the aerosol extinguishing units so that any gases produced were essentially trapped within the compartment. In other situations the gases would likely be quickly diluted through mixing and ventilation throughout the space.

Even though these fire scenarios represent aerosol suppression of diesel fires in small closed compartments, and the high reported concentrations are measured deep within the hot upper layer gases and are often sustained for only a short period of time, the data presented here do indicate potential emissions from both units. This potential underlines the fact that appropriate safety and operational guidelines should accompany use of these units on board naval vessels in order to minimize the likelihood that personnel could be exposed to levels above OSHA thresholds during conduct of normal fire response activities.

4.6 Results for Obstructed Diesel Burn with StatX Suppression

Following tests with the open diesel fire discussed above, additional tests were conducted to measure concentrations of NO, NO_2 and NO_x as they evolved during obstructed diesel fire tests. In these tests, a 1.4 m x 1.3 m x 0.46 m steel structure was suspended above the diesel pool fire to simulate a fuel spill fire under an engine enclosure. After agent discharge, the compartment door was held 0.3m open so hot upper layer gases were not fully trapped within the compartment. The aerosol agent did not fully suppress the fire due to re-radiation of heat from the hot engine enclosure, so the obstructed diesel pool fire continued to burn until the compartment door was closed, after which the fire was suppressed by confinement. Following this, the door was fully opened to vent the compartment of aerosol and fire gases.

Measured concentrations of NO, NO_2 and NO_x (left axis) for one of the obstructed diesel burns with StatX aerosol agent suppression are plotted against time in Figure 4-11 for a representative test in which the door was held open. Measured O_2 concentrations are plotted against the right axis to indicate the state of the fire in the compartment. Results from a repeat test followed similar trends, although some test-to-test variation was observed in measured values of peak concentration and in the duration of high levels of all three gases.

As can be seen in Figure 4-11, after ignition of the diesel pool, NO levels gradually increased to values typical of those measured during the diesel characterization fire discussed in Section 4.2. Upon activation of the StatX aerosol unit (150 seconds), measured concentrations of NO increased sharply to values of around 150 ppm in this test (118 ppm in the repeat test). They then decreased

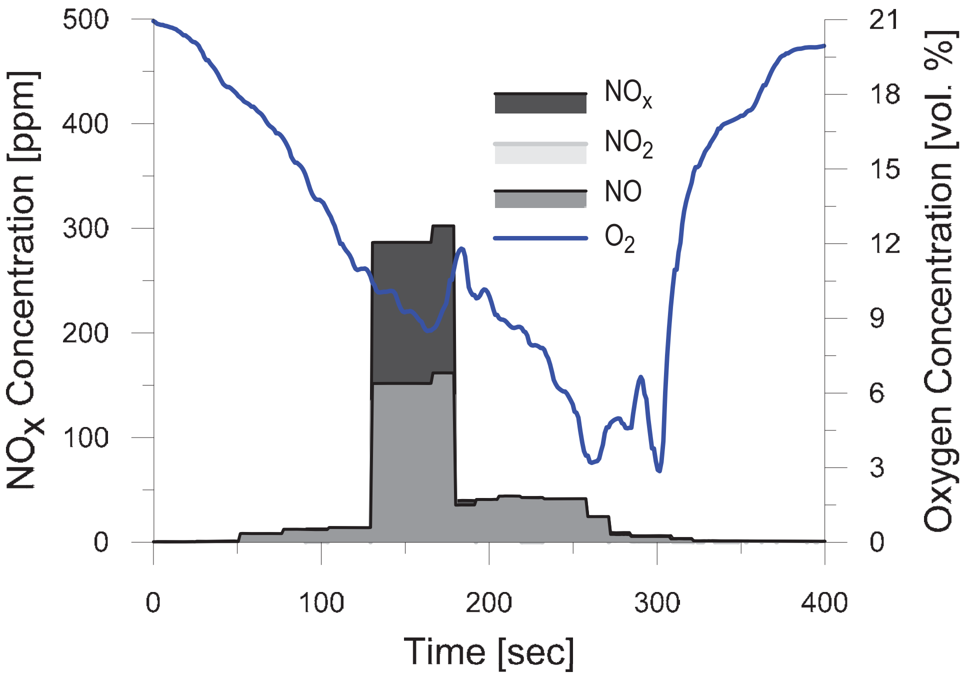

Figure 4-11: Measured NO_x concentrations during an obstructed diesel burn using Stat X suppression, door open 0.3m

back to levels of around 50 ppm until the fire extinguished (310 seconds). As concentrations of NO increased, measured concentrations of NO_2 simultaneously increased to around 140 ppm (90 ppm in the repeat test), then decreased back to ambient levels more quickly than for NO. High values of NO, NO_2 and NO_x appeared to be sustained throughout the 50 second period during which the agent was discharged and the aerosol successfully acted to decrease the overall intensity of the fire[7], reducing the temperatures within the compartment. As the fire re-established itself, still with the door open, concentrations of NO_2 decreased quickly down to ambient while NO and NO_x concentrations fell to values more consistent with, albeit slightly higher than, levels seen during the diesel characterization fires until after the fuel was burned out. After the compartment door was fully opened, all measured concentrations dropped back to ambient levels.

4.7 Results for Obstructed Diesel Burn with DSPA Suppression

Concentrations of NO, NO_2 and NO_x were measured during two obstructed diesel burns with DSPA aerosol agent suppression, using the same compartment configuration as that described for the Stat X obstructed diesel burns in Section 4.6 above. As was the case for the Stat X tests, the aerosol did not immediately suppress the fire in either of these tests[8]. Measured concentrations of NO, NO_2 and NO_x (left axis) for one of the burns with DSPA aerosol agent suppression are plotted against time in Figure 4-12 with oxygen levels again plotted on the right hand axis. Results from

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[7] This corresponds to a marked increase in the measured concentrations of O_2 which correlates inversely to the strength of fire in the compartment (O_2 concentrations decrease as fire grows and increase as fire is suppressed)

[8] A low flame flicker was seen as the door was opened; however, the fire did extinguish shortly thereafter.

the repeat experiment were very similar in terms of both peak concentrations and the duration of high levels of all three measured gases, suggesting that the aerosol agent and fire interacted in much the same fashion for both tests.

After ignition of the diesel pool, NO levels gradually increased to values typical of those measured during the diesel characterization fire and discussed in Section 4.2. Upon activation of the DSPA aerosol unit (148 seconds), the concentration of NO increased sharply to values approaching 375 ppm then decreased again as aerosol acted to decrease the intensity of the fire. In contrast to the previous tests using Stat X suppression, concentrations of NO_2 did not appear to increase until the NO concentrations reached their peak values (178 seconds) and began to decay. Peak values of at least 50 ppm[9] NO_2 were measured before the door was fully opened (250 seconds), the fire went out[8] and the compartment was ventilated. All measured concentrations dropped back to ambient levels in the same fashion as observed in the other tests.

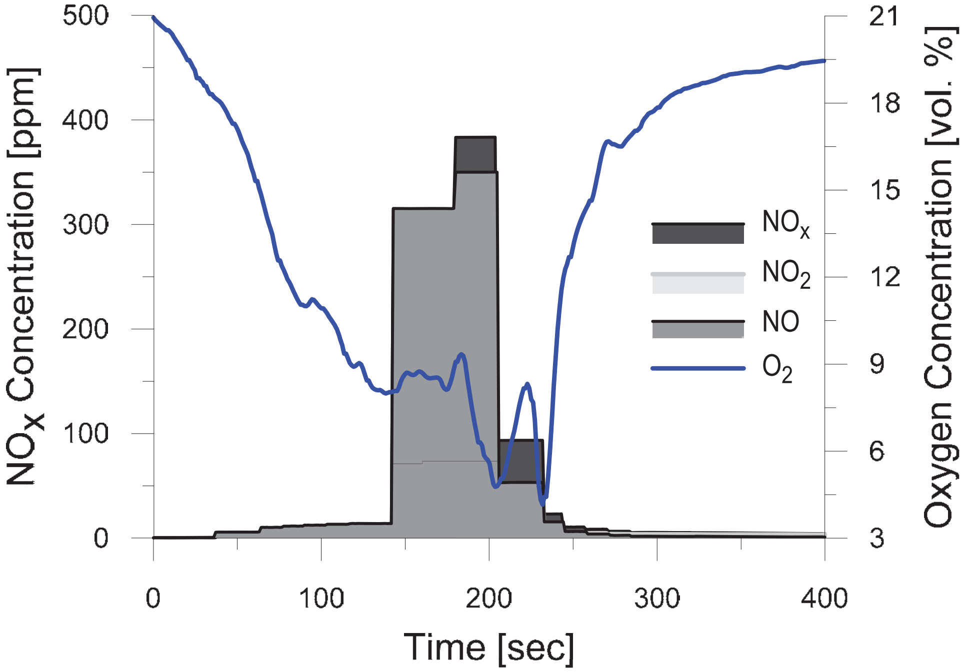

Figure 4-12: Measured NO_x concentrations during an obstructed diesel burn using DSPA suppression, door open 0.3m[9]

4.8 Summary and Discussion of Obstructed Diesel Fire Results

Comparison of NO_x concentrations measured during StatX and DSPA activation and aerosol suppression of the obstructed diesel fires, Figure 4-11 and Figure 4-12 respectively, suggest that some nitrogen oxides are produced via interaction of the agent with the hot fire gases in the burn

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[9] As concentrations of NO and NO_x reach values near 400 ppm, the signal may exceed the detection limit of the detectors. Measured values of NO_2 are then suspect since they are determined as the difference between the NO and the NO_x values and are therefore incorrect if the signal from one or both detectors saturates.

compartment both during and immediately after activation of both variants of aerosol extinguisher. Concentrations of NO measured in the present location surpassed the OSHA IDLH limit for occupational exposure of 100 ppm [11, 13, 14]; however, it would again be expected that high concentrations would persist for only short periods of time, being quickly diluted through mixing and ventilation.

Trends in the time evolution of NO_2 concentration are more difficult to discern since in the DSPA test, it is thought that the NO_x detector saturated. Nonetheless, NO_2 concentrations were observed to increase to levels of at least 50 - 150 ppm after activation of the unit, simultaneously with measured increases in NO concentration in the hot gas layer. As in previous tests, concentrations decayed relatively quickly back to ambient levels once the fire was fully suppressed. In both cases, NO_2 concentrations exceeded the 1-hour continuous exposure limit proposed by WHO [10], as well as both the OSHA IDLH and OSHA 15-minute exposure thresholds [11, 12]; again noting that these high concentrations are measured at a single point deep within the hot upper layer gases and are sustained for only very short periods of time. The results further support the importance of appropriate operational procedures to minimize the likelihood that any personnel could be exposed to such levels of NO or NO_2 during conduct of normal fire response activities.

4.9 Results for Obstructed Bilge Fire with StatX Agent Suppression

Concentrations of NO, NO_2 and NO_x were measured during two different obstructed bilge fire diesel tests, with StatX aerosol agent suppression. Measured concentrations of NO, NO_2 and NO_x (left axis) are plotted against time in Figure 4-13 for a case where the door was closed on suppression, then opened to a 0.3m opening at 230 seconds into the test. Figure 4-14 contains data taken during the same scenario in which the door was closed and sealed immediately after agent was discharged into the compartment, then held closed until the end of test. Measured O_2 concentrations are plotted against the right hand axis to indicate the state of the fire in the compartment during each test. These scenarios were intended to generate ‘worst’ case situations in which any gases generated due to the combined action of the agent and pre-existing hot fire gases would remain trapped in the compartment. Measurements of NH_3 and HCN concentration were made using the Gastec sampling system for the scenario shown in Figure 4-14 as well.

In Figure 4-13, NO and NO_2 levels first increased to values similar to those observed during the diesel characterization fires discussed in Section 4.1. Upon activation of the Stat X unit (120 seconds), concentrations of NO and NO_x increased sharply to very high values, reaching levels near 260 – 275 ppm. Levels of NO_2 rose to values of between 50 and 75 ppm after discharge of the agent and as the concentration of NO decreased, possibly due to a shift in equilibrium between production of NO and NO_2 as the compartment cooled with the suppression of the fire. When the door was opened at 230 seconds into the test, the concentrations of all species returned to ambient values as the hot gases exited the compartment and mixed with fresh air. The concentrations of NO, NO_2 and NO_x may not be quantitatively correct during time periods over which very high values of NO_x were observed[9]; however, high concentrations of both NO and NO_2 were present in

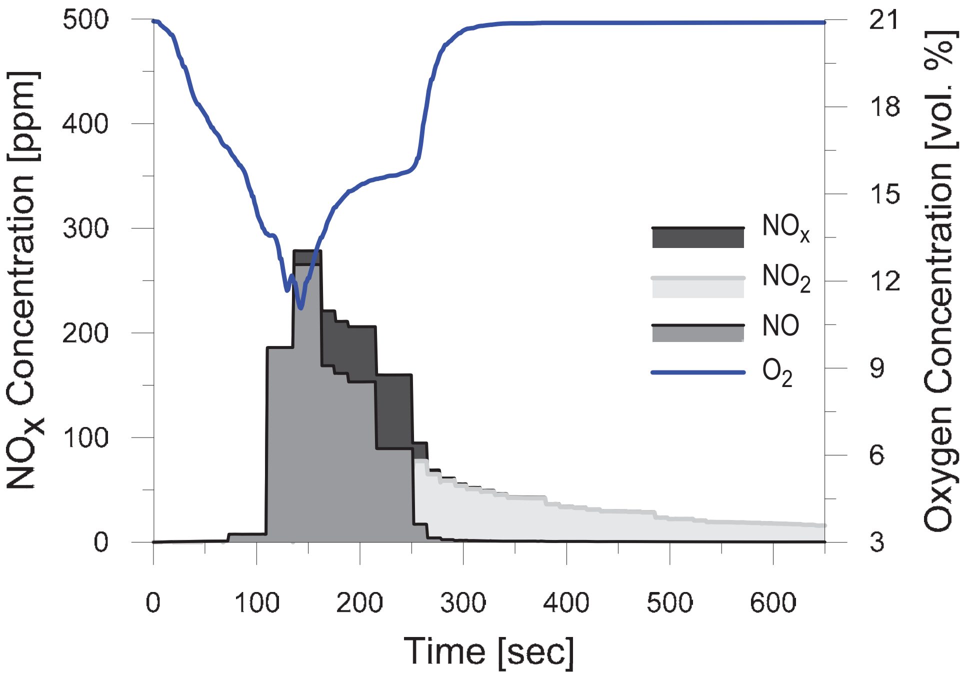

Figure 4-13: Measured NO_x concentrations during an obstructed bilge fire with StatX suppression (door closed at suppression; opened 230 seconds into test)

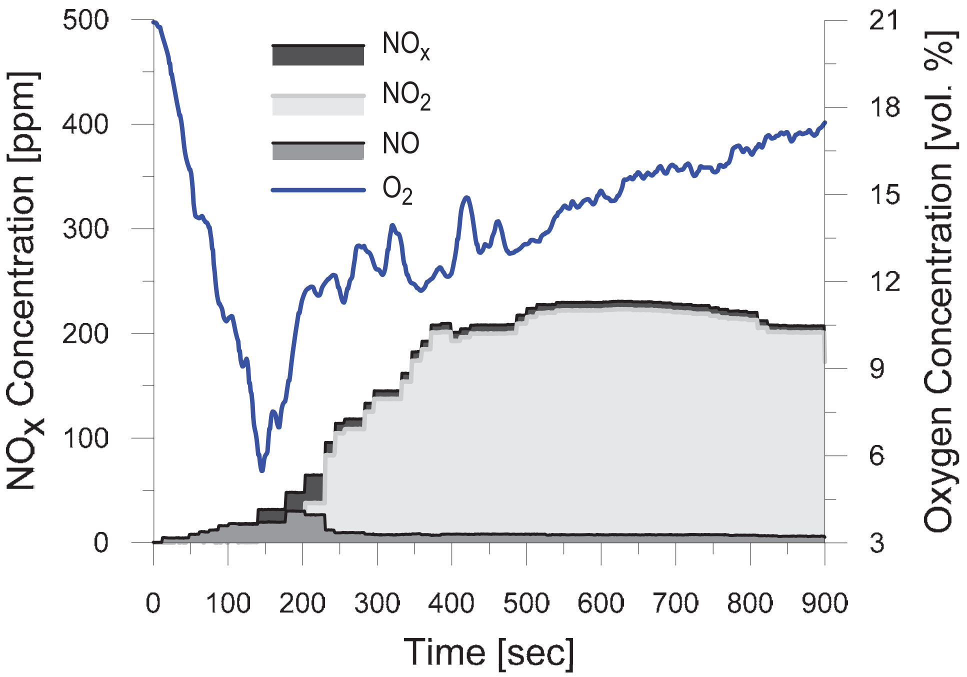

Figure 4-14: Measured NOx concentrations in an obstructed bilge fire during StatX suppression (door held closed throughout the experiment)

the upper layers of the burn compartment after agent discharge and until the door to the compartment was opened.

Subsequently, the same test as shown in Figure 4-13 was repeated except the compartment door was closed for the 10 minute duration of the experiment. Due to the high concentrations of gas seen in previous tests, the Novatech NO and NO_x detectors were modified and recalibrated to allow detection of concentrations as high as 1800 ppm. Results from one of several repeat tests of this scenario are plotted against time in Figure 4-14. As in the first stages of all previous tests, measured concentrations of NO and NO_2 were consistent with those measured during the diesel characterization fires discussed in Section 4.2. After activation of the aerosol unit (170 seconds), the compartment door was closed and the concentration of NO_x increased gradually. Measured concentrations of NO first increased slightly and then dropped to values of around 25-30 ppm for the duration of the experiment. At the same time, measured concentrations of NO_2 remained very high, at between 200 and 220 ppm throughout the test. The time evolution of nitrogen oxide concentrations varied significantly from those seen in earlier tests, possibly as a result of a shift in the equilibrium between NO and NO_2 production as the fire was suppressed and the hot gases cooled with the compartment door closed.

The shifts in concentrations of NO and NO_2 measured using the Novatech system were further confirmed via Gastec samples taken at 770 seconds into the test. As presented in Figure 4-15, Gastec samples indicated concentrations of NO of around 5 ppm (left edge of black tape in upper tube), while that for NO_2 (lower) was much higher, around 200 ppm.

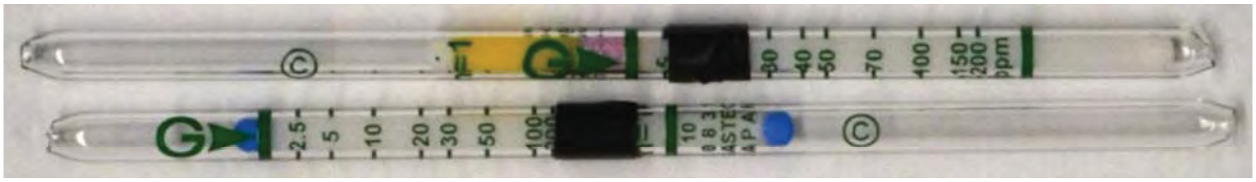

Figure 4-15: NO and NO_2 concentrations measured using Gastec tubes during suppression of an obstructed bilge fire using a StatX aerosol unit (770 seconds)

In addition to the NO_x measurements presented above, additional Gastec samples were withdrawn at times of 409 seconds and 521 seconds respectively, to determine whether any HCN or NH_3 was present in the hot layer gases after discharge of the aerosol unit. Again, no measurable concentration of HCN was seen, while measured concentrations of NH_3 were approximately 300 ppm, as shown in Figure 4-16.

Figure 4-16: NH_3 concentration measured using Gastec tube during suppression of an obstructed bilge fire using a StatX aerosol unit (521 seconds)

4.10 Results for Obstructed Bilge Fire with DSPA Agent Suppression

Concentrations of NO, NO_2 and NO_x were measured during two different obstructed bilge fire tests, suppressed using DSPA 5-4 aerosol units. Measured concentrations of each gas (left axis) are plotted against time in Figure 4-17 for a case where the door was closed on suppression, then opened to a 0.3m opening at 240 seconds into the test. Figure 4-18 contains data taken during the same scenario in which the door was closed and sealed immediately after agent was discharged into the compartment, then held closed until the end of test. Measured O_2 concentrations are plotted against the right hand axis of each plot. These scenarios were intended to generate a 'worst' case scenario in which any gases generated due to the combined interaction of the agent with the pre-existing hot fire gases would be trapped in the upper hot gas layers. Measurements of NH_3 and HCN concentrations were also made using the Gastec sampling system for the scenario in Figure 4-18.

In the test with the door initially shut, Figure 4-17, NO and NO_2 levels initially remained lower than values typically observed during the initial stages of these fires. Upon activation of the aerosol unit (120 seconds), concentrations of NO and NO_x in the upper hot gases increased sharply to values near 490-500 ppm. Levels of NO_x also rose significantly after discharge of the agent. Once the NO and NO_x values decreased well below the detector saturation limit, more representative values of NO_2 were detected (240 seconds into the test); as the concentration of NO decreased, NO_2 concentrations reached values of at least 400-425 ppm[9] suggesting again a possible shift in equilibrium between NO and NO_2 production as the fire is suppressed. Since this corresponded closely with the time at which the compartment door was opened to 0.3 m, concentrations of all three gases subsequently decreased back to ambient levels as they cooled, mixed with air and exited the compartment.

The same test as shown in Figure 4-17 was repeated except the compartment door was left closed for the 10 minute duration of the experiment. Results from one of several repeat tests are plotted against time in Figure 4-18. For this test, the Novatech NO and NOx detectors were recalibrated to allow detection of concentrations as high as 1800 ppm.

In Figure 4-18, measured concentrations of NO and NO_2 before activation of the DSPA unit are consistent with those measured during DSPA suppression of the open diesel fires shown in Figure 4-9. After activation of the aerosol unit (145 seconds), the compartment door was re-closed and the concentration of NO_x increased quickly to values as high as 600-700 ppm (lower than in Figure 4-9), with concentrations of NO reaching 200 ppm and those for NO_2 ranging between 400 and 500 ppm for the duration of the experiment. Peak concentrations of NO are less than those observed in Figure 4-17, while those for NO_2 are approximately the same, again suggesting possible shifts in equilibrium between production of those two gases when an aerosol is discharged into a working fire environment such as the one encountered in these tests.

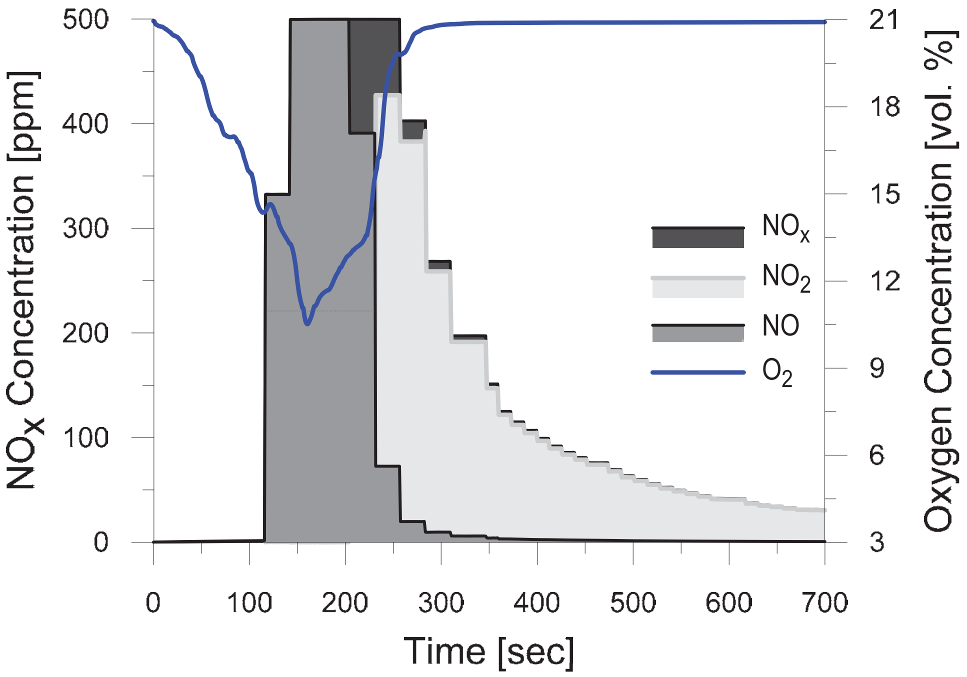

Figure 4-17: Measured NO_x concentrations in an obstructed bilge fire with DSPA 5-4 suppression (door closed at suppression; opened 240 seconds into test)

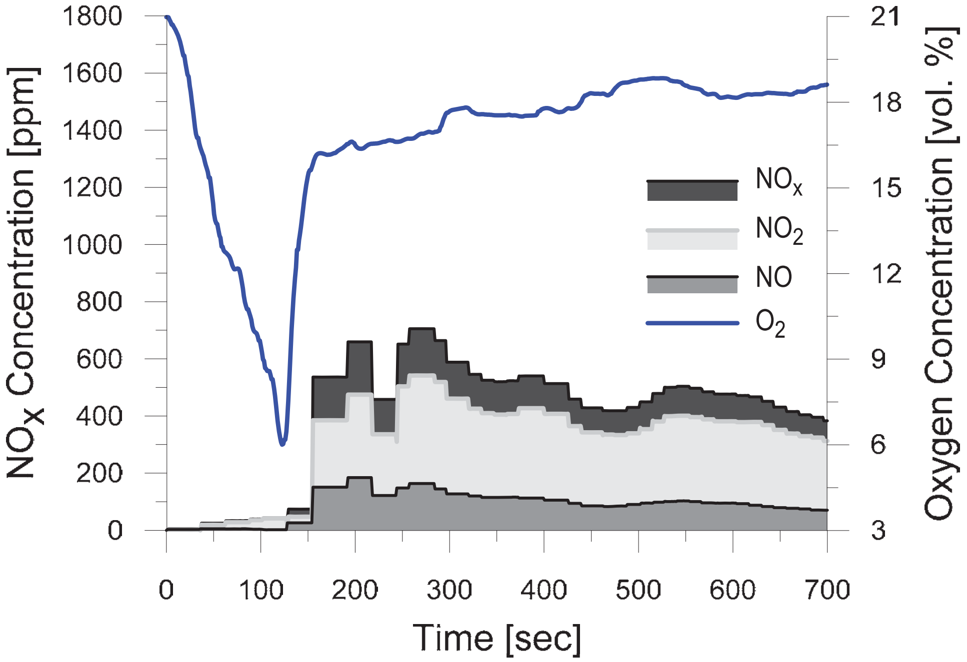

Figure 4-18: Measured NO_x concentrations in an obstructed bilge fire with DSPA 5-4 suppression (door held closed throughout the experiment)

Concentrations of NO and NO_2 measured using the Novatech system were confirmed via Gastec samples taken at 385 seconds into the test and presented in Figure 4-19. Sampling tubes for NO (upper tube) and NO_2 (lower tube) both indicated concentrations at or above 200 ppm.

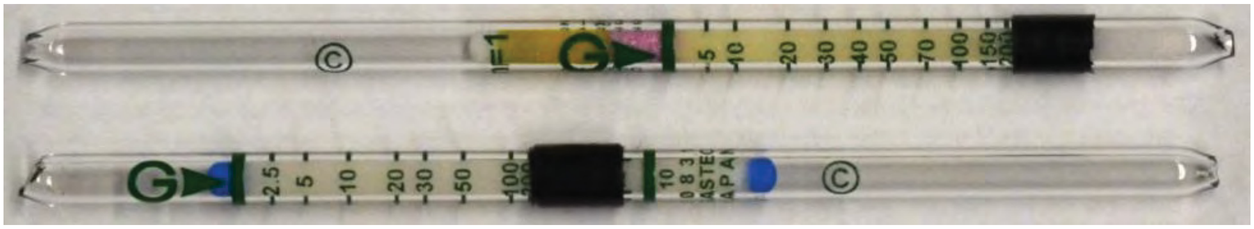

Figure 4-19: NO and NO_2 concentrations measured using Gastec tubes during suppression of an obstructed bilge fire using DSPA 5-4 aerosol unit (385 seconds)

In addition to the NO_x measurements presented above, additional Gastec samples were withdrawn at times of 525 seconds and 618 seconds to determine whether any HCN or NH_3, respectively, was present in the hot layer gases after discharge of the aerosol unit. Again, no measurable concentration of HCN was seen, while NH_3 concentrations of approximately 260 ppm were recorded as seen in Figure 4-20. These values are consistent with previous tests where concentrations of nitrogen oxides (Section 4.9, for example) were also similar.

Figure 4-20: NH_3 concentration measured using Gastec tube during suppression of an obstructed bilge fire using a DSPA 5-4 aerosol unit (618 seconds)

4.11 Summary and Discussion of Obstructed Bilge Fire Test Results

Comparison of NO_x concentrations measured during StatX and DSPA activation and aerosol suppression of the bilge fire scenarios, Figure 4-13 and Figure 4-17, respectively, suggest that nitrogen oxide levels are high in the hot fire gases in the burn compartment both during and immediately after activation of both variants of aerosol extinguisher. Depending on the environment that evolves after agent activation, concentrations of NO and NO_2 may also shift relative to one another. Nevertheless, in most tests, peak concentrations of NO measured at the current sampling location surpassed the IDLH limit for occupational exposure of 100 ppm set by OSHA [11, 13, 14], noting again of course that these values are measured at a single location deep in the hot layer gases.

Trends in the time evolution of NO_2 during suppression of diesel bilge fires with both StatX and DSPA units are also similar for comparable test situations. NO_2 concentrations increased after the units were activated and, depending on the ensuing compartment environment, reached levels of at least 100 ppm in tests where the door was opened a few minutes after agent discharge, but much higher, between 200 and over 500 ppm, in situations where the door was sealed shut and the compartment confined for a longer period of time. As such, NO_2 concentrations measured during these tests greatly exceed the 1-hour continuous exposure limit proposed by WHO [10], as well as both the OSHA IDLH and OSHA 15-minute exposure thresholds [11]. Again, it is clearly important to implement appropriate operational procedures to minimize the likelihood that personnel could be exposed to high levels of NO or NO_2 during conduct of normal fire response activities.

4.12 Softwood Fire Characterization Test Results

To establish baseline concentration levels of NO, NO_2 and NO_x generated by wood crib fires, gas concentration measurements were made during a wood crib characterization fire as it grew to a fully developed fire in the UW burn compartment with the door open to 0.3 m. After it reached steady burning conditions and a marked hot layer had developed, the door was closed to mimic fire confinement on board a naval vessel. Concentrations of NO, NO_2 and NO_x measured using the Novatech system during a representative wood crib fire are plotted (left axis) against time in Figure 4-21, with corresponding oxygen concentrations plotted on the right axis. The Gastec sampling system was used to cross check values of NO and NO_2 concentration from the Novatech, and to take measurements of NH_3 and HCN concentration during some of the tests.

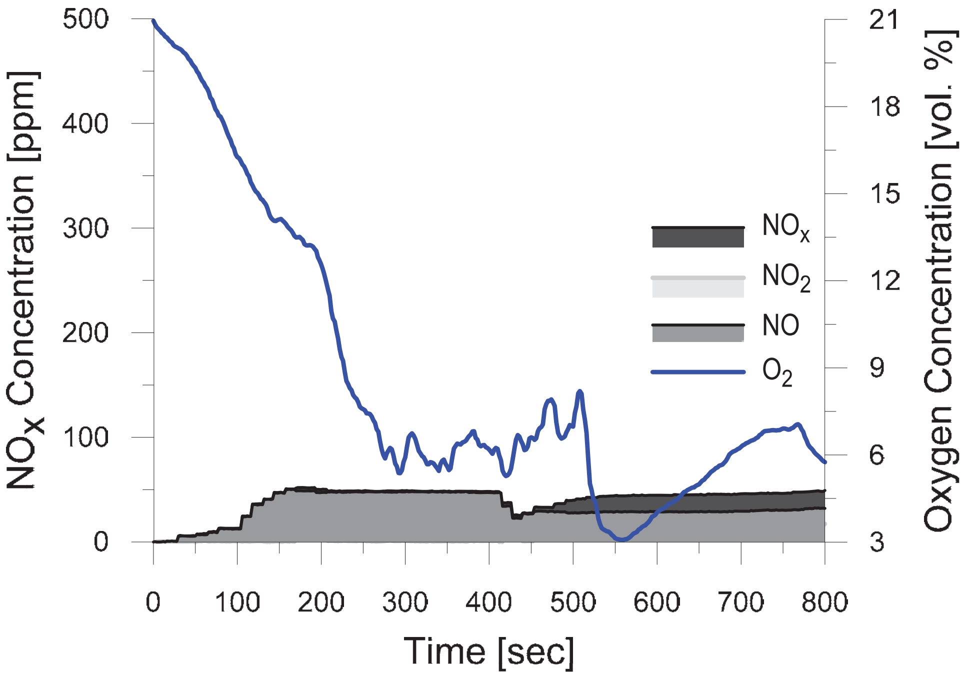

Figure 4-21: Measured NOx concentrations during a wood crib characterization fire with door initially open then closed after development of hot layer

It can be seen that after ignition, the concentration of NO increased gradually to levels of approximately 50 ppm as the fire reached steady state burning. As peak concentrations of NO were reached, small concentrations of NO_2 were measured (less than 5 ppm); however, combined concentrations of NO and NO_2 from the wood crib fire alone remained below 55 ppm throughout the test.

Gastec samples withdrawn from the upper layer at 659 seconds (not shown here) indicated NO concentrations of approximately 13-15 ppm and of NO_2 below 15 ppm, confirming the levels of concentration measured using the Novatech (given the potential errors discussed previously).

A concentration of around 10 ppm of HCN and no measurable concentration of NH_3 were detected in the Gastec samples withdrawn at 800 and 915 seconds after ignition, respectively.

4.13 Discussion of Wood Crib Fire Characterization Test Results

Both NO and NO_2 contribute to the total NO_x produced during the wood crib characterization fires. As expected based on literature relating to the combustion of wood cribs, measured concentrations of NO_x are around 50 ppm [42]. Measured concentrations of NO remain well below threshold values suggested in the OSHA guidelines [11, 13, 14] over the 10-15 minute period of the open wood crib fires. Average concentrations of NO_2 in the hot gases from the wood crib fire are similarly well below threshold levels established by OSHA [11, 12] and barely exceed one hour average exposure levels proposed by WHO [10]. Additional NO or NO_2 generated as a result of the aerosol activation, however, might exacerbate this situation during aerosol suppression of wood crib compartment fires. Therefore, NO_x concentration data measured during various softwood crib suppression scenarios are presented and discussed in the following sections.

4.14 Results for Softwood Crib Fire with StatX Agent Suppression

Concentrations of NO, NO_2 and NO_x measured during two different wood crib fire tests with StatX aerosol agent suppression (left axis) are plotted against time in Figure 4-22 and Figure 4-23. On both plots, corresponding O_2 concentrations are plotted using the right axis to provide an indication of the fire development with time. Results in Figure 4-22 are for a scenario in which the door was initially open while the fire built, then closed after aerosol discharge (220 seconds), opened and closed again (345 and 465 seconds respectively) and finally opened (585 seconds) until the end of the test. In comparison, Figure 4-23 contains results for a test in which a fully developed fire was established within the compartment (hot layer temperatures of 900K), then an aerosol unit was discharged and the compartment door was immediately closed and kept sealed for 10-15 minutes. Measurements of NH_3 and HCN concentration were also made using the Gastec system for the test shown in Figure 4-23.

For the test shown in Figure 4-22, both NO and NO_2 concentrations increased after ignition of the wood cribs, with NO concentrations reaching values of over 100 ppm and NO_2 concentrations over 150 ppm as the fire grew to steady state with the compartment door closed. These concentrations are higher than those measured during the wood crib characterization fire (open door) discussed in Section 4.12. With the door initially open, both NO and NO_2 concentrations increased until activation of the StatX aerosol unit (220 seconds) after which concentrations jumped for a short period of time and then decreased gradually, likely since the compartment door was closed. When the door was opened again (345 seconds), concentrations of NO began to decrease sharply to values of around 40 ppm, while concentrations of NO_2 rose for a period of time before decreasing to average values of around 150 ppm. Changes in concentrations of NO and NO_2 observed as the door was opened and closed during this test support the idea expressed in Sections 4.11 that the equilibrium between the two gases may change significantly as the local conditions within the fire compartment change.

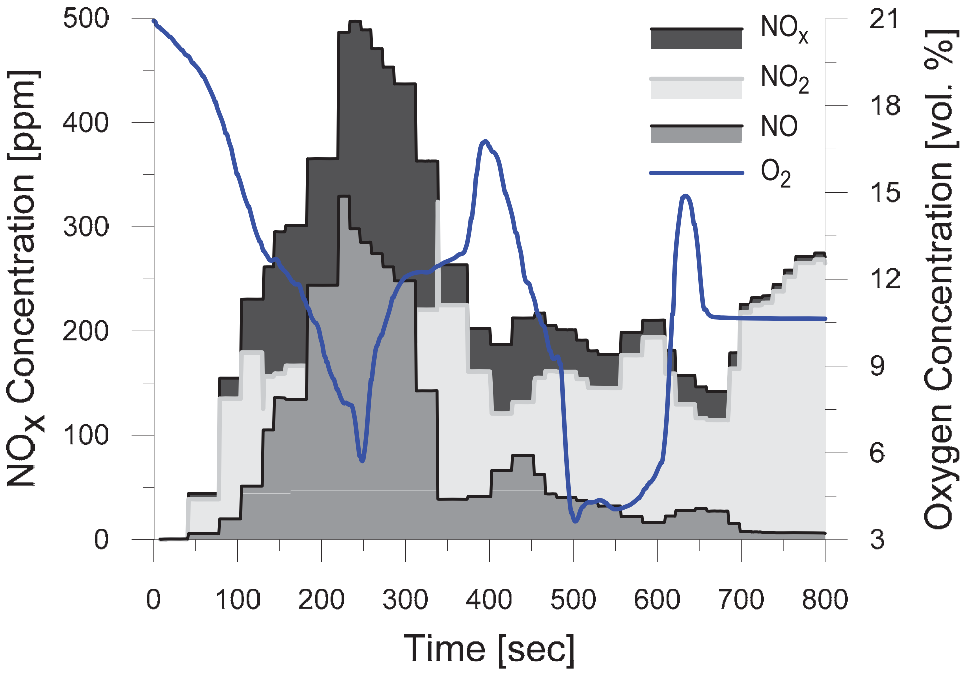

Figure 4-22: Measured NO_x concentrations during softwood crib burn with Stat X suppression (door opened and closed during the experiment)

Plotted in Figure 4-23 are measured concentrations of NO, NO_2 and NO_x (left axis) and O_2 (right axis) from a similar test in which the wood crib fire grew to steady state with the door open, after which the aerosol was discharged (385 seconds) and then the door immediately closed and held closed for the duration of the experiment. This scenario was intended as a 'worst' case scenario in which hot fire gases would be trapped in the upper hot gas layers. Since high concentrations of NO and NO_x were expected, as had been observed in the tests described in Sections 4.9 and 4.10, the detectors were recalibrated to allow detection of concentrations as high as 1800 ppm.

Seen in Figure 4-23, measured concentrations of NO and NO_2 increased after ignition and were consistent with those measured during the wood crib characterization fires (door open; Section 4.12) before activation of the Stat X unit. After activation of the unit (385 seconds), the compartment door was closed and measured concentrations of NO_x did not increase as expected. This may have been due to excessive confinement of the fire or erroroneous measurement due to

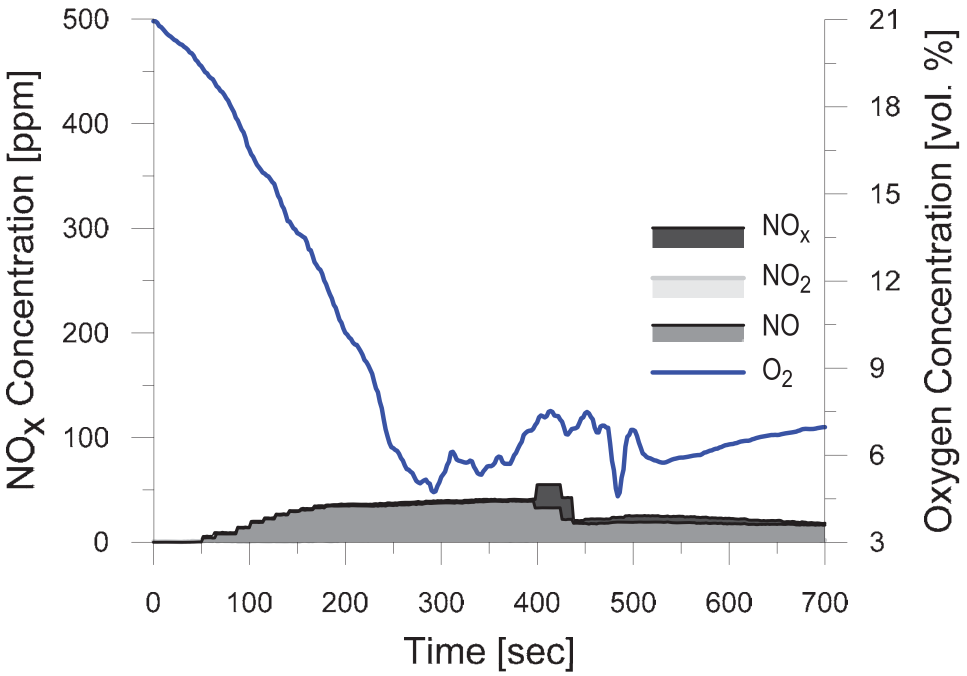

Figure 4-23: Measured NOx concentrations during softwood crib burn with Stat X suppression (door closed after suppression)

accumulation of moisture inside the sampling probe during the lengthy test. The concentrations of NO and NO_2 measured using the Gastec sampling tubes confirmed that the levels of NO and NO_2 remained quite low. Gastec samples taken at 600 seconds indicated concentrations of NO (left side of black tape upper tube) and NO_2 (lower tube) of around 7 and 10 ppm, respectively, as shown in Figure 4-24.

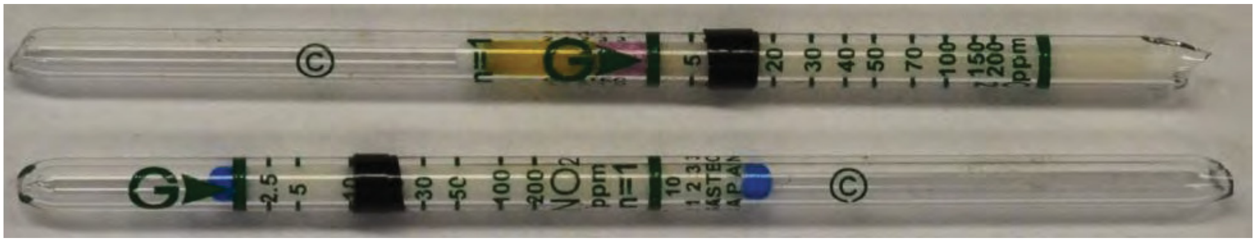

Figure 4-24: NO and NO_2 concentrations measured using Gastec tubes during suppression of a wood crib fire using a Stat X aerosol unit (600 seconds)

In addition to the NO and NO_2 concentration measurements presented above, Gastec samples were withdrawn at 724 seconds and 844 seconds into the test to determine, respectively, whether any HCN or NH_3 was present in the hot layer gases. Unlike previous tests, no measurable concentrations of NH_3 were observed; however, HCN concentrations of approximately 17-20 ppm were recorded as marked by the left side of the thick black tape in Figure 4-25.

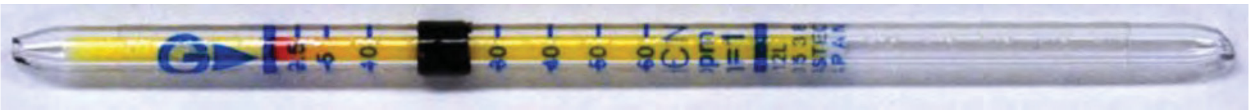

Figure 4-25: HCN concentrations measured using Gastec sampling tubes during suppression of a wood crib fire using a StatX aerosol unit (724 seconds)

4.15 Results for Softwood Crib Fire with DSPA Agent Suppression

Concentrations of NO, NO_2 and NO_x measured during two different wood crib fire tests with DSPA 5-4 aerosol agent suppression are plotted (left axis) against time in Figure 4-26 and Figure 4-27, with corresponding concentrations of O_2 plotted on the right axis in each figure to indicate fire development with time. Figure 4-26 shows data for the case in which the fire was allowed to grow for a set period of time after ignition (approximately 245 seconds), then the DSPA 5-4 unit was discharged and the door held closed for 155 seconds. The door was then opened again to see if the aerosol had extinguished the fire and the hot gases were vented. Figure 4-27 shows representative results for a comparable test in which a fully developed fire was established within the compartment (hot layer temperatures of 900K), then an aerosol unit was discharged and the compartment door was immediately closed and kept sealed for the 10-15 minute duration of the test. To again supplement the information on NO_x evolution, additional measurements of NH_3 and HCN concentration were made using the Gastec sampling system during the test plotted in Figure 4-27.

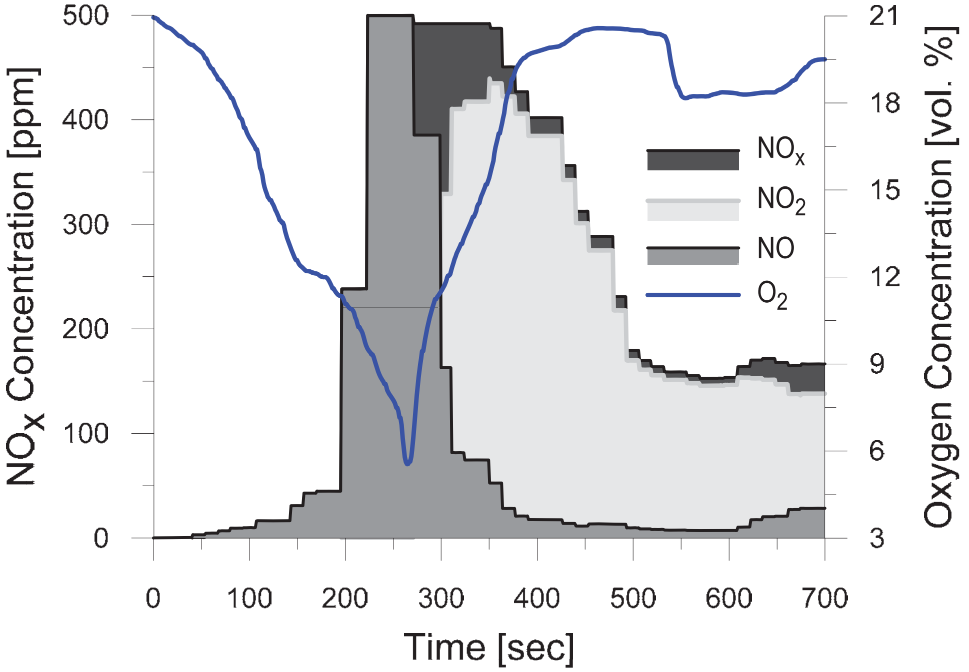

Figure 4-26: Measured NO_x concentrations during a softwood crib fire with suppression by a DSPA 5-4 aerosol unit (door opened and closed during experiment)

For the DSPA 5-4 wood crib fire suppression test shown in Figure 4-26, NO levels increased after ignition of the wood cribs and appeared to reach values of over 150 ppm, higher than those measured during the wood crib characterization fire (Section 4.12) before the DSPA 5-4 aerosol unit was activated (245 seconds). Measured concentrations of NO grew to over 500 ppm and remained at those levels for a period of time until the aerosol decreased the intensity of the fire and NO concentration decreased back to values of around 25 ppm. Potentially due to saturation of the detectors, measured values of NO_2 followed trends similar to those seen for other tests; as the concentrations of NO decreased with the compartment door closed, the compartment environment cooled somewhat and concentrations of NO_2 grew to very high values, in this case over 400 ppm. Both NO and NO_2 concentrations decreased as expected after the door was opened and the compartment ventilated (400 seconds)[10]. Accounting for saturation of the detectors, it is evident that relatively high concentrations of both NO and NO_2 were present in the upper layers of the burn compartment during DSPA 5-4 suppression of the wood crib fire.

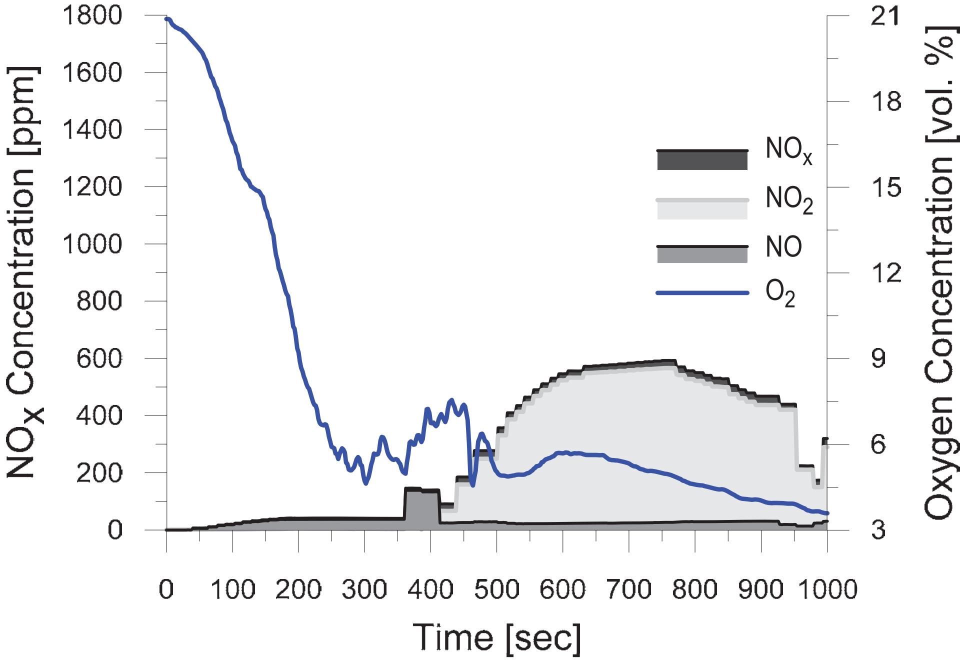

Figure 4-27: Measured NOx concentrations during a softwood crib burn with suppression by a DSPA 5-4 aerosol unit (door closed after suppression)

Plotted in Figure 4-27 are measured concentrations of NO, NO_2 and NO_x (left axis) and O_2 (right axis) from a repeat test in which the wood crib fire was allowed to grow to steady state with the door open, after which the DSPA 5-4 aerosol was discharged (405 seconds) and then the door immediately closed and held closed for the duration of the experiment. This scenario was again intended as a 'worst' case scenario with hot fire gases trapped in the upper hot layer of the

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[10] It should be noted that the compartment door was actually opened and closed several times after 500 seconds into the test which accounts for the sustained higher levels of NO concentration seen on the plot in Figure 4-26.

compartment. Since high concentrations of NO and NO_x were expected, the detectors were recalibrated to allow detection of concentrations as high as 1800 ppm.

Measured concentrations of NO and NO_2 increased after ignition, first grew to values that were consistent with those measured during wood crib characterization fires discussed in Section 4.12 for a period of time and then rose to higher values of over 100 ppm before activation of the aerosol. After activation of the unit (405 seconds), the compartment door was closed, the concentration of NO decreased to values of around 20 ppm and concentrations of NO_2 grew to high values (in this case 590-600 ppm) as had been seen for other tests in which the door was closed after activation of an aerosol unit. Although there was moisture detected in the lines during this test, as there had been during the test plotted in Figure 4-23, these results appear to follow trends in data observed for other tests.

The concentrations of NO and NO_2 measured using the Gastec system again confirmed the levels of NO and NO_2 measured using the Novatech. Gastec samples taken at 560 seconds into the test indicated concentrations of NO (left hand side of black tape upper tube) of around 20 ppm and saturated the tube at 200 ppm for NO_2 (lower tube) as shown in Figure 4-28.

Figure 4-28: NOx concentrations measured using Gastec sampling tubes during suppression of a wood crib fire with a DSPA 5-4 aerosol unit (560 seconds)

Additional Gastec samples were withdrawn at times of 705 seconds and 815 seconds into the test respectively, to determine whether any HCN or NH_3 was present in the hot layer gases. While no measurable concentrations of HCN were observed, NH_3 concentrations of approximately 500 ppm were recorded, as marked by the left hand side of the black tape in Figure 4-29.

Figure 4-29: NH3 Concentrations measured using Gastec sampling tubes during suppression of a wood crib fire with a DSPA aerosol unit (815 seconds)

4.16 Summary and Discussion of Softwood Crib Test Results

Comparison of NO_x concentrations measured during StatX and DSPA activation and aerosol suppression of the softwood fires, Figure 4-22 and Figure 4-23, as well as Figure 4-26 and Figure 4-27, suggest that interactions between the crib fire and the aerosol, coupled with confinement of the compartment by closing the door, led to varying concentrations of NO, NO_2, HCN and NH_3 across the tests. This is consistent with general expectation, since of all of these species are likely to be involved with NO_x production during a fire. Further, the concentrations of each would be anticipated to change as the compartment temperature and ventilation characteristics vary due to opening and closing of the door, since their relative generation is known to be very dependent on local factors such as temperature and oxygen concentration.

Measured concentrations of NO appeared to be lower than in many of the tests conducted using the diesel fire scenarios, and in many of the tests did not surpass the IDLH limit for occupational exposure of 100 ppm set by OSHA [11]; however, in one of the tests higher concentrations were measured at the sampling position for a period of time suggesting that there is still the possibility for NO to collect in the hot upper layer gases. Due to combined aerosol activation and compartment confinement, concentrations of NO_2 were very high in many of the tests, exceeding the 1-hour continuous exposure limit proposed by WHO [10], as well as both the OSHA IDLH and OSHA 15-minute exposure thresholds [11, 12]. Measurable concentrations of HCN and NH_3 were also observed in some of the tests. Even if such concentrations are sustained only locally around the measurement point deep in the hot layer, development of appropriate operational procedures for aerosol use coupled with compartment confinement are necessary in order to minimize the likelihood that personnel could be exposed to levels of any of these gases above threshold values during conduct of normal fire response activities.

Results thus far focussed on discussion of the combined interactions between the StatX and DSPA 5-4 aerosol units as they were applied to suppress various diesel and softwood crib fires, with and without confinement of the compartment after activation of the extinguishing unit. Additional tests were conducted in order to assess the potential for generation of NO_x, HCN, NH_3 and other gases such as CO and CO_2 should an aerosol unit discharge accidentally into a compartment where there was no fire. The results of these ‘aerosol only’ tests are presented in Section 4.17 for the StatX unit and Section 4.18 for the DSPA 5-4 unit.

4.17 Results of Aerosol Agent Only Tests for StatX Unit

Concentrations of NO, NO_2 and NO_x were measured using the Novatech system during three tests conducted by discharging a Stat X aerosol unit into the empty fire compartment, then immediately closing the door and keeping the compartment door sealed for 10 minutes. In test 1, Figure 4-30 and Figure 4-31, gas concentrations were measured low in the compartment, near the outlet of the aerosol unit. For Test 2, Figure 4-32 through 4-35, and Test 3, Figure 4-36 though Figure 4-39, they were measured in the gases near the ceiling of the compartment through the sampling port that was used in the fire test scenarios. To supplement the information on NO_x evolution, additional measurements of NH_3 and HCN concentration were made using the Gastec system in the latter two experiments.

These tests were intended to benchmark the quantity of NO, NO_2, NO_x and CO that was created due to thermal decomposition of base aerosol compounds (such as KNO_3) and fuel binder during and immediately after activation of the aerosol unit. In addition, results were compared against 10 and 15 minute short term exposure limits for NO_x [9, 11, 12, 13, 14] and CO [43] to better appreciate the potential impact of an accidental discharge of a unit into an occupied space.

Upon activation of the StatX aerosol unit for the first test, Figure 4-30, concentrations of NO measured near the outlet of the unit (left axis) increased sharply to values of about 225 ppm, and then decreased back to 100 ppm where they remained for the duration of the experiment. Trends in the measured concentrations of CO (Figure 4-31) and O_2 (right axis on both plots) at the same position closely followed those of NO confirming that the NO was being formed through combustion reactions taking place during generation of the aerosol powder. CO concentrations sharply increased to peak values of 120 ppm and then decreased back to more steady levels of 60-70 ppm. As NO concentrations increased, NO_2 concentrations also increased, reaching peak values of around 40 ppm for a period of time and then decreasing to sustained levels of around 25 ppm for the duration of the 10 minute test. The observed decreasing concentrations of each gas was a result of buoyancy of the hot gases at the discharge of the unit, as well as diffusion and mixing of gases throughout the compartment with time. When the door was opened, the compartment ventilated (640 seconds) and concentrations of all gases returned to ambient levels.

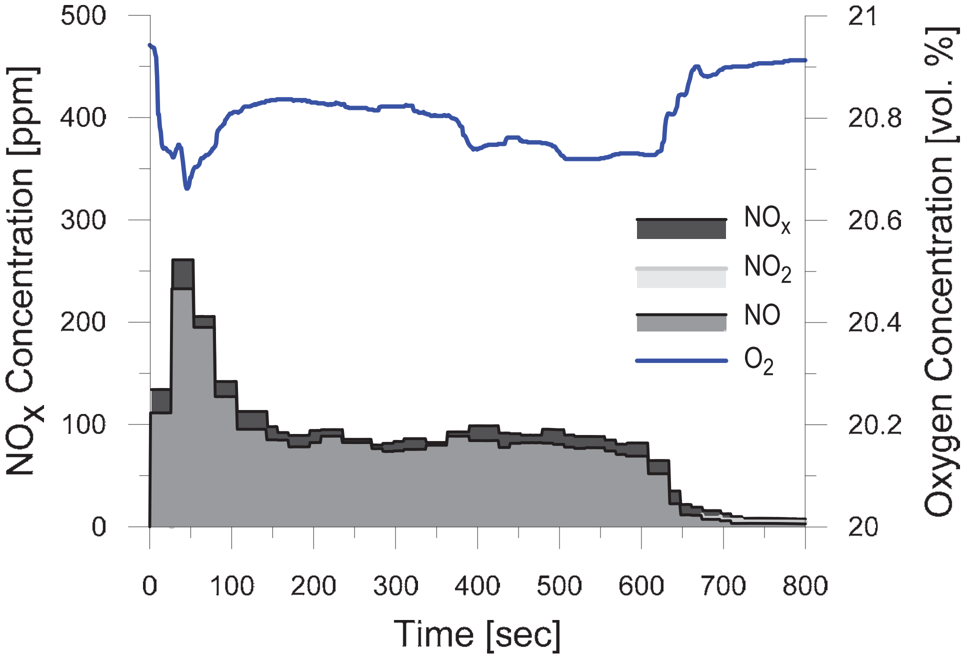

Figure 4-30: NO_x concentrations measured near the outlet of the StatX unit during and after aerosol generation in a cold test compartment with no fire (Test 1)

Subsequent to Test 1 where measurements of gas concentration were taken near the outlet of the StatX unit, in Test 2 concentrations of NO, NO_2 and NO_x were measured in the upper layer of the compartment during and after StatX aerosol generation. Time evolution of the concentrations of NO_x (left axis, Figure 4-32) and CO (left axis, Figure 4-33) overplotted with concentration of O_2

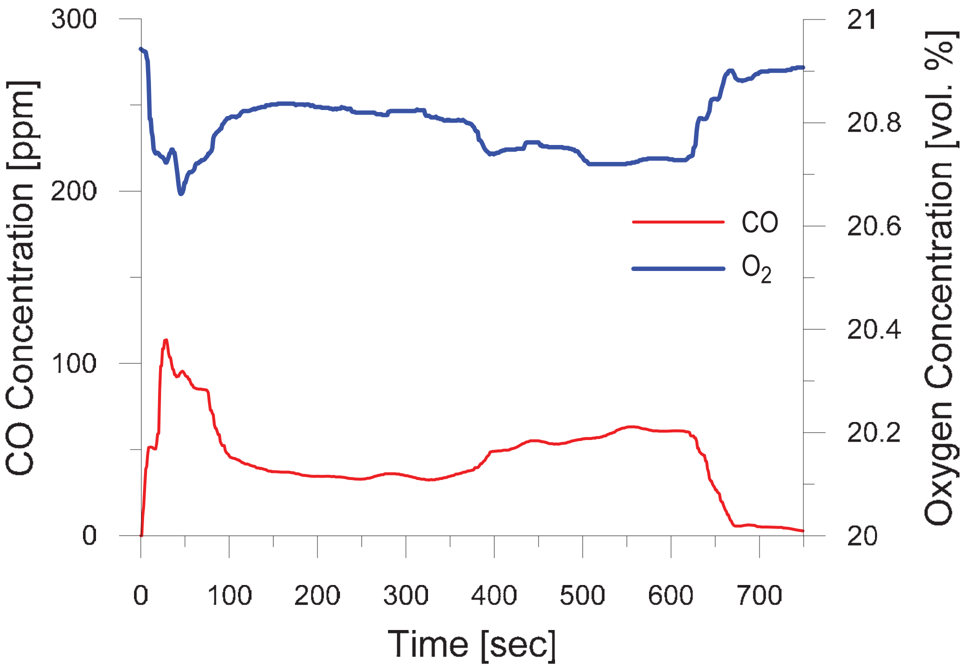

Figure 4-31: CO concentrations measured near the outlet of the StatX unit during and after aerosol generation in a cold test compartment with no fire (Test 1)

(right axis on both plots) indicate that upon activation of the unit, NO concentration immediately increased to peak values of 350 ppm and CO to peak values of 290 ppm, both higher than the peaks measured in the previous test. Concentrations of O_2 followed the inverse trend suggesting that this was a result of the heated aerosol discharge gases rising and collecting near the measurement location at the ceiling. NO and CO concentrations decayed after a short period of time, to much lower sustained values of 20-50 ppm for the remainder of the 10 minute test. As NO concentrations decreased, NO_2 concentrations increased to correspondingly higher peak values of around 100-110 ppm, then also decreased to levels of around 25 ppm for the duration of the test. The steep decrease to lower concentrations can likely be attributed to mixing in the upper regions of the compartment in this scenario, as well as leakage of agent and gases observed around the compartment door. Once the door was opened and the compartment ventilated, all gas concentrations returned to ambient levels.

As in previous tests, Gastec samples were taken to compare concentrations of NO and NO_2 to those measured using the Novatech system. The samples, taken at approximately 100 seconds into the test, suggest concentrations of NO and NO_2 of 70 and 200 ppm, respectively, as presented in Figure 4-34. Differences in concentration from those measured using the Novatech unit may be explained through a combination of the differences in system resolution and sampling locations, as well as gas residence time during which an equilibrium shift between NO and NO_2 production might well have taken place.

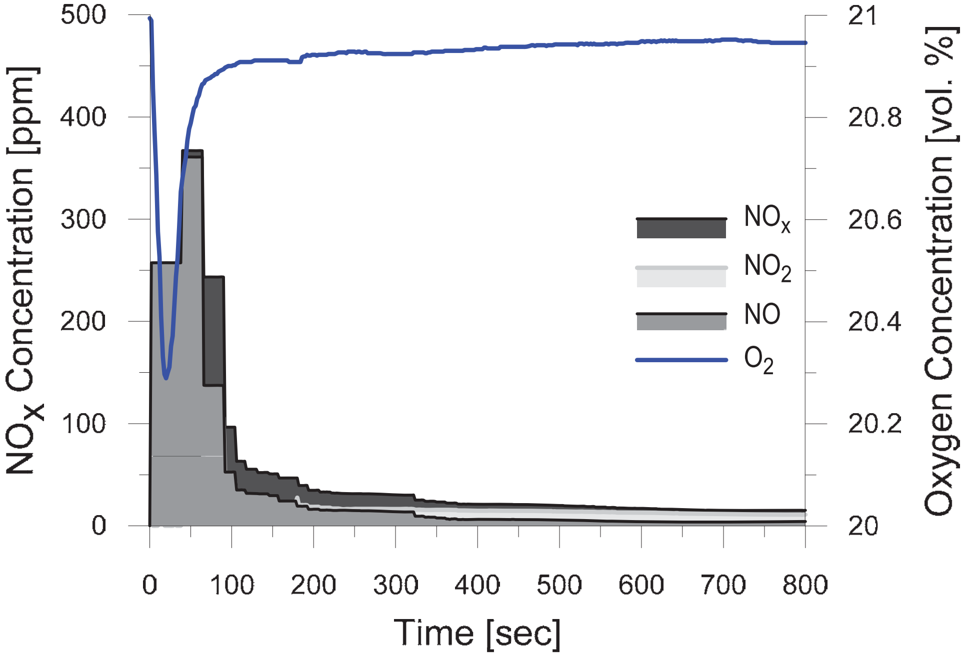

Figure 4-32: Measured NO_x concentrations during and after aerosol generation from a StatX unit into a cold test compartment with no fire (Test 2)

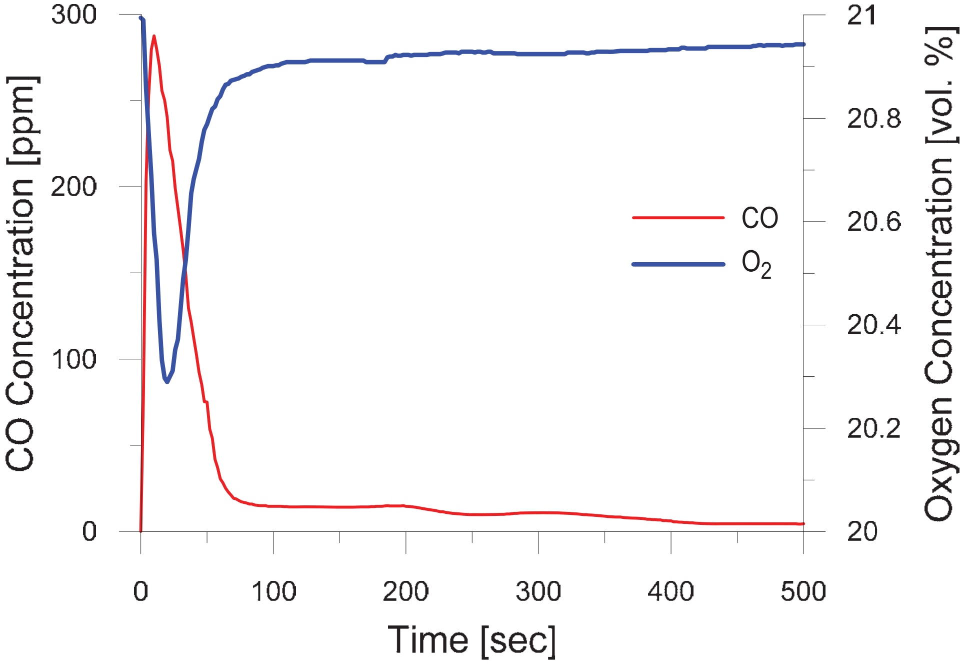

Figure 4-33: Measured CO concentrations during and after aerosol generation from a StatX unit into a cold test compartment with no fire (Test 2)

Figure 4-34: NOx concentrations measured using Gastec sampling tubes during release of Stat X aerosol unit in a test compartment with no fire (Test 2, 100 seconds)

In addition to the NO_x measurements, additional Gastec samples were withdrawn at times of 229 seconds and 339 seconds into the test to determine whether any HCN or NH_3, respectively, was present in the hot layer gases after discharge of the aerosol unit. While no measurable concentrations of HCN were observed, NH_3 concentrations of 25-30 ppm were recorded as indicated by the left edge of the black tape in Figure 4-35.

Figure 4-35: NH_3 Concentrations measured using Gastec sampling tubes during release of Stat X aerosol unit in a test compartment with no fire (Test 2, 339 seconds)

A repeat test of the above agent only discharge scenario was performed, but with the compartment door kept better sealed after discharge of the agent. In

Figure 4-36 is a plot of NO_x concentrations (left axis) and in Figure 4-37 CO concentrations (left axis), both with O_2 concentrations (right axis) as measured over time in the upper ceiling gases during activation of the StatX aerosol unit. Concentrations of NO increased to peak values of 400 ppm immediately on activation of the aerosol with a corresponding decrease in O_2 concentration as was seen in the other tests. CO concentrations did not peak, but instead increased to around 100 - 115 ppm (a lower level than for the test above) and remained at that level for the remainder of the test. Similar in trend to CO, concentrations of NO_2 increased to peak values of around 25-30 ppm and remained constant, while NO concentrations slowly decayed as a function of time, leveling out at values around 100 ppm until the compartment door was opened and the compartment ventilated (not shown in this plot). Such test to test variation can again likely be explained by shifts in chemical equilibrium amongst the oxidation reactions involving CO, CO_2 and NO_x.

The concentrations of NO and NO_2 measured using the Novatech system (Figure 4-36) were further confirmed via Gastec samples taken at 170 seconds into the test which indicated concentrations of NO (upper tube) and NO_2 (lower tube) of around 150 and 20 ppm respectively, as marked by the right hand edge of the black tape around the two tubes shown in Figure 4-38.

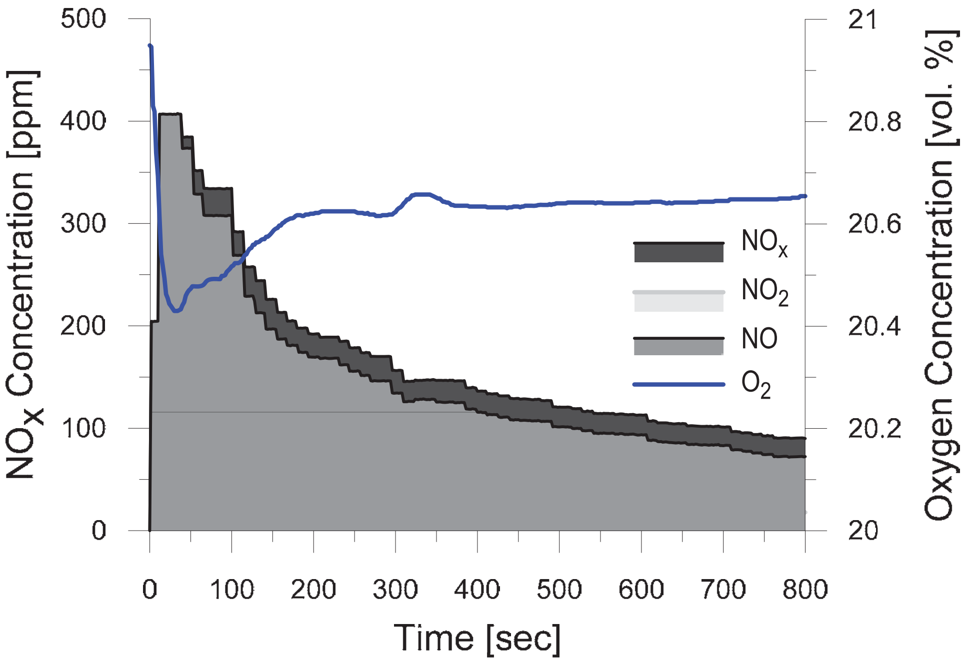

Figure 4-36: Measured NOx concentrations during release of StatX unit into a cold test compartment with no fire (Test 3)

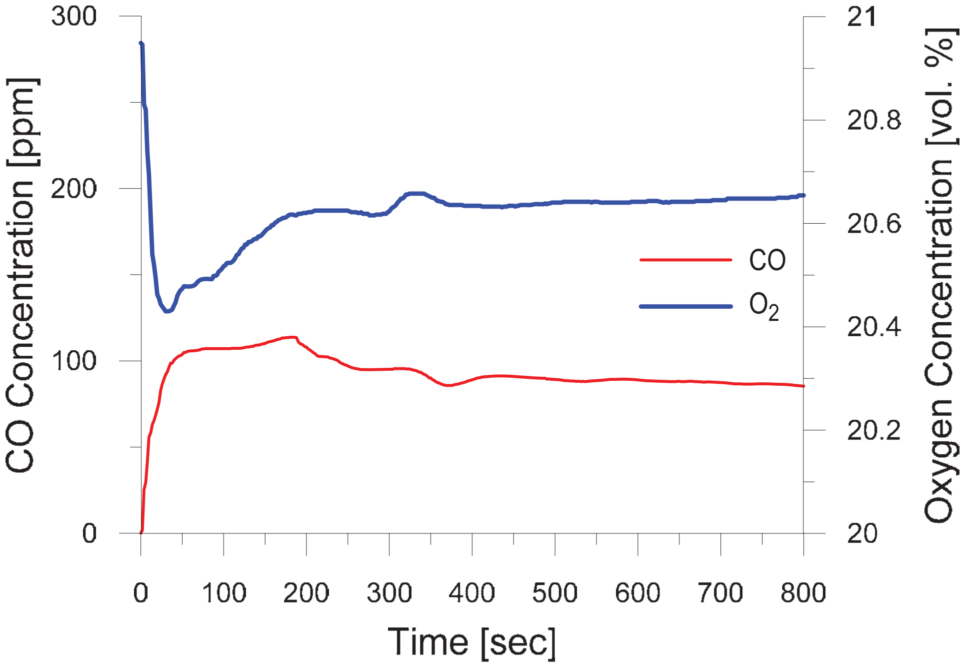

Figure 4-37: Measured CO concentrations during release of a StatX unit into a cold test compartment with no fire (Test 3)

Figure 4-38: NOx concentrations measured using Gastec sampling tubes during release of a StatX unit in a cold test compartment with no fire (Test 3, 170 seconds)

Additional Gastec samples were withdrawn at times of 330 seconds and 450 seconds into the test, respectively, to determine whether any HCN or NH_3 was present in the hot layer gases after discharge of the aerosol unit. While no measurable concentrations of HCN were observed, an NH_3 concentration of 50 ppm was recorded, as indicated by the left side of the black tape on the tube in Figure 4-39. This would again be consistent with the oxidation pathways expected due to aerosol agent discharge.

Figure 4-39: NH_3 Concentrations measured using Gastec sampling tubes during release of a StatX unit in a cold test compartment with no fire (Test 3, 450 seconds)

4.18 Results of Aerosol Agent Only Tests for DSPA Unit

Concentrations of NO, NO_2, NO_x, and CO were measured using the Novatech system during three tests conducted by discharging a DSPA 5-4 aerosol unit into the empty fire compartment, then immediately closing the door and keeping the compartment door sealed for 10 minutes. In Test 1, Figure 4-40 and Figure 4-41, gas concentrations were measured low in the compartment and near the outlet of the aerosol unit. For Test 2, Figure 4-42 through Figure 4-45 and Test 3, Figure 4-46 through Figure 4-50, they were measured in the gases near the ceiling of the compartment using the sampling port that was used in the fire test scenarios. To supplement the information on NO_x evolution, additional measurements of NH_3 and HCN concentration were made using the Gastec sampling systems in the latter two tests.

As with the Stat X agent only tests above, the quantity of NO, NO_2, NO_x and CO that was created due to thermal decomposition of base aerosol compounds (such as KNO_3) and fuel binder was determined during and immediately after activation of the aerosol unit. Results were compared against 10 and 15 minute exposure limits for NO_x [9, 11, 12] and CO [43] to better appreciate the potential impact from an accidental discharge into an occupied space.

Upon activation of the DSPA aerosol unit for the test plotted in Figure 4-40, concentrations of NO measured near the outlet of the unit (left axis) increased sharply to values of 500 ppm, and then slowly decreased for the duration of the experiment. CO concentrations sharply increased to peak

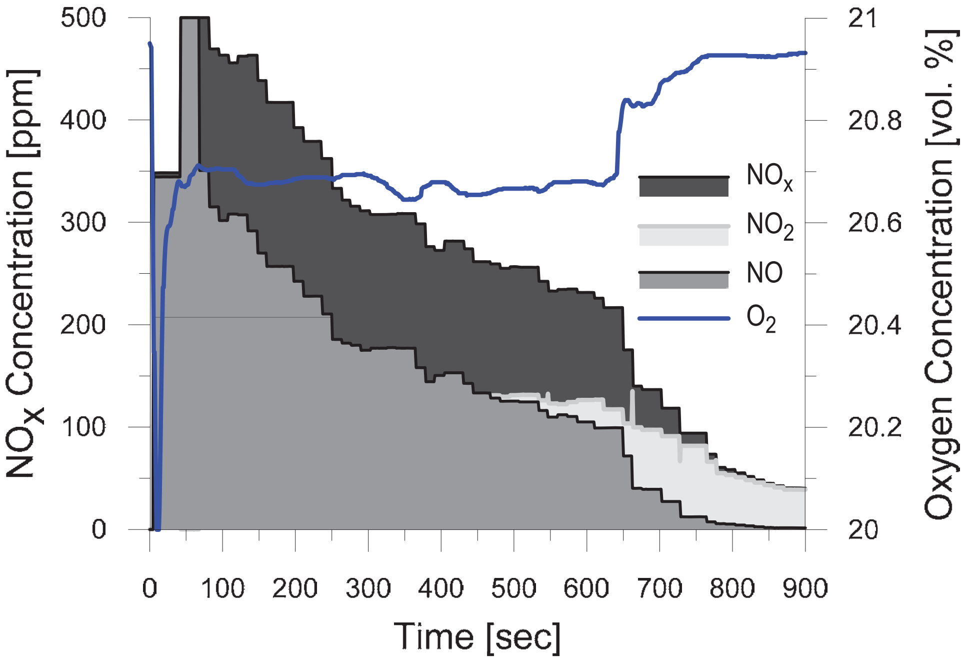

Figure 4-40: Measured NO$_x$ concentrations during release of DSPA unit into a cold test compartment with no fire (Test 1)

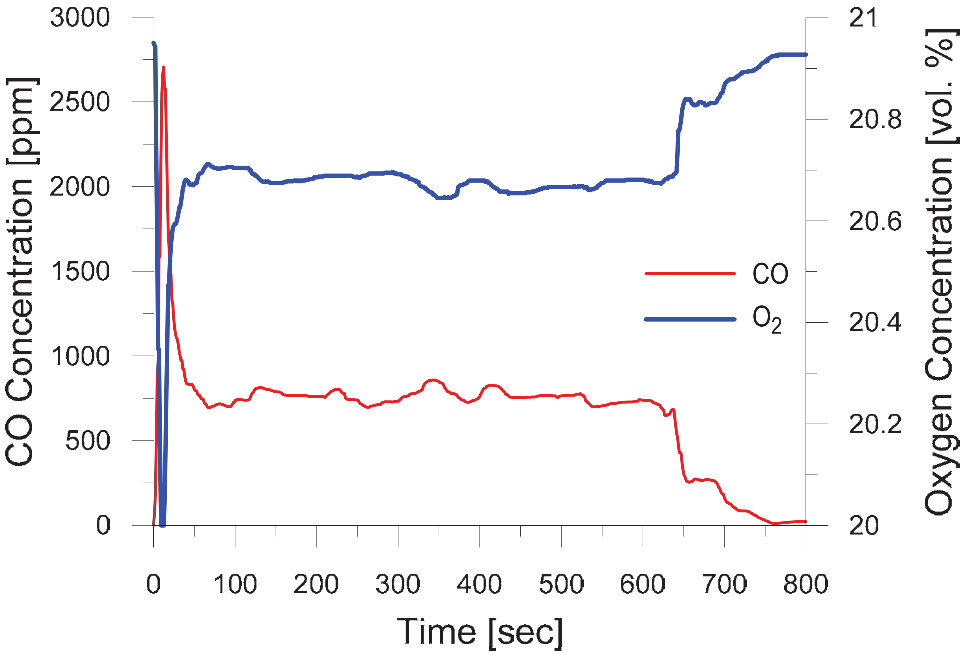

Figure 4-41: Measured CO concentrations during release of DSPA unit into a cold test compartment with no fire (Test 1)

values of 2700 ppm and then decreased back to more steady levels around 750 ppm while concentrations of O_2 exhibited the inverse trends as expected for an oxidation process. As NO concentrations decreased below saturation, NO_2 concentrations increased and then leveled at values of 125 - 150 ppm. All measured concentrations returned to ambient levels as the door was opened and compartment ventilated.

Subsequent to the measurements of gas concentration near the outlet of the DSPA 5-4 unit, Figure 4-42 and Figure 4-43, measurements of NO, NO_2 and NO_x were made in the upper layer of the test compartment during and after DSPA aerosol generation. Time evolution of the concentrations of NO_x (left axis, Figure 4-42) and CO (left axis, Figure 4-43) overplotted with concentrations of O_2 (right axis on both plots) indicate that upon activation of the unit, NO concentration immediately increased to peak values of over 500 ppm and saturated the Novatech detector system. CO similarly increased to high peak values, over 3000 ppm, slightly higher than the peak values measured in the previous test. Concentrations of O_2 followed the inverse trend. NO and CO concentrations then gradually decayed over time, to lower sustained values of 100 ppm (NO) and 1200 ppm (CO) for the remainder of the test.

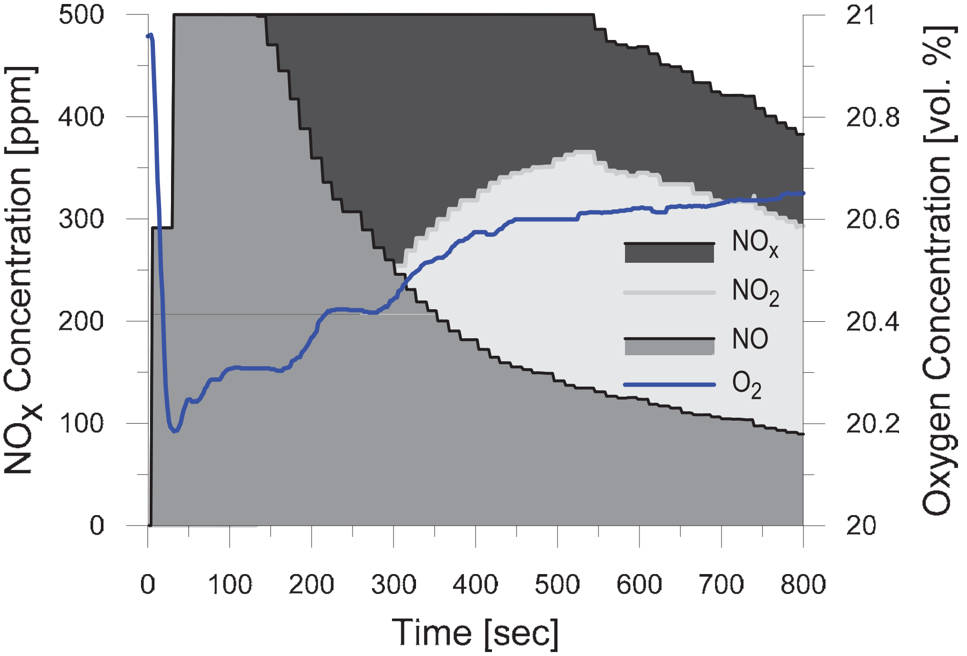

Figure 4-42: Measured NO_x concentrations during release of DSPA unit into a cold test compartment with no fire (Test 2)

As NO concentrations decreased such that the detector was no longer saturated, NO_2 concentrations increased to peak values exceeding those of NO, around 350 ppm, before decreasing again. In comparison to measurements made right at the outlet of the DSPA unit, the concentrations in this test are higher which can likely be attributed to heated aerosol exhaust gases rising and collecting near the measurement location at the ceiling. Once the door was opened and the compartment ventilated, all gas concentrations returned to ambient levels.

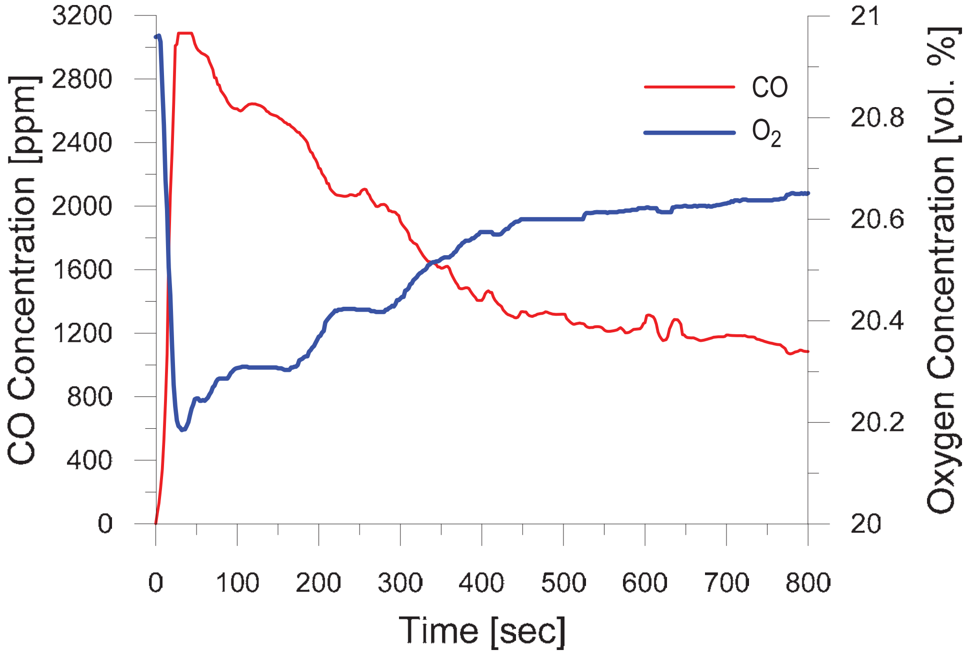

Figure 4-43: Measured CO concentrations during release of DSPA unit into a cold test compartment with no fire (Test 2)

Concentrations of NO and NO_2 were also measured via Gastec samples taken at 100 seconds into the test. These indicated concentrations of NO (upper tube) and NO_2 (lower tube) of over 200 and around 50 ppm respectively, as demarcated by the left side of the black tube around each tube in Figure 4-44, confirming that the Novatech measurements are in error due to saturation of the detector.

Figure 4-44: NOx concentrations measured using Gastec sampling tubes during release of a DSPA 5-4 unit into a cold test compartment with no fire (Test 2, 100 seconds)

Gastec samples were also withdrawn at times of 258 seconds and 378 seconds to determine, respectively, whether any HCN or NH_3 was present in the hot layer gases after discharge of the unit. While no measurable concentrations of HCN were observed, high NH_3 concentrations, 300 ppm, were recorded as indicated by the left hand side of the black tape in Figure 4-45.

Figure 4-45: NH$_3$ concentrations measured using Gastec sampling tubes during release of a DSPA 5-4 unit into a cold test compartment with no fire (Test 2, 378 seconds)

A repeat test of the above DSPA 5-4 agent only discharge scenario was performed with the detectors recalibrated to allow detection of concentrations as high as 1800 ppm. In Figure 4-46 is a plot of NO$_x$ concentrations (left axis) and in Figure 4-47 are CO concentrations (left axis), both overplotted with O$_2$ concentrations (right axis) as measured with time. Trends were similar to those seen in other tests. Concentrations of NO (Figure 4-46) and CO (Figure 4-47) increased, respectively, to peak values of 600 ppm and 1370 ppm on activation of the aerosol with a corresponding decrease in O$_2$ concentration. In contrast, concentrations of NO$_2$ (Figure 4-46) increased to around 200 ppm and remained constant, while NO and CO concentrations slowly decayed to lower sustained values of around 100 ppm and 800 - 1000 ppm, respectively. When the compartment door was opened (not shown here), concentrations returned to ambient.

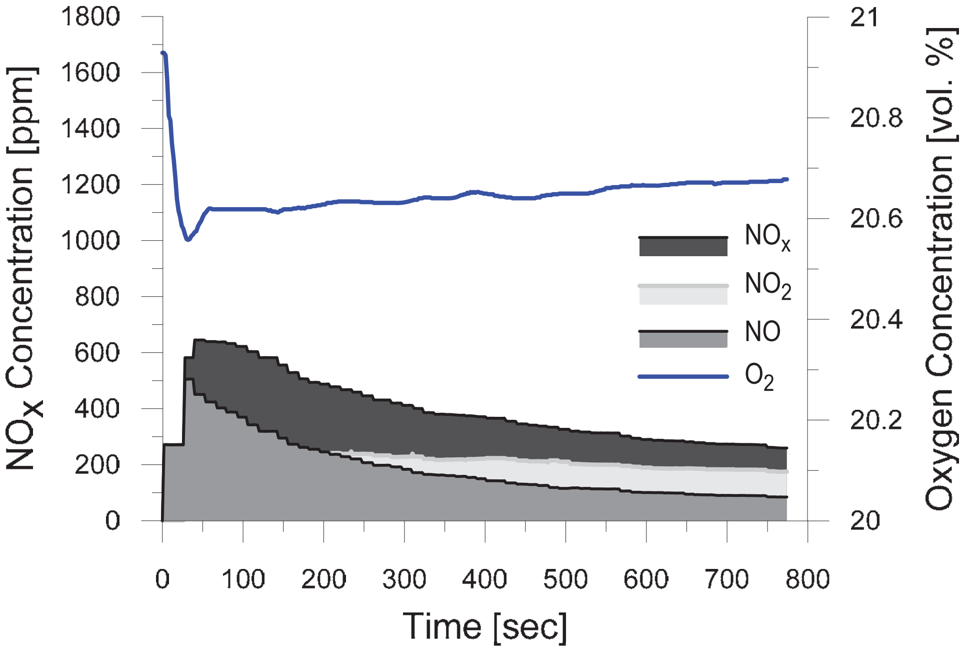

Figure 4-46: Measured NOx concentrations during release of DSPA 5-4 unit into a cold test compartment with no fire (Test 3)

The relative level of NO and NO$_2$ measured using the Novatech system was again confirmed via Gastec samples taken at 162 seconds into the test. As indicated by the left hand edge of the black tape around the tubes shown in Figure 4-48, concentrations of both NO (upper tube) and NO$_2$ (lower tube) were above 200 ppm.

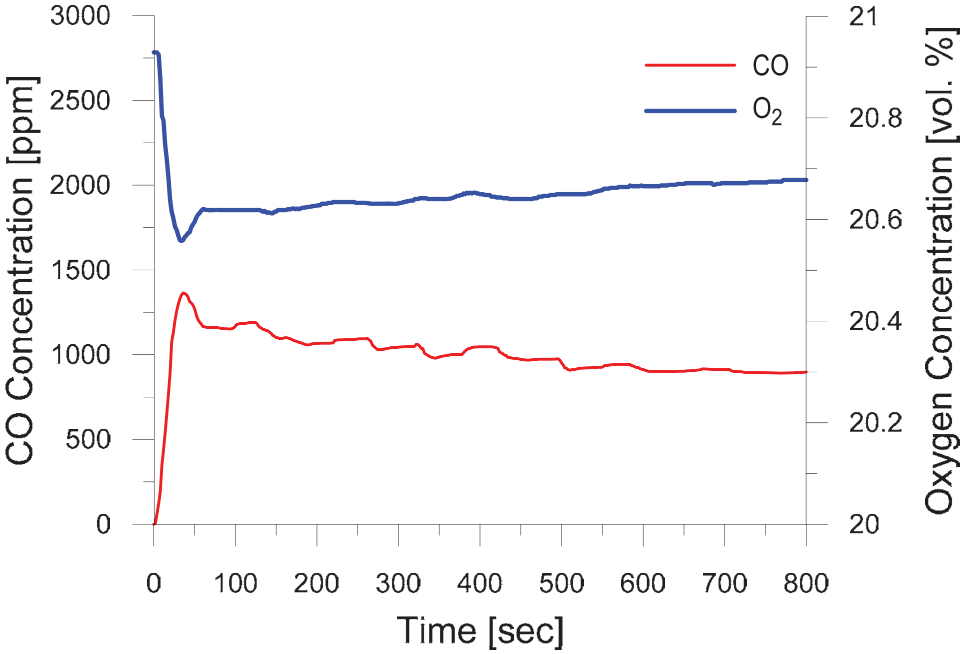

Figure 4-47: Measured CO concentrations during release of DSPA 5-4 unit into a cold test compartment with no fire (Test 3)

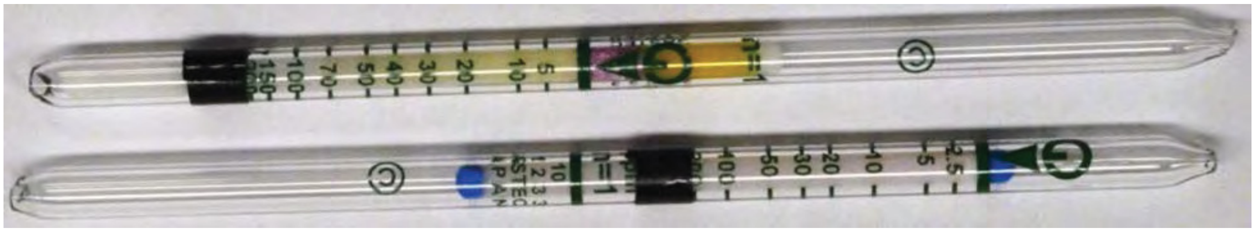

Figure 4-48: Measured NOx concentrations using Gastec sampling tubes during release of a DSPA 5-4 unit into a cold compartment with no fire (Test 3, 162 seconds)

Additional Gastec samples were withdrawn at times of 297 seconds and 417 seconds into the test to determine, respectively, whether any HCN or NH_3 was present in the hot layer gases after discharge of the aerosol unit. As shown by the left edge of the black tape in Figure 4-49, the measured concentration of HCN was 40 ppm, while that of NH_3 (Figure 4-50) was 60 ppm. The presence of these gases, coupled with the fact that NO_2 concentrations exceeded those of NO, suggest variations in reaction equilibrium due to the conditions within the closed compartment.

Figure 4-49: HCN concentrations measured using Gastec sampling tubes during release of a DSPA 5-4 unit into a cold compartment with no fire (Test 3, 297 seconds)

Figure 4-50: NH_3 concentrations measured using Gastec sampling tubes during release of a DSPA 5-4 unit into a cold test compartment with no fire (Test 3, 417 seconds)

4.19 Summary and Discussion of Aerosol Agent Only Test Results

Concentrations measured during and after activation of StatX and DSPA 5-4 aerosol units in agent only tests shown in Sections 4.17 and 4.18, indicate different temporal distributions of hot gases in different regions of the compartment during activation and aerosol generation from the two units. Differences in total aerosol loading and generation reactions in each unit, coupled with confinement of the compartment by closing the door, led to varying concentrations of NO, NO_2, CO, HCN and NH_3 across the tests. Results were consistent with general expectation, since of all of the species of interest are linked to oxidation and NO_x production during agent generation. The relative concentrations of each change as the compartment temperature and ventilation characteristics vary, since their relative generation is known to be very dependent on local factors such as temperature and oxygen concentration.

NO was produced during and immediately after activation for each variant of aerosol extinguisher, both in the regions immediately adjacent to the unit and in the upper layers of the compartment. Measured concentrations of NO appeared higher near the ceiling than in the immediate vicinity of either unit, due to the single point sampling method and strong air currents around the discharging aerosol units. In all cases, local NO concentrations surpassed the short term exposure thresholds and the IDLH limit for occupational exposure of 100 ppm set by OSHA [11, 13, 14]. Differences in NO_2 concentration were seen between aerosol variants and from test to test depending on compartment confinement. They exceeded the 1-hour continuous exposure limit proposed by WHO [10], as well as both the OSHA IDLH and OSHA 15-minute exposure thresholds [11, 12] in all tests. CO concentrations measured during and after StatX and DSPA 5-4 activation in the sealed compartment indicate peak concentrations of CO varied significantly between tests with the two aerosol variants as well. For most tests with the compartment door closed, CO concentrations significantly surpassed the ceiling level of 200 ppm set by NIOSH for occupational exposure [22]; in others, CO concentrations fell between the OSHA and NIOSH limits. Measurable concentrations of HCN and NH_3 were also observed in some of the tests, reaching levels as high as 300 ppm of NH_3 and 40 ppm of HCN in separate tests where the door was closed after aerosol activation.

From the above discussion the potential exists for significant concentrations of all gases to accumulate, at least locally, when the compartment door is closed, suggesting that care should be taken regarding potential exposure of personnel should an aerosol unit release into a cold, relatively well sealed compartment. When air flow promoted mixing and ventilation of gases in the compartment, high concentrations were generally seen for only short periods of time. Even if such concentrations are sustained only for short times in the depths of the upper layer of a compartment, it is extremely important to develop appropriate operational procedures for aerosol storage and use in order to minimize the likelihood that any personnel could be exposed to levels of any of these gases above threshold values should an accidental release take place.

5 Powder Characterization Using X-Ray Diffraction (XRD)

The nature of the raw solid aerosol tablet as well as the aerosol powder that was generated during discharge of each handheld unit was assessed using X-ray diffraction. Manufacturer documentation and other literature suggested that the tablet/powder composition might include compounds such as potassium bicarbonate ($KHCO_3$), potassium nitrate (KNO_3), ammonium bicarbonate (NH_4HCO_3), potassium hydroxide (KOH) and other potassium salts.

5.1 Powder Characterization of Stat X and DSPA 5-4 Raw Tablets

Diffraction patterns obtained via X-ray diffraction of the raw StatX and DSPA 5-4 tablets are contained in Figure 5-1 and Figure 5-2. Comparison with patterns in existing X-ray diffraction libraries [39], identified the main component in the raw tablet for each unit as a mineral form of potassium nitrate, niter. No other compounds could be identified.

Niter is a strong oxidizing agent, known to be employed in aerosol powder generation [44]. While it is noted to have a relatively low acute toxicity, it is listed as a carcinogen and can be harmful if swallowed, especially for vulnerable populations. It also forms an acid (pH 5.5 – pH 8) in the presence of water. As it thermally decomposes, it produces nitrogen and potassium oxides and may partake in further reactions to produce a wide variety of chemical compounds.

5.2 Powder Characterization of Stat X and DSPA 5-4 Aerosol Powder

The aerosol extinguishing powder generated during discharge of each unit was collected and analyzed using the same X-ray diffraction unit as was used for analysis of the raw aerosol tablets. Figure 5-3 and Figure 5-4 below, contain the patterns obtained from the Stat X and DSPA 5-4 aerosols, respectively.

The diffraction patterns from both the StatX and DSPA 5-4 aerosol powders indicated that a major component was potassium carbonate (K_2CO_3), which may also be a decomposition product of potassium bicarbonate ($KHCO_3$) when temperatures are in the excess of 500°C [45]. In the case of the DSPA aerosol, another potassium salt - potassium cyanate (KCNO) – was also seen perhaps pointing to the source of HCN seen in the DSPA 5-4 agent only test. No other compounds were identified in the aerosols for either variant of extinguisher.

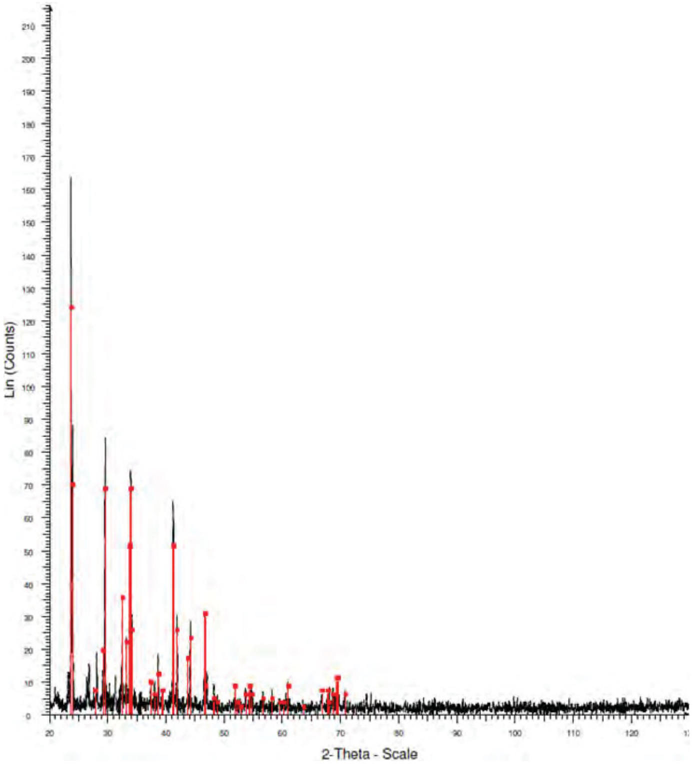

Figure 5-1: Diffractogram of raw StatX aerosol tablet

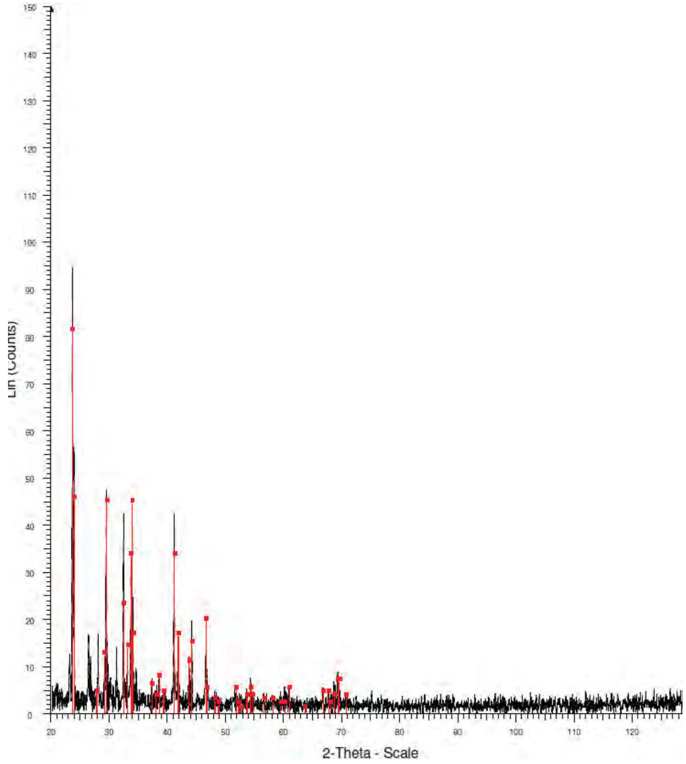

Figure 5-2: Diffractogram of the raw DSPA 5-4 aerosol agent

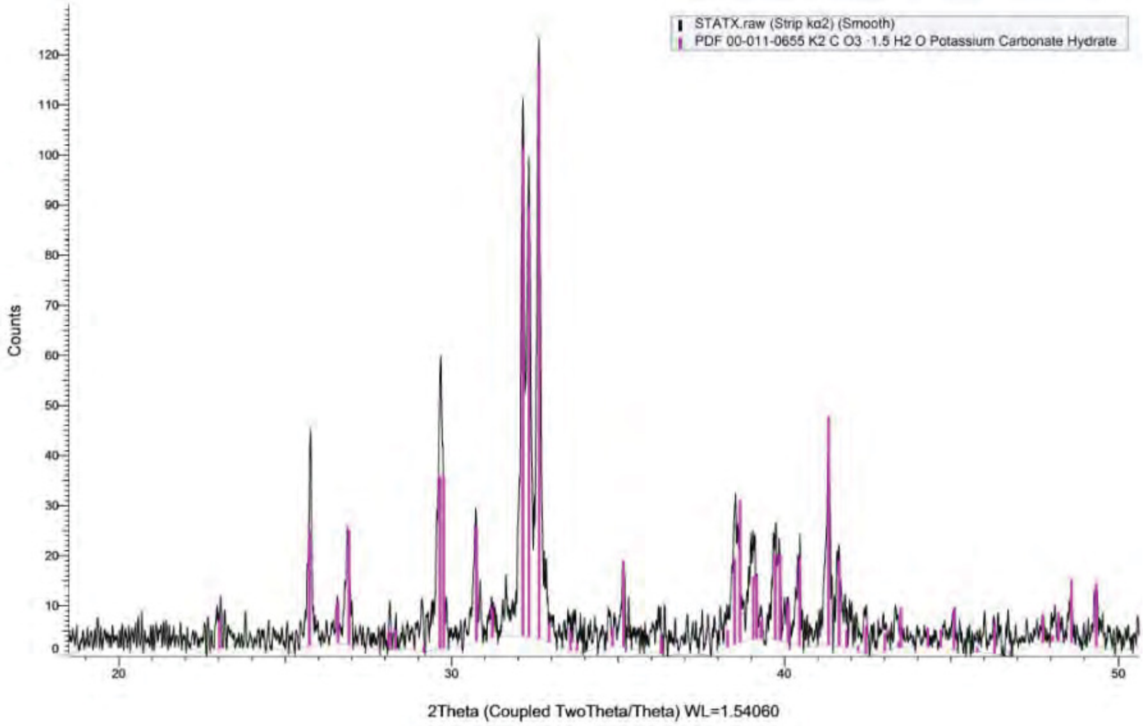

Figure 5-3: Difractogram of the StatX aerosol extinguishing powder

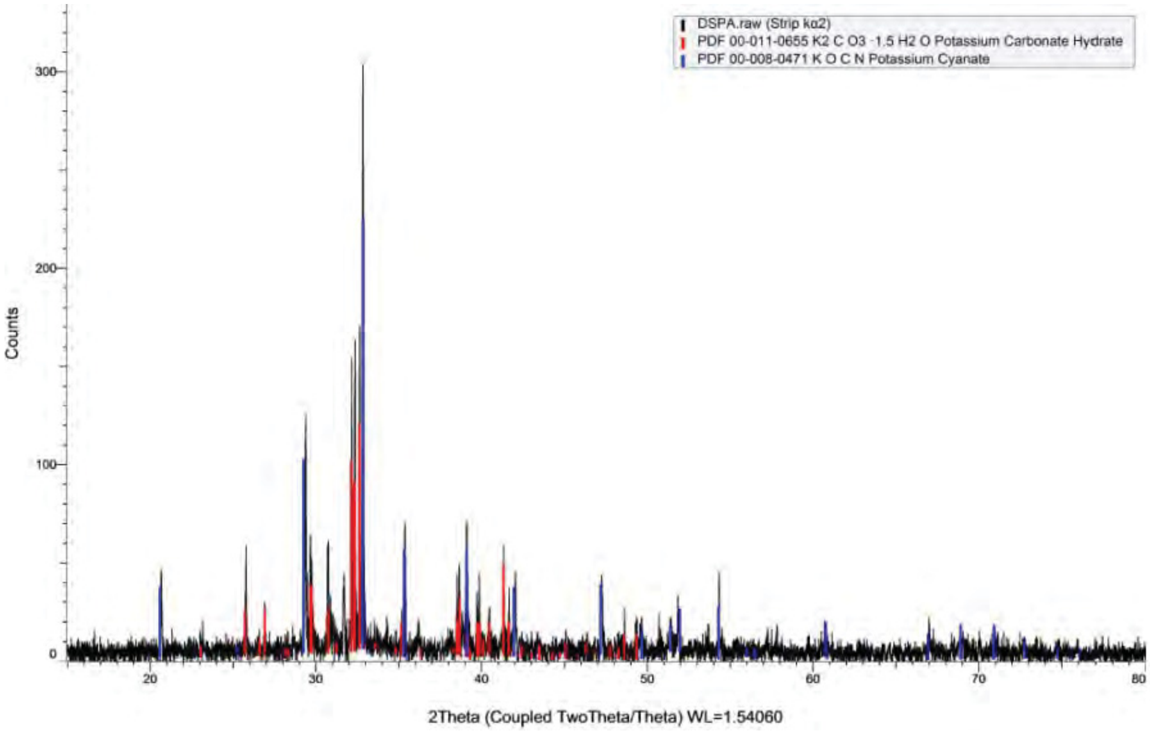

Figure 5-4: Difractogram of the DSPA 5-4 aerosol extinguishing powder

6 Impacts of Aerosol Powder on Various Materials and Equipment

One key component of the aerosol forming agent in both the StatX and DSPA 5-4 handheld aerosol extinguishing units is potassium nitrate, KNO_3, which is an ionic salt, a strong oxidizing agent and a natural solid source of nitrogen [46]. Upon activation, the KNO_3 as well as any organic oxidizers and binding agents react to generate fluid aerosols in the proximity of the extinguishing units. The aerosols can be comprised of particulates such as potassium carbonate (K_2CO_3) and potassium bicarbonate ($KHCO_3$), as well as ammonium bicarbonate (NH_4HCO_3), potassium cyanate (KCNO) and other materials depending on the nature of the reacting compounds and details of the reaction and decomposition processes. The particles are expelled into the fire environment and, when exposed to high temperatures, the potassium carbonate can dissociate into potassium radicals which interact with the hydroxyl, OH, oxygen, O, and hydrogen, H, radicals that normally drive the hydrocarbon combustion process. This interaction not only works to suppress the fire, but also leads to production of other stable molecules such as potassium hydroxide (KOH) [27], as well as gases such as H_2O, CO_2, and NO_x [47].

Both potassium hydroxide (KOH) and potassium carbonate can dissociate in water to form the potassium ion (K+) and either hydroxide (OH^-) or carbonate (CO_3^{-2}) ions, respectively. The resulting solutions are strongly basic, with pH levels on the order of 12-13. Potassium hydroxide is classified as a highly corrosive chemical [48, 49]. As such, the potential for the powders generated by an aerosol extinguisher to impact their surrounding environment may relate to both their effects on humans and on various materials. In fact, direct contact with KOH can cause skin burns, eye damage and potentially also damage to the lungs when inhaled [49, 50]. In terms of impact on materials, strong bases can lead to corrosion, damage and eventual failure of a material.

To evaluate the impacts of the aerosol powders on various materials and sensitive electrical equipment such as might be on board a naval vessel, a number of common metals, marine materials, commercially available personal computer towers and electronic boards, and Nomex fabric specimens were placed in the UW burn compartment during the series of agent only tests, diesel fire tests and diesel fire tests with agent suppression that were described in Chapter 4 above. Early tests were conducted using either StatX or DSPA units, while in later tests the impacts of both aerosol units on various materials were compared under similar test conditions.

Across the tests, specimens can be grouped into two test series and several main categories of materials as follows. In a preliminary set of tests, the following materials were exposed to aerosols: 1) chrome plated aluminum and nickel plated aluminum; 2) copper; and 3) chrome plated steel; while in the extended tests, the following materials were exposed: 4) high tensile and mild steel; 5) copper-beryllium alloys; 6) NOMEX fabric 7) CD discs; and 8) computer and electronic boards. The following discussion is split into two sections; the first outlines the results of the preliminary tests and the second, those of the extended tests.

Control and test specimens were cut for each material. The control sample was cleaned using acetone to remove any oils and other residue on the surface and then scanned using an optical microscope to visualize the unexposed surface characteristics of that material. These specimens were then stored in electrostatic bags and set aside as reference samples for on-going comparison against the exposed material coupons.

The surfaces of chrome and nickel plated aluminum, chrome plated stainless steel, copper and copper beryllium test specimens were also cleaned using acetone and then exposed to either the aerosol particulate in a cold compartment (agent only test) or to the smoke and hot gases developed during a diesel fire, with and without suppression by one or both of the aerosol variants. During the agent only tests, the specimens were dispersed throughout the test compartment and were exposed to the aerosol particulate for the entire ten minute duration of the test. In the diesel fire tests, with and without suppression, each set of samples was placed along the wall of the compartment so that they would be exposed to the products of combustion from the fire as well as to the aerosol powder but would not be directly impacted by the flames. Again samples were exposed for the duration of each test.

After exposure to the test environment, samples were stored in electrostatic bags and examined on a weekly or on a six-month basis to qualitatively monitor any effects that long term exposure to the aerosol particulate may have had on the sample, as well as to visually document any cumulative damage that might accrue due to exposure to the fire gases and/or aerosol particulates. A Nikon D7000 high resolution digital camera was used in conjunction with Nikkor AF 85mm f/1.8 D portrait lens to capture the overall nature of particle deposition on some of the samples. An Olympus FV optical microscope at 50X magnification was used for more detailed analysis of the impacts of exposure to the surface of each sample. Microscope images were recorded using a Photometrics Coolsnap camera and image processing done through Image-Pro Premium, version 6.3.0.512 [51]. No quantitative characterization of corrosion damage was attempted.

Images of control samples and test specimens for the various groups of materials and equipment are presented in the following sections, beginning with the description of the control sample for each material followed by presentation of results for specimens of that material that were exposed to agent only, then diesel fires, without and with aerosol suppression.

6.1 Preliminary Test Series

6.1.1 Exposure of Chrome Plated Aluminum Specimens

Figure 6-1a) contains an image of the surface of the reference chrome plated aluminum specimen and Figure 6-1 b) an image of the surface of a chrome plated aluminum sample 6 months after it was exposed to aerosol powder generated by the StatX unit in an agent only test. Both were taken at 50X magnification with a 300 μm reference located on each image. In comparison to the surface of the reference sample (Figure 6-1a)), moderate to significant damage can be seen on the surface of the exposed specimen (Figure 6-1b)), mainly in the form of large pits that have eaten away the surface coating after exposure to the aerosol agent alone. Some particulate residue can be seen as small white dots in the image in Figure 6-1b) as well.

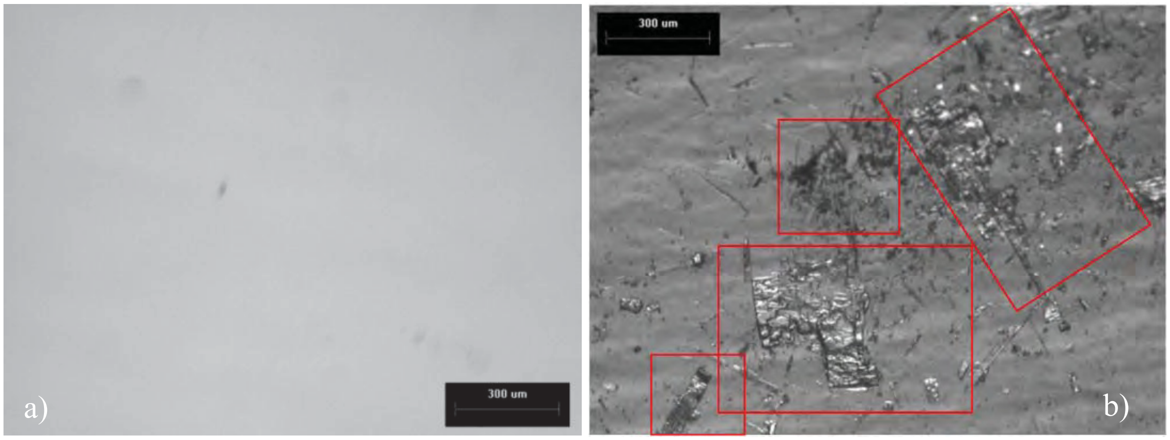

Figure 6-1: Surface of chrome plated aluminum sample (50x magnification) a) reference specimen b) six months after exposure to Stat X aerosol agent

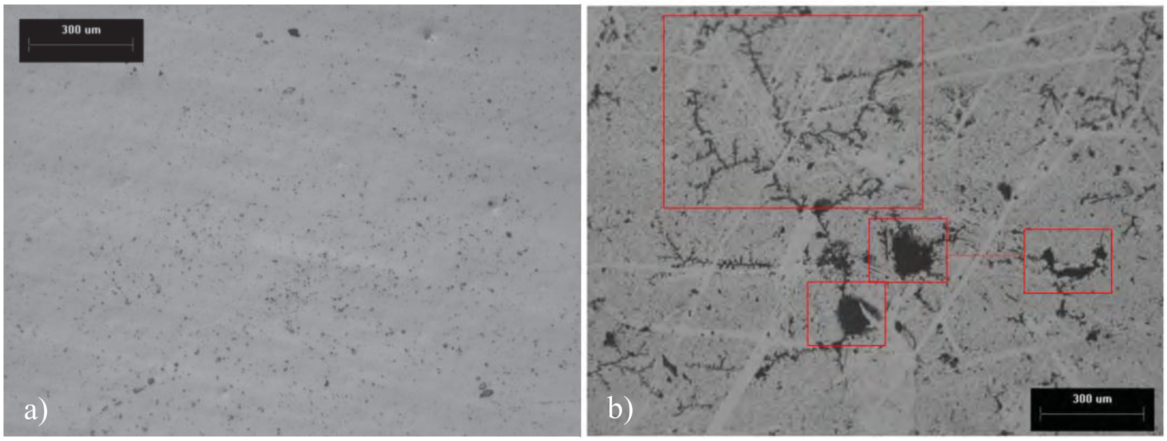

Figure 6-2: Surface of chrome plated aluminum sample (50X magnification) six months after exposure to a) diesel fire gases b) diesel fire gases and DSPA 5-4 aerosol agent

Figure 6-2 a) and Figure 6-2 b) contain images of the surfaces of chrome plated aluminum specimens 6 months after they were exposed to diesel fire gases alone (Figure 6-2 a)) and to a combination of diesel fire gases and aerosol powder generated by the DSPA 5-4 unit in an agent only test (Figure 6-2 b)). Both were again taken at 50X magnification with a 300 µm reference located on each image. In comparison to the reference image in Figure 6-1a), only minor damage in the form of small pits and cavities in the chrome plate can be observed on the surface of the sample that was exposed to the diesel fire environment. In contrast, in the section of the surface of the chrome plated aluminum sample exposed to the diesel fire with DSPA 5-4 agent suppression Figure 6-2 b), there appears again to have been significant damage in the form of both deeper, larger pits and long deep fingers which appear to have penetrated the surface coating and potentially reached the aluminum substrate underneath.

6.1.2 Exposure of Nickel Plated Aluminum Samples

Figure 6-3a) contains an image of the surface of the reference nickel plated aluminum specimen and Figure 6-3b) an image of the surface of a sample of the same material 6 months after it was exposed to aerosol powder generated by the StatX unit in an agent only test. Both were taken at 50X magnification with a 300 µm reference located on each image. In comparison to the smooth surface of the reference sample, there are dark striations across the surface of the exposed sample indicating some interaction between the aerosol and the surface, possibly in places where the coating may have already been scratched. The absence of deep pits or fingers similar to those seen for the chrome plated aluminum samples suggests general but superficial damage to the surface coating with little evidence of penetration to the aluminum beneath.

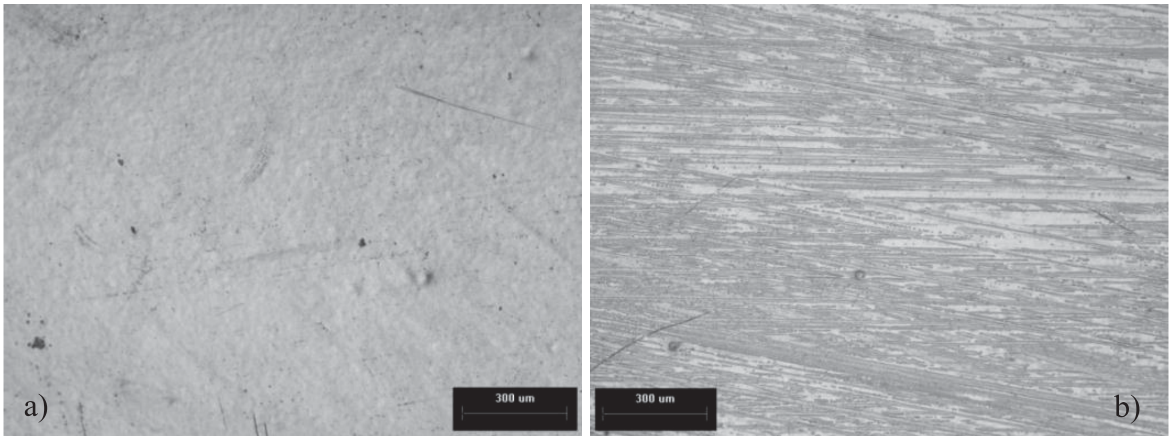

Figure 6-3: Surface of nickel plated aluminum sample (50x magnification) a) reference specimen b) six months after exposure to Stat X aerosol agent

In comparison to the above, Figure 6-4 a) contains an image of the surface of a nickel plated aluminum specimen six months after it was exposed to diesel fire gases and Figure 6-4 b) an image of the surface of a nickel plated aluminum sample six months after it was exposed to a combination of diesel fire gases and aerosol powder generated by the DSPA 5-4 unit (agent only test). Both were taken at 50X magnification with a 300 µm reference located on each image. In comparison to the reference image in Figure 6-3a), minor damage in the form of small pits and cavities in the nickel plate can be observed on the exposed surface due to exposure to the hot gases from the diesel fire (Figure 6-4 a)). On the surface exposed to the diesel fire with agent suppression, Figure 6-4 b), additional damage has occurred, leading to deeper, but still localised, small cavities or holes. There was no evidence of the large pits and fingers seen for the chrome plated aluminum samples discussed in the previous section. While the surface characteristics of the coating are impacted and it is clear that exposure to the aerosol has led to some damage to the surface, the level of damage is relatively minor and does not appear as though it will significantly affect the overall integrity of the coating or the material beneath.

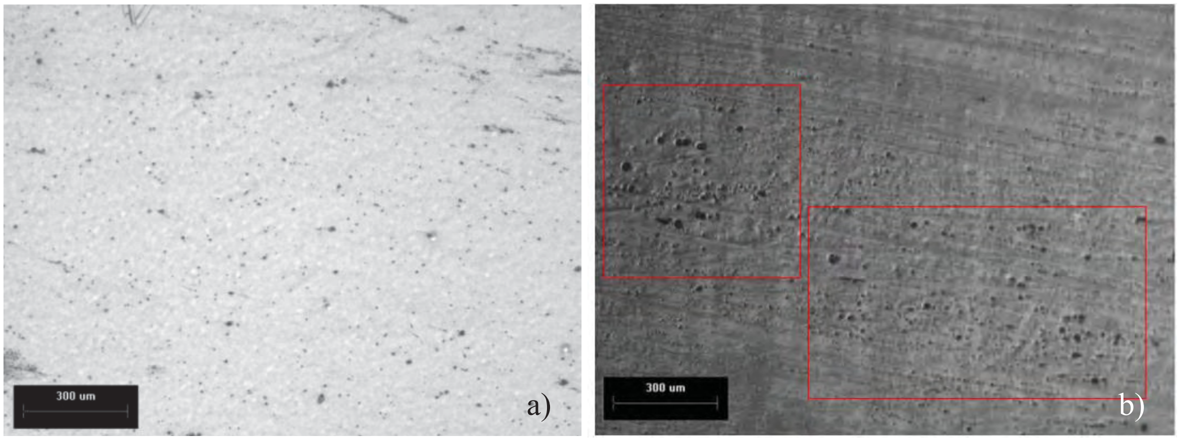

Figure 6-4: Surface of nickel plated aluminum sample (50X magnification) six months after exposure to a) diesel fire gases b) diesel fire gases and DSPA 5-4 aerosol agent

6.1.3 Exposure of Copper Samples

Figure 6-5 a) contains an image of the surface of the reference copper pipe specimen and Figure 6-5 b) a magnified image of the surface of the reference sample on which there is clear evidence of marking due to the pipe manufacturing process. Figure 6-5 c) contains an image of the surface of the copper sample taken six months after it was exposed to aerosol powder generated by the StatX unit in an agent only test. The latter two images were taken at 50X magnification and 300 µm references are located on each. Direct exposure to the gases and particulates formed during generation and discharge of the Stat X agent, and continuing interactions after exposure, have resulted in the large pits in evidence across much of the copper surface in Figure 6-5 c). Slight discolouration of the surface suggested the presence of an oxide layer as well, but examination of sample cross sections indicated that the discoloured layer was extremely thin.

Figure 6-6 contains an image of the reference copper specimen (left) with that of a different sample taken six months after it was exposed to a combination of diesel fire gases and aerosol powder generated by the DSPA 5-4 unit during a diesel fire suppression test. Comparison of the images shows that there is notable discolouration of the copper, suggesting oxidation of the surface during exposure to the heat, diesel fire gases and aerosol agent generated during suppression.

A magnified image of a section of the surface of the exposed copper sample is in Figure 6-7 a) with a cross-section through the same sample shown in Figure 6-7 b). Both images are taken at 50X magnification with a 300 µm scale in the bottom corners. Surface pitting caused by exposure to the diesel fire gases and aerosol suppression agent can be seen in Figure 6-7 a); however, the rough surface of the pipe makes it difficult to discern these pits in the cross-sectional sample, Figure 6-7 b). More evident in the cross-sectional image is a thin black layer on the outer edge of the surface along the length of the section. This layer appears to indicate surface oxidation;

however, additional quantitative investigation would be required to better identify the nature and extent of the surface interactions that took place during exposure of these samples.

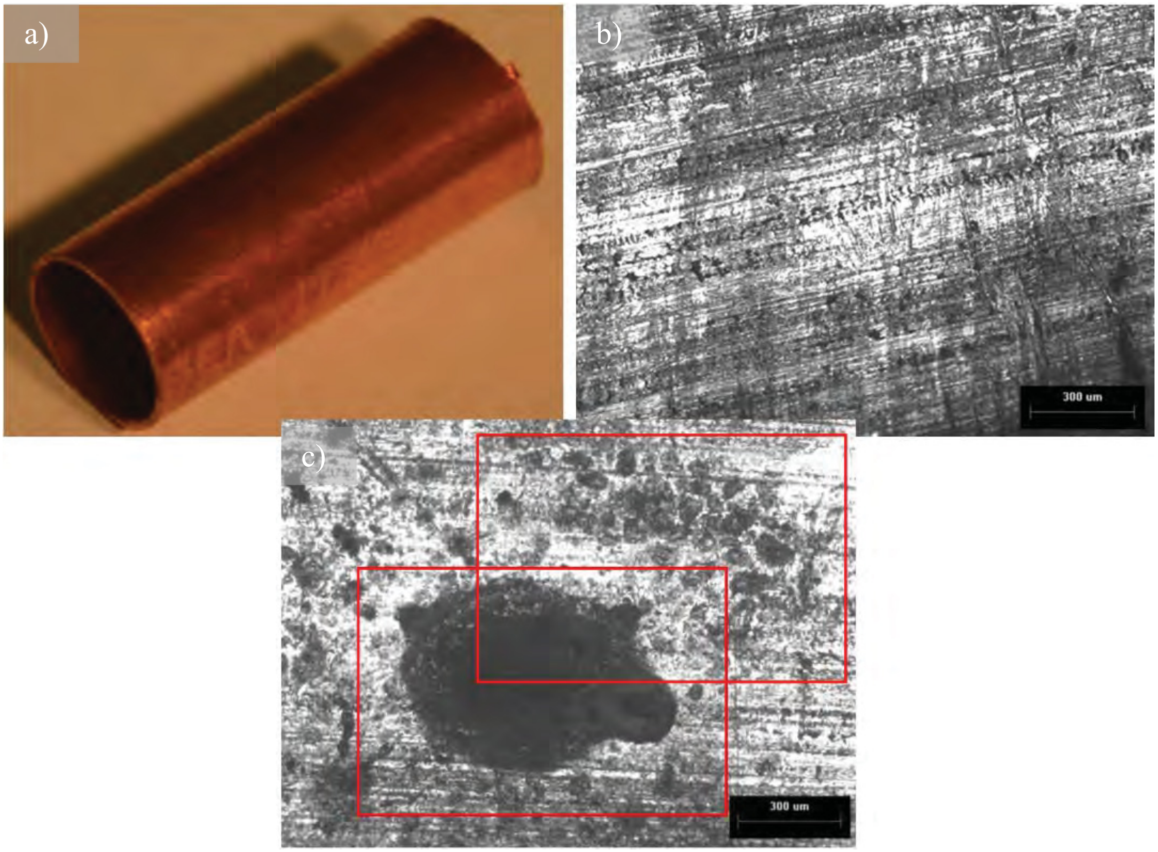

Figure 6-5: Surface of copper sample a) reference, no magnification b) reference, 50X magnification c) six months after exposure to aerosol, 50X magnification

Figure 6-6: Surface of control sample (left) and sample six months after exposure to the diesel fire gases with aerosol agent suppression (right) showing discolouration of surface

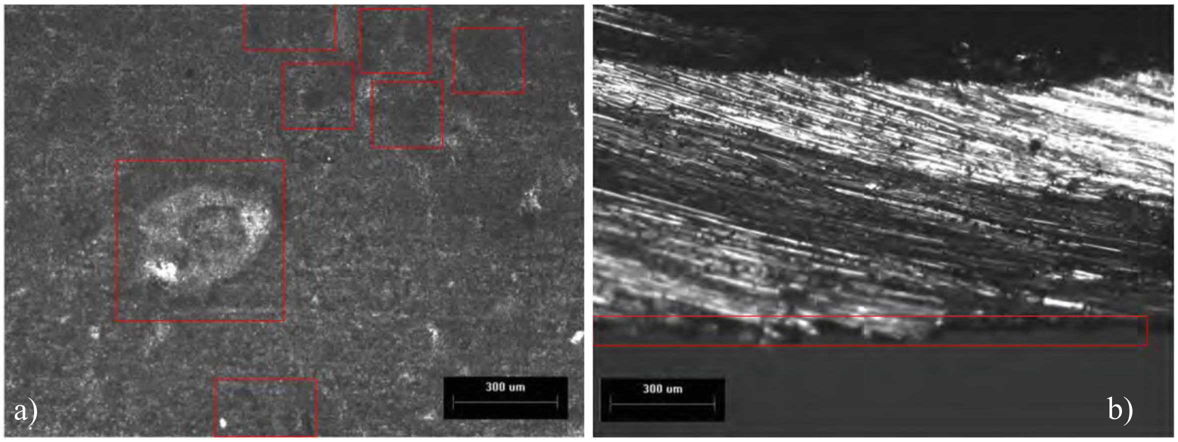

Figure 6-7: Surface of copper sample (50X magnification) six months after exposure to diesel fire gases and DSPA 5-4 aerosol agent a) surface view b) cross-sectional view

6.1.4 Exposure of Chrome Plated Steel Samples

Figure 6-8a) contains an image of the surface of the reference chrome plated steel specimen and Figure 6-8b) an image of the surface of a chrome plated steel sample six months after it was exposed to aerosol powder generated by the StatX unit in an agent only test. Both were taken at 50X magnification with a 300 µm reference located on each image. Some denting and small pits are evident on the surface of the reference sample in Figure 6-8a) due to handling of the sample (A1). As can be seen in Figure 6-8b), six months after exposure to aerosol agent, there appears to be significant damage to the surface. This appears to be in the form of long deep fingers which have penetrated the surface coating, perhaps along pre-existing cracks, and large deep pits potentially reaching the steel substrate underneath. The damage to the chrome layer appears similar to damage previously noted for chrome plated aluminum samples after exposure to the combined effects of diesel fire gases and DSPA 5-4 aerosol agent.

Figure 6-8: Surface of chrome plated steel sample (50X magnification) a) reference specimen b) six months after exposure to aerosol

Figure 6-9 contains an image of the surface of a chrome plated steel specimen six months after it was exposed to a combination of diesel fire gases and aerosol powder generated by the DSPA 5-4 unit. The image was taken at 50X magnification with a 300 µm scale in the upper left hand corner. Much of the surface appears to have been damaged, with large deep pits and finger crevices that penetrate through the coating and into the steel substrate. While the patterns are similar to the surface damage observed in the images of the other chrome plated aluminum and steel samples above, the damage on this sample appears more severe than on any of the other samples tested.

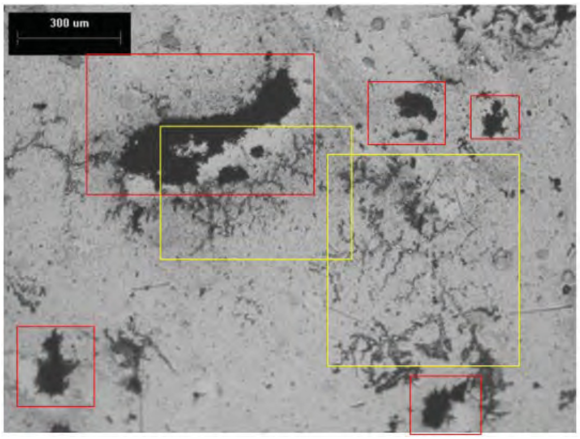

Figure 6-9: Chrome plated steel six months after exposure to the diesel fire gases with aerosol agent suppression (50x magnification)

6.1.5 Summary of Preliminary Corrosion Test Results

Aerosol powder residue was visible on all of the surfaces of all samples set in the compartment during and after aerosol only or aerosol suppression tests with Stat X and DSPA 5-4 handheld aerosol extinguishers. Although much of the residue could be wiped away with a cloth, some deposition of aerosol particulate did occur on the exposed surfaces. There was little evidence of corrosion of either chrome or nickel plated aluminum samples after exposure only to the hot gases produced by a diesel fire. On the other hand, exposure to the gases and particulate generated and discharged during aerosol activation, either alone or in combination with exposure to hot diesel fire gases, led to varying levels of corrosion on all sample surfaces.

Nickel plated aluminum samples appeared to be impacted the least while copper, chrome plated aluminum and chrome plated stainless steel samples experienced increasing degrees of damage, respectively. A thin oxide film may have formed on the surface of the nickel plated aluminum sample and acted to increase the corrosion resistance of the surface so that only small localized pits were observed. Interaction with the copper samples was manifest through a significant change in colour of the surface which may be attributed to surface oxidation (Figure 6-6). Deeper pits on the surface of the copper may suggest a significant potential for corrosion of copper surfaces exposed to the aerosol powders (Figure 6-5 and Figure 6-7). Chrome plated aluminum and stainless steel samples were most impacted by exposure to the diesel fire gases and aerosol powder exhibiting fairly deep pits and finger crevices in the surface (Figure 6-2, Figure 6-8 and Figure 6-9). Should these cracks grow through the coating and impact the substrate below during exposure over longer periods of time, more serious corrosion could take place.

6.2 Extended Test Series

Based on the findings of the preliminary tests outlined above, additional work was focussed towards extending the assessment to evaluate the potential impact of aerosol suppression agent generation and deposition on other materials and critical systems on board naval vessels. These included copper beryllium alloys, AISI 1018 mild steel and AISI 4140 high tensile steel (MS and HTS), NOMEX fabric found in personal protective equipment, as well as CD's, circuit boards and other computer components.

Copper beryllium alloys are similar to copper, but generally exhibit improved corrosion characteristics over many steels, particularly against alkalis and some organic acids [52, 53], so tests to determine impact of aerosols on those alloys were considered as complementary to the results above. Mild and high tensile steels are very common onboard navy vessels but generally exhibit poor corrosion resistance so those samples were painted with an anti-corrosion paint as would be typically found on board the vessel. The other samples were representative of the protective equipment worn by the attack teams (Nomex) and of the wide range of materials typically found in an electronics room, CD's, computer cabinets and circuit boards.

The results of these tests are discussed in the next sections beginning with macroscopic observations of particle deposition from StatX and DSPA 5-4 agent releases during agent only and obstructed diesel fire tests, followed by more specific results from exposure of the materials during agent only tests and combined diesel fire gases and agent suppression tests for each variant of extinguisher.

6.2.1 StatX Aerosol Tests

Macroscopic Observation of Sample Surfaces Pre and Post Exposure

Figure 6-10 contains photographs of the material samples that were exposed to the thermal decomposition products and aerosol powder generated during an StatX agent only test, while those in Figure 6-11 are for samples exposed to hot gases from a diesel fire with StatX aerosol suppression. Each set is discussed in turn.

The photographs in Figure 6-10 are taken at three different time intervals - prior to exposure to the aerosol, immediately after exposure to the aerosol and one month after exposure to the aerosol - chosen to assess the severity of corrosion that might occur to different materials during and, over a period of time after, discharge of an aerosol unit. The material coupons in the images include from top left to bottom right: a computer discs (CD), MS (strip), HTS (disc), a circuit board with electronic components and copper terminal strips, NOMEX fire resistant cloth (blue), and a copper beryllium disc (bronze disc).

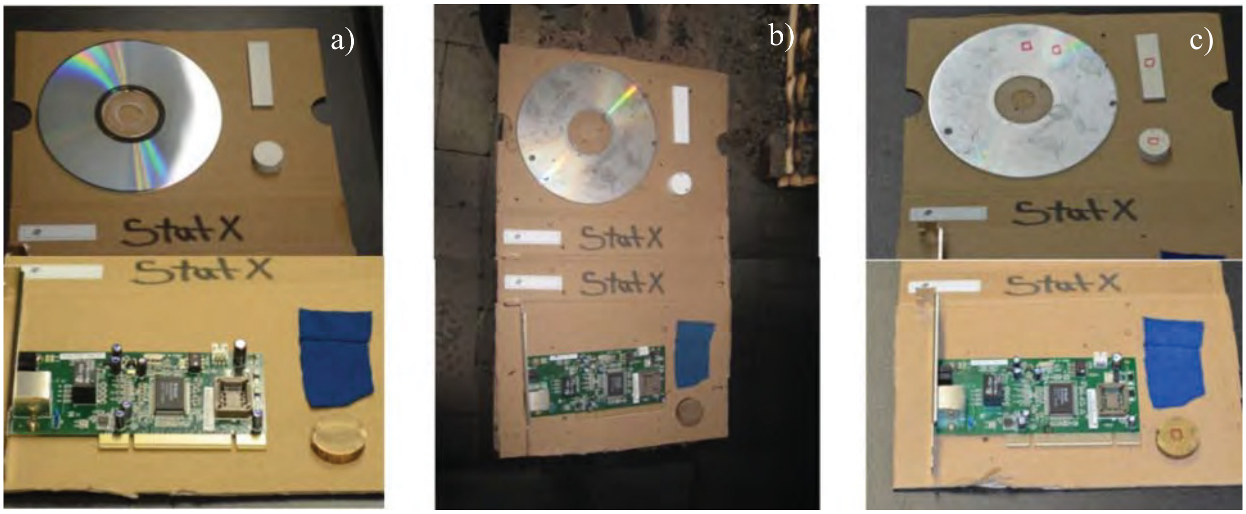

Figure 6-10: Nikon D7000 photographs of material samples used in StatX agent only test a) reference specimens b) specimens immediately after exposure to aerosol c) specimens one month after exposure to aerosol

Comparison of Figure 6-10 a) and b) indicates the deposition of a thin layer of aerosol powder on all surfaces, as evidenced by the discolouration of all samples after exposure to the aerosol. This layer was subsequently left on the surface of each sample, and the samples were examined on a weekly basis using optical microscopy to chart the progress of any corrosion or other impact that the aerosol powder might have on the various materials over time. Figure 6-10 c) shows a macroscopic view of the same samples one month after exposure.

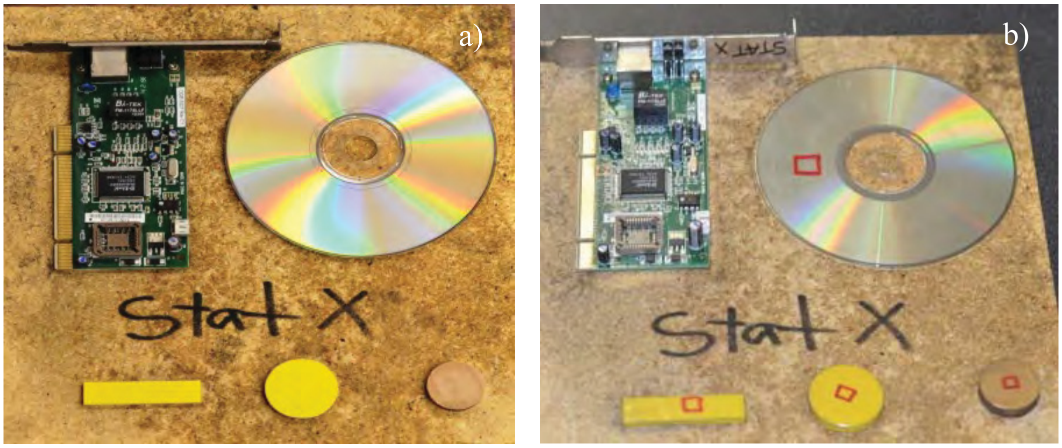

Figure 6-11: Nikon D7000 photographs of material samples in a StatX unobstructed fire suppression test a) reference specimens b) specimens one month after exposure to aerosol

Figure 6-11 contains photographs of similar samples exposed to an unobstructed diesel fire test that was suppressed using the Stat X aerosol unit. Figure 6-11 a) shows the samples prior to exposure and Figure 6-11 b) the same samples one month after exposure. The material coupons in these images are (from top left to bottom right): a circuit board with electronic components and copper terminal strips, a computer disc (CD), MS painted with anti-corrosion paint (strip), HTS painted with anti-corrosion paint (disc), and a copper beryllium disc (bronze disc).

As was the case for the agent only test, comparison of the two images, Figure 6-11 a) and b) indicates slight discolouration of the surfaces of the samples, due to a thin layer of soot from the fire and aerosol powder that has deposited there.

More detailed results of the microscopic surface examinations conducted pre-exposure and at certain times after exposure are contained in the following sections.

Exposure of Wiped and Unwiped Computer Discs

Two commercially available computer discs (CD) were exposed during an agent only and an unobstructed diesel fire suppression test with a StatX aerosol unit. Immediately after the agent only test, one disc was wiped clean with a micro fiber cloth such that most, if not all, of the agent residue was removed from the surface (wiped). To investigate the effects of cleaning the aerosol residue from the surface, the other two CDs were not wiped after exposure. Figure 6-12 a) contains a magnified image of the surface of a CD before exposure, Figure 6-12 b) of a disc which was exposed to aerosol agent only and wiped clean, Figure 6-12 c) of a disc which was exposed to aerosol agent only and not wiped clean and Figure 6-12 d) of a disc which was exposed to a diesel fire with aerosol agent suppression and not wiped. Figure 6-12 b) and c) were recorded three months after exposure, while Figure 6-12 d) was taken two months after exposure. All were imaged at 50X magnification and have a 200 μm scale in the bottom right hand corner.

Discolouration of the CD surface occurred in all tests. In comparison to the reference image in Figure 6-12 a), marked damage occurred to the surfaces of all discs that were exposed during aerosol activation and discharge, whether or not there was a fire burning. The smaller pits seen in Figure 6-12 b) for the test in which the surface was wiped after exposure versus the combination of smaller and more severe pits and other residue seen in Figure 6-12 c) for the test where the surface was not wiped clean and d) in which the CD was also exposed to diesel fire gases, indicated that wiping the surface of the disc might mitigate the damage somewhat; however, in all cases, pitting damage to the surface was sufficient to suggest that exposure of the CD to the aerosol agent may lead to a loss of integrity of the CD tracks with resultant corruption or loss of stored data. This is consistent with degradation and oxidation of CDs that has been reported in the literature [for example, [54]]. Although not as clear in these images, the damage was exacerbated further in the latter two cases by the additional deposition of other particulates and soot on the surface due to the aerosol generation process and from the diesel fire respectively.

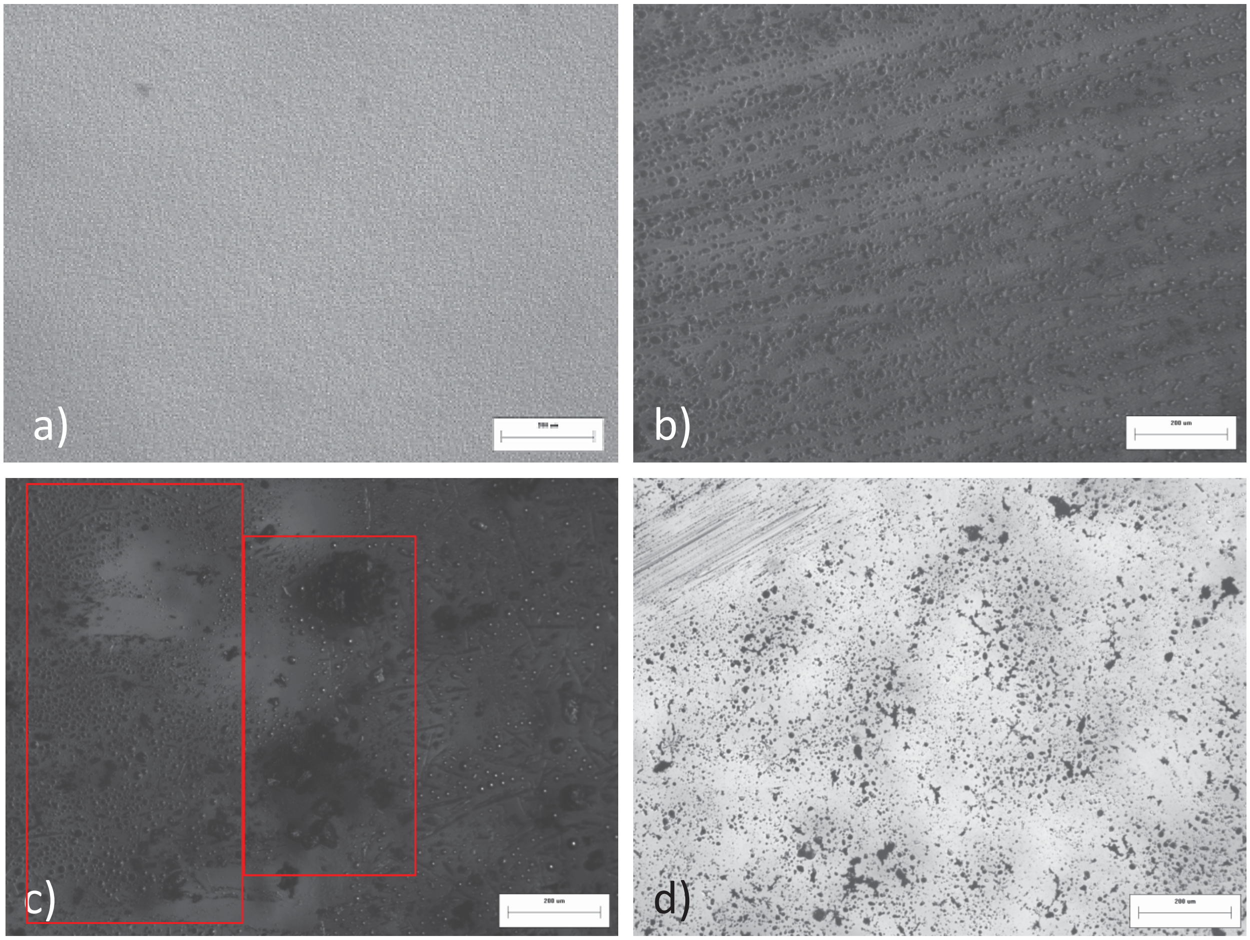

Figure 6-12: Surface of computer disc (50X magnification) a) reference specimen b) three months after exposure to StatX aerosol only (cleaned) c) three months after exposure to StatX aerosol only (uncleaned) and d) two months after exposure to diesel fire with StatX suppression

Copper Beryllium

Figure 6-13 a) contains an image of the surface of the reference copper beryllium disc, Figure 6-13 b) an image of the copper beryllium surface taken three months after it was exposed to aerosol powder in a StatX agent only test and Figure 6-13 c) an image of the surface two months after it was exposed to a combination of diesel fire gases and aerosol powder generated by the StatX unit. All were imaged at 50X magnification and have a 200 µm scale in the bottom right hand corner.

Direct exposure to the gases and particulates formed during generation and discharge of the aerosol, with or without a diesel fire, resulted in discolouration and mild pitting on the surfaces of each sample [55]; the latter evidenced by small deep marks distributed across the surface. The larger, less well defined black discoloured areas were due to the deposition of soot and other particulates on the surfaces during the tests; they did not change in size or shape with time after exposure suggesting that no on-going material interactions were taking place in those areas.

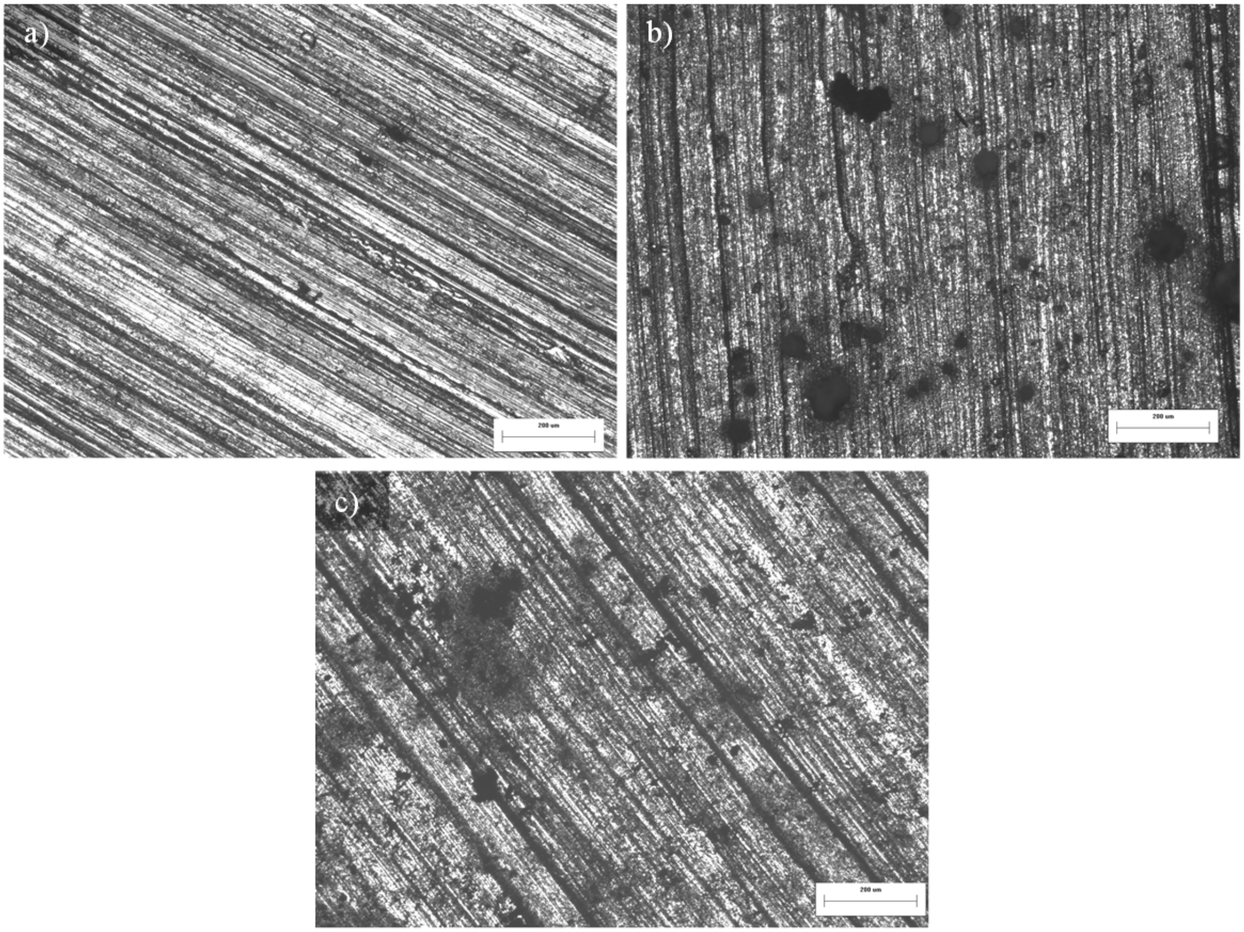

Figure 6-13: Surface of copper beryllium disc (50x magnification) a) reference specimen b) three months after exposure to StatX aerosol only c) two months after exposure to diesel fire with StatX suppression

AISI 4140 High Tensile Steel (HTS) Coated in Anti-Corrosion Paint

Commercially available high tensile steel was coated with an anti-corrosion marine paint to mimic painted surfaces onboard a naval vessel. The samples were exposed to the gases and particulate generated during an agent only and an unobstructed diesel fire suppression test with a StatX aerosol unit. Figure 6-14 a) contains an image of the painted surface of a reference high tensile steel specimen, Figure 6-14 b) an image of the painted surface of the high tensile steel sample taken three months after it was exposed to aerosol powder in a StatX agent only test and Figure 6-14 c) an image of the surface two months after it was exposed to a combination of diesel fire gases and aerosol powder generated by the StatX unit. All were imaged at 50X magnification and have a 200 µm scale in the corners.

In both aerosol only and diesel suppression tests, surface discolouration and black deposits indicated soot and other particulates on the sample surfaces. In addition for the diesel fire suppression test, Figure 6-14 c), there was evidence of small shallow pits forming on the painted

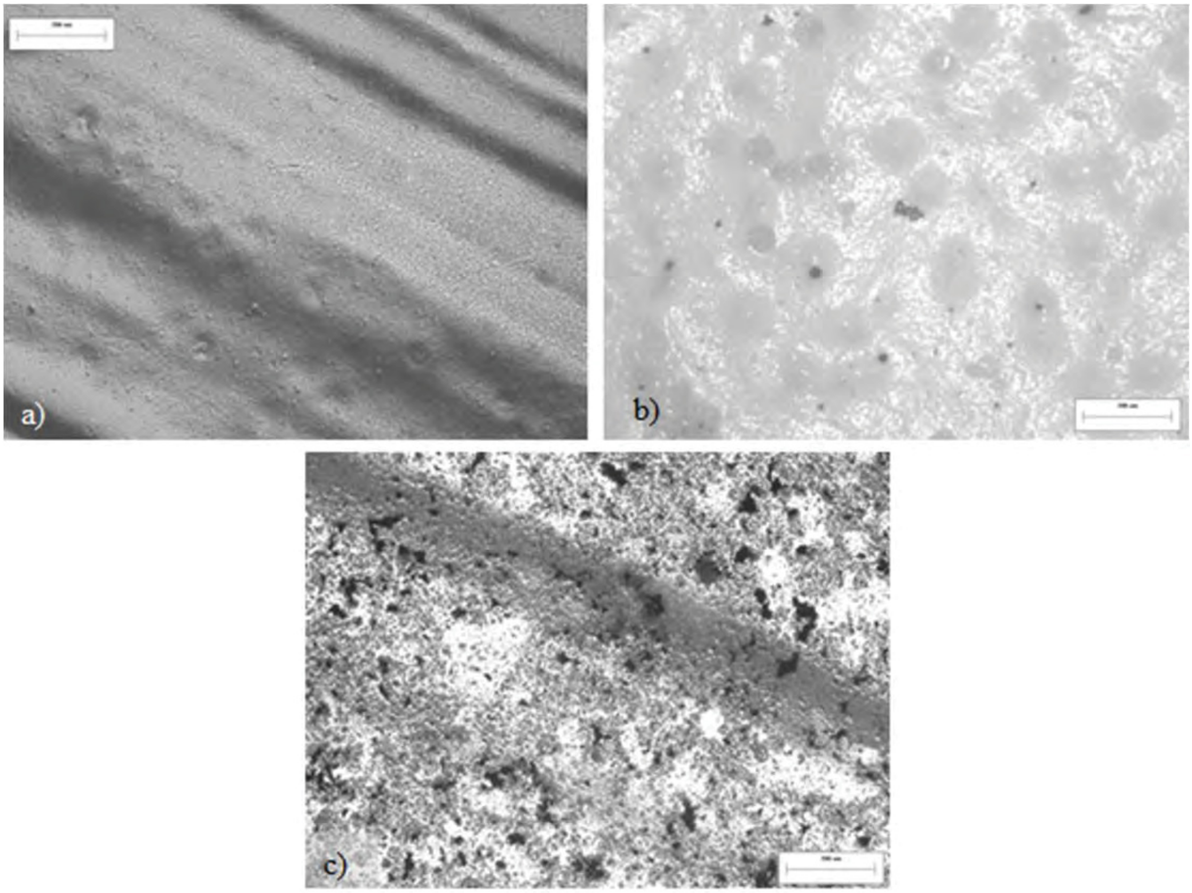

Figure 6-14: Surface of AISI 4140 high tensile steel specimen (50x magnification) a) reference specimen b) three months after exposure to StatX aerosol only and c) two months after exposure to diesel fire with StatX suppression

surface in spots. Overall, however, the anti-corrosion marine paint appeared to have limited the interaction between the high tensile steel specimen and any corrosive agents that may have formed during aerosol extinguisher activation or suppression of the fire.

AISI 1018 Mild Steel (MS) Coated in Anti-Corrosion Paint

Commercially available mild steel was coated with the same anti-corrosion marine paint that was used for the HTS specimens above. The samples were exposed to the gases and particulate generated during an agent only and an unobstructed diesel fire suppression test with a StatX aerosol unit. Figure 6-15 a) contains an image of the surface of the reference mild steel specimen, Figure 6-15 b) an image of the painted surface of the mild steel sample taken three months after it was exposed to aerosol powder in a StatX agent only test and Figure 6-15 c) an image of the surface two months after it was exposed to a combination of diesel fire gases and aerosol powder generated by the StatX unit. All were imaged at 50X magnification and have a 200 µm scale in one corner.

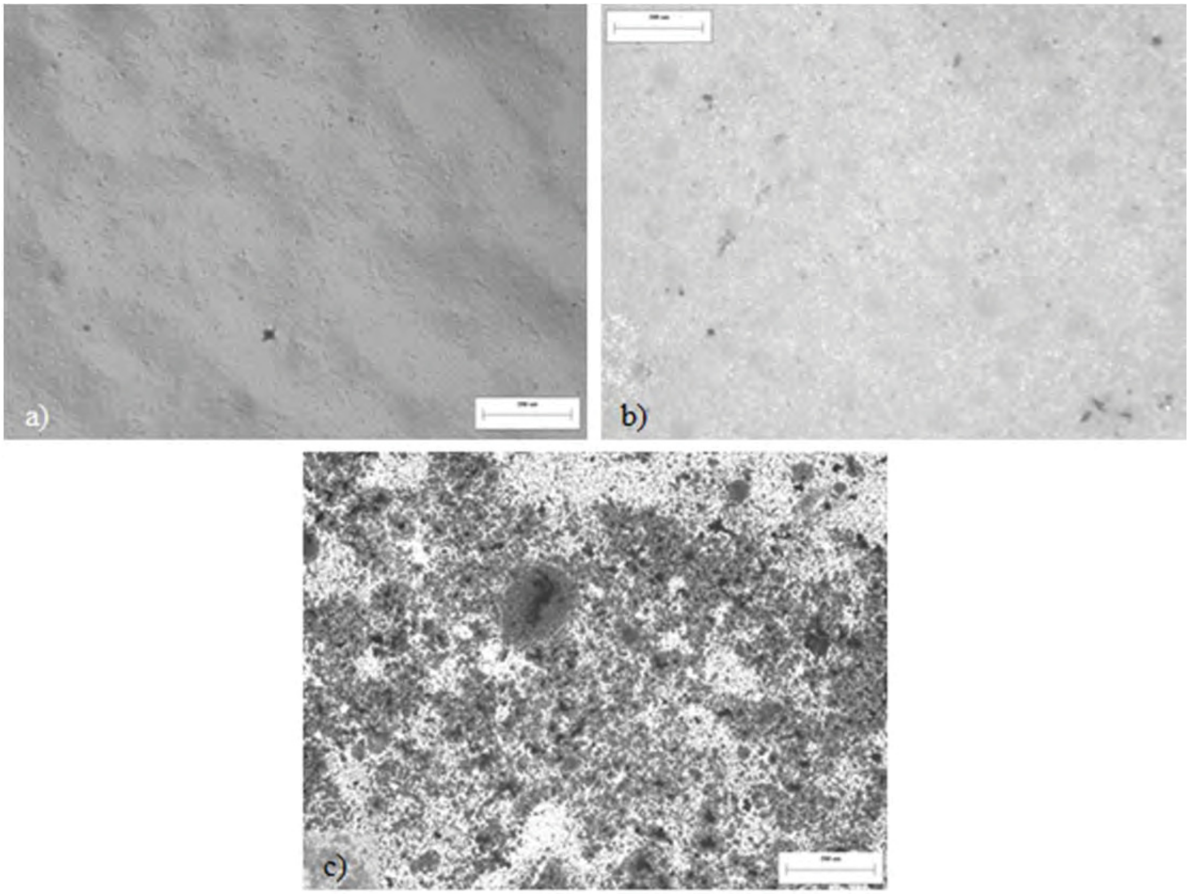

Figure 6-15: Surface of AISI 1018 mild steel specimen (50x magnification) a) reference specimen b) three months after exposure to StatX aerosol only and c) two months after exposure to diesel fire with StatX suppression

There was some discolouration of the surface after the agent only test, however, no significant effect on the painted surface or deposition of particulate or soot can be seen in Figure 6-15 b). After exposure in the diesel fire test with agent suppression, the painted surface of the mild steel sample was noticeably discoloured due to interaction with the environment, but also because of soot and particle deposition. As was the case for the painted high tensile steel specimens above, there was some evidence of small shallow pits in the painted surface but the anti-corrosion marine paint appeared to have limited the interaction between the mild steel specimen and any corrosive agents that may have formed during aerosol extinguisher activation or suppression of the fire.

NOMEX Fire Resistant Clothing

NOMEX fabric swatches were exposed to the gases and particulate generated during activation and discharge of the extinguisher in an agent only test with a StatX aerosol unit. Figure 6-16 a) contains an image of the surface of the reference fabric swatch and Figure 6-16 b) an image of the swatch taken three months after it was exposed to aerosol powder in a StatX agent only test.

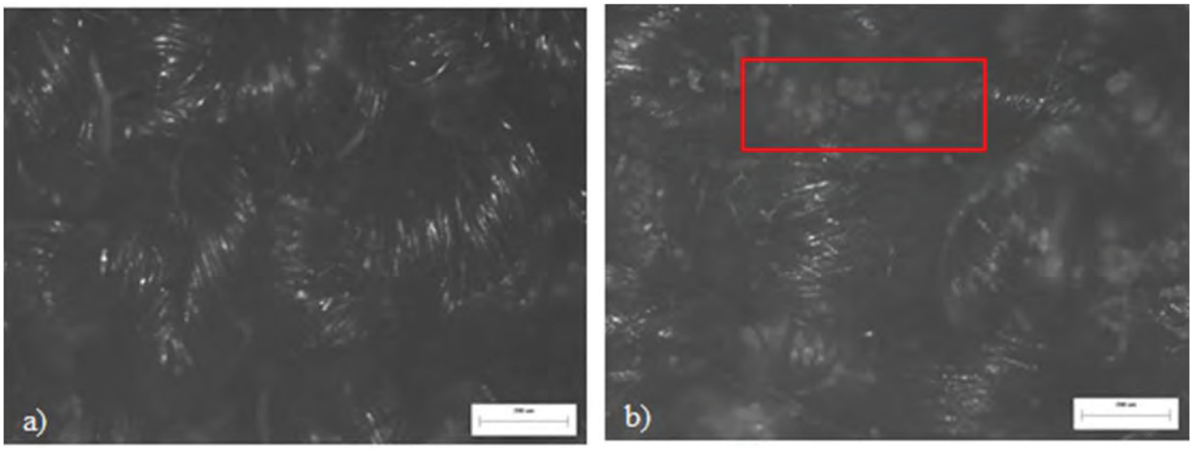

Figure 6-16: NOMEX fabric specimen (50x magnification) a) reference specimen and b) three months after exposure to StatX aerosol only

Visual comparison of the swatches indicated general discolouration of the fabric due to exposure suggesting that aerosol particles may get trapped in the fibres. Evidence of this can be seen in the highlighted section in the upper middle section of Figure 6-16 b). Overall, however, there appears to be little or no damage to the fibres from exposure during generation and discharge of the aerosol powder.

Computer Circuit Board

Functioning computers and/or individual circuit boards were placed inside the test compartment in an effort to determine the impact of aerosol extinguishment on electronic equipment. In these tests, functioning circuit boards were left inside the testing compartment and exposed to the gases and particulate generated during agent only and unobstructed diesel fire suppression tests with a StatX aerosol unit. In all cases, powder residue was visible on the electronic circuit boards at the end of the tests. At regular intervals after exposure, the circuit boards were examined for obvious visual damage and if none was evident, each was installed in the computer, the computer was powered on and the operating system booted. The system was then turned off, the circuit board removed and examined under the microscope. Unless otherwise noted for the results below, the circuit boards shown did boot properly and did run normally before the images were taken.

Figure 6-17 and 6-18 a) contain reference images of the surfaces of connectors and conductive pathways, respectively, before exposure while Figure 6-17 and 6-18 b) are images of these components taken three months after exposure to aerosol powder in a StatX agent only test and Figure 6-17 and 6-18 c) are images of the surfaces of comparable components (different boards) two months after exposure to a combination of diesel fire gases and aerosol powder generated by the StatX unit. All were imaged at 50X magnification and have a 200 µm scale in one corner.

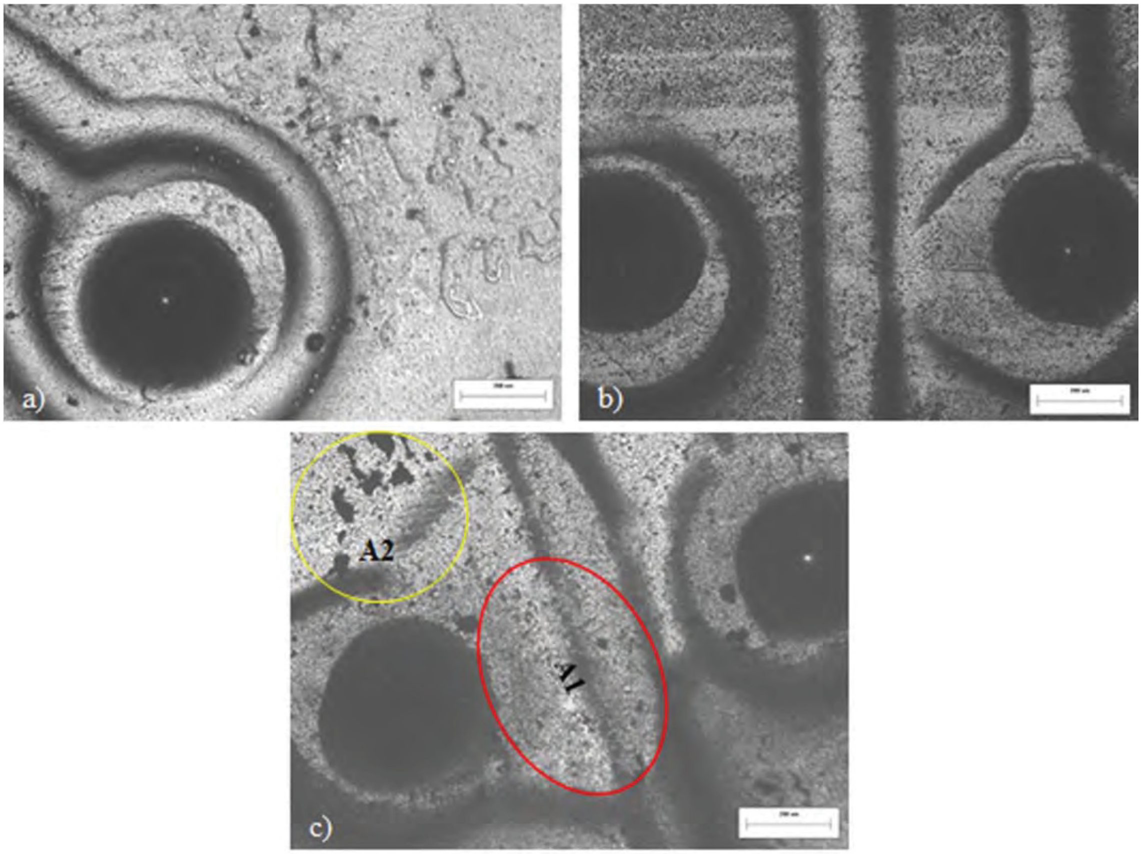

Figure 6-17: Connectors on computer circuit board (50X magnification) a) reference specimen b) three months after exposure to StatX aerosol only c) two months after exposure to diesel fire with StatX suppression

Comparing the reference image of the connector (Figure 6-17 a)) to that taken after exposure to the StatX agent only (Figure 6-17 b)), it can be seen that this exposure did not lead to significant evidence of corrosion or damage three months after exposure. Two months after exposure to the combined diesel fire gases with StatX suppression (Figure 6-17 c)), some small pits appear to have developed in the centre of the image (A1)[11]. Other markings due to surface soot deposition are also evident in this image.

Comparison of the reference image of the conductive pathways (Figure 6-18 a)) to those taken after testing, it can be seen that the exposure to the StatX agent alone (Figure 6-18 b)) and to the diesel fire gases with StatX suppression (Figure 6-18 c)) again led to formation of some shallow pits on the surfaces, noting as above that there was also some soot deposition on the surface in Figure 6-18 c) and some of the deeper pits seen in all of these images were due to bubbling of the silicone coating during the manufacturing of the circuit board.

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[11] The larger pits that are evident to some extent in Figure 6-17 a) and in A2 in Figure 6-17 c) are not linked to the exposure, but rather are due to bubbling of the silicone coating during the manufacturing process.

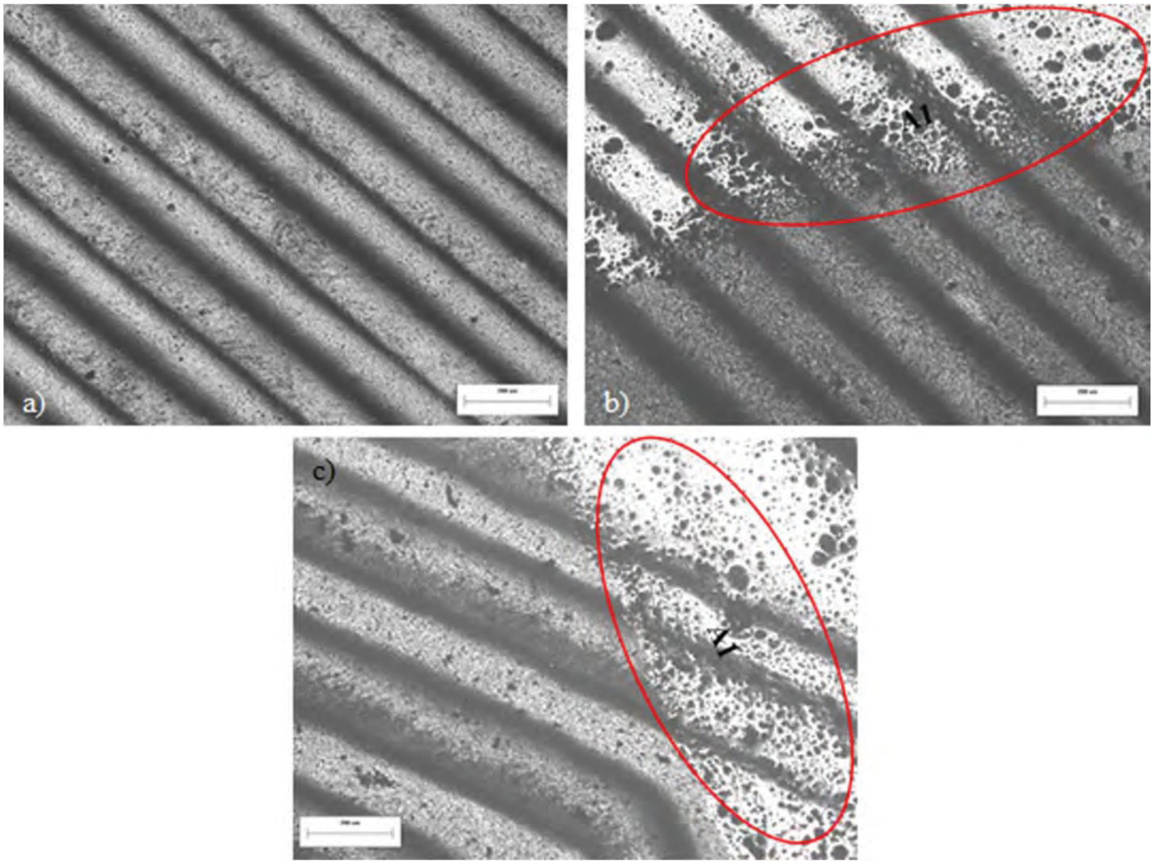

Figure 6-18: Conductive pathways on computer circuit board (50X magnification) a) reference specimen b) three months after exposure to aerosol only c) two months after exposure to diesel fire with aerosol suppression

An additional longer term test was also conducted to determine whether extended exposure to the aerosol alone would lead to more evident degradation of a computer circuit board. In this case, the circuit board was exposed to aerosol particulate during a StatX agent only test and then was held in a conditioning chamber for six months after exposure. After six months, it was inserted into the computer which was turned on to see if it would operate properly. The computer failed to boot from the exposed circuit board, but the computer fan and auxiliary systems did run for over half an hour with no change in status. Figure 6-19 shows the computer card after exposure to the aerosol and at the time of disassembly of the system. Evidence of degradation of the card due to exposure is evident in the highlighted section on the right hand side of the picture.

Figure 6-20 a) through c) are images of conductive pathways and electrical connectors on the computer board (50X magnification with a 300 µm scale in the lower left and lower right hand corners, respectively). Comparison of Figure 6-20 a) to Figure 6-20 b) and c) indicates the deposition of aerosol residue, as well as the significant pitting that had occurred to both circuit board components six months after exposure to the StatX aerosol agent. This represents notable damage to the board and may be one possible reason for the computer system malfunction.

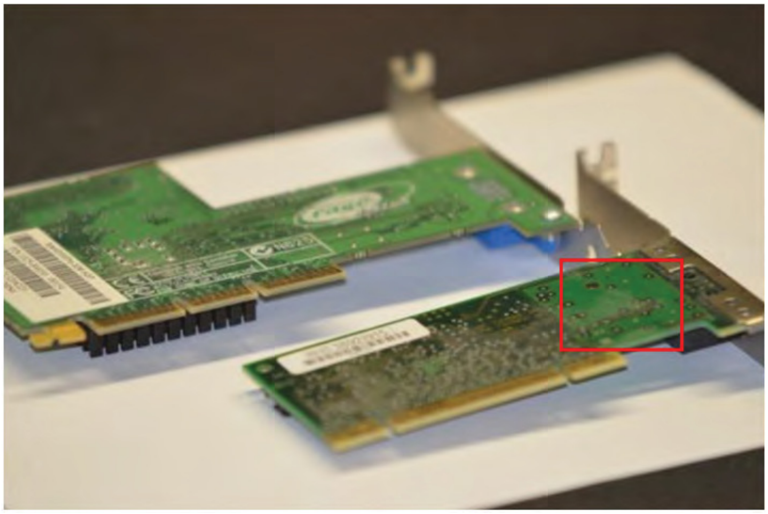

Figure 6-19: Computer card after six months after exposure to StatX aerosol agent

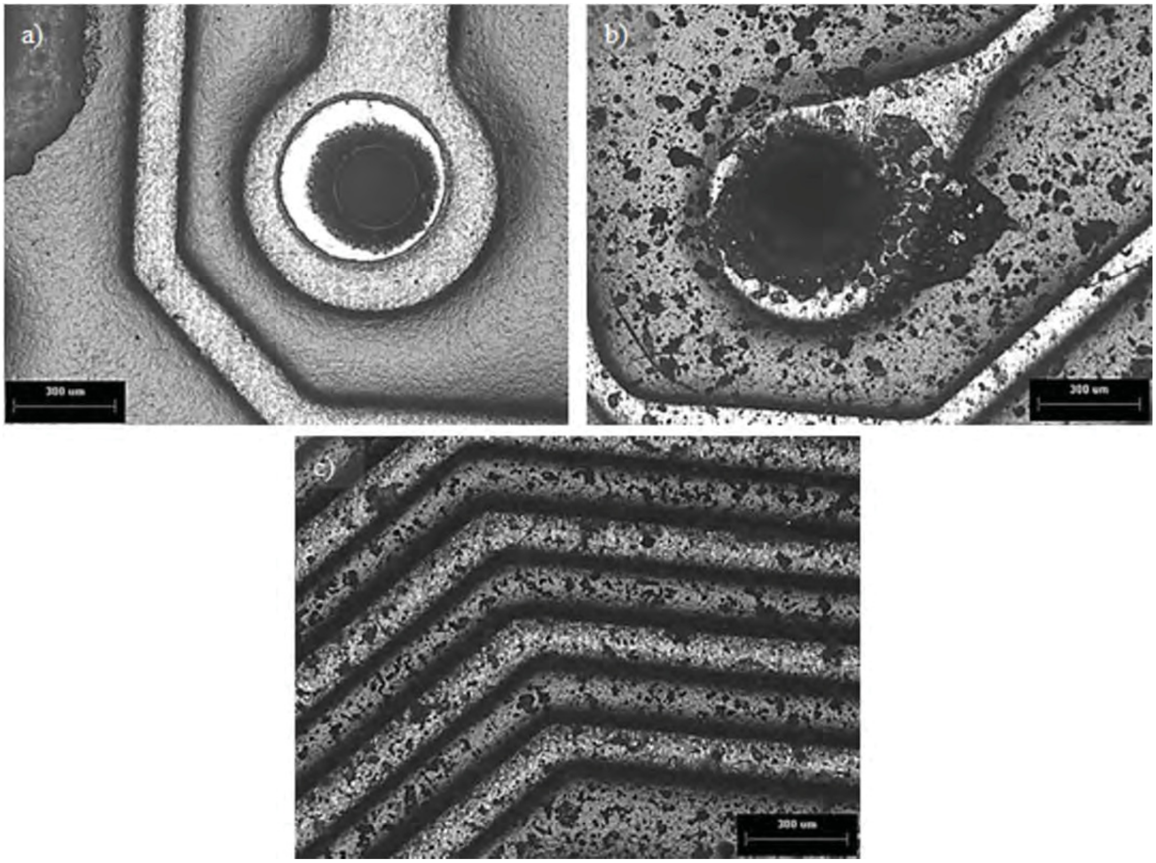

Figure 6-20: Connectors and conductive pathways on computer circuit board (50x magnification) a) reference specimen b) conductor six months after exposure to StatX aerosol only c) conductive pathway six months after exposure

The combined results presented in this section point to the potential for minor impact through to significant damage of sensitive electronic equipment during generation and discharge of StatX aerosol, either alone or during suppression of a diesel fire. After exposure, pitting and corrosion of the board, connectors and/or conductive pathways might occur, and if electronic equipment was poorly cleaned or left uncleaned for extended periods after an exposure, this could potentially be sufficiently severe to lead to malfunction of a computer board.

6.2.2 DSPA Aerosol Tests

Macroscopic Observation of Sample Surfaces Pre and Post Exposure

Figure 6-21 contains photographs of the material samples that were exposed to the thermal decomposition products and aerosol powder generated during a DSPA 5-4 agent only test, while those in Figure 6-22 are for samples exposed to hot gases from a diesel fire with DSPA 5-4 aerosol suppression. Each set is discussed in turn.

The photographs in Figure 6-21 are taken at three different time intervals - prior to exposure to the aerosol, immediately after exposure to the aerosol and one month after exposure to the aerosol - chosen to assess the severity of corrosion that might occur to different materials during and, over a period of time after, discharge of an aerosol unit. The material coupons in the images are the same as those used for the StatX aerosol tests above – with samples from top left to bottom right: a computer disc (CD), MS (strip), HTS (disc), NOMEX fire resistant cloth (blue), a copper beryllium disc (bronze disc) and a circuit board with electronic components and copper terminal strips.

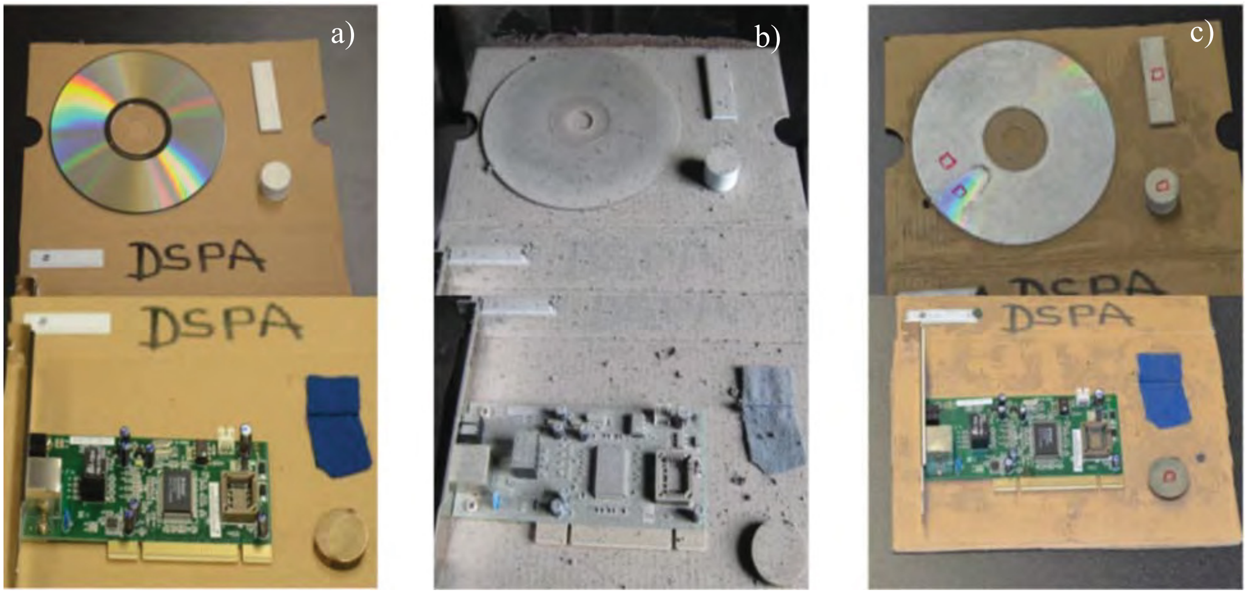

Figure 6-21: Nikon D7000 photographs of material samples used in DSPA 5-4 agent only test a) reference specimens b) specimens immediately after exposure to aerosol c) specimens one month after exposure to aerosol

Comparison of Figure 6-21 a) and b) indicates the deposition of a significant layer of aerosol powder on all surfaces, as evidenced by the grey colour of all samples. This layer was left for the initial week and then dusted off to leave only a thin layer of aerosol powder. The samples were then examined on a weekly basis using optical microscopy to chart the progress of any corrosion or other impact that the aerosol powder might have had on the various materials over time. Figure 6-21 c) shows a macroscopic view of the same samples one month after exposure. More detailed results of surface examinations conducted before exposure and two to three months after exposure are contained in subsequent sections of the report.

Figure 6-22 contains photographs of similar samples exposed to an unobstructed diesel fire test that was suppressed using the DSPA 5-4 aerosol unit. Figure 6-22 a) shows the samples prior to exposure and Figure 6-22 b) the same samples one month after exposure. The material coupons in these images are (from top left to bottom right): a circuit board with electronic components and copper terminal strips, a computer disc (CD), MS painted with anti-corrosion paint (strip), HTS painted with anti-corrosion paint (disc), and a copper beryllium disc (bronze disc). As was the case for the agent only test, comparison of the two images, Figure 6-22 a) and b) indicates slight discolouration of the surfaces of the samples, due to a thin layer of soot from the fire and aerosol powder that had deposited there.

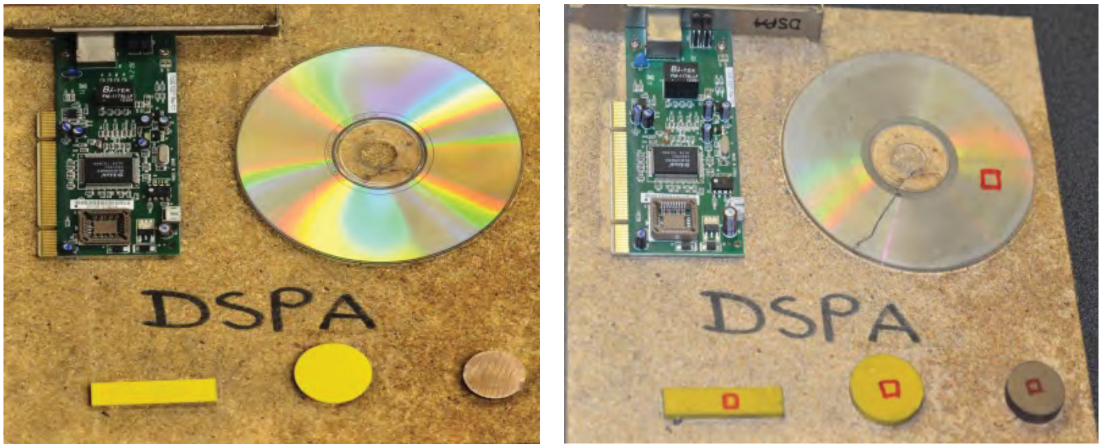

Figure 6-22: Nikon D7000 photographs of material samples in a DSPA 5-4 unobstructed fire suppression test a) reference specimens b) specimens one month after exposure to aerosol

More detailed results of the microscopic surface examinations conducted pre-exposure and at certain times after exposure are contained in the following sections.

Exposure of Wiped and Unwiped Computer Discs

Two commercially available computer discs (CD) were exposed during an agent only and an unobstructed diesel fire suppression test with a DSPA 5-4 aerosol unit. Immediately after the agent only test, one disc was wiped clean with a micro fiber cloth such that most, if not all, of the agent residue was removed from the surface (wiped). In order to investigate any effects of cleaning the aerosol residue from the surface, the other two CDs were not wiped after exposure. Figure 6-23 a) contains a magnified image of the surface of a CD before exposure, Figure 6-12b) of a disc which was exposed to aerosol agent only and wiped clean, Figure 6-23 c) of a disc which was exposed to aerosol agent only and not wiped clean and Figure 6-23 d) of a disc which was exposed to a diesel fire with aerosol agent suppression and not wiped. Figure 6-23 b) and c) were recorded three months after exposure, while Figure 6-23 d) was taken two months after exposure. All were imaged at 50X magnification and have a 200 µm scale in the bottom right hand corner.

Discolouration of the CD surface occurred in all tests. In comparison to the reference image in Figure 6-23 a), marked damage occurred to the surface of all discs that were exposed during aerosol activation and discharge, whether or not there was fire burning. Smaller pits were seen in Figure 6-23 b) for the test in which the surface was wiped after exposure; while a combination of smaller and more severe pits were engraved into the surface across the entire disc as seen in Figure 6-23 c) for the tests in which the surface was not wiped clean and Figure 6-23 d) when the CD was

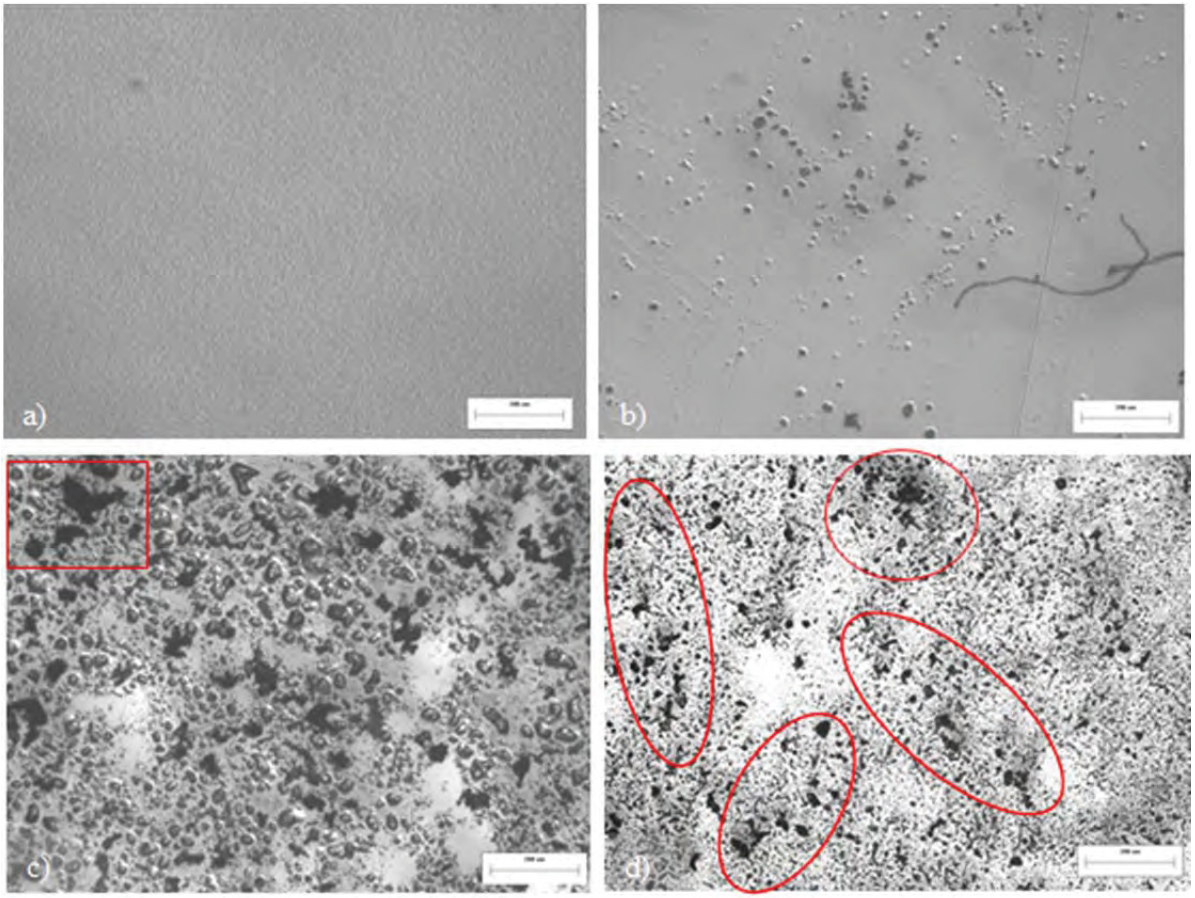

Figure 6-23: Surface of computer disc (50X magnification) a) reference specimen b) three months after exposure to DSPA 5-4 aerosol only (cleaned) c) three months after exposure to DSPA 5-4 aerosol only (uncleaned) and d) two months after exposure to diesel fire with DSPA 5-4 suppression

also exposed to diesel fire gases. The potential damage was exacerbated further in the latter two cases by the additional deposition of other particulates and soot from the aerosol generation process and from the diesel fire. These are indicated by the areas outlined in red in the images. Results indicate that wiping the surface of the disc might mitigate the damage somewhat; however, in all cases, pitting damage to the surface appeared sufficient to suggest that the interaction of the aerosol agent with the surface of the CD might lead to a loss of integrity of the CD tracks with resultant corruption or loss of stored data, particularly if left unwiped for a period of time [54].

Copper Beryllium

Figure 6-24 a) contains an image of the surface of the reference copper beryllium disc, Figure 6-24 b) an image of the copper beryllium surface taken three months after it was exposed to aerosol powder in a DSPA 5-4 agent only test and Figure 6-24 c) an image of the surface two months after exposure to a combination of diesel fire gases and aerosol powder generated by a DSPA 5-4 unit. All were imaged at 50X magnification and have a 200 µm scale in the bottom right hand corner.

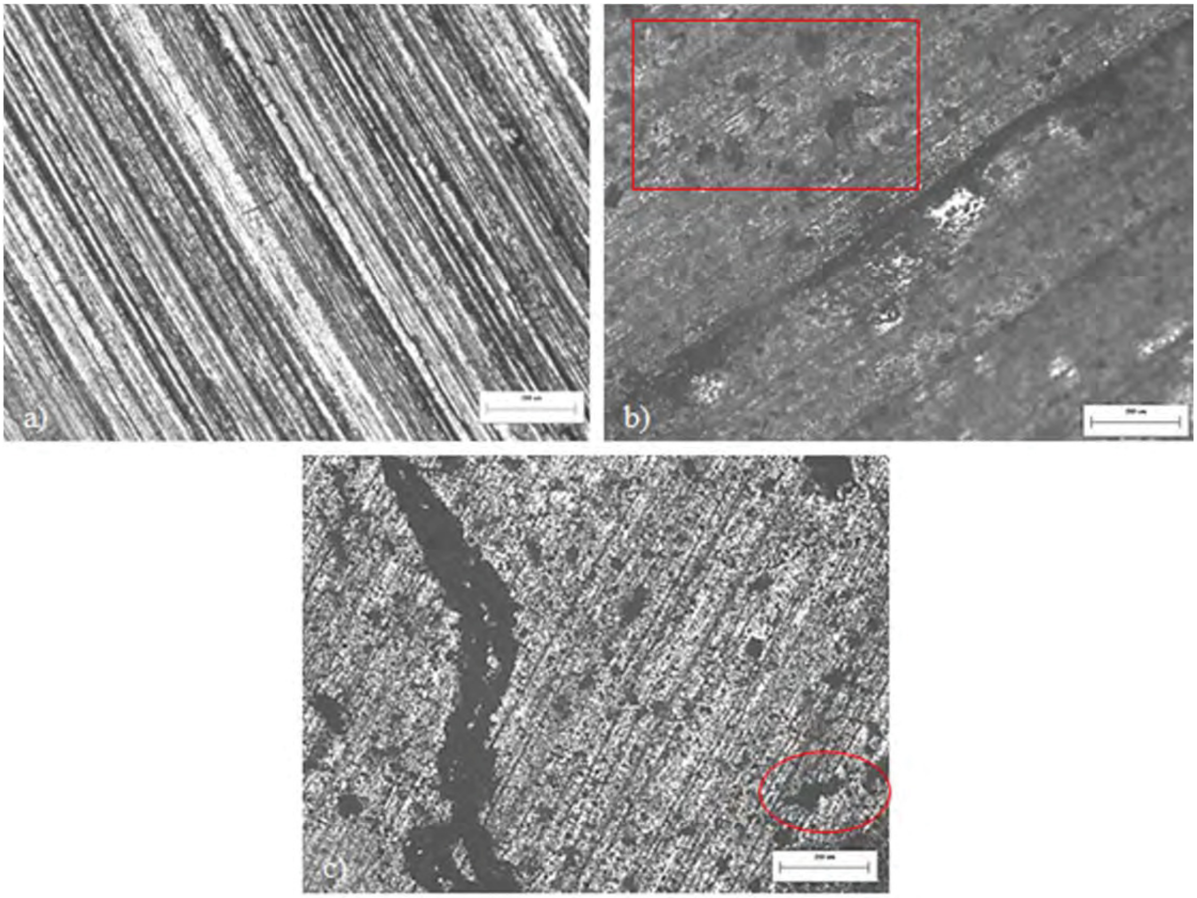

Figure 6-24: Surface of copper beryllium disc (50x magnification) a) reference specimen b) three months after exposure to DSPA 5-4 aerosol only c) two months after exposure to diesel fire with DSPA 5-4 suppression

Direct exposure to the gases and particulates formed during generation and discharge of the aerosol agent, with or without a diesel fire, resulted in only very mild, if any interaction with the surfaces of each sample. Although the serrations in Figure 6-24 b) do not appear to be as dominant as those in the reference specimen, the large cracks shown in Figure 6-24 b) and c) did not appear to change during the two and three month exposure periods supporting the idea that there was minimal interaction between the CuBe and DSPA 5-4 aerosol particulate. The larger, less well defined black discoloured areas marked in Figure 6-24 b) were due to deposition of soot and other particulates on the surfaces during the tests; they did not change in size or shape with time after exposure again suggesting that no on-going material interactions were taking place in those areas.

AISI 4140 High Tensile Steel (HTS) Coated in Anti-Corrosion Paint

Commercially available high tensile steel was coated with an anti-corrosion marine paint to mimic painted surfaces onboard a naval vessel. The samples were exposed to the gases and particulate generated during an agent only and an unobstructed diesel fire suppression test with a DSPA 5-4 aerosol unit. Figure 6-25 a) contains an image of the painted surface of a reference high tensile steel specimen, Figure 6-25 b) an image of the painted surface of the high tensile steel sample

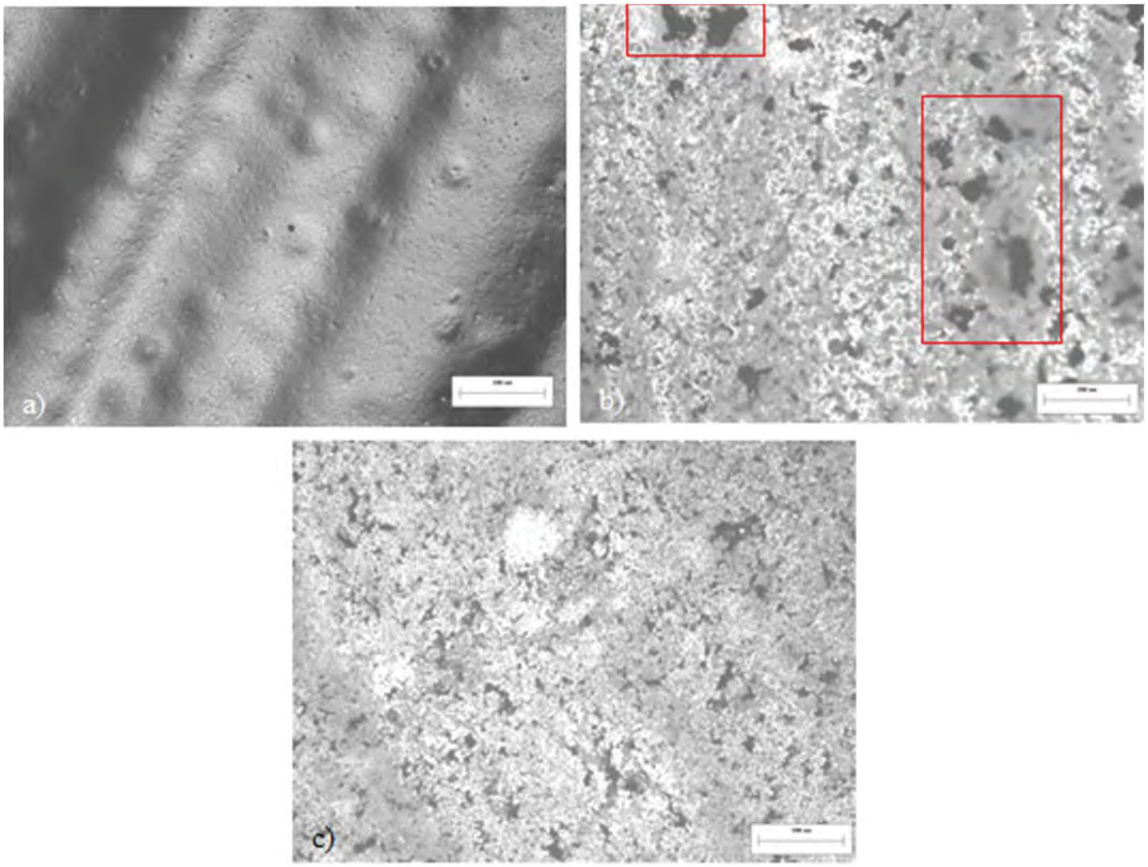

Figure 6-25: Surface of high tensile steel specimen (50x magnification) a) reference specimen b) three months after exposure to DSPA 5-4 aerosol only and c) two months after exposure to diesel fire with DSPA 5-4 suppression

three months after it was exposed to aerosol powder in a DSPA 5-4 agent only test and Figure 6-25 c) an image of the surface two months after it was exposed to a combination of diesel fire gases and aerosol powder generated by the DSPA 5-4 unit. All were imaged at 50X magnification and have a 200 µm scale in the corners.

In both aerosol only and diesel suppression tests, surface discolouration, as well as the white and black demarcations outlined in Figure 6-25 b) indicated the presence of aerosol powder, soot and other particulates on the sample surfaces. There was some preliminary evidence of small shallow pits forming on the painted surface in some spots; however, for the two and three month duration of these tests, the anti-corrosion marine paint appeared to have limited the interaction between the high tensile steel specimen and any corrosive agents that may have formed during aerosol extinguisher activation or suppression of the fire.

AISI 1018 Mild Steel (MS) Coated in Anti-Corrosion Paint

Commercially available mild steel was coated with the same anti-corrosion marine paint that was used for the HTS specimens above. Figure 6-26 a) contains an image of the surface of the reference mild steel specimen, Figure 6-26 b) an image of the painted surface of the mild steel

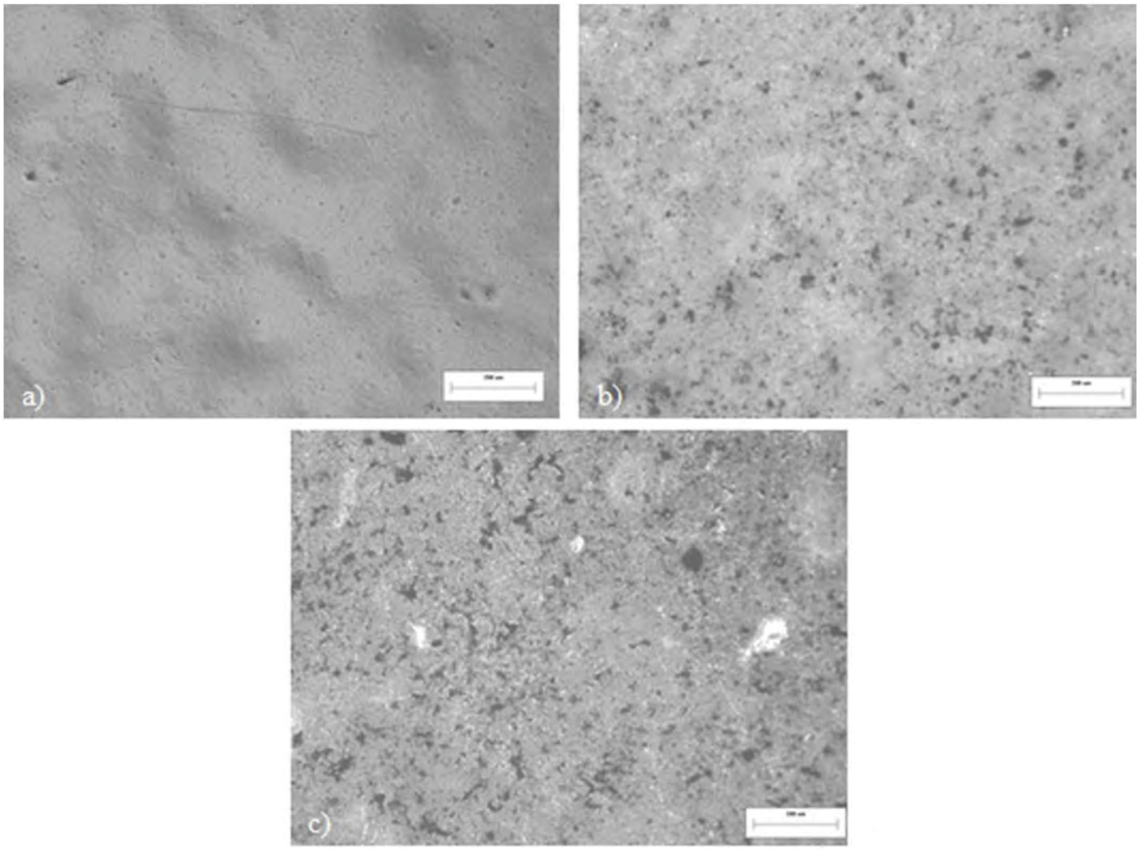

Figure 6-26: Surface of AISI 1018 mild steel specimen (50x magnification) a) reference specimen b) three months after exposure to DSPA 5-4 aerosol only and c) two months after exposure to diesel fire with DSPA 5-4 suppression

sample taken three months after it was exposed to aerosol powder in a DSPA 5-4 agent only test and Figure 6-26 c) an image of the surface two months after it was exposed to a combination of diesel fire gases and aerosol powder generated by the DSPA 5-4 unit. All were imaged at 50X magnification and have a 200 µm scale in one corner.

Comparison of Figure 6-26 a) with Figure 6-26 b) and c) indicates some deposition of aerosol and soot on the surface of the sample; however, no significant degradation was evident. As was the case for the high tensile steel specimens above, there was some evidence of small shallow pits forming in the painted surface, but the anti-corrosion marine paint appeared to have limited the interaction between the mild steel specimen and any corrosive agents that may have formed during aerosol extinguisher activation or suppression of the fire.

NOMEX Fire Resistant Clothing

NOMEX fabric swatches were exposed to the gases and particulate generated during activation and discharge of the extinguisher in an agent only test with a DSPA 5-4 aerosol unit. Figure 6-27 a) contains an image of the surface of the reference fabric swatch and Figure 6-27 b) an image of the swatch taken three months after it was exposed to aerosol powder in the test.

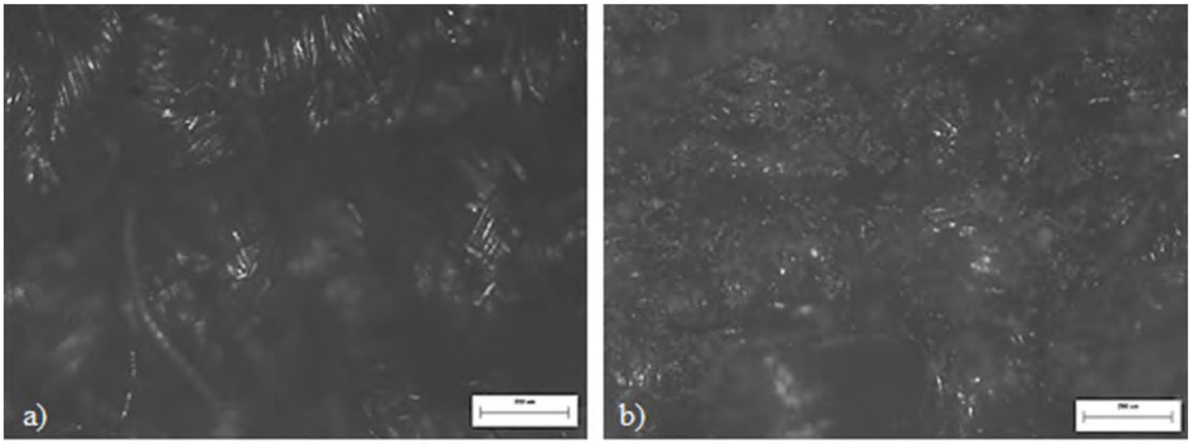

Figure 6-27: NOMEX fabric specimen (50x magnification) a) reference specimen and b) three months after exposure to DSPA 5-4 aerosol only

Visual comparison of the swatches indicated general discolouration and evidence of aerosol particles trapped in the fibres. Overall, however, there appeared to be little or no direct damage to the fibres from exposure during generation and discharge of the aerosol powder.

Computer Circuit Board

Functioning computers and/or individual circuit boards were placed inside the test compartment and exposed to the gases and particulate generated during agent only and unobstructed diesel fire suppression tests with a DSPA 5-4 aerosol unit in an effort to determine the impact of aerosol extinguishment on electronic equipment. In all cases, powder residue was visible on the electronic circuit boards at the end of the tests. At regular intervals after exposure, the circuit boards were examined for obvious visual damage and if none was evident, each was installed in a computer, the computer was powered on and the operating system booted. The system was then turned off, the circuit board removed and examined under the microscope.

The circuit boards exposed to aerosol particulate in the DSPA 5-4 agent only tests ceased operating in late June, approximately 3 months after the test, while those exposed during DSPA 5-4 suppression of the diesel fire continued to operate for the duration of this investigation.

Figure 6-28 and 6-29 a) contain reference images of the surfaces of connectors and conductive pathways, respectively, before exposure while Figure 6-28 and 6-29 b) are images of these components taken three months after exposure to aerosol powder in a DSPA 5-4 agent only test and Figure 6-28 and 6-29 c) are images of the surfaces of comparable components (different boards) two months after exposure to a combination of diesel fire gases and aerosol powder generated by the DSPA 5-4 unit. All were imaged at 50X magnification and have a 200 µm scale in one corner.

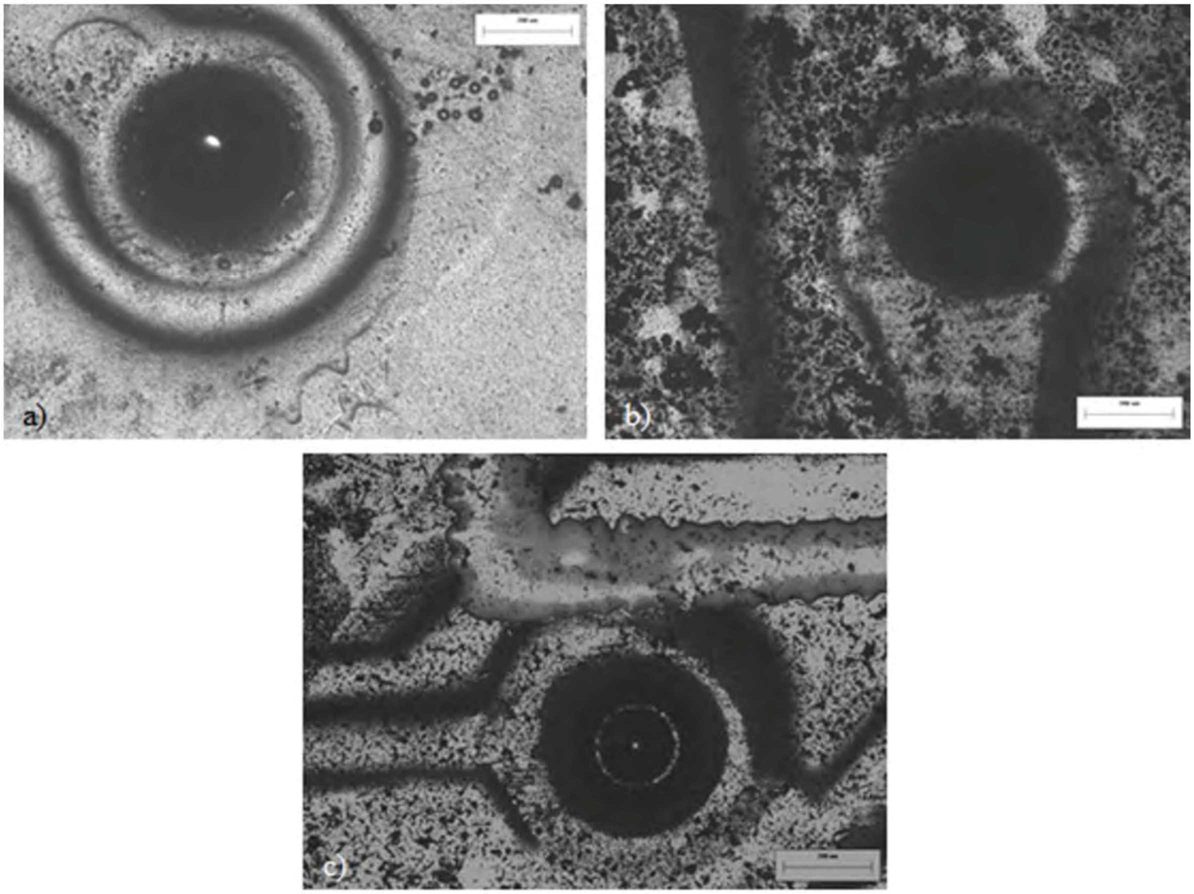

Figure 6-28: Connectors on computer circuit board (50X magnification) a) reference specimen b) three months after exposure to DSPA 5-4 aerosol only c) two months after exposure to diesel fire with DSPA 5-4 suppression

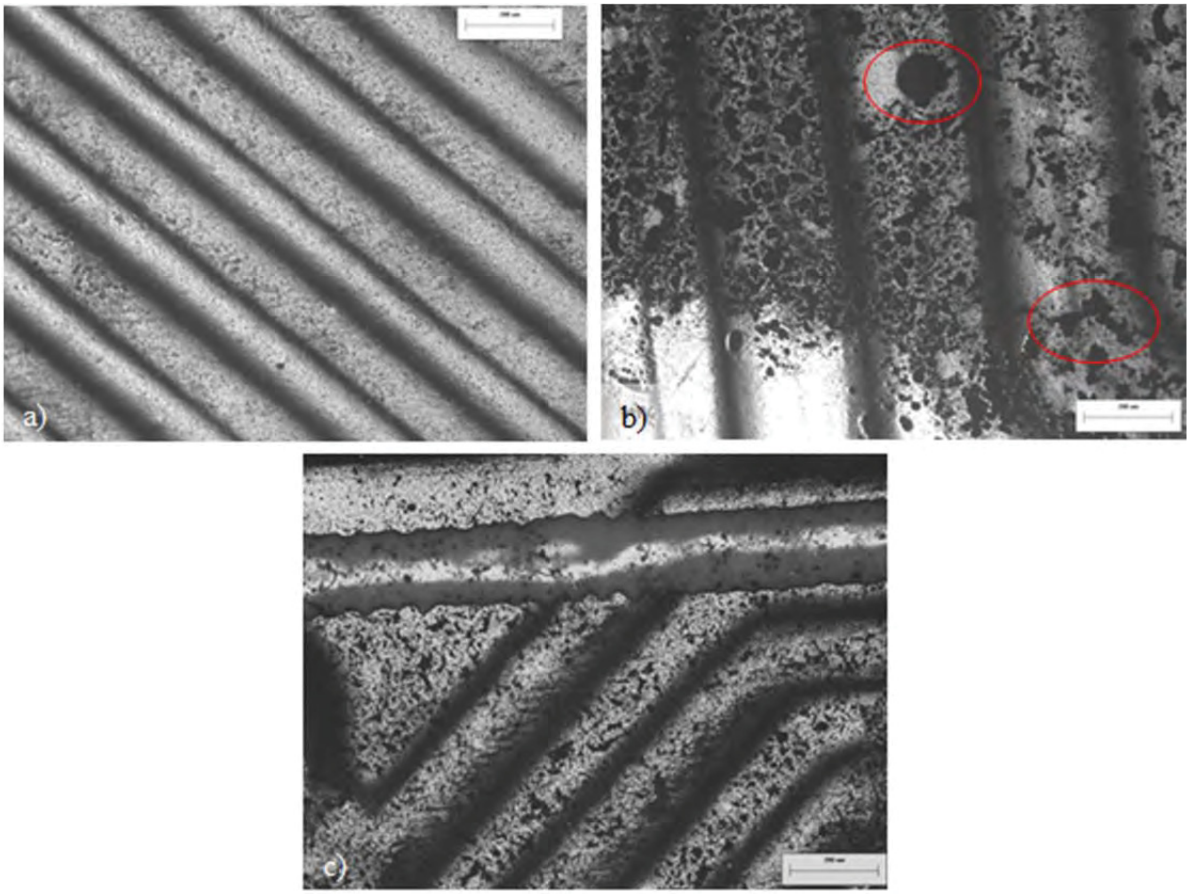

Figure 6-29: Conductive pathways on computer circuit board (50X magnification)
a) reference specimen b) three months after exposure to DSPA 5-4 aerosol only
c) two months after exposure to diesel fire with DSPA 5-4 suppression

Significant discolouration and generalized pitting of the connectors and surrounding areas can be seen by comparing the reference image (Figure 6-28 a)) to the images taken after exposure of the circuit boards in the agent only and diesel suppression tests (Figure 6-28 b) and c)). Similar discolouration and extensive pitting was also evident in the images of the conductive pathways (Figure 6-29 a) through c)). Coupled to this was some soot deposition on the surfaces in all images and marked specifically in Figure 6-29 b).

An additional longer term test was also conducted to determine whether extended exposure to the DSPA 5-4 aerosol alone would lead to more evident degradation of a computer circuit board. In this case, the circuit board was exposed to aerosol particulate during an agent only test and then was held in a conditioning chamber for six months after exposure. After six months, it was inserted into the computer which was turned on to see if it would operate properly. The computer did boot from the exposed circuit board and ran normally for half an hour with no change in status. Figure 6-30 shows the computer card after exposure to the aerosol and at the time of disassembly of the system. Evidence of degradation of the card due to exposure was evident in that section of the circuit board highlighted in the image.

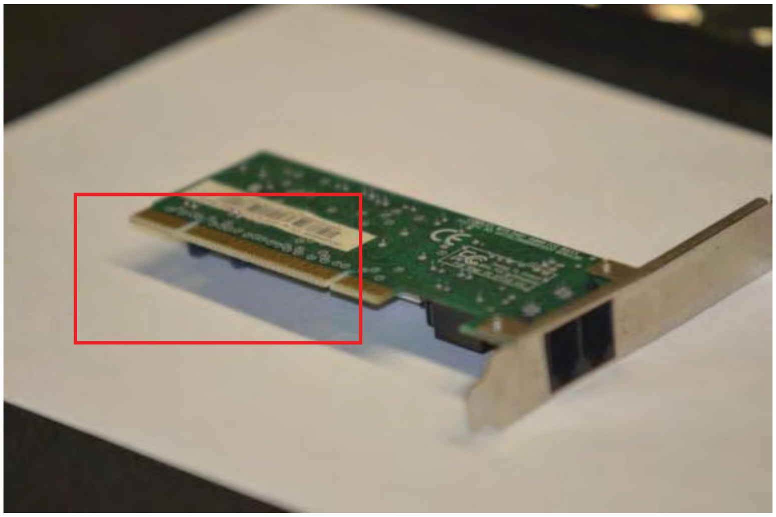

Figure 6-30: Computer Card after six months of exposure to DSPA aerosol agent

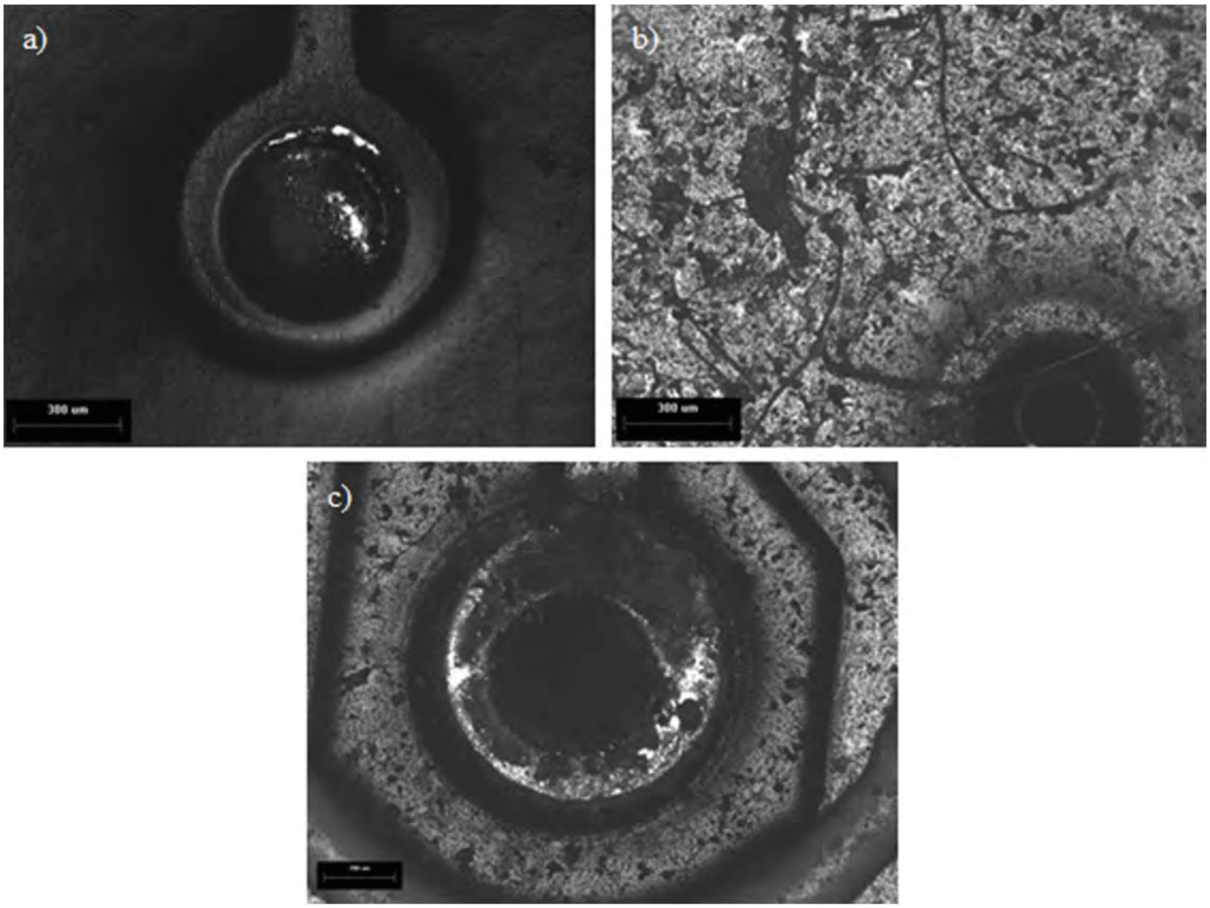

Figure 6-31: Connectors on computer circuit board (50x magnification) a) reference specimen b) section of board near connector six months after exposure to DSPA 5-4 aerosol only c) connector six months after exposure

Figure 6-31 a) through c) are images of the electrical connectors on the computer circuit board taken at 50X magnification with a 300 µm scale in the lower left hand corners. Comparison of Figure 6-31 a) to Figure 6-31 b) and c) indicates the aerosol residue deposition from the test, as well as the deep pitting and apparent cracking that had occurred to both the circuit board and connectors six months after exposure to the DSPA 5-4 aerosol agent. While in this case it did not lead to malfunction of the circuit board, the apparent level of damage suggests that it is quite possible that computers or other electrical equipment could malfunction during or after exposure to the aerosol agent generated by this unit.

The combined results presented in this section point to the potential for minor impact through to significant damage of sensitive electronic equipment during generation and discharge of DSPA 5-4 aerosol units, either alone or during suppression of a diesel fire. After exposure, pitting and corrosion of the board, connectors and/or conductive pathways can occur, and if electronic equipment was poorly cleaned or left unwiped for extended periods after an exposure, this could potentially be sufficiently severe to lead to complete malfunction of a computer board.

6.3 Summary

A film of soot and aerosol powder remained on the surfaces of materials exposed during generation and discharge of both aerosol units in agent only and in diesel fire suppression tests. Discolouration of most surfaces did occur during these tests and if the residue was not cleaned from the surfaces, low to moderate levels of surface pitting occurred on some materials over a period of months after exposure. After exposure, pitting and corrosion of CD discs, circuit boards and other electronic components could occur, and if these were poorly cleaned or not cleaned for extended periods after an exposure, this could potentially be sufficiently severe to lead to complete malfunction. Similarly, chrome plated, and to a lesser degree nickel plated materials, were subject to the formation of crevices and pits in the plating after exposure to the aerosol agent. While copper surfaces appeared to oxidize during agent generation and suppression tests, other materials, such as painted HTS or MS and copper beryllium alloy, appeared to suffer only minor discolouration and deterioration in the form of some shallow pitting after extended periods of time. Finally, particulate deposition was evident in micrographs of the NOMEX fabric samples, but no degradation of the fabric itself was evident in the microscopic images taken in this study.

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