

REDUCING HYDROGEN FLUORIDE AND OTHER DECOMPOSITION USING POWDERS AND HALOCARONS

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INTRODUCTION

The principal toxic species produced during combat vehicle fires is carbon monoxide (CO). The yield is strongly dependent on the amount of combustion air and other burning conditions. Levels can exceed human toxic levels, sometimes very quickly. Other toxics can be generated depending upon the material(s) that are burning. Paper and clothing fires typically produce CO, as do most hydrocarbon fuel fires. Plastics from circuit boards, wire and cables, and fabrics, however, tend to generate other toxic products, such as hydrochloric acid (HCl) and hydrogen cyanide (HCN), in addition to CO.

Using halons and their replacement fire extinguishing agents on fires increases the amount and types of toxic products. These decomposition products can be severely toxic. In addition to increased CO, acid gases, such as hydrogen fluoride (HF) and hydrogen bromide (HBr) (with Halons 1301 and 1211), as well as carbonyl fluoride (COF₂) are formed. In some cases, chemical intermediaries have also been identified. These toxic compounds have been measured to be 10 to 1000 times those limits set by the Occupational Safety and Health Administration (OSHA) and other safety and health organizations. Various fire suppression test programs have shown that the concentration of toxic products generated by the current halon replacements exceeds levels generated by the existing halons by 5 to 10 times. These high levels continue to be a serious concern being addressed as new replacements are introduced to replace existing halon systems on combat vehicles.

RELEVANT RESEARCH

During the spring of 1991, NMERI performed testing with a powder halocarbon mixture designated as Envirogel™ – a blend of a halocarbon gas, a gelling agent, and a finely ground powder. The halocarbons evaluated included hydrofluorocarbons (HFC)-125 and -134a. The powders were ammonium polyphosphate (APP) and monoammonium phosphate (MAP). Two powder grinds were also investigated, including a fine grind (nominally 7 μm particle size) and a coarse grind (nominally 35 μm particle size). Testing was performed using the two gases in combination with the two powders at different ratios [1]. Test scenarios included small (18 m³) and large (500 m³) total flood chamber tests. Portable extinguisher and combat vehicle engine compartment tests were also conducted.

The measured HF concentrations were very low (< 100 ppm), both for large fires and those with excessively long extinguishment times (> 30 sec). In all cases no HF or other measured decomposition products (COF₂ and CO) were detected during the extinguished Envirogel™ tests. The HF concentrations were 2000 to 3000 times lower than those measured during comparable extinguishment tests using the current halon replacements (FM-200, FE-I 3, CEA-410, NAF S-III, etc.). Also, COF₂ concentrations were 1 to 10 times lower. The low decomposition products associated with the Envirogel™ agent made it a significantly attractive halon substitute, worthy

of consideration for a variety of applications: however, interest in the product has been low to nonexistent.

No significant metal corrosion was shown when the Envirogel™ product was discharged onto heated metal surfaces. The Envirogel™ product had good suspension qualities; it had the ability to remain suspended in the test chamber after discharge preventing reignition of the fuel. No significant toxicological effects were found that would cause concern. Moore et al. [1] present test data and additional information on the evaluation of the Envirogel™ concept (e.g., mixing powders with halocarbon to reduce decomposition products).

The major drawback of the Envirogel™ product was the cleanup required after the agent was discharged. It was not a clean agent as compared to Halon 1301 and the current halon replacements. However, because no decomposition products were detected with Envirogel™, even when applied to large fires, it was worthy of further investigation. Based on the Envirogel test results and research carried out by **NASA**, the addition of HF scavenging powders to halocarbon gases will reduce decomposition products. The fire suppression studies with the Envirogel™ product were carried out at 55 to 45 wt% powder amounts.

OBJECTIVE

The objective of the research presented in this paper is to show the effects on decomposition product formation and fire suppression performance by adding small amounts of various powders to halocarbon compounds during portable fire extinguisher development for US Army combat vehicles and during crew compartment test conducted for the **US Marine Corps**. Specifically we were interested in determining the effect of powders, their amount, and particle size related to HF scavenging. Initial laboratory testing with various powder particle sizes and types was performed to investigate relative HF reduction. The laboratory testing was used to define and determine the parameters that reduce decomposition product formation when powders are added to halocarbon gases. Combinations acceptable for use in occupied spaces were important. Based on the limited laboratory results, ~~desired~~/**known** characteristics of the powders, and discussion with the project officers, agent blends were selected for field-scale fire suppression testing.

LABORATORY TESTS

The apparatuses shown Figures 1 and 2 were used to evaluate the gaseous HF scavenging capability of the tested powders. In the first apparatus 1 g of powder was placed on a porous polymer plate and HF gas at -3000 ppm was flowed through the apparatus while a Fast Fourier Infrared (FTIR) apparatus was used to monitor HF concentrations in real time. HF adsorption by the equivalent amounts of powders was measured. With the second apparatus, the HF gas flow was initiated, steady HF concentration was maintained through the apparatus, 5 g of powder were “puffed” in the HF gas stream, and after 20 to 40 sec the HF gas flow was turned off, monitoring was performed with the FTIR until the HF concentrations lowered. Powder dispersion and “floating” characteristics were monitored, as well as HF adsorption capability.

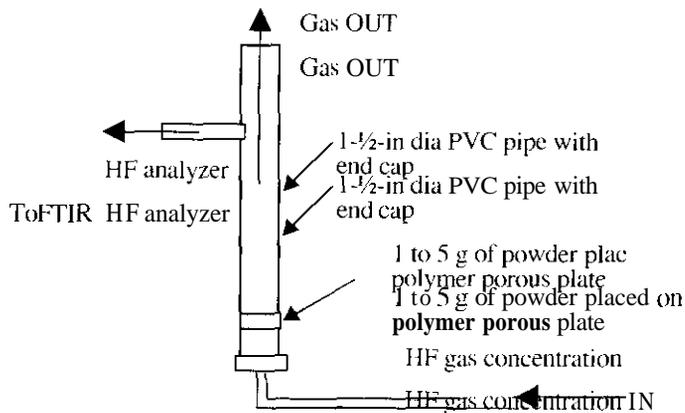


Figure 1. Initial laboratory apparatus.

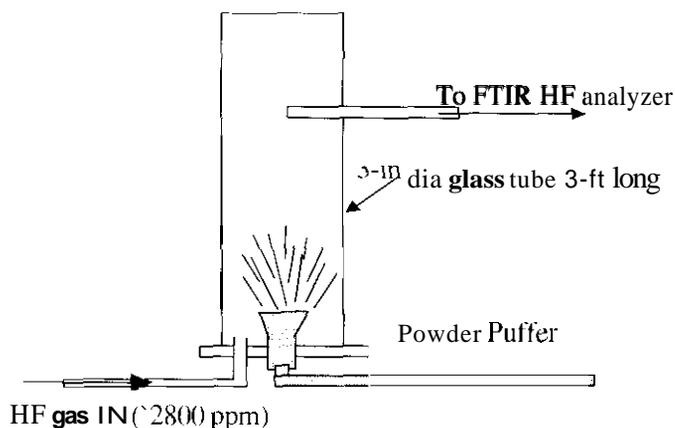


Figure 2. Laboratory "Powder Puffer" apparatus.

RESULTS

Several tests were performed with the first apparatus. Initially, 5 g of APP (nominally $<7 \mu\text{m}$ in size) were placed on the porous plate. No HF was measured over 1 min. The apparatus was cleaned and smaller amounts of powder were placed on the porous plate. It was not until 1 g was reached that useful data was generated. This amount of powder (1 g) would just evenly cover the entire porous plate. The measured HF concentration above the porous plate was very low at the beginning (*HF was being adsorbed by the powder*), but began to increase over time as the adsorbing capacity of the powder decreased overtime. This test was repeated, with same results for the two powders tested (Figure 3).

The results using the first apparatus show that sodium bicarbonate was a significantly better HF adsorber than APP. While these laboratory tests were being conducted, field-scale tests with APP/FM-200 and sodium bicarbonate/FM-200 were being performed. Only small differences in fire suppression effectiveness were observed. The sodium bicarbonate results were slightly better. Thus, sodium bicarbonate was selected for further evaluation in the laboratory.

Using the apparatus shown in Figure 2 several tests were performed. Typical results are illustrated in Figures 4 to 7. For the first test shown (Figure 4), the HF concentration was reduced by almost 45% from 1190 to 660 ppm when the powder was "puffed" into the HF gas stream. Similar results were seen with other particle sizes. Figures 6 and 7 show typical test results for calcium carbonate and potassium bicarbonate. The calcium carbonate was not an effective

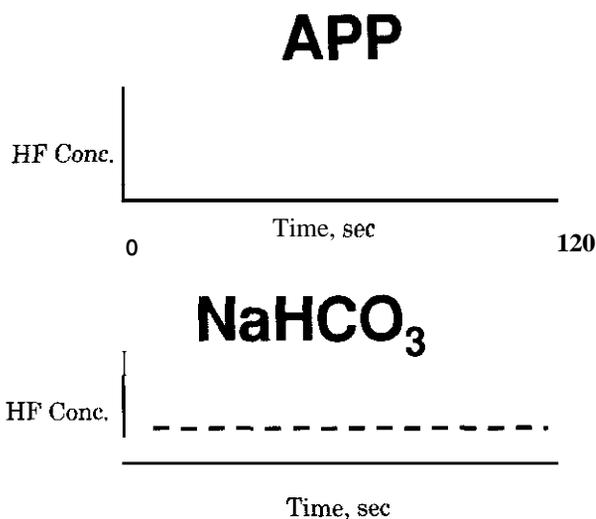


Figure 3. Typical HF concentration versus time plots using the initial laboratory apparatus.

scavenger. The potassium bicarbonate performed similar to the sodium bicarbonate, in terms of percent HF reduction. Results for several other tests are not shown.

The NMERI “Puffer” test apparatus proved to be an effective tool in evaluating the potential HF scavenging capability of powders to be blended with halocarbons. The most effective powder tested was sodium bicarbonate and the smaller the particle size the better. Sodium bicarbonate was also significantly better than **APP** at adsorbing HF during these tests. Based upon limited preliminary testing, it is recommended that minor refinement of the second test apparatus be performed and several other powders at various sizes be tested and evaluated.

PORTABLE FIRE EXTINGUISHER TESTS

Two options were considered for obtaining and analyzing the concentrations and types of decomposition products during portable fire extinguisher testing: (1) conduct tests in the open and hope that the sampling probe and fire plume location relationships would remain the same from test to test, thus ensuring test repeatability, or (2) conduct tests in an enclosure (Figure 8), eliminating wind and other related variables which would affect test repeatability. Option 2 was chosen. The tests were conducted to compare the results from one agent to another and not necessarily to measure the exact exposures one would expect in suppressing an outdoor fire with a slight wind at ones back. However, the test scenario may represent the exposure one would get if the agent were discharged within a crew compartment on a relatively “large” fire.

Several decomposition product tests conducted. Figure 9 shows HF concentration profiles for the FM-200 only tests. During Test No. 33 the fire was not extinguished and the HF levels exceeded 6000 ppm for over 10 sec. The results for Test Nos. 1, 2, 3, and 32 were similar; after about 50 sec, the HF concentration levels off to ~1200 ppm. Figure 10 compares the typical/average FM-200 HF data Halon 1301 results. The average HF concentrations for FM-200 are 2–6 times higher than for Halon 1301. Figure 11 shows HF concentrations for four of the FM-200 blended with sodium bicarbonate tests. The initial HF peak values are significantly reduced with the addition of the sodium bicarbonate; however, residual HF concentrations are still high (e.g., 700–1200 ppm).

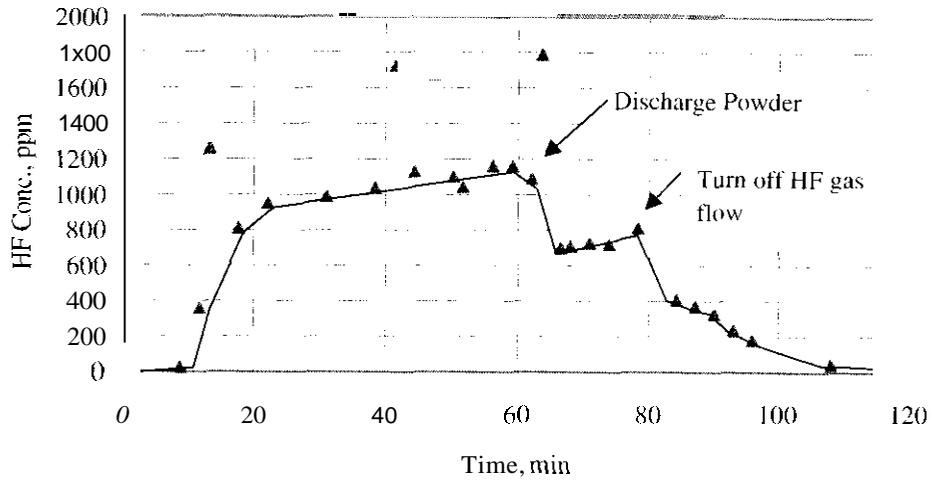


Figure 4. Sodium bicarbonate (43 to 53 μm) results (NMERI Puffer apparatus).

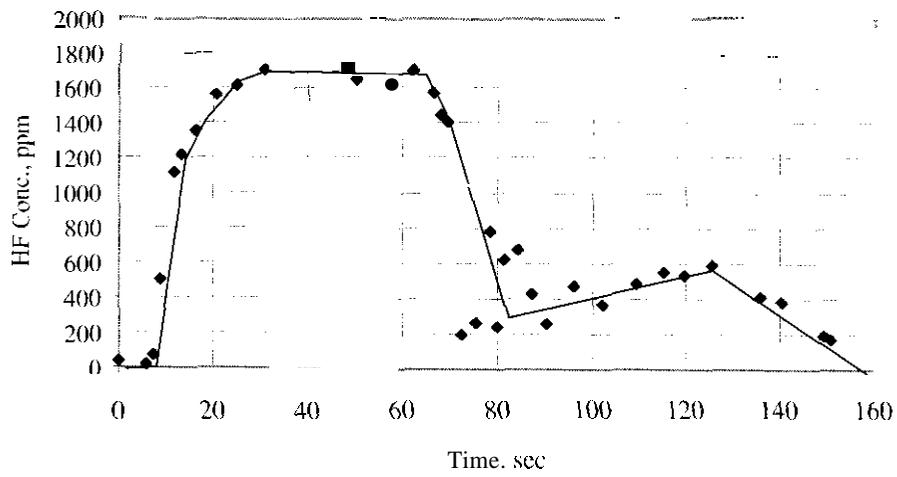
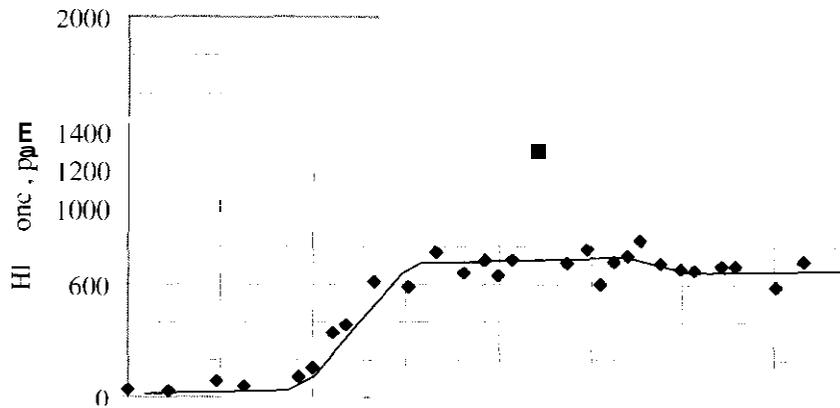


Figure 5. Sodium bicarbonate (< 7 μm) results (NMERI Puffer apparatus).



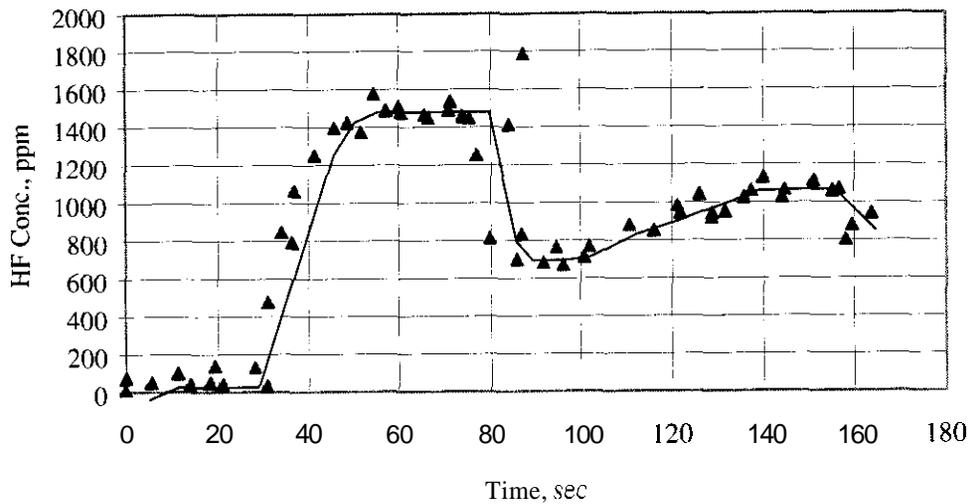


Figure 7. Potassium bicarbonate (43 to 53 μm) results (NMERI Puffer apparatus).

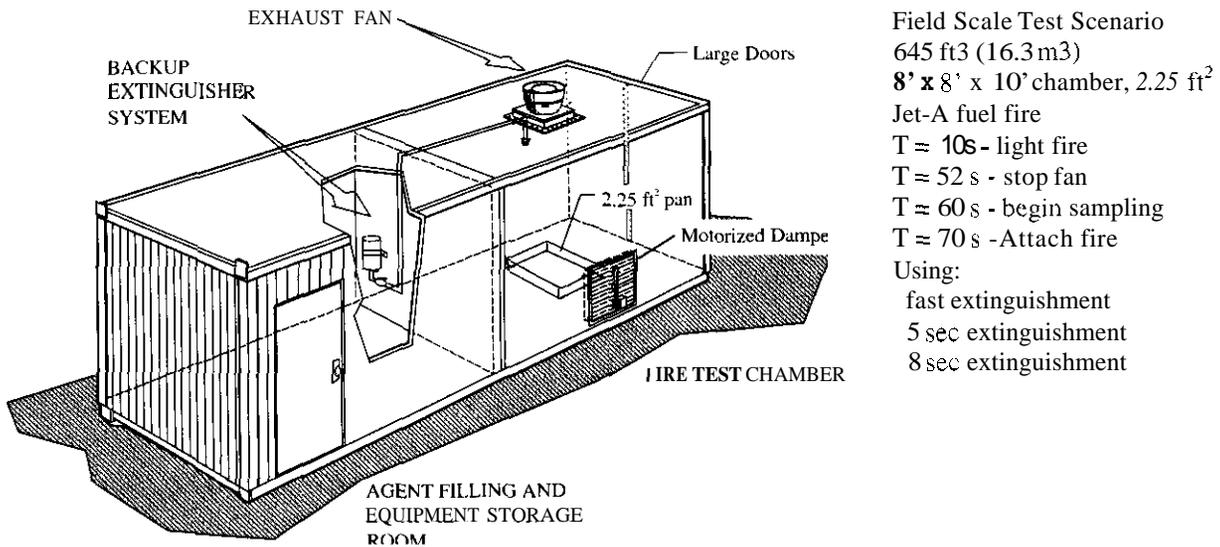


Figure 8. NMERI Field-Scale Test Chamber.

The amount of decomposition products generated during a fire suppression event is dependent upon the fire size, extinguishment time, and the amount of extinguishing agent discharged. The extinguishment time, discharge time, and amount of agent discharged were varied for each of the tested agents. The firefighter was instructed to vary the flow rate during each test in an attempt to increase or decrease the extinguishment time from test to test. The flow rate was varied by changing how much the firefighter depressed the extinguisher handle. The further the handle was depressed the higher the flow rate and thus, the shorter the extinguishment time. By varying the extinguishment time, the effect of fire extinguishment time on decomposition product generation was determined.

The data collected show that the concentrations of the decomposition products generated by the tested compounds exceed that generated with Halon 1301 by two to six times (depending on the

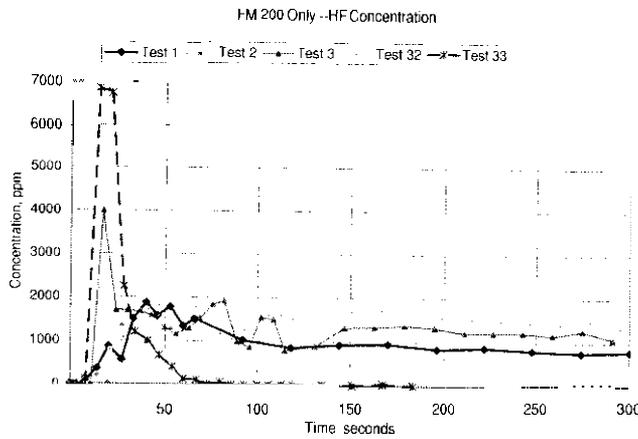


Figure 9. Typical FM-200 only HF concentrations measured in the NMERI Field-Scale Test Chamber during streaming agent tests.

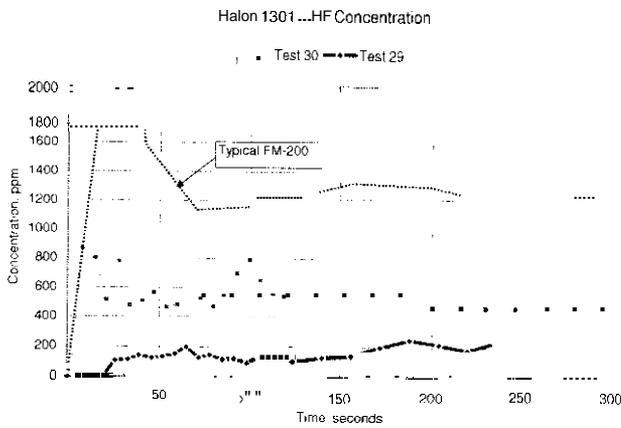


Figure 10. Typical Halon 1301 HF concentrations compared to average FM-200 only test results in the NMERI Field-Scale Test Chamber (agents tested as streaming agents).

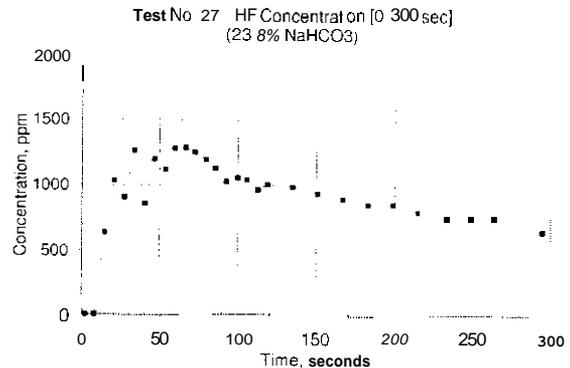
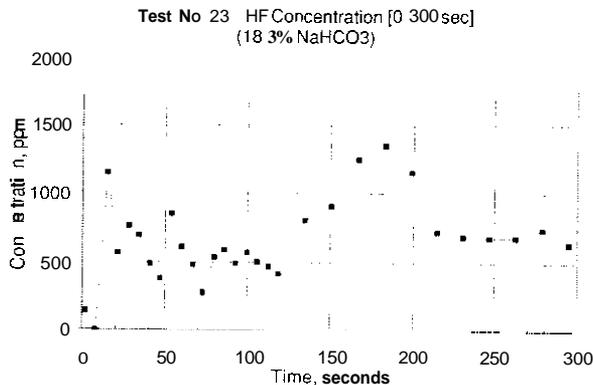
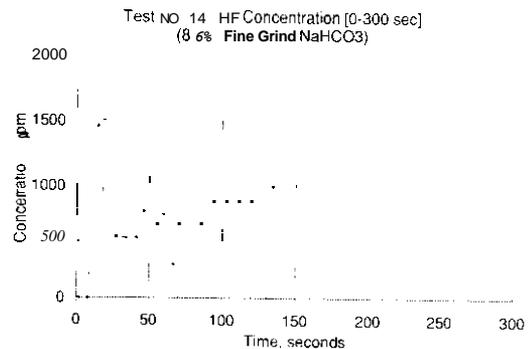
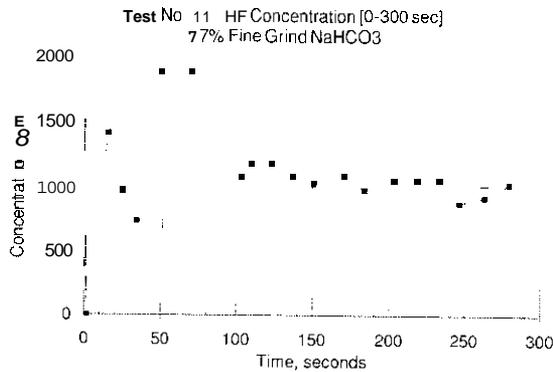


Figure 11. HF concentration versus time for selected FM-200 and sodium bicarbonate tests.

time to extinguish the fire). As expected the least amount of HF was formed with Halon 1301. Straight FM-200 generated higher HF concentrations than when blended with the powders due to both decreased extinguishment time and HF adsorption by the powders. The decomposition data indicates that there is a two-fold benefit when blending powders with halocarbons. The benefits are increased agent effectiveness and reduced decomposition products (mainly HF). The resulting HF concentrations with the addition of the tested powders were still higher than when Halon 1301 was used. These HF concentrations exceeded toxic levels for human inhalation exposure.

US MARINE CORPS AAV TEST PROGRAM

NMERI personnel under contract to Santa Barbara Dual Spectrum performed agent and decomposition product measurement tasks during tests planned and conducted by General Dynamics Amphibious Systems and Santa Barbara Dual Spectrum. Test site support was provided by the Marine Corp Amphibious Vehicle Test Branch (AVTB) (Camp Pendleton, CA), March–June 1999. The sampling and analysis of extinguishing agent and decomposition products were required to determine agent mixing/distribution within the test vehicle, and decomposition product concentrations resulting during each of the fire suppression tests. Data regarding carbon dioxide (CO₂), CO, HF, HBr, oxygen (O₂), noise level, and limited COF₂ were collected.

The test vehicle and NMERI sampling trailer are shown in Figure 12. The test events were fast growth fire conditions that may occur in the AAV crew and sub-floor compartments. The test sampling duration was 5 min. The fuel was military JP-8 heated to –160 °F. Over 100 tests were conducted. Limited data are presented in this paper. The majority of the tests were performed using FM-200 as the halocarbon agent blended with Ansul +50 sodium bicarbonate dry chemical powder (contains an anti-caking agent). A limited number of tests were also performed using a fine grind (< 7 micron) sodium bicarbonate powder. Test comparison plots are presented in Figures 13 through 16.

HF TOXICITY CONCERNS

There were several tests in which the maximum HF concentration requirement was exceeded for both 0–30 sec and for less than 5 min. Increasing the amount of added powder amount helped to minimize the HF levels; however, there is a concern that sodium fluoride (NaF) particulates are being formed. Insufficient data are available on the short-term (possibly high level, >1000 ppm) inhalation toxicity exposure to this compound. Concentration levels of this compound were not monitored in the test vehicle.

If NaF was not being formed, then the HF may likely be sticking to the outside of the powder particles. This may have made it non-detectable with the technique being used (no studies have been performed to investigate the effects of or if HF is “sticking” to the powder.) In the event HF is sticking to the particle surfaces then, there may still be serious toxicity exposure concerns (e.g., irritation, burning, etc. of the throat, nose, eyes, skin, lungs, etc.).

The discussion of HF exposure is becoming a serious topic as the testing and implementation of halon replacements continues. Dr. Brock [2] wrote in response to questions and concerns being raised by a Subcommittee following the issue for the National Fire Protection Association (NFPA) 2001 Standard Committee. The next revision (Year 2000 Edition) of NFPA 2001 will

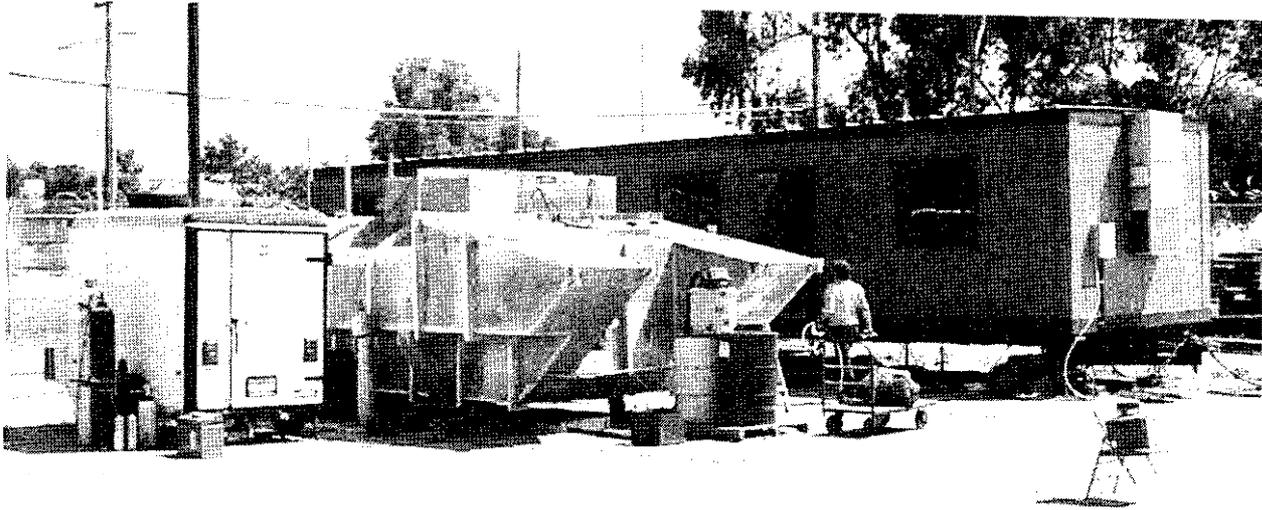


Figure 12. AAV crew compartment test setup, Camp Pendleton, CA.

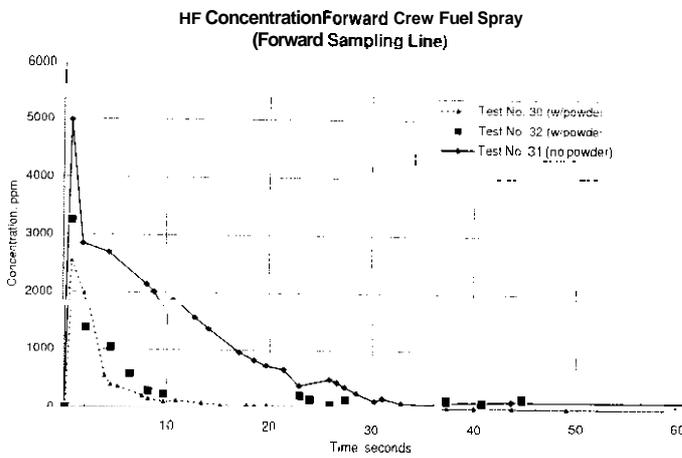


Figure 13. Comparison of forward crew fuel spray fire suppression HF concentration levels with and without the addition of Ansul +50 NaHCO₃ powder to FM-200.

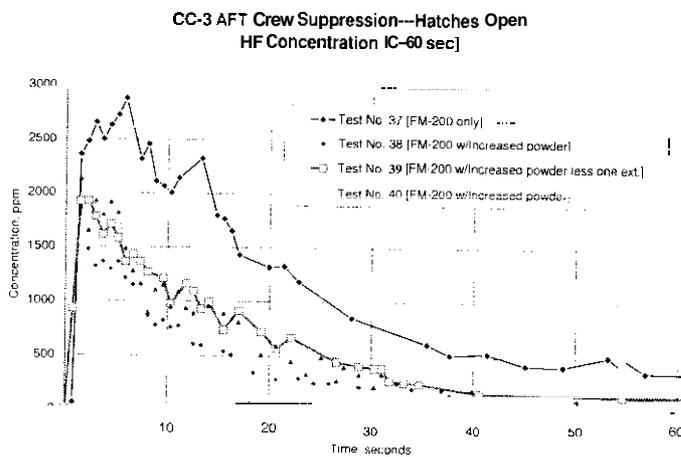


Figure 14. AFT (CC-3) Crew Suppression test data with hatches open showing the decrease in HF generation and the adsorption affect when NaHCO₃ powder was discharged into the test vehicle during the most severe test event.

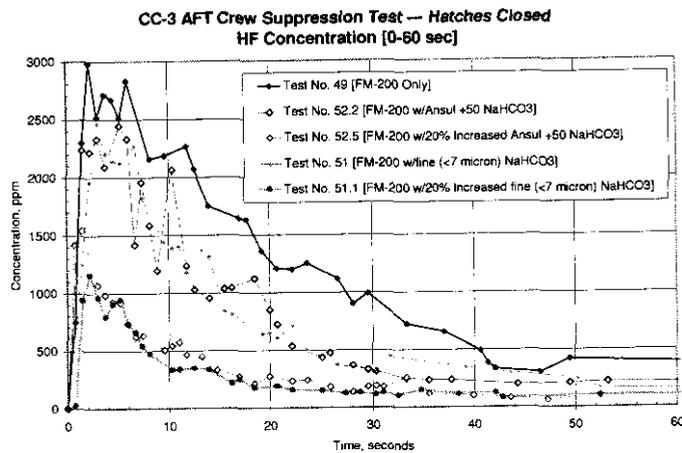


Figure 15. **AFT** (CC-3) Crew Suppression test data with hatches closed showing the decrease in HF generation and the adsorption affect when NaHCO_3 powder was discharged into the test vehicle during the most sever test event. Differences between Ansul +SO and fine grind ($<7 \mu\text{m}$) powder are illustrated.

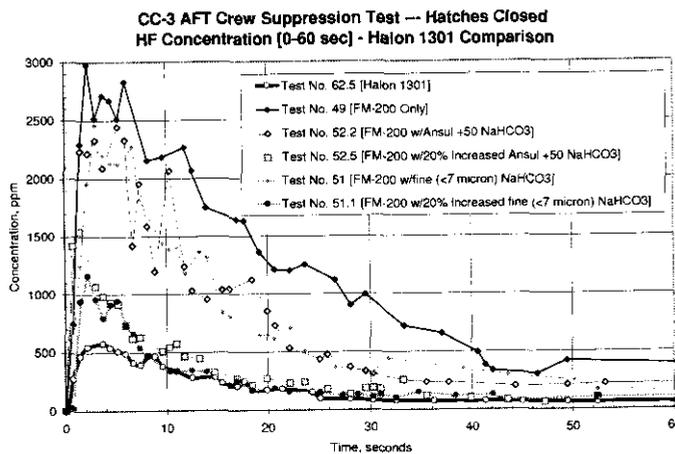


Figure 16. **AFT** (CC-3) Crew Suppression HF test data with hatches closed, comparing halon replacement test data with Halon 1301 baseline results. The superior performance of Halon 1301 over FM-200 and FM-200 with powders added is shown.

provide a detailed summary of HF exposure concern levels that were identified by the Subcommittee. The current thinking is that HF exposure concentrations greater than 200 ppm will likely impair personnel egress (Figure 17). Based upon these data, the HF concentrations measured during this test series are likely to be life threatening, taking in account the $C^2 \cdot t$ relationship discussed by Brock [2].

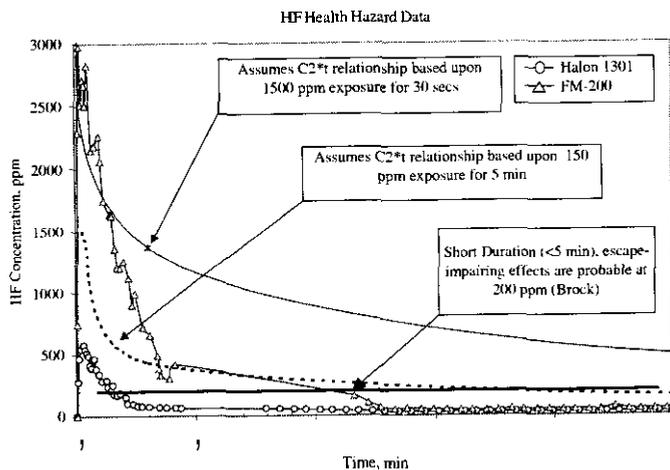


Figure 17. Comparison of HF levels generated during Halon 1301 and FM-200 CC-3 Fire Suppression scenario test (closed hatch) to HF health effect levels based on concentration versus time relationships.

CONCLUSIONS

The large amount of HF generated with commercial agents is a concern; therefore, other fire suppression agent solutions are being investigated for combat vehicle applications. The addition of powders (>5 wt%) to halocarbons reduces HF concentrations. The addition of powders also increases fire suppression performance. It has been shown that the powder act as HF scavengers. In general, the halocarbon/powder blend extinguishing agent successfully suppressed all of the test fires. There was good repeatability between the various tests that have been conducted. Measured HF levels exceeded human toxicity level of concern for some of the tests conducted.

HF scavenging was successful with the addition of NaHCO₃ powder to FM-200. Based upon the limited testing, powder particle size had little effect on HF reduction for the larger fire scenarios. The HF reduction was more dependent upon the amount of powder that was added however, for the small (less intense) fire scenarios, the smaller powder was a better HF scavenger, and stayed more dispersed throughout the test chambers.

RECOMMENDATIONS

1. The health related issues associated with inhalation of NaF should be investigated, as well as particle size effects. These issues need to be related to expected exposure times.
2. Additional scavenging powders should be investigated, as should the effect of particle size and amount of powder discharged.
3. Cleanup, corrosion, and related issues need to be addressed.
4. The effects of the agent distribution system on discharge time and agent dispersion need to be investigated. Faster discharges (through addition of more bottles, with less agent) will result in faster extinguishment times, thereby, reducing HF levels.

REFERENCES

1. Moore, Ted A., Manspeaker, Christopher E., and Lifke, Joseph L., *An Evaluation of Envirogel™ as a Halon Alternative*, POWSUS, Inc., Wayne, PA, August 1995. NMERI 1995/14.
2. Brock, W.J., "Hydrogen Fluoride: How Toxic is Toxic"? (A Hazard and Risk Analysis)," *Proceedings*, Halon Options Technical Working Conference, Albuquerque, NM, pp. 559-566. 1999.