NEXT GENERATION FIRE SUPPRESSION TECHNOLOGY PROGRAM: FY2005 PROGRESS

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INTRODUCTION

Initiated in 1997, the Department of Defense's Next Generation Fire Suppression Technology Program (NGP) has completed its eighth year of research. The NGP goal is to "develop and demonstrate technology for economically feasible, environmentally acceptable and user-safe processes, techniques, and fluids that meet the operational requirements currently satisfied by halon 1301 systems in aircraft."

Fires and explosions continue to be among the greatest threats to the safety of personnel and the survivability of military aircraft, ships, and land vehicles in peacetime and during combat operations. However, over the past eight years, research to identify replacement fire suppressants has declined considerably, despite the continuing need. To date, no commercial or military aircraft have had their halon 1301 systems replaced, while new systems are being installed in the cargo bays of commercial jetliners. Meanwhile, the international community is continuing to cast an eye on the necessity of maintaining the large halon 1301 reserves and even considering the requirement of a total phaseout. Thus, the demands on research to identify new approaches to aircraft fire suppression are unabated, nor have the demands on the new technologies lessened.

NGP technology is already having an impact on fire suppression systems, and NGP research has generated unparalleled contributions to the published literature, all of which can be obtained via the NGP web site: www.bfrl.nist.gov/866/NGP. Much of the most recent progress is being reported at this Conference. The following pages highlight the new knowledge gained from the NGP research and the progress made towards the NGP Goal. Recent publications are listed at the end. A concluding section summarizes the concluding steps for the Program.

TECHNICAL PROGRESS

Knowledge of the Flame Suppression Process

The NGP search for alternative suppressant technologies has included those for both volatile fluids and compounds whose vapor pressures were sufficiently low that they had to be dispensed as powders or aerosols. Research on the latter category has been completed. New technology for the dispersion of such compounds in solid propellant fire extinguishers and powder panels has been passed to the testing and evaluation community.

Through this year, NGP research has evolved the following structure for describing the potential for an agent to emerge from its storage bottle, flow through distribution plumbing, be dispersed

into the engine nacelle or dry bay, transport around obstructions to reach the site of the fire, and volatilize sufficiently to overwhelm the flames. More complete exposition of some of these components is the subject of remaining NGP research.

- If the agent is above its freezing point and if the pressure in the storage bottle is maintained as the agent is ejected, then nearly all the mass of stored chemical will reach the distribution plumbing.
- In different systems, the length of the distribution plumbing ranges from well under a meter to several meters. The flow through the piping depends on the temperature, the phase distribution of the fluid, the number and severity of bends, etc. The NGP has modeled (and validated) the transport of this transient two-phase flow in past years.¹
- The dispersed agent is generally a combination of vapor and liquid.
 - If the boiling point of the fluid is at or below the gas temperature in the nacelle, the liquid that emerges from the storage bottle will flash evaporate. The fraction converted to gas is estimated using the Jakob number, the ratio of the fluid's sensible heat to its heat of vaporization. This flashing is rapid relative to the transit time of the air flow through a nacelle and imparts substantial momentum to the gas and the smaller droplets that are formed. This favors rapid and efficient dispersion throughout the nacelle.
 - If the fluid's boiling point is above the nacelle air temperature and if the fluid is dispensed, rather than atomized, gravity will cause most of the fluid to drop to the bottom surface of the nacelle. At that point its entry into the air stream is by evaporation. Unless the evaporation rate is high, the storage of large amounts of suppressant is necessary to achieve the concentration needed to extinguish flames.
 - If there are nozzles at the end of the distribution plumbing, then some ensemble of droplet sizes is generated.
 - If the pressurizing gas is highly soluble in the liquid suppressant, flashing can occur at temperatures somewhat below the boiling point.
- The gaseous agent and the finer droplets are transported downstream within the nacelle. The larger droplets will generally fail to follow the main flow streamlines around any clutter and will impact the surfaces, forming pools from which evaporation is needed to resume transport downstream.
- Upon reaching the site of the flames, the agent available for suppression is the sum of the gaseous component plus that fraction of the droplets that can evaporate while in the high temperature environment of the flame. Smaller diameter droplets evaporate more

¹ Tuzla, K., Palmer, T., Chen, J., Sundaram, R., Yeung, W., "Development Of Computer Program for Fire Suppressant Fluid Flow Final Technical Report Volume I -- Main Report," (<u>6b1 Suppressant Flow Through Piping Final Report Vol. 1</u>), September, 2000.

Tuzla, K., Palmer, T., Chen, J., Sundaram, R., Yeung, W., "Development Of Computer Program for Fire Suppressant Fluid Flow Final Technical Report Volume II -- Input Manual for the Program Experimental Data Assessment of the Program," (<u>6b1 Suppressant Flow Through Piping Final Report Vol. 2</u>), September, 2000.

efficiently than larger ones. However, the nozzles that can generate such fine sprays generally have low throughput.

• The sustaining of a sufficient concentration of agent bathing the flame zone leads to flame extinction.

The NGP has also developed a new understanding of how efficient volatile chemicals interact with flames and eventually suppress them. This is summarized as follows:

Flame propagation results from the fast reactions of key species (H and O atoms, OH radicals) with vaporized fuel molecules. These species exist at concentrations far above those expected from thermal equilibrium at flame temperatures. Chemically active agents catalytically reduce the radical concentrations toward equilibrium levels. While this process slows the flame, it does not necessarily extinguish it. The suppressant also increases the heat capacity of the fuel/air mixture, reducing the flame temperature and thus the flame reaction rates below the level needed to sustain combustion. These two effects are synergistic. The contribution of both effects suggests that the lower limit for a suppression concentration may be at about 1 % by volume.

With this knowledge the NGP had developed a list of criteria to guide the search for candidate suppressant fluids:

- 1. Fire suppression efficiency at least comparable to halon 1301 (volume fraction about 0.03) and certainly higher than the hydrofluorocarbons (HFCs). Based on prior experience, this focuses the search on compounds that contain at least one bromine, iodine or phosphorus atom.
- 2. Short atmospheric lifetime (current preference of the order of a month), to keep ozone depletion potential (ODP), global warming potential (GWP) and any future unidentified environmental contamination issues to a minimum.
- 3. Boiling point sufficiently low that for gaseous agents, an extinguishing concentration can be achieved within a specified time following discharge. New knowledge of this process is described below.
- 4. Low toxicity relative to the concentration needed for suppression.

Minimum Release Temperature

There are few viable chemicals with boiling points, T_b , below the specified minimum operating temperature of -40 °C (-40 °F). Prior NGP experiments with CF₃I ($T_b = -22$ °C) have shown that it does not flash at this minimum temperature. All chemicals currently under consideration have boiling points higher than this, and their dispersion is thus characterized by the ability to evaporate rapidly.

Incorporating the chemical features that effect low atmospheric lifetime (criterion 2) generally results in molecules that are larger than halon 1301 and thus tends toward higher boiling points. Any increase in the specification for minimum operating temperature would allow consideration of molecules with higher T_b values. As T_b rises, there are more compounds per, *e.g.*, 10 °C band, so the domain of eligible chemicals increases significantly.

In September 2004, following a yearlong examination of mishaps, the DoD reaffirmed that

systems safety risk management should be integrated into overall safety engineering.² In anticipation of this, the NGP revisited the basis for the operating temperature requirement for halon (replacement) fire suppression systems.

Aviation fire incident data for the years 1980 through 2002 were obtained from the U.S. Army, Navy and Air Force Safety Centers, a total of 5236 incidents involving fixed wing aircraft and 1435 rotary aircraft. Each Safety Center also provided information on the altitude, outside air temperature (OAT), and location associated with many of the incidents.

Each fire incident was reviewed to determine whether agent release had occurred to protect an engine nacelle, auxiliary power unit (APU), auxiliary power plant (APP), or gas turbine compressor (GTC) compartment. For those incident reports in which the OAT was not included, it was estimated using the reported altitude and standard altitude-temperature curves. [The pertinence of these curves was verified using the incidents for which complete data were reported.] For incidents in which neither altitude nor temperature information were recorded, a methodology for assuming flight altitude based on aircraft flight phase³ was applied. The resulting distributions of discharges are shown in Figures 1 and 2 for fixed-wing and rotary wing aircraft, respectively.

The evaporation rate of a fire suppressant is also affected by the air temperature within the engine nacelle. Accordingly, an in-flight nacelle air temperature model was constructed to estimate nacelle air temperature during flight conditions. The accuracy of the model was checked using data from recent in-flight temperature measurements in rotary aircraft. The model tended to predict temperatures lower than those measured and is thus conservative.

The data indicate that only about 1 % of the incidents occurred in cold or severe cold climates. The principal findings of this analysis are:

- Nearly all releases of halon 1301 in military aircraft have been at temperatures higher than the design temperature of -40 °C. For fixed-wing aircraft, 75 % of the releases were at OATs above -25 °C (-13 °F); for rotary aircraft, 97 % were above -21 °C (-6 °F).
- The gas temperature in the engine nacelle has almost always been above -18 °C (0 °F).

This does not, of course, represent relief from the current specification; that is a DoD policy matter. Moreover, even if the specification were raised to -25 °C (-13 °F), this would not increase the list of otherwise acceptable chemicals that could flash. It would, however, increase the evaporation rate of those chemicals with moderately higher boiling points.

² Memorandum on Defense Acquisition System Safety from M.W. Wynne, USD(AT&L) of 23 September 2004.

³ Kolleck, M. L. and Jeffery, K., *Halon Discharges at Altitude*, Booz-Allen, Dayton, OH, June 1994.



CF₃I Properties

This chemical has flame suppression capability similar to halon 1301, but a higher boiling point and toxic potency. To date, it has been rejected for use within the U.S., but is being considered for application in other countries. The NGP conducted two small efforts on this chemical.

A fire extinguishing agent must be able to be stored for long periods of time at high pressure in metal containers without degrading and losing its effectiveness. CF_3I (and a variety of other candidate suppressants) had been placed in individual PTFE-lined steel stainless cylinders that also contained coupons of various metals from which agent storage bottles might be fabricated. These cylinders were stored at temperatures ranging from 22 °C to 150 °C for three years. Most of the samples showed no degradation. However, the combination of elevated temperature and copper-containing metals had caused serious degradation of the CF_3I in some of the vessels. The samples were then stored at about 22 °C for another five years. The subsequent analyses indicated no new compounds and no significant loss of the CF_3I .

Were CF_3I to be substituted for halon 1301, it would likely be released to the environment in a similar manner and frequency. When released at altitudes below the stratosphere, CF_3I has a very short atmospheric lifetime compared to halon 1301. A prior analysis of such a substitution

for fuel tank inerting in the F-16 showed that the substitution might not have a significant benefit for that application. The historic profile and magnitude of halon 1301 releases for engine nacelle fire suppression are different from that for fuel tank inerting. A calculation to estimate the effect of the substitution for the nacelle application is underway. The data for the altitude release profile came from the compilation discussed in the prior section of this Report.

New Candidate Suppressants

The NGP identified nine chemical families whose consideration would complete the screening for new alternatives. These are described in Table 3.

Chemical Family	Initial Compound(s)	Notes	
bromofluoroalkenes	CHF ₂ CBr=CF ₂	Cup burner value was 0.033. $T_b \approx 30$ °C. Only consider other compounds with lower T_b values.	
bromofluoroalkylethers	CBrHFOCF ₃ CBrF ₂ OCHF ₂	T_b expected to be 5 °C to 15 °C. However, attempts at synthesizing them failed.	
	CF ₂ HCFBrOCF ₃ CFBrHCFHOCF ₃	Compounds are on order. Estimated T_b values are 42 °C and 37 °C. Other compounds will be acquired only if they have lower T_b values.	
bromofluorovinylethers	CF ₂ BrCF ₂ OCF=CF ₂	T_b measured as ≈ 55 °C, and the cup burner value was 0.045. Only consider other compounds with lower T_b values.	
fluoronitriles	CF ₃ CN	Commercially available; $T_b = 4 ^{\circ}C$. Cup burner value was 0.09, no better than HFC-125. No compounds from this group to be acquired.	
bromofluoronitriles	CF ₂ BrCN	T_b is 3 °C, cup burner value < 0.04; should have a short atmospheric lifetime. A recent, unpublished report indicates this compound is highly toxic. This is being checked.	
bromofluoropropeneoxides	CF ₃ CBr(O)CF ₂	Cup burner value was a marginal 0.049. $T_b \approx 20$ °C. A low atmospheric lifetime was expected. Only consider other compounds with lower T_b values, not a likely occurrence.	
N-bromofluoroalkylamines	(CF ₃) ₂ NBr	The compound has been ordered. $T_b \approx 22$ °C. Additional compounds will be considered only if they have lower T_b .	
bromofluoroalkylamines		No sources of any compounds have been found.	
N-bromofluoroimines	CF ₂ =NBr	T _b is 14 °C. The compound has been ordered. Additional low boiling analogs to be checked if the first suppression result is favorable.	

Table 1.Representative Compounds for Screening

Limits to Effectiveness of Metal-containing Compounds

There has been extensive research on the extraordinary flame *inhibition* effectiveness of ironcontaining compounds. In these laboratory tests, small amounts of the compounds fractionally reduced the flame burning velocity far more efficiently than did halon 1301. However, in no cases were the flames extinguished. NGP research has developed an explanation for this binary behavior. The addition of small amounts of the compound catalytically recombines hydrogen atoms, reducing the concentration of the prime attacker of fuel molecules. As more of the compound is added, the higher concentration favors condensation to inert iron oxide particles. Thus, there is never enough of the flame retarding species to extinguish the flame.

Compounds of other metals, if they were effective flame suppressants, would likely be either solids or viscous liquids, not suitable for use as suppressant fluids. They could, however, be incorporated into solid propellant fire extinguishers (SPFE). [In fact, it was NGP SPFE experiments with ferrocene that demonstrated the inability of an iron-containing compound to quench larger flames.] It was thus important to know whether any other metal-containing compounds might have potential for this use.

The NGP undertook a review and analysis of the literature to understand metal chemistry in flames. This included a detailed examination of the mechanism of inhibition of iron and the reasons for its loss of effectiveness, the demonstrated flame inhibiting properties of other metals, and the potential loss of effectiveness for them. The literature analyzed included that on engine knock, premixed and diffusion flames, flame retardancy, ignition, rocket nozzles, and NO formation. The metals covered were chromium, lead, manganese, tungsten, molybdenum, tin, cobalt copper, and antimony. This work has uncovered that tungsten, molybdenum and cobalt are likely to be effective inhibitors at low concentrations, results that have not been suggested in previous reviews of flame inhibition by metal-containing compounds.

There are several screens for estimating whether other metallics will have a loss of effectiveness similar to that of iron. Table 4 summarizes the results of this screening analysis for whatever compounds of these metals have been examined. The metals are listed in roughly decreasing order of inhibition effectiveness, based on the literature review. A prospective SPFE additive should have a mark in the first column and no marks in the three right-hand columns. The absence of a mark indicates that there are no reported studies or that the results are inconclusive.

For W, Mo, Co, and Cu, there is no direct evidence of the potential for loss of effectiveness, and the vapor pressures of the suggested flame-quenching species (for which data are available) are reasonably high. For Co, the monoxide CoO is likely to be an important intermediate in the inhibition cycle. Its low vapor pressure can be taken as evidence for the potential for condensation. Nonetheless, the potential for condensation of metal species really depends upon the local super-saturation ratio in the inhibited flame. Calculation of the super-saturation ratio depends upon knowing both the detailed kinetic mechanism of inhibition as well as the vapor pressure of all of the intermediate species. Further, the kinetics of the condensation (and potential re-evaporation of particles) will be highly dependent on the flow-field of the particular flame system to be extinguished. *Prediction* of the potential loss of effectiveness due to condensation is beyond the current state-of-the-art.

Table 2. Evidence Regarding Potential for High Flame Suppression Efficiency of Metalcontaining Compounds

Metal	High Inhibition Efficiency	Loss of Effectiveness	Presence of Particles	Evidence of Saturation
Cr	Y	Y	Y	Y
Pb	Y	Y	Y	Y
Mn	Y	Y	Y	Y
W				
Мо				
Sn	Y	Y	Y	Y
Со	Y			
Cu				
Sb	Y	Y	Y	Y

Prior NGP experiments with K_2CO_3 added to an SPFE have shown a significant increase in flame extinguishment efficiency relative to the same formulation without the potassium salt. These results were verified in real-scale engine nacelle fire tests. Thus, the current results provide backup only in case potassium salts manifest some other undesirable behavior.

Should more definitive information on compounds containing these metals be desired, two possible screening experiments are suggested:

- Cup burner tests would determine the amount of a diluent (e.g., CO₂, or N₂) added to the air stream necessary to cause blow-off of the cup-burner flame, both with and without the metal agent added at increasing concentration in the oxidizer stream.
- Addition of metal-containing compounds to an SPFE. There is inert gas in the effluent, as well as fragmented metal-containing species, so that by proper application to an appropriate fire, the utility of the metal additive could be assessed at larger scale. The challenge would be to find a configuration that has the proper sensitivity to the inert gas flow so that the effects of the additive could be quantified.

Fire Suppressant Dynamics in Cluttered Engine Nacelles

The objective in this portion of the NGP is to provide the basis for optimizing the distribution of suppressants, thereby improving the suppression efficiency of gases and aerosols that are less effective than halon 1301. The tool by which this guidance is to be delivered is a validated computational fluid dynamic (CFD) model of suppressant flow, a fire, and fire extinguishment in cluttered environments. Earlier components of this effort had been development of understanding of suppressant droplet dynamics around obstacles and upon impact on cold and heated surfaces, extension of this knowledge to spray-clutter interactions in a wind tunnel, adaptation of the Vulcan CFD model for simulating these suppressant-laden flows, and examination of the effect on agent distribution of varying the number of agent injection nozzles.

This year, a first series of fire suppression tests were conducted in the NAVAIR F-18 E/F Ground Engine Nacelle Simulator and the results compared with simulations previously made using the CFD computer code. The 25 experiments were designed to explore the envelope of

test conditions under which flame extinguishment did and did not occur. Figure 3 is a photograph of the test fixture. The nacelle is ca. 3.18 m (125 in.) in length. The height and width vary along the length, but they are contained within a region 1.45 m high and 1.15 m wide. The engine surface, a hollow cylinder, has a diameter of 0.77 m in the front (the left in the Figure), narrowing to 0.62 m at the rear. Air and agent are introduced into the nacelle through the diagonal pipe at the lower left of the photograph. The intake air flow is turbulent even without the clutter-induced mixing. Clutter objects are located along its length. There are ribs and longerons, along with other clutter, along the length of the nacelle (Figure 4a) and a gearbox assembly located 0.1 m to 0.75 m from the forward end and mostly below the engine (Figure 4b).



Figure 3. Photograph of the NAVAIR F-18 E/F Ground Engine Nacelle Simulator



4a

4b

Figure 4. Photographs of Ribs/Longerons and Gear Box Assembly

Before conducting fire suppression tests, determinations were made of the accuracy with which the model simulated the distribution of fire suppressant in the fixture. Measurements of HFC- 125 (C₂HF₅) were made at 12 locations using a Halonyzer II. Figure 5 compares the predicted concentration of HFC-125 at two of those locations with the predicted concentrations for two different injection durations. The actual agent release duration was 2.7 s. As the agent concentration rises, the simulation with a 3 s injection period replicates both sets of test data well. The model reasonably replicates the flushing of the agent from the nacelle at location 3. For location 1, the model flushes the agent too quickly. The discrepancy is likely due to two idealizations in the model. First, the agent dispensing is simulated as a square wave, while in the test there is a "tail" to the ejection as the pressure in the storage bottle decreases. Second, the model assumes that the agent flashes completely upon injection, while in the tests there was some downstream evaporation of liquid. The discrepancies on the "down" side of the curves are relatively unimportant since the fires will typically have already been quenched.

For the fire suppression tests, pools of JP-8, each 0.09 m^2 in area, were situated at three locations (all downstream of ribs) on the nacelle floor below the engine. Variables in the tests included mass of suppressant in the storage bottle, discharge rate of the agent, air flow, and one-at-a-time capping of three of the four agent injection nozzles. Within the apparatus geometric limits and the physical properties of the suppressant, it was not possible to replicate exactly the Vulcan simulations in all cases. However, the test matrix did preserve the trends of configuration and flows from the simulations.



Figure 5. Comparison of Measured and Simulated Concentration Throughout a Discharge Test

Two parameters determined the average overall suppressant mass fraction in the test fixture:

1. The ratio of "suppressant" mass inflow to "suppressant plus air" mass flow determined

the maximum value attainable for long times, referred to as the inflow ratio.

2. The "suppressant plus air" flow determined the time to reach these maximum values. This time was generally much less than the injection duration, indicating that the maximum values were closely approached.

It was a very successful series of tests. In all but two cases, the model and the test agreed as to whether the fire was extinguished or not. Figure 6 shows the inflow ratio in the tests for which Vulcan simulation had been performed. For each test, the top three bars are the estimated inflow ratio based on the measured pressure drop at the storage bottle over 1 s, 2 s, and 3, s. The "target" bar represents the theoretical fraction, as employed in the Vulcan simulations.

When the agent inflow ratio, based on the bottle discharge was below about 0.43 (mole fraction about 0.15), the fires were not extinguished. This inflow ratio corresponds to an average mole fraction of 0.15, almost twice the cup burner suppression value. This indicates the significance of inhomogeneities within the nacelle, i.e., some regions have a much lower mole fraction than the average.



Figure 6. Agent Injection Ratios

Additional tests were also conducted where individual nozzles were removed to increase the degree of inhomogeneity of agent distribution. The results indicate that Vulcan predicts somewhat greater sensitivity to removing nozzles than is observed in the tests. Analysis of all the data from the experiments and simulations is underway.

Verification of NGP-Developed Fire Suppression Principles

Planning is underway for a series of about 1000 real-scale engine nacelle fire suppression tests. These are scheduled for summer 2005. Their purposes will be (a) to verify the fire suppression principles developed in the NGP by comparing the outcome of the tests with predictions based on NGP-developed technology and (b) to identify any as-yet unexplained suppression phenomena. Candidates for test variables include nacelle temperature; agent storage temperature; number, nature and location of injection ports; agent chemistry and thermophysical properties; fire type, and agent mass.

Each test sequence involves tests at several agent concentrations (to determine the mass needed for flame extinguishment) and replicate tests (to mitigate the occurrence of single anomalous results). A factorial experimental design will be used to extract the maximum amount of information from the modest number of tests.

WHAT LIES AHEAD?

The Next Generation Fire Suppression Technology Program will reach completion in FY2006. At that time, the NGP will have met its goal to develop and demonstrate technology for economically feasible, environmentally acceptable and user-safe processes, techniques, and fluids that meet the operational requirements currently satisfied by halon 1301 systems in aircraft. The completion of the NGP will mark the end of DDR&E's program in fire suppression and will provide a sound technical basis for future fire suppression systems and research efforts.

The remaining tasks are completion of assessment of the nine chemical families, completion of guidance for efficient agent delivery, verification of the effectiveness of the new distribution principles and the relative performance of chemicals, and preparation of the NGP final report. In book form, this will pull together the new knowledge into a unified package. In addition to these, the NGP expects to continue sponsorship of the Halon Options Technical Working Conferences through FY2006.

RECENT PUBLICATIONS

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