Propellant Off-Gassing and Implications for Triage and Rescue

Hansjörg Schwertz; Lisa A. Roth; Daniel Woodard

INTRODUCTION: Hypergolic propellants can be released in large amounts during space launch contingencies. Whether propellant-contaminated suit fabric poses a significant risk to rescue crews, due to off-gassing, has not been explored in detail. In this study, we addressed this issue experimentally, exposing space suit fabric to propellants (dinitrogen tetroxide [N_2O_4] and monomethyl hydrazine [MMH]).

METHODS: The NASA Space Shuttle Program Advanced Crew Escape System II (ACES II) is similar to the NASA Orion Crew Survival System (OCSS) and was utilized here. Suit fabric was placed and sealed into permeation cells. Fabric exterior surface was exposed to constant concentrated hypergolics, simulating permeation and leakage. Fabric was rinsed, and permeation and off-gassing kinetics were measured. Experimental parameters were selected, simulating suited flight crewmembers during an evacuation transport without cabin air flow.

RESULTS: The fabric allows for immediate permeation of liquid or vaporized MMH and N_2O_4. NO_2 off-gassing never exceeded the AEGL-1 8-h level (acute exposure guideline level). In contrast, MMH off-gassing levels culminated in peak levels, approaching AEGL-2 10-min levels, paralleling the drying process of the fabric layers.

DISCUSSION: Our findings demonstrate that MMH off-gassing is promoted by the drying of suit material in a delayed fashion, resulting in MMH concentrations having the potential for adverse health effects for flight and rescue crews. This indicates that shorter decontamination times could be implemented, provided that suit material is either kept moist to prevent off-gassing or removed prior to medical evacuation. Additional studies using OCSS or commercial crew suits might be needed in the future.

KEYWORDS: hypergolic, monomethyl hydrazine, N_2O_4, off-gassing, emergency egress.

Schwertz H, Roth LA, Woodard D. *Propellant off-gassing and implications for triage and rescue.* Aerosp Med Hum Perform. 2020; 91(12):956–961.

Space launch systems are used in a multitude of contexts ranging from space exploration to scientific experiments to orbital satellite-based communication systems. While these systems have expanded the possibilities of science and commerce, they also present the potential for acute exposure of astronauts to toxic rocket fuel propellants during multiple stages of flight, including launch and launch anomalies, in flight, and upon descent and touch-down. Hypergolic fuel and oxidizer fluids or vapors such as monomethyl hydrazine (MMH) and dinitrogen tetroxide (N_2O_4) can present serious health risks to astronauts, ground crews (during handling), and rescue crews (contact with contaminated surfaces and off-gassing). Whether propellant-contaminated suit fabric poses a significant risk to rescue crews, as outlined below for each chemical, has not been studied in detail. Accordingly, we designed a test series to simulate spacesuit contamination (astronaut risk) and subsequent off-gassing (rescue crew risk) in an enclosed environment, followed by thorough analyses and comparison with existing and recommended exposure limits for MMH and N_2O_4.

Hypergolic propellant combinations are used for upper stage or maneuvering propulsion rocket engines and ignite spontaneously when coming in contact with each other. The simple construction and reliability is advantageous, since no

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This manuscript was received for review in April 2020. It was accepted for publication in October 2020.

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DOI: https://doi.org/10.3357/AMHP.5637.2020

ignition system is needed. In addition, the propellants can be stored as liquids at ordinary pressures and temperatures; however, this necessitates expensive safety precautions because of their toxicity, corrosiveness, and carcinogenicity.[11]

MMH is considered the strongest convulsant and most toxic of the methyl-substituted hydrazine derivatives.[1] It can be absorbed by any route (i.e., skin, mucous membranes, digestive tract, respiratory system), and has been categorized as probably carcinogenic to humans (Group 2A)[7] by the International Agency for Research on Cancer (IARC). Following acute exposure, MMH is immediately irritating and corrosive to the skin and eyes, and can induce mucous membrane damage and pulmonary edema. It has been linked to numerous other adverse health effects throughout the body, including respiratory arrest secondary to seizures or coma due to its potency as a central nervous system (CNS) stimulant.[8,10] The induction of Heinz bodies during MMH exposure is suggestive of methemoglobinemia and hemolysis.

As N_2O_4 is in equilibrium with NO_2, previous clinical and toxicological cases have generally not distinguished between the toxic properties of the two. Exposure to N_2O_4 chiefly happens via skin contact or inhalation of vapors. N_2O_4, which reacts with water and water vapor to form nitric acid, causes skin and eye irritations, burns, and corrosion.[1] Acute inhalation of N_2O_4 can induce cough, fatigue, and nausea, and may result in pulmonary edema and pneumonitis.[6] It is important to note that the pulmonary edema can present with a delay of onset as long as 36 h,[3] as well as additional development of bronchiolitis obliterans.[3]

As defense against these and other hazards, crewmembers in future NASA, international collaborated, or commercial spaceflight missions will wear appropriate spacesuits, as the SpaceX spacesuit, or the recently presented NASA Orion Crew Survival System (OCSS), which is equipped with adequate pressurization capabilities in case of emergency. OCSS is similar in design and materials both to the Advanced Crew Escape System II (ACES II), which was part of the gear worn by Space Shuttle crewmembers. Critically, the ACES II facilitated quick and safe egress in an emergency occurring during prelaunch, launch, in flight, or postlanding. ACES II is capable of being pressurized at 3.5 psi, and is structured as a single pressure bladder made of a single layer of nylon fabric, which is laminated to Gore-Tex and covered by the flame-retardant Nomex.[2] The waterproof main zipper is designed to seal out water and other fluids.

During emergency situations, astronauts wearing the ACES II or an equivalent suit might be exposed to significant amounts of MMH and N_2O_4, leading to the suit fabric layers becoming impregnated with propellant and subsequent off-gassing effects. While the pressurized suit should protect crewmembers against inward leakage of fluids and vapors, contaminants could pose a contact and inhalation risk to rescue workers. In light of these concerns, existing egress protocols contain prolonged decontamination times (15 min), and the use of sensors to ensure adequate decontamination is implemented. However, these extended procedures could potentially lead to delayed triage assessment and emergency treatment of critically injured personnel.

METHODS

Materials

N_2O_4 and MMH were aliquoted from a fuel container at NASA Kennedy Space Center (Cape Canaveral, FL, USA). ACES II bilayer fabric (Nomex; Gore-Tex) was provided by the manufacturer (David Clark Company, Worcester, MA, USA), and 20 cm^2 pieces were used.

Procedures

IRB approval was not needed since experiments did not require human or animal studies. Liquid and vapor exposures were chosen since emergency situations could result in direct contact with liquids, as well as vapor production due to the volatility (low vapor pressure at 20°C) of MMH and N_2O_4. It is important to keep in mind that vapor refers to a gas phase at a temperature where the same substance can also exist in the liquid state in equilibrium. ACES II fabric sandwich (Nomex, meta-aramid; Gore-Tex, 20 cm^2) was placed and sealed into 5 cm glass permeation cells (LABC, Hennef, Germany) equipped with exposure and detection ports **(Fig. 1)**.

The fabric's exterior surface (outer layer, Nomex) was exposed to liquid or concentrated MMH and N_2O_4 vapor for 60 min to simulate permeation and leakage (measuring vapor on inner side of fabric). A standard generator and Flow Unit (Kin-Tec Analytical, La Marque, TX, USA) allowed for constant airflow ($28.3\ L \cdot h^{-1}$) and vapor concentration to a permeation cell ($188\ mg \cdot m^{-3}$ [100 ppm] and $1880\ mg \cdot m^{-3}$ [1000 ppm] N_2O_4, $189\ mg \cdot m^{-3}$ [100 ppm] and $945\ mg \cdot m^{-3}$ [500 ppm] MMH). Air flow and fabric size were extrapolated to simulate 2 m^2 suit surface area and evacuation transport in a 12,472.6 L helicopter (NASA UH-1H) cabin without airflow. A 30-s water spray (100 ml), simulating transition through water spray during emergency egress was performed. Material deterioration was assessed subjectively based on discoloration (yes – no), and spontaneous disintegration of fabric (yes – no). It is important to point out that these observations are a first

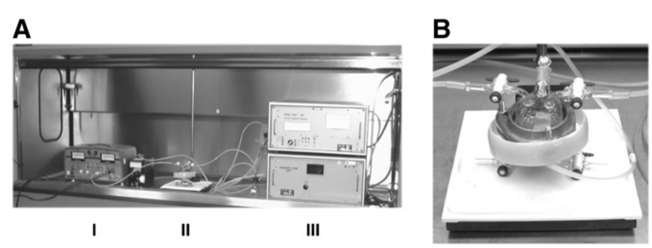

Fig. 1. Experimental set-up. (A) Experimental set-up for N_2O_4/NO_2 testing in a fume hood. Vapor and off-gassing concentrations were measured using a concentration monitor (I). Fabric was enclosed and sealed into a permeation cell (II). Vapor was generated using a standard vapor generator, and an auxiliary flow unit, for defined air flow parameters (III). MMH experiments were set up accordingly, using different detection monitor. (B) Glass permeation cell with access ports for application and removal of exposure vapors.

orientation for potential detrimental effects of chemical exposure, but may not have relevance to potential health risks. Off-gassing was continuously measured after exposure of the fabric layers to aforementioned concentrations of N_2O_4 and MMH using standardized detection equipment (Energetics Science, Elmsford, NY, USA) detecting NO_2 based on the equilibrium $N_2O_4 \rightleftharpoons 2\,NO_2$ and MMH, and values were recorded every 2 min.

Statistical Analysis

Data were analyzed using Prism 8 (GraphPad Software, San Diego, CA, USA). Because of the original definition of acute exposure guideline level (AEGL) by the Environmental Protection Agency (EPA), the aforementioned off-gassing values were converted from SI-unit ($mg \cdot m^{-3}$) to ppm.

Extrapolation is used to estimate data beyond the original observation range. However, extrapolation can lead to incorrect predictions if the method is not used appropriately and without robust data sets being implemented. Here, we used extrapolation to cross-predict low and high concentration values from each other data set. To verify dose-dependency and plausibility, we extrapolated the 945 $mg \cdot m^{-3}$ results from the 189 $mg \cdot m^{-3}$ values, and the 189 $mg \cdot m^{-3}$ data points from the 945 $mg \cdot m^{-3}$ measurements. Peak permeation or off-gassing were aligned accordingly to adjust for time-dependency of different vapor concentrations.

RESULTS

When exposing the suit material to liquid N_2O_4, we observed immediate penetration through the two tested layers. Furthermore, after 30 – 60 min exposure time we noticed a dark discoloration of the Nomex layer (**Fig. 2A**, left panel), and even spontaneous disintegration of the Gore-Tex fabric (Fig. 2A, right panel). MMH also immediately penetrated through Nomex and Gore-Tex. However, in contrast to the N_2O_4 induced effects, liquid MMH induced less damage to the suit fabric. As demonstrated in **Fig. 2B**, MMH did have a discoloring effect on the Nomex layer (Fig. 2B, left panel) but Gore-Tex did not demonstrate color or visible integrity changes post MMH exposure (Fig. 2B, right panel).

Neither exposure of the fabric layers with N_2O_4 vapor (1880 $mg \cdot m^{-3}$, **Fig. 3A,** left panel Nomex, right panel Gore-Tex), nor with MMH vapor (945 $mg \cdot m^{-3}$, **Fig. 3B**, left panel Nomex, right panel Gore-Tex) resulted in noticeable color changes or even destruction of the fabric. Measuring N_2O_4 vapor at the inside of the fabric layers, a measure of astronaut risk, did demonstrate a peak concentration of 0.19 $mg \cdot m^{-3}$ (0.1 ppm) after 16 min (188 $mg \cdot m^{-3}$ vapor, **Fig. 3C**, double dashed line), and 1.69 $mg \cdot m^{-3}$ (0.9 ppm) after 52 min (1880 $mg \cdot m^{-3}$ vapor, Fig. 3C, solid line). The 189 $mg \cdot m^{-3}$ MMH vapor reached its peak inside concentration after 47 min (0.19 $mg \cdot m^{-3}$, 0.1 ppm, **Fig. 3D**, dotted line). In contrast, exposure to MMH vapor at a concentration of 945 $mg \cdot m^{-3}$ permeated to the inside, reaching a peak concentration of 2.82 $mg \cdot m^{-3}$ (1.49 ppm) after 2 min (Fig. 3D, dashed line). **Fig. 3E** depicts the extrapolated data points. While the overall trend and dynamic was preserved, extrapolation resulted in lower permeation concentrations for 945 $mg \cdot m^{-3}$ vapor. This was most likely due to the 189 $mg \cdot m^{-3}$ vapor permeation concentration staying below the limit of effective detection, leading to skewed data representation.

NO_2 off-gassing, putting rescue workers at risk, was initially the highest, peaking at 0.564 $mg \cdot m^{-3}$ (0.3 ppm) at 12 min (**Fig. 4A**), and decreased during the reminder of the detection period. Off-gassing of the 945 $mg \cdot m^{-3}$ MMH vapor demonstrated an initial peak at 0.2268 $mg \cdot m^{-3}$ (0.12 ppm) at 2 min (**Fig. 4B**, dashed line), but subsequently stayed undetected till 52 min, reaching a peak of 5.103 $mg \cdot m^{-3}$ (2.7 ppm) at 106 min, followed by a gradual decrease in off-gassing concentrations. Off-gassing of the 189 $mg \cdot m^{-3}$ MMH vapor followed the same trend; it was detected at 78 min and reached a peak concentration of 1.002 $mg \cdot m^{-3}$ (0.53 ppm) at 94 min (Fig. 4B, dotted line). Extrapolation of our results verified the accuracy and repeatability of the measurements. **Fig. 4C** depicts the resulting graph.

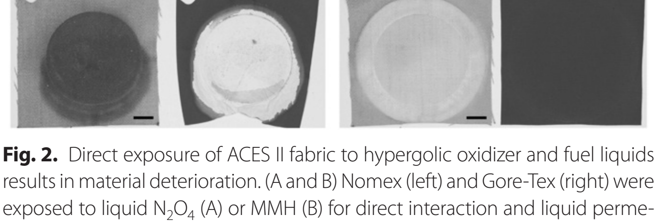

Fig. 2. Direct exposure of ACES II fabric to hypergolic oxidizer and fuel liquids results in material deterioration. (A and B) Nomex (left) and Gore-Tex (right) were exposed to liquid N_2O_4 (A) or MMH (B) for direct interaction and liquid permeation testing. Scale bars = 1 cm.

DISCUSSION

It is generally accepted that direct contact of flight crews to hypergolic propellants during emergency egress is a likely scenario,[9] but can also happen in flight. Important insights into acute MMH and N_2O_4 toxicity for space crews were generated during the Apollo-Soyuz incident. During the vehicle descent, hypergolic fumes were filtered into the space ship through an open air intake valve, located in close proximity to a thruster, due to a mishap.[3] Members of the crew were found to have experienced loss of consciousness, pulmonary edema, with delayed onset, skin and mucosal irritation, and neurologic findings (i.e., nystagmus).[3] For better protection of NASA flight crews from hazards before, during, and after spaceflight operations (NASA, or commercial), including pressure loss, fluid and fire exposure, the ACES II was designed. ACES II and more contemporary suit designs (e.g., the OCSS and commercial crew suits) have pressurization capabilities that prevent the entry of vapors, and therefore, add a protective layer for the astronauts.

In case of a launch anomaly, flight crew protection is of the highest importance, and exposure is minimized by initially spraying water along the space vehicle access arm on the launch pad (Firex System) and additional decontamination efforts are

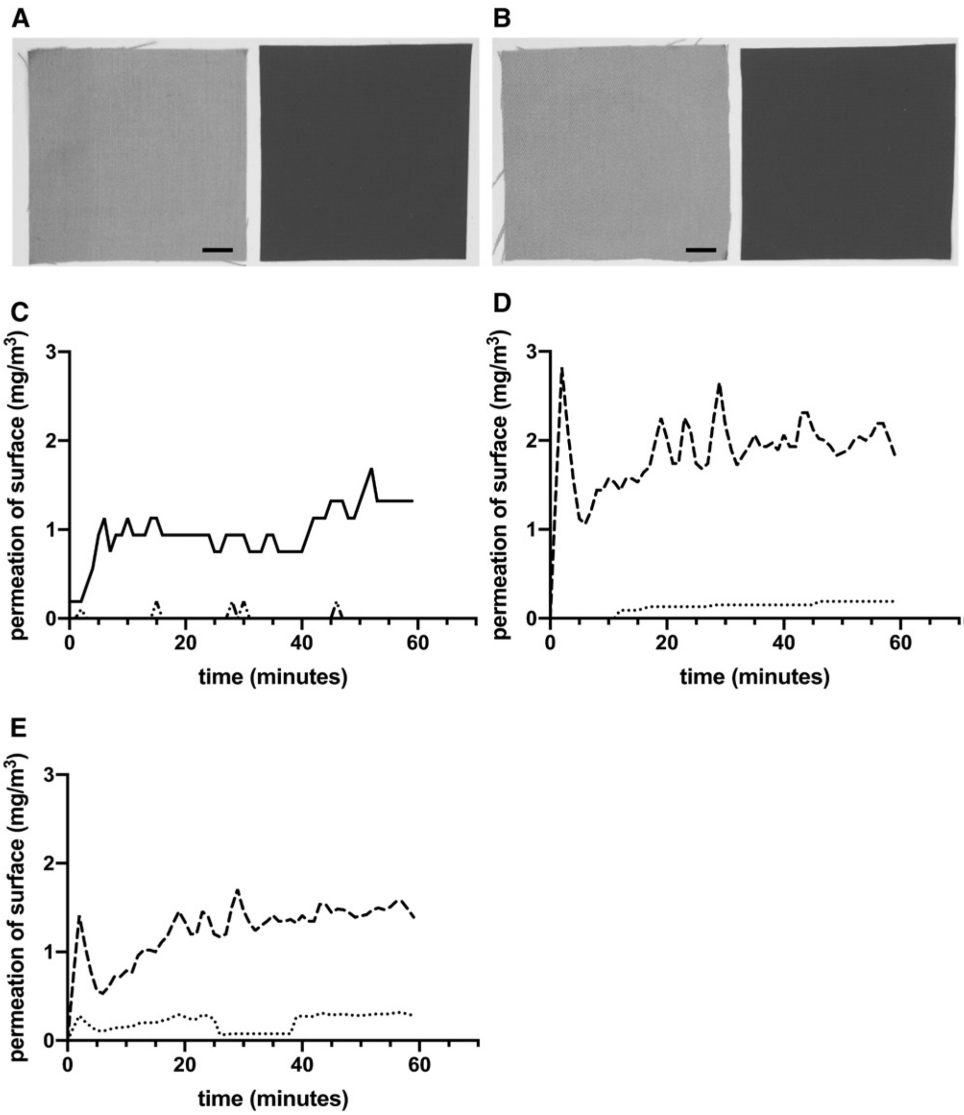

Fig. 3. Exposure of suit fabric to hypergolic vapor does lead to time-dependent permeation in a nonpressurized setting. (A and B) Nomex (left) and Gore-Tex (right) were exposed to 1880 mg/m^3 N_2O_4 vapor (A) or 945 mg · m^{23} MMH vapor (B). Scale bars = 1 cm. (C) N_2O_4 vapor permeates suit fabric. The bar graph demonstrates the measurements of permeated N_2O_4 concentrations on the inside of the fabric sandwich (double dashed line, 188 mg · m^{-3}, solid line 1880 mg · m^{-3}). (D) MMH vapor permeates suit fabric. The bar graph demonstrates the measurements of permeated MMH concentrations on the inside of the fabric sandwich (dotted line, 189 mg · m^{-3}, dashed line 945 mg · m^{-3}). (E) The bar graph demonstrates the extrapolated MMH penetration using all concentrations (dotted line, 189 mg · m^{-3}, dashed line 945 mg · m^{-3}).

employed at respective triage sites, as well as engineering controls in the spacecraft. However, there is a paucity of data examining rescue crew hazard exposure due to direct contact or potential off-gassing of MMH and N_2O_4/NO_2. During emergency egress, evacuation transport, triage evaluation, and treatment, off-gassing effects from propellant-impregnated fabric could pose a significant risk to rescue crews. Therefore, to investigate the rescue crew risk in this study, we used an experimental approach.

Direct exposure of ACES II fabric to N_2O_4 and MMH fluids did result in differential suit material deterioration (Fig. 2). In contrast to these experiments using liquid chemicals, the exposure of ACES II fabric layers to hypergolic vapor did not result in obvious structural changes of the suit material (Fig. 3A and B). However, vaporized N_2O_4 and MMH did permeate through the fabric layers in a concentration-dependent manner (Fig. 3C, D, and E). Furthermore, while N_2O_4 demonstrated a negligible off-gassing effect, exposure of the fabric layers to MMH did lead to substantial off-gassing (Fig. 4).

Being left structurally intact after the exposure to hypergolic vapors, suit layers were demonstrated to be permeated by the hazardous vapors. Exposure to N_2O_4 vapor resulted in permeation peak values below NIOSH Recommended Exposure Limit (REL, 1.8 mg · m^{-3}), OSHA Permissible Exposure Limit (PEL, 9 mg · m^{-3}), and EPA Acute Exposure Guideline Level (AEGL) -2 levels. While NIOSH REL and OSHA PEL are averaging exposure over a certain time period, and are therefore more suitable for the analysis of a longer-term exposure risk, the EPA AEGL describe the human health effects from once-in-a-lifetime, or rare, exposure. AEGLs are defined as airborne concentration, which it is predicted to cause irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape. Therefore, AEGLs seem to be more suitable when dealing with short-term emergency responses as is the case for rescue crews in the setting of emergency egress and space crew rescue.

For N_2O_4, it is important to note that, that during emergency launch pad situations, N_2O_4 will react with launch pad spray water and result in nitrous and nitric acid, which has the potential to induce direct skin injuries in crewmembers and rescue crews alike.

Contrasting N_2O_4, MMH vapor permeated through the fabric layers, reaching dose dependent peak concentrations, which were above the current NIOSH REL (0.08 mg · m^{-3}) and OSHA PEL (0.35 mg · m^{-3}). In addition, the concentrations reached during our permeation experiments would have

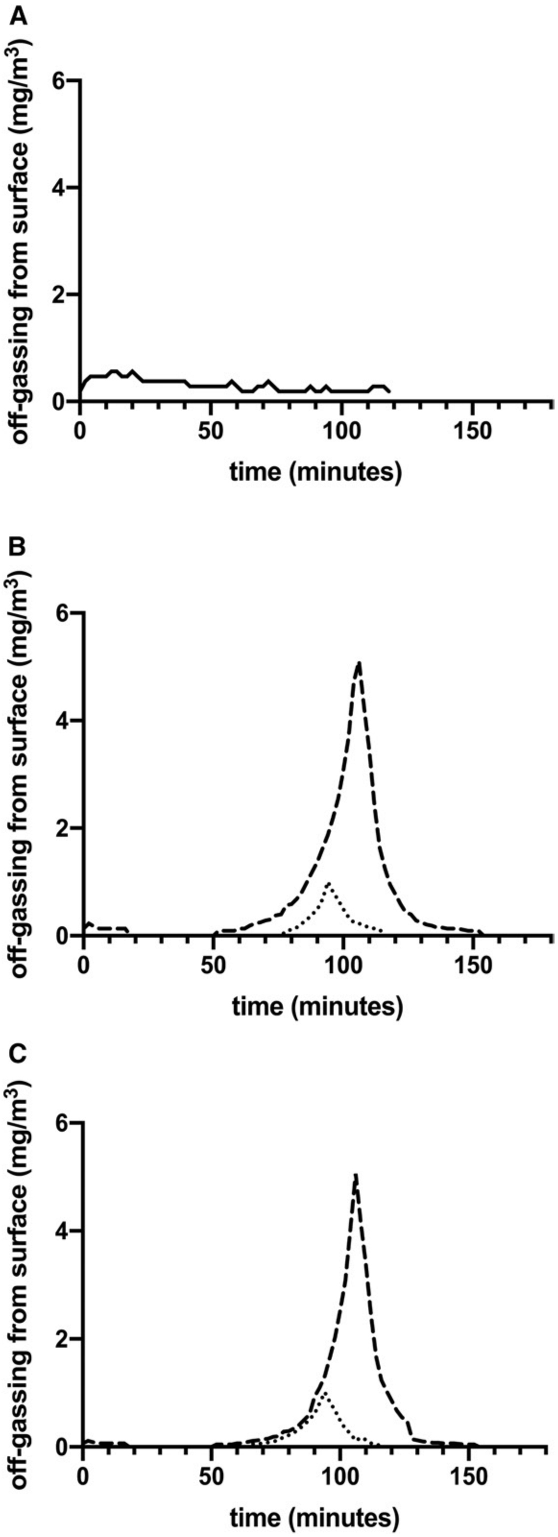

Fig. 4. Oxidizer and fuel off-gassing demonstrate differential kinetics. (A) Exposure of suit fabric to N_2O_4 vapor (1880 mg · m^{-3}) leaves minimal volatile residues. The bar graph demonstrates the measurements of off-gassed NO_2 (solid line, based on the equilibrium $N_2O_4 \rightleftharpoons 2\,NO_2$). (B) Fabric exposure to MMH vapor induces time and concentration dependent off-gassing. The bar graph demonstrates the measurements of off-gassed MMH concentrations from the fabric (dotted line, 189 mg · m^{-3}, dashed line 945 mg · m^{-3}). (C) The bar graph demonstrates the extrapolated MMH off-gassing using all concentrations (dotted line, 189 mg · m^{-3}, dashed line 945 mg · m^{-3}).

exposed individuals to MMH levels around or above the 1 h AEGL-2 limit and the NASA Spacecraft Maximum Allowable Concentrations (SMACs), potentially inducing irreversible or serious, long-lasting adverse health effects or an impaired ability to escape.[4,5] The exposure risk for flight crews should be limited due to pressurization of their escape suits, a condition that was beyond the scope of our experimental design. Nevertheless, based on these results, and to reduce potential contact and inhalation risk to rescue workers, removing a permeated suit for triage evaluation and treatment purposes should be performed only when adequate ventilation is available.

Current NASA emergency egress procedures require a 15-min decontamination interval (Personal communication. Philip J. Scarpa, M.D., and Cathy Dibiase, R.N.; 2020) that allows medical personnel to safely evaluate and treat evacuated injured flight-, closeout-, or fire-crews. The decontamination time does, however, lead to delays in evaluation and treatment. For mitigation purposes, alternative approaches have been tested, including equipping paramedics with respiratory protection and performing the primary survey without the removal of ACES II suits and helmets. However, evaluations and advanced life support are difficult to perform when using respiratory protection, and may potentially lead to adverse patient outcomes.

In light of this problem, our NO_2-off-gassing tests demonstrated no increased health risk for rescue crews during triage site evaluation or evacuation transport simulating conditions. In contrast, the MMH experiments showed MMH peak off-gassing levels, approaching AEGL-2 10-min concentrations. It is interesting to note that the MMH off-gassing was initially undetectable, followed by a timed peak exposure burst, paralleling the drying process of the fabric layers. These results demonstrate that MMH off-gassing is mostly problematic if fabric is allowed to dry. This could result in a substantial exposure risk of rescue workers causing corrosive and irritating effects to the skin and eyes, mucous membrane damage, pulmonary edema, respiratory arrest, seizures, or coma, and resulting in a hazardous accumulation of MMH in an enclosed environment (e.g., a rescue vehicle) if fabric is allowed to dry.

There are some limitations to this study we would like to address. First, we did not use a pressurized experimental set-up or supplemental oxygen flow systems.[12] The addition of these measures would have most likely decreased inward leakage of fluids and vapors and provided additional protection against the low-level permeation detected in our experiments. Second, our study was limited to the use of the ACES II fabric instead of testing OCSS or commercial crew suit material. It is important to note that ACES II and the newest generation suits use similar fabric designs, and our results should therefore be, at least in part, representative of OCSS exposure situations. Nevertheless, N_2O_4 and MMH exposure studies using the OCSS or commercial crew suits should be performed in the near future.

In conclusion, our data demonstrate that MMH off-gassing is promoted by the drying of suit material and therefore in a delayed fashion. This indicates that shorter decontamination times could be implemented and utilized, provided that escape suit material is either kept moist to prevent off-gassing or removed prior to medical evacuation while ample ventilation is available. In addition, we show that prolonged direct exposure to hypergolic propellant fluid could result in suit fabric disintegration. Furthermore, unpressurized ACES II suit fabric layers allow for permeation of propellant vapors. While N_2O_4 did not reach critical values, MMH permeated at concentrations having the potential for adverse health effects for flight and rescue crews.

ACKNOWLEDGMENTS

We thank Dr. Philip J. Scarpa, Aerospace Medicine and Occupational Health Branch NASA, KSC, for his support, and Dr. Julielynn Wong for critical review of the manuscript and invaluable comments and recommendations.

Financial Disclosure Statement: The authors have no competing interests to disclose.

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