NIST Technical Note 1437

FY2000 Annual Report
Next Generation Fire Suppression Technology Program (NGP)

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National Institute of Standards and Technology
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NGP
NEXT GENERATION FIRE SUPPRESSION TECHNOLOGY PROGRAM

FY2000 ANNUAL REPORT

Next Generation Fire Suppression Technology Program (NGP)

[PP-1059]

Richard G. Gann
Technical Program Manager
January 22, 2001

ABSTRACT

The Department of Defense's Next Generation Fire Suppression Technology Program (NGP) has completed its fourth year of research with a revised goal to develop and demonstrate, by 2005, 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. Research to complete a suite of suppressant screening tests is virtually complete. Research on new flame suppression chemistry, new and improved aerosol suppressants, improved suppressant delivery, and viability of new suppressant technologies has produced substantive results. The NGP has also completed a scoping study on technologies for improved fuel tank inertion.

Keywords: fire research, fire suppression, halon, aircraft

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I. INTRODUCTION

This is a year of transition for the Next Generation Fire Suppression Technology Program (NGP).

The Department of Defense (DoD) had initiated the NGP in FY1997, with a goal to develop and demonstrate, by 2004, retrofitable, economically feasible, environmentally acceptable, and user-safe processes, techniques, and fluids that meet the operational requirements currently satisfied by halon 1301 systems in existing weapons systems. Fires and explosions were (and are) 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. Production of halon 1301 (CF_3Br), long the fire suppressant of choice, had ceased as of January 1, 1994 due to its high ozone-depleting potential (ODP). By 1997 the DoD had identified the best available replacements for halon 1301, but each had unresolved operational features that compromised its implementation. The new Program was to identify fire suppression technologies with reduced compromises.

Support for the NGP was to come from the DoD Strategic Environmental Research and Development Program (SERDP), the Military Department Science and Technology Programs, and cost sharing from the participating laboratories. However, full support from the Military Departments did not materialize, and in November 1999, agreement was reached on an NGP of about half its original size. SERDP committed to maintaining its support, but at a lower level beginning in FY2002. The NGP goal was modified in keeping with the new level of resources:

> "Develop and demonstrate, by 2005, 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 focus on aircraft fire suppression emerged from the aircraft safety and survivability engineering teams from all three Services having fire suppression needs for engine nacelles and dry bays that were not being supported by research efforts outside the NGP. The NGP strategy has been updated and can be found at the NGP web site: www.dtic.mil/ngp/.

The demands on the new fire suppression technologies have not lessened. They need to be of low mass and volume and compatible with the host aircraft design. New chemicals must have high suppression efficiency and perform well in evaluations of ODP, global warming potential, atmospheric lifetime, reignition quenching, residue level, electrical conductivity, corrosivity to metals, polymeric materials compatibility, long-term storage stability, toxicity of the chemical and its combustion and decomposition products, speed of dispersion, and occupational safety.

The expectations from the NGP were reduced. By FY2001, the NGP would deliver understanding of how chemicals must interact with flames to be as effective as halon 1301, appraisal of the world of useful chemicals, identification of the best places to look for alternative suppressants and a first set of "best looks," a suite of screening tests and guidance for their use, and a method for comparing the life-cycle costs of new fire suppression technologies.

At the end of FY2000, the NGP has completed its fourth year of research, having expended about two thirds of the planned resources and having produced nearly all of these deliverables. The following section of the report highlights the new knowledge gained from the NGP research and the progress made towards the NGP Goal. A concluding section forecasts where the research will proceed from this time forward. An appendix lists all the NGP projects.

II. TECHNICAL PROGRESS

A. SUPPRESSANT SCREENING TESTS

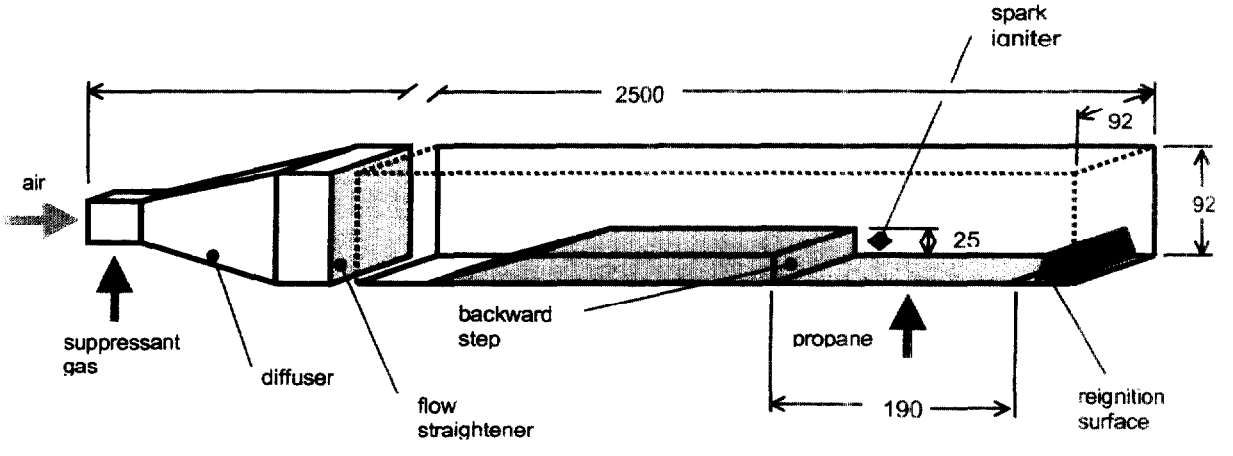
The NGP development of a set of efficient, accurate screening tests for new suppressant chemicals will soon be completed. Already completed and published are protocols for:

- Progressive evaluation of compounds for environmental impact, toxicity, and materials compatibility
- Evaluation of inhalation toxicity using a human pharmacokinetic model
- Screening for fire suppression efficiency of gases and liquid aerosols. As discussed below in Section II.A.2, our research has uncovered complexities in the use of some laboratory flames to assess the suppression performance of certain types of agents. Resources will be dedicated in FY2001 to identify one or more proper burners and operating conditions.

1. Transient Application, Recirculating Pool Fire (TARPF) Facility

We have completed work on this last screening tool (Figure 1), one which can simulate situations not possible in cup or Tsuji burners: impulsively discharged gases (such as from a pressurized storage bottle or solid propellant gas generator, SPGG); the impact of a hot surface on continuous suppression, the impact of a recirculating flow; and the impact of a liquid spray. Current resource levels will defer the inclusion of aerosol suppressants until the demand arises.

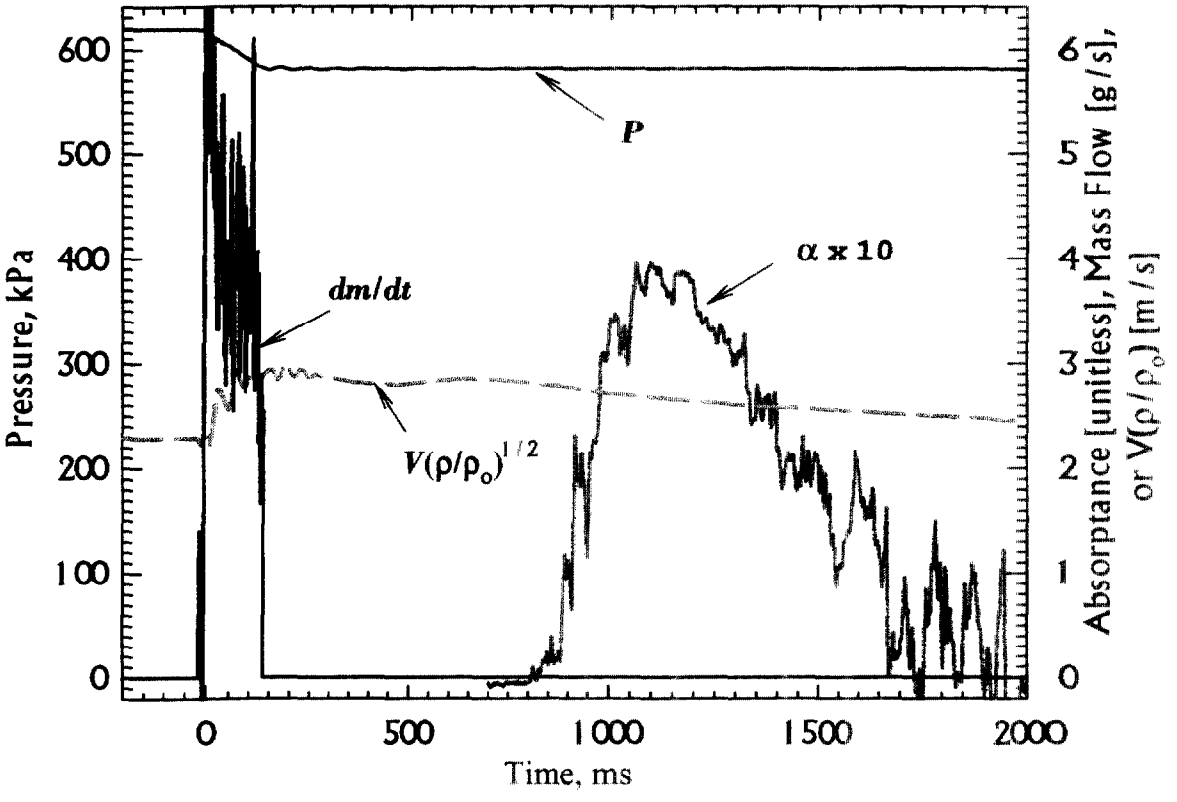
Figure 1. Schematic of TARPF (dimensions in mm)



In a successful test of a transient-discharged suppressant, the agent must be present in the flame zone at a design concentration for a sufficient residence time to ensure that the flames are quenched and do not re-ignite. Because of the complex flow pattern, the concentration/time profile of the agent in the flame zone will not be the same as the mass loss profile from the storage container. Figure 2 shows the time history of a typical HFC-125 discharge in the TARPF. The absorbance (α) of the chemical is measured downstream of the backward step

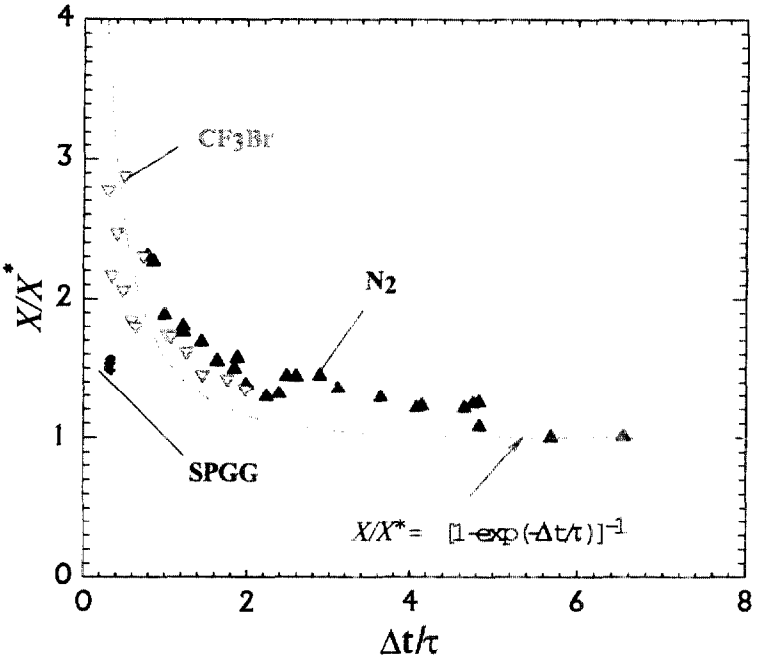
using the DIRRACS (Differential Infrared Rapid Agent Concentration Sensor) instrument described further in Section II.E. The velocity 76 mm upstream of the burner was measured using a pitot probe and the mass flow from the change in pressure in the bottle. The broadening of the agent arrival at the flames highlights the importance of measuring the agent concentration locally and the difficulty in relating changes in bottle pressure to actual mixing conditions.

Figure 2. Time History of a HFC-125 Discharge in the TARPF



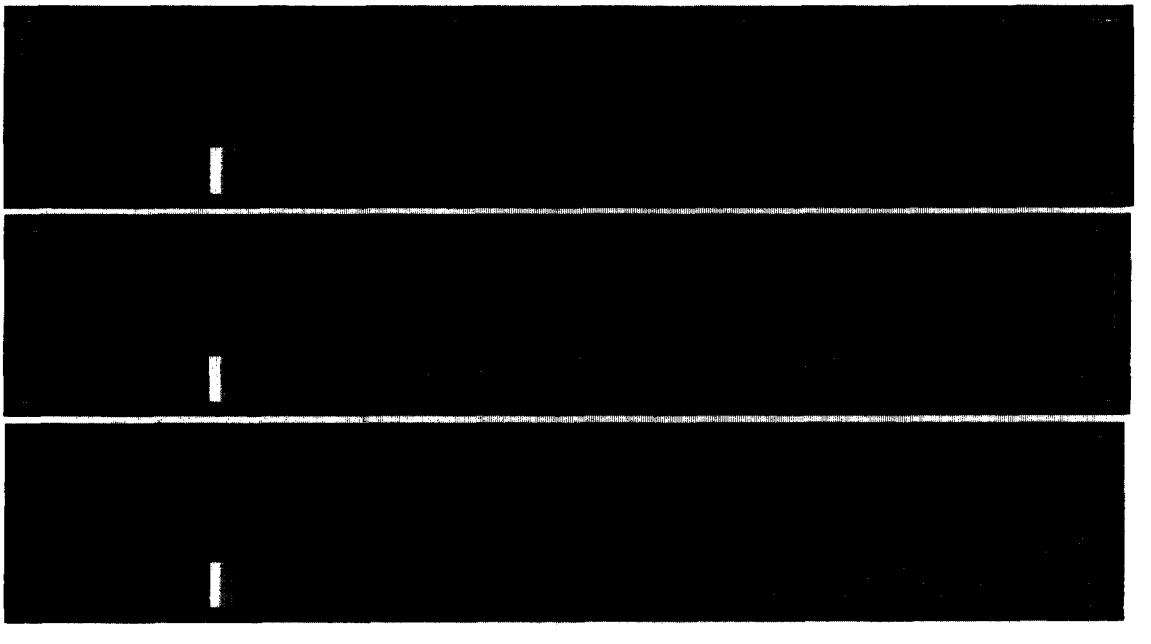
The capability to test SPGGs has been added to the TARPF. For the first time, both compressed and solid-propellant-generated gases can be compared side by side, and the effect on performance of different formulations, particle loadings and burning rates for various SPGG designs can be unambiguously discriminated. The fact that in Figure 3, the different agents all lie close to the theoretical equation in the attached plot shows the value of this new apparatus, whether the agent is chemically active or physically active and whether the agent is discharged from an SPGG or a compressed gas storage bottle. A workshop with SPGG manufacturers was held in September to identify issues regarding the measurement and use of SPGGs in various fire suppression applications including weapons systems. A summary report is in preparation.

Figure 3. Comparison of N_2, CF_3Br, and SPGG Effectiveness in the TARPF



One-step chemistry has been added to the direct numerical simulation discussed last year to enable flame extinction by a thermal gaseous agent to be modeled. The computer output in Figure 4 indicates how the heat release rate (red implies high values and black no reaction) is diminished shortly after the agent (N_2) enters the flow impulsively from the left. The simulation reproduces the experimental extinguishment data for N_2 effluent quite well.

Figure 4. Simulated Extinction of a Propane Flame by N_2



From such simulations and related experiments, it was determined that the most difficult fire to extinguish results when the flame is anchored to the trailing edge of an obstacle in the flow and is established in the mixing layer between the re-circulation zone immediately behind the step and the main flow.

A JP-8 spray was added to the TARPF to supplement the gaseous propane pool. The presence of the spray had little effect on the amount of gaseous agent required for flame extinction. At hot surface temperatures above 800 °C, the flame would almost always re-ignite and stabilize on the hot surface. At temperatures much below 800 °C, the number of re-ignitions approached zero. When the hot surface is moved between the stabilizing step and the propane pool, ignition delays on the order of seconds occurred at temperatures as low as about 400 °C. This difference occurs because the time interval in which a flammable mixture is in contact with the hot surface increases by about an order of magnitude. In general, the worst case for re-ignition (minimum re-ignition time) occurs when the time required to mix the air and fuel is short compared to the time necessary for the fuel surface to cool.

Experiments were begun with HFE-7100 (1-$CH_3OC_4F_9$), a thermally active aerosol suppressant which had been shown to be more efficient that halon 1301 in suppressing open diffusion flames in the DLAFSS (Dispersed Liquid Agent Fire Suppression Screen). Thermal suppressants should be less effective at suppressing fires stabilized behind clutter, and that was the case in the first TARPF tests. Further experiments will be needed to explore the role of mixing and fluid flow/droplet interactions in extinguishment effectiveness for agents released as liquids.

2. Laminar Flame Burners for Fire Suppression Effectiveness Screening

NGP research has now investigated a range of chemical families, looking for candidate agents and for understanding of how they function to quench flames. The latter is especially important, both for considering the potential of agents that have not yet been synthesized and for gaining confidence that the chemicals will be effective on the practical fires of concern.

Late in this process, we have found that the effectiveness of some types of chemicals varies significantly in different laboratory tests. The following discussion presents the information derived to date and a sense of where it is important to find resolution.

a. Inert Agents. NGP experiments with gaseous thermal agents indicate that extinguishing concentrations for diffusion flames are dependent on both the flow configuration of the burner and the fuel that is used, but the relative effectiveness of a set of thermal agents remains fixed.

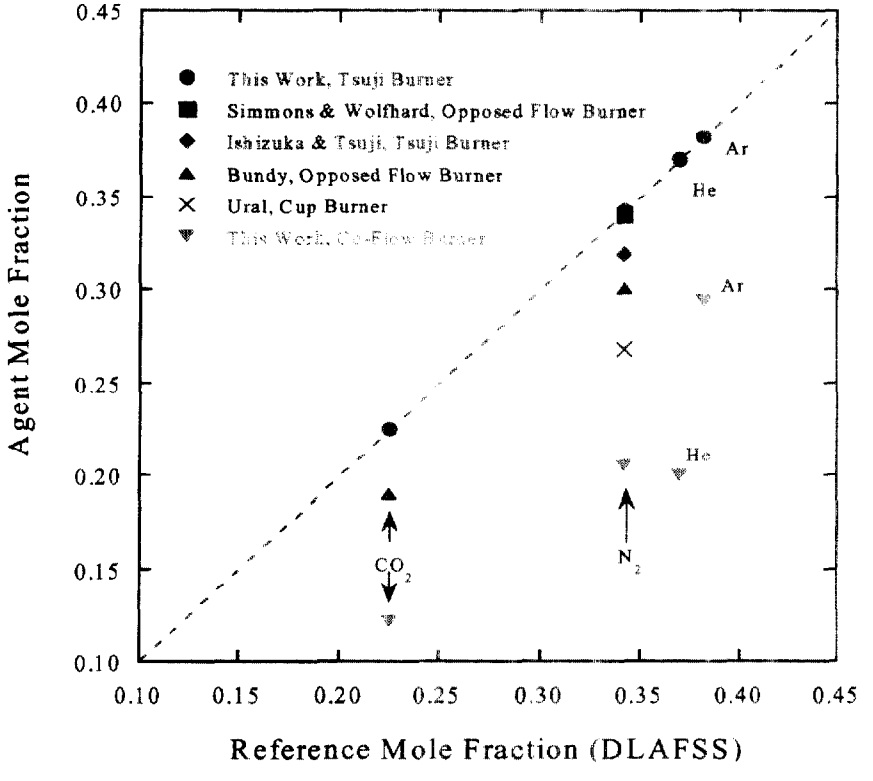
Experiments in a cup-burner-like apparatus (co-flow diffusion flame) showed that about 20 % more by volume of an inert agent (nitrogen, carbon dioxide, argon, or helium) was needed to extinguish a propane/air laminar diffusion flame than a similar methane flame. The relative extinguishing concentrations of the agents were the same as measured in a cup burner, but the absolute values were lower, an effect apparently associated with the smaller diameter of the fuel tube used in the current system. Similar experiments were conducted in the counterflow diffusion flame of the DLAFSS. Once again, the extinguishing concentration of each agent was

higher for the propane flames than for the methane flames and the relative order of effectiveness for the thermal agents was maintained. The absolute extinguishing concentrations for the various thermal agents were higher than observed in both the current co-flow studies as well as published cup burner studies. Figure 5 compares the measurements from the DLAFSS with those observed for the co-flowing burner as well as literature measurements for other types of diffusion flame burners.

Detailed kinetic modeling of laminar propane and methane diffusion flames indicates the following reason for the difference in their ease of extinguishment. Reducing the maximum flame temperature to 1550 K results in extinguishment of a laminar methane flame diluted with a thermal agent, while the corresponding temperature for a propane flame is 1433 K.

In summary, different types of laboratory diffusion flames produce similar *relative* values for inert suppressants. There are reasonable explanations for the differences in *absolute* extinguishing concentrations. The DLAFSS (Tsuji burner) produces the most conservative results.

Figure 5. Extinguishing Mole Fractions of Inert Suppressants in Various Methane/Air Laboratory Burners

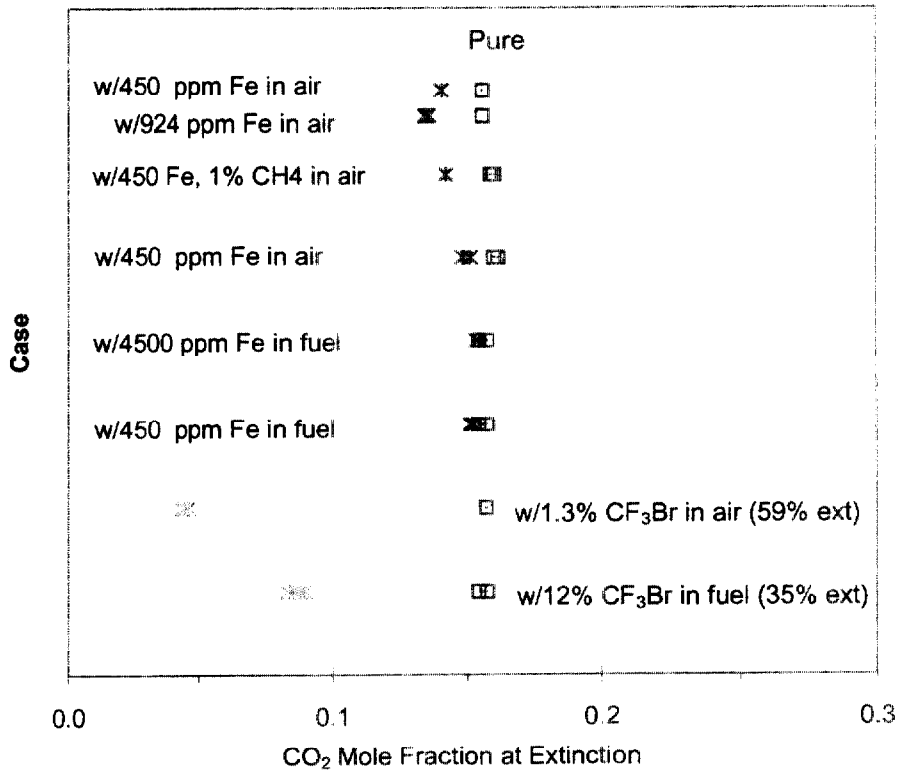


b. Metal-containing Compounds. The NGP has developed evidence that further examination is needed regarding the use of premixed and highly strained diffusion flames to

assess the suppression efficiency of "super-effective" chemicals such as those containing metal atoms. Based on NGP modeling and experiments with such flames, it was expected that ferrocene in a thermal bath should be a powerful suppressant of practical flames. Experiments (discussed below in Section II.D.1.c) were performed in which hot product gases supplied from an SPGG passed through a bed of ferrocene and then to a spray flame. Surprisingly, the combination did not have the intended high efficiency and failed to extinguish the flame. While, as discussed below, this may well be attributed to inefficient delivery of the ferrocene to the flame, further examination at laboratory scale seemed warranted.

Tests were then performed in cup burner flames to explore possible reasons for this lack of effectiveness. The addition of $Fe(CO)_5$ alone to the air stream of a cup burner would not be expected to be efficient at extinguishing the flame since particle formation keeps the maximum inhibiting species mole fractions below the extinguishing value. However, the addition of small amounts of ferrocene or $Fe(CO)_5$ to the air stream should significantly reduce the amount of CO_2 necessary to extinguish the cup burner flame. Surprisingly, the addition of about 450 ppm (v/v) of $Fe(CO)_5$ to the air stream of a heptane-fueled cup burner barely reduced the amount of added CO_2 required for extinction (Figure 6). (Adding 150 ppm of $Fe(CO)_5$ to a premixed methane-air flame reduces by a factor of eight the amount of CO_2 required to halve the burning velocity.)

Figure 6. Extinction Mole Fraction of CO_2 in Methane/Air Cup Burner Flames



Similar ineffectiveness was observed with non-sooting methanol as the fuel and even in a methane diffusion flame, with the suppressant mixture added to either the air or fuel stream of the latter. The methane data suggest that agent transport to the flame front is not the cause of the conflicting extinguishing concentrations. These results contrast with those for a CF_3Br-CO_2 mixture, where addition of CF_3Br to either stream at mole fractions which would approximately halve the premixed flame burning velocity leads to a reduction of the CO_2 required for extinction by a factor of two to three.

Aqueous solutions of several metallic compounds were tested in the DLAFSS to determine whether the suppressing concentrations were statistically indistinguishable from what was obtained with pure H_2O. Solutions of two copper salts, $CuBr_2$ and $CuSO_4$, were not. As can be seen from Table 1, the iron, sodium and manganese salts were highly effective additives. The iron result is consistent with the finding from the opposed flow diffusion flame, OFDF (which has a higher flame strain rate), and at odds with the lower strained cup burner flames.

Table 1. Agent Concentrations at Blow-off in the DLAFSS

Molecule	Mass Fraction	Mole Fraction
H_2O	5.7×10^{-2}	9.0×10^{-2}
$FeNH_4SO_4$	2.0×10^{-3}	3.4×10^{-4}
NaH_2PO_2	5.0×10^{-3}	1.4×10^{-3}
$Mn(C_2H_3O_2)_2$	2.3×10^{-3}	4.7×10^{-4}

c. Halogenated Agents. Numerous experiments with diverse laboratory burners and practical flames (notwithstanding the poor performance in the SPGG experiments reported in Section II.D.1.c) have shown reasonable consistency in the concentrations of gaseous halogenated agents needed for flame extinguishment. This includes chemicals including fluorine, chlorine, bromine and/or iodine atoms and both chemicals with catalytic activity and those with none. There are larger effects from differences in the dispersion of the chemicals and in the fractions in the liquid or gaseous state when nearing the flame zone. To a first approximation, the flame quenching efficiency of gaseous halogenated chemicals depends on the density of bromine, chlorine, and/or iodine atoms delivered to the flame zone. CF_3 groups provide some enhancement; combustible groups contribute to the fuel load and reduce suppressant effectiveness. Any of the laboratory diffusion flames are thus useful to verify that a halogenated chemical is not unusual. The DLAFSS allows examination of the added contribution of the heat of vaporization.

There may be some clues regarding this disparate behavior of metal atoms from kinetic modeling of inhibited premixed flames. There, CF_3Br only reduces radical concentrations to a significant extent in the early, low temperature region of the flame, unlike iron and sodium which reduce radical concentrations wherever they exceed equilibrium values. Further, there are almost no effects of saturation with CF_3Br, whereas they are quite pronounced for both NaOH and $Fe(CO)_5$. It is difficult to relate these premixed flame results to the diffusion flames in real fires, but it is clear that there is a delicate balance between the thermal and catalytic components of

flame quenching. The thermal effect lowers the temperature, which leaves the flame radicals further away from equilibrium, making catalytic processes more efficient. However, if the temperature is too low to permit adequate generation of the catalytic species from the parent compound in the available amount of time, the suppression efficiency will be diminished, not enhanced. Thus, for flame geometries in which suppressants will have short residence times in the flame zone, the rate and temperature at which the catalytic species is released is a critical property of a prospective agent. This will be especially important for suppressants added as droplets or solid particles.

These results provide only circumstantial indications as to the source of this large difference in suppressant effectiveness. Recent modeling of manganese-containing compounds (and the data in Table 1) indicates a similarity to the iron-based mechanism, and it may be that we could expect the same anomalies with all metal-containing compounds. Thus, resolving this issue on both a laboratory and practical scale will be a priority for FY2001 research.

d. Phosphorus-containing Compounds (PCCs). In the DLAFSS, $CH_3P(O)(OCH_3)_2$ (dimethylmethylphosphonate, DMMP) extinguished the flames at about 0.8 % by volume, nominally in agreement with the OFDF results. However, extinction of a cup burner flame by this compound required the addition to the air stream of about 5 % by volume, about the same extinguishing mass fraction as CO_2, a strictly physically active agent. Thus, this class of compounds manifests the same type of disparity as metal-containing compounds in suppression behavior between the low strain, co-flow diffusion flame and the higher strain, counterflow diffusion flames. There are no quantitative data on the effectiveness of PCCs on practical fires.

Suppressant Screening Test Publications

Grosshandler, W.L., Hamins, A., Charagundla, S.R., and Presser, C., "Suppression Effectiveness Screening for Impulsively Discharged Agents," *Proceedings of the 2000 Halon Options Technical Working Conference*, pp.15-25, Albuquerque, 2000.

Jomaas, G., Roberts, B.T., DuBois, J., and Torero, J.L.,"A Study of the Mechanisms Leading to Re-ignition in a 'Worst Case' Fire Scenario," Final Report, Cooperative Agreement No. 70NANB8H0043, Department of Fire Protection Engineering, University of Maryland College Park, MD, June 2000.

Grosshandler, W.L., Hamins, A., McGrattan, K., Charagundla, R., and Presser, C., "Suppression of a Non-premixed Flame Behind a Step," *Proceedings of the Combustion Institute* **28**, in press, 2001.

Takahashi, F., Schmoll, W.J., Strader, E.A. and Belovich, V.M., "Suppression of a Nonpremixed Flame Stabilized by a Backward Facing Step," *Combustion and Flame* **122**, 105-116 (2000).

Yang, J.C., Donnelly, M.K., Prive, N.C., and Grosshandler, W.L., "An Apparatus for Screening Fire Suppression Efficiency of Dispersed Liquid Agents," *Fire Safety Journal*, in press, 2001.

Vinegar, A., Jepson, G., Cisneros, M., Rubenstein, R., and Brock, W. "Setting Safe Exposure Limits for Halon Replacement Chemicals Using Physiologically-based Pharmacokinetic Modeling," *Inhalation Toxicology* **12**, 751-763 (2000).

Vinegar, A., "Toxicological Assessment of Human Health Consequences Associated with Inhalation of Halon Replacement Chemicals," Final Report to the Next Generation Fire Suppression Technology Program, (2000).

Vinegar, A., "Modeling Cardiac Sensitization Potential of Humans Exposed to Halon 1301 and Halon 1211 Aboard Aircraft," *Aviation, Space, and Environmental Medicine*, submitted for publication, 2000

Vinegar, A., "PBPK Modeling of Canine Inhalation Exposures to Halogenated Hydrocarbons," *Toxicological Sciences*, in press, 2001.

Dodd, D.E., Jepson, G.W., and Macko, J.A., Jr., "Human Health Safety Evaluation of Halon Replacement Candidates," *Air Force Technical Report, AFRL-HE-WP-TR-2000-0104* (2000).

Nyden, M.R., Yang, J.C., Mather, J.D., "Screening of Candidate Fire Suppressants," *Proceedings of the 2000 Halon Options Technical Working Conference*, pp.104-115, Albuquerque, 2000.

B. NEW FLAME SUPPRESSION CHEMISTRY

A continuing NGP priority is the search for new chemicals that perform as well as CF_3Br, but without the environmental limitations. The research follows two directions: (a) learning more about how different chemicals effect suppression, then looking for optimal analogs and (b) identifying the best chemicals from the various families of chemicals. The principal desirable properties guiding the search are:

- Fire suppression efficiency at least comparable to halon 1301 and certainly higher than the HFCs.
- Short atmospheric lifetime (current preference of the order of a month), to keep ozone depletion, global warming and any future unidentified environmental contamination issues to a minimum.
- Low toxicity relative to the concentration needed for suppression.
- Boiling point sufficiently low that for gaseous agents, an extinguishing concentration can be achieved within a specified time following discharge. An approximate upper limit is 80 °C, but slow evaporation or poor dispersion may reduce this significantly for some chemicals.

There are a large number of families of chemicals, and the NGP is working systematically to ensure examination of all pertinent compounds.

1. Tropodegradable Bromocarbon Extinguishants

Previous NGP research had established that there are several families of compounds that contain both a bromine atom for fire suppression efficiency and an additional feature that leads to rapid degradation of the compound in the troposphere. These chemical families include the bromofluoroalkenes, bromofluoroethers, and bromofluoroamines.

A first look at these compounds focussed on those with a carbon-carbon double bond. From a list of over 80 promising chemicals, four have emerged as particularly encouraging:

1-Bromo-3,3,3-trifluoropropene	$CF_3CH=CHBr$
2-Bromo-3,3,3-trifluoropropene	$CF_3CBr=CH_2$
4-Bromo-3,3,4,4-tetrafluorobutene	$CF_2BrCF_2CH=CH_2$
2-Bromo-3,3,4,4,4-pentafluorobutene	$CF_3CF_2CBr=CH_2$

Evaluation of the various measures of toxicity for these compounds is being pursued under the auspices of the Advanced Agent Working Group. A summary of the findings for these bromofluoroalkenes is presented in Table 2.

Flash photolysis/resonance fluorescence measurements made on the second of these indicates a high reactivity with OH and a very short atmospheric lifetime.

Table 2. Bromofluoroalkene Data Summary

Attribute	Observation
Flame extinction (cup-burner and DLAFSS)	2.6 % to 4.5 % (v/v)
Boiling point	34 °C to 56 °C
Current Cost	\$0.02 to \$100.00 per gram (\$10 to \$50,000 per pound)
Acute Inhalation Toxicity	Minimal for lower boiling compounds
Ames Test	Negative
Chromosomal Aberration	Negative
Estimated Atmospheric Lifetimes	4 to 8 days

The flame suppression efficiencies, estimated atmospheric lifetimes and toxicity values are all within desirable ranges. The high prices reflect the fact that these compounds are currently available only by small-batch synthesis; far lower prices are likely to be achieved if they are manufactured in quantity.

The main caution with these chemicals is their high boiling points. Prior research had indicated that there might be problems dispersing chemicals with boiling points of about –20 °C when the storage container and the environment are as low as -40 °C. The latter temperature is a design specification for fire suppressants in aircraft. NGP research is underway to determine whether CF_3I (with a boiling point of –22 °C) will disperse well. (See Section II.D.2). If CF_3I floods the volume efficiently, the developed test procedures will be used to examine higher boiling chemicals.

Meanwhile, a rigorous search is underway to identify and procure for testing additional bromofluoroalkenes, as well as bromofluoroamines and bromofluoroethers with significantly lower boiling points. Fortunately, there is evidence that there are such compounds with acceptable toxicity. For instance, the bromofluoroether CH_3OCF_2CFHBr has an estimated cup-burner value of 4.2 % and an estimated atmospheric lifetime of 14 days. Its toxicity is low enough that the compound was once proposed as an anesthetic. Its boiling point is unfortunately too high (89 °C) for consideration as a halon replacement. The initial compounds, with estimated boiling points between being 15 °C and 30 °C, are being prepared:

Bromofluoroalkenes:	CH_2=CBr-CHF_2	CHF=CBr-CH_2F	CHBr=CF-CFH_2	
	CF_2=$CHCF_2Br$	CFBr=$CHCF_3$	CHF=$CBrCF_3$	
Bromofluoroethers:	$CF_3OCH_2CH_2Br$	CHF_2OCH_2Br	CF_3OCH_2Br	CH_3OCF_2Br

These estimations are based on comparisons to fluorinated and brominated propenes with known boiling points. The prediction quality for compounds like these is limited at present, but will improve when the above series has been synthesized.

Because the viability of these brominated compounds depends on their having low atmospheric lifetimes, NGP research is continuing to improve our ability to predict these values. Alkenes have a high reactivity toward OH and thus it has been presumed that bromoalkenes or bromofluoroalkenes will also have this high reactivity. To establish this, a series of bromofluoroalkenes was chosen to determine the effect of Br on the reactivity of OH with the carbon-carbon double bond. In all cases, the addition of bromine to one of the carbon atoms around the double bond had the effect of activating the bond toward addition. Thus, bromination shortens the atmospheric lifetime. There was also an increase in the UV absorption at wavelengths greater than 190 nm, but this was not sufficient to reduce atmospheric lifetimes, which, due to the rapid reaction with OH, are already on the order of days to weeks.

We have also embarked on the development of an alternate method to predict rate constants for reactions of other candidate chemicals where computational expense becomes a limiting factor. In this procedure, we calculate the reaction energetics and relate this result to the activation energy or the rate constant at any temperaure. The first predictions from this approach (Table 3, third column) seem quite reasonable and the method is likely to be utilized in subsequent calculations for larger molecules.

Table 3. Rate Constants for Reaction of OH with Halogenated Methanes (in units of 10^{-14} cm^3 s^{-1})

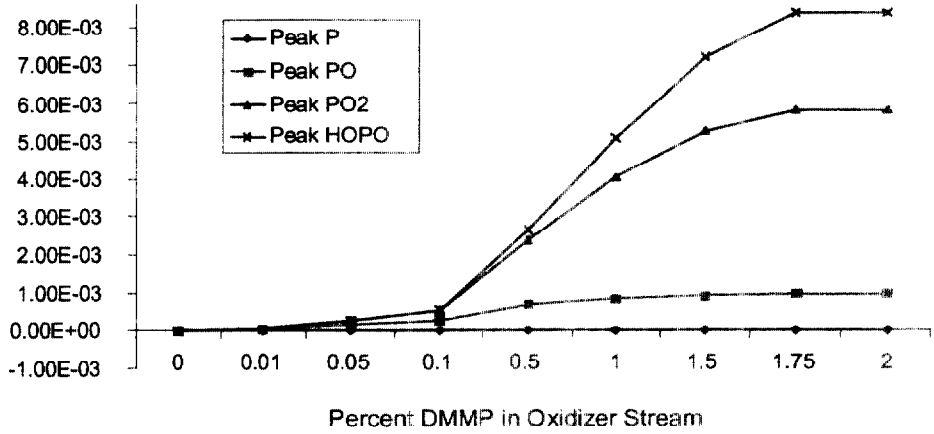
	$k_{prediction}$	k_{theory}	k_{exp}
CH_2FBr	2.7	3.0	Unknown
$CHFBr_2$	6.8	10.0	Unknown
CHFClBr	5.9	6.8	Unknown
$CHCl_2Br$	14	27	12
$CHClBr_2$	14	35	Unknown
$CHBr_3$	14	---	15

2. Phosphorus-Containing Compounds (PCCs)

Prior NGP research had demonstrated the high flame quenching efficiency of PCCs in an opposed flow diffusion flame (OFDF). New results show that the suppression efficiencies of PCCs are determined by the number of phosphorus atoms delivered to the flame with little sensitivity to the bonding environment. Extinguishment of a propane-air OFDF was achieved by the addition of either (0.20 ± 0.03) volume percent of $P_3N_3F_6$ or (0.67 ± 0.11) percent volume fraction of DMMP to the air stream. The products of the extinguishing concentration and the number of phosphorus atoms per molecule are indistinguishable for these two very different molecular structures.

Detailed chemical modeling of the flame with added DMMP shows that the concentrations of the key P-containing radicals reach a plateau before an extinguishing concentration is added (Figure 7). This further supports the concept that even though small amounts of agent may reduce flame radicals to equilibrium levels, the heat capacity of additional agent is needed to effect extinction.

Figure 7. Calculations of Species Concentrations for Propane/Air/DMMP flames



An environmental impact assessment for DMMP was made on the basis of quantitative structure activity relationships (QSARs) using its octanol/water partition coefficient. The results of this

study suggest that the aquatic toxicity of this compound is lower than ethanol, which is considered to be benign.

3. Survey of Chemical Families

In the planning for the NGP, some judgment was made regarding good chemical families to investigate as sources of alternative fire suppressants. Some of these choices have proved fruitful, as noted earlier in this report. Others have proved counter to expectations.

With this updated knowledge, a comprehensive review of the world of chemicals has now been performed to identify those chemical families still ripe for examination in the NGP. For each type of chemical functionality, assessments were made of the extent of prior fire suppression studies and the potential for success in any (further) study. Expected flame suppression efficiency, atmospheric persistence, boiling point, and toxicity were the main screening criteria.

The following families were identified as the most promising:

▪ N compounds:	amines	nitriles		
▪ P Compounds:	*acids*	*esters*	*nitriles*	*halides*
▪ S Compounds:	sulfides	mercaptans	sulfoxides	
▪ Metal Compounds:	*manganese*	*tin*		
▪ Halogenated Organics:	alkenes (I)	*fluoroethers (Br,I)*		

It was expected that substantial fluorination would be needed to obtain the desired low boiling points. Those families in italics will be examined in the FY2001 program.

New Flame Suppression Chemistry Publications

Tapscott, R.E. and Mather, J.D., "Tropodegradable Fluorocarbon Replacements for Ozone Depleting and Global Warming Chemicals," *Journal of Fluorine Chemistry* **101**, 209-213 (2000).

Mather, J.D., and Tapscott, R.E., "Tropodegradable Bromocarbon Extinguishants – Progress Overview," *Proceedings of the 2000 Halon Options Technical Working Conference*, pp. 154-163, Albuquerque, 2000.

Orkin, V.L., Villenave, E., Huie, R.E., and Kurylo, M.J., Atmospheric Lifetimes and Global Warming Potentials of Hydrofluoroethers: Reactivity toward OH, UV Spectra, and IR Absorption Cross Sections, *J. Phys. Chem. A* **103**, 9770-9779 (1999).

Louis, F., Gonzalez, C., Huie, R. E., and Kurylo, M. J., An *ab Initio* Study of the Reaction of Halomethanes with the Hydroxyl Radical. Part 1: CH_2Br_2, *J. Phys Chem. A* **104**, 2931-2938 (2000).

Louis, F., Gonzalez, C., Huie, R. E., and Kurylo, M. J., An Ab Initio Study of the Kinetics of the Reactions of Halomethanes with the Hydroxyl Radical. Part 2: A Comparison between

Theoretical and Experimental Values of the Kinetic Parameters for 12 Partially Halogenated Substituted Methanes., *J. Phys Chem. A* **104**, 8773-8778 (2000).

Louis, F., Gonzalez, C., Huie, R. E., and Kurylo, M. J., An Ab Initio Study of the Kinetics of the Reactions of Halomethanes with the Hydroxyl Radical. Part 3. Reactivity Trends and Kinetics Parameter Predictions for the Potential Halon Replacements CH_2FBr, $CHFBr_2$, CHFClBr, $CHCl_2Br$, and $CHClBr_2$, *J. Phys. Chem. A*, in press (2001).

Huie, R. E., Louis, F., Gonzalez, C. A., and Kurylo, M. J., An *Ab initio*-Based Screening Tool for the Atmospheric Lifetimes of Halon Replacements, *Proceedings of the 2000 Halon Options Technical Working Conference,* pp.87-92, Albuquerque, 2000.

Yang, J.C., Cleary, T.C., and Donnelly, M.K., "Performance Data on Cold Temperature Dispersion of CF_3I," *Proceedings of the 2000 Halon Options Technical Working Conference*, pp. 175-179, Albuquerque, New Mexico (2000).

Williams, B.A. and Fleming, J.W., "Influence of Bond Energies on Chemical Flame Inhibition: Implications for the Search for New Fire Suppressants," *Combustion and Flame*, submitted for publication, 2000.

Babushok, V., Tsang, W., and Grosshandler, W.L., "Inhibitor Rankings for Hydrocarbon Combustion," *Combustion and Flame*, submitted for publication, 2000.

Fuss, S.P., Dye, D.J., Williams, B.A., and Fleming, J.W., "Inhibition of Premixed Methane-Air Flames by Submicron Water Mists," *Proceedings of the 2000 Halon Options Technical Working Conference*, pp. 242-250, Albuquerque, 2000.

Babushok, V. and Tsang, W., "Influence of Phosphorus-Containing Fire Suppressants on Flame Propagation," *Proceedings of the Third International Conference on Fire Research and Engineering*, pp.257-267, Chicago, IL, 1999.

Yang, J.C., Bryant, R.A., Huber, M.L., and Pitts, W.M., "Experimental Investigation of Extinguishment of Laminar Diffusion Flames by Thermal Agents," *Proceedings of the 2000 Halon Options Technical Working Conference*, Albuquerque, pp. 433-446, 2000.

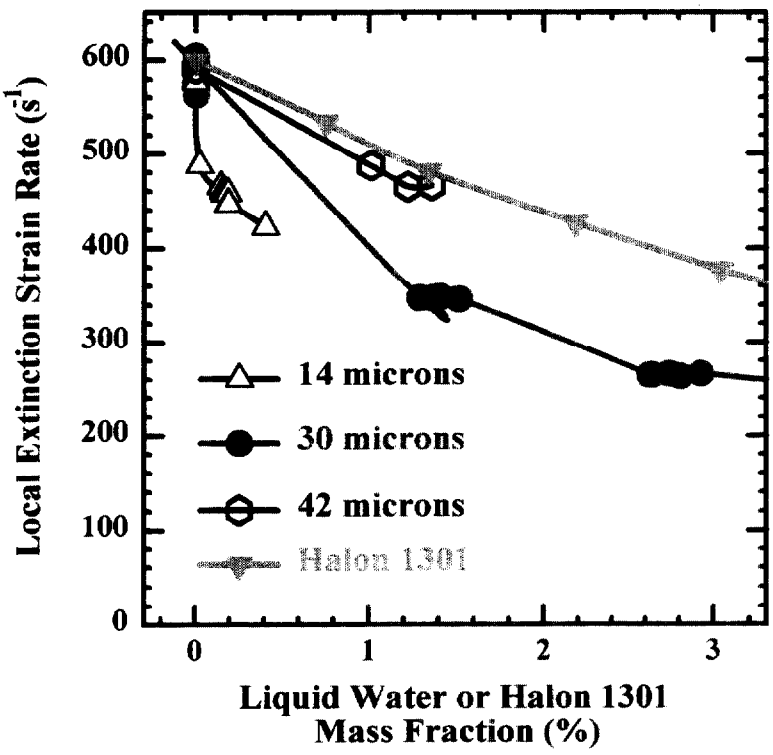
C. NEW AND IMPROVED AEROSOL SUPPRESSANTS

Nearly all suppressants of interest emerge from pressurized storage containers as liquids or powders, along with a gaseous component. NGP research has already shown that the properties of the dispensed aerosol can have a profound effect on the mass of suppressant needed to quench flames. The work this year has proceeded in two directions. The first involves improving the effectiveness of water-based aerosols. Since water dispersion and vaporization are problematic at the lower temperatures experienced by aircraft in flight, this aspect will not be pursued further. The second explores the use of chemical or physical hosts for highly effective suppressants whose use in the pure state is not acceptable for toxicity or environmental reasons. As noted in Section II.A, there are now questions regarding the effectiveness of some of these "super suppressants" on some types of flames. Thus, research on their transport will be suspended until the effectiveness issue is resolved.

1. Water-based Suppressants

A picture has emerged of the suppression of propane/air and methane/air opposed flow diffusion flames by water droplets. On a mass basis, water droplets are at least as efficient as gaseous halon 1301 (Figure 8). The efficiency improves when the endothermicity from vaporization of the water is realized. As noted last year, droplets with diameters ≤18 μm completely evaporated and a significant number of droplets with diameters ≥30 μm survived in most flames. When the residence time is long enough, the sensible enthalpy of liquid water (including complete vaporization) can be completely utilized. The transition diameter from very effective, smaller particles/droplets to larger, less effective ones depends on the aerosol boiling or decomposition temperature, the density of the liquid or solid, the local temperature, and the residence time of the aerosol at that temperature.

Figure 8. Measurements of Extinction Strain Rates in Non-premixed Propane/Air Flames Inhibited by Halon 1301 (CF_3Br) and by Monodisperse Water Droplets of Various Diameters



The strain rate (defined in terms of the velocities of the air and fuel streams, their densities, and a characteristic length) is a flame property that enables relating laboratory burners to actual fires. Velocity determination is particularly difficult to measure for aerosol-laden air streams, in which the particles or drops in the air stream carry a substantial amount of momentum but the

individual particles or drops may be too large to follow the gas flow. NGP research has developed a technique for measuring the true air stream velocity by saturating (to minimize evaporation) the air with fine (<1 μm diameter) droplets and following their movement using Phase Doppler Particle Anemometry. The derived strain rates are not significantly impacted by the addition of up to 5 % by mass of large water droplets (20 μm - 40 μm diameter). However, in both propane/air and methane/air extinction studies for water loadings > 5 % by mass, the local strain rate is strongly impacted by the presence of the added drops and work is continuing to develop a suitable metric.

NGP research has pursued the use of additives to water to increase its effectiveness and lower the freezing point. Calculations had shown that lactic acid (CH_2OHCH_2COOH), a compound with a high heat of vaporization, might significantly reduce the number of moles of water required for extinguishment. However, measurements of the effectiveness of lactic acid/water mixtures as extinguishing agents in the DLAFSS system revealed that as the amount of lactic acid was increased, it became *more* difficult to extinguish the flame. The enhanced extinguishing ability due to heat extraction is more than compensated for by the additional heat released by the lactic acid's contribution as a fuel.

We attempted to generalize the water droplet suppression model by generating experimental data with HFE-7100 ($CH_3OC_4F_9$) and n-C_6F_{14}. While it was possible to generate monodisperse aerosols of these two fluids, their high vapor pressures (> 30 kPa at room temperature) required saturating the air carrier stream to avoid evaporation. At such high air-stream loadings, no stable flame could be established. A search for fluids with much lower vapor pressures is underway.

2. Adsorbed Suppressants

There are potentially a number of chemicals that are highly effective flame suppressants that cannot be used for toxicological or environmental reasons. The NGP is exploring the concept of storing such chemicals stably in a safe medium, which would then release the chemical when the medium was discharged and reached the high-temperature neighborhood of the flame. Last year, NGP research had shown that it is indeed possible to absorb/adsorb a practical mass of a suppressant onto an inert host for transport to the fire. The remaining question was the speed of release in the flame.

We have designed, built, and tested an effective particle seeding system for introduction of zeolite, silica, or aerogel particles into either a premixed or counterflow diffusion flame. For the proof-of-concept tests, a premixed flame was used because of safety concerns over inhalation of escaped suppressant-laden particles from a counterflow diffusion flame system. Fortunately, we were able to establish a good correlation between the inhibition effects of $NaHCO_3$ in premixed and diffusion flames (Figures 9 and 10), despite the significantly different structures of these flames. Hence, we expect that tests with the two flames should be roughly comparable in demonstrating the effectiveness of chemically acting agents.

Figure 9. Methane-air Counterflow Diffusion Flame, without (left) and with (right) $NaHCO_3$ Particles

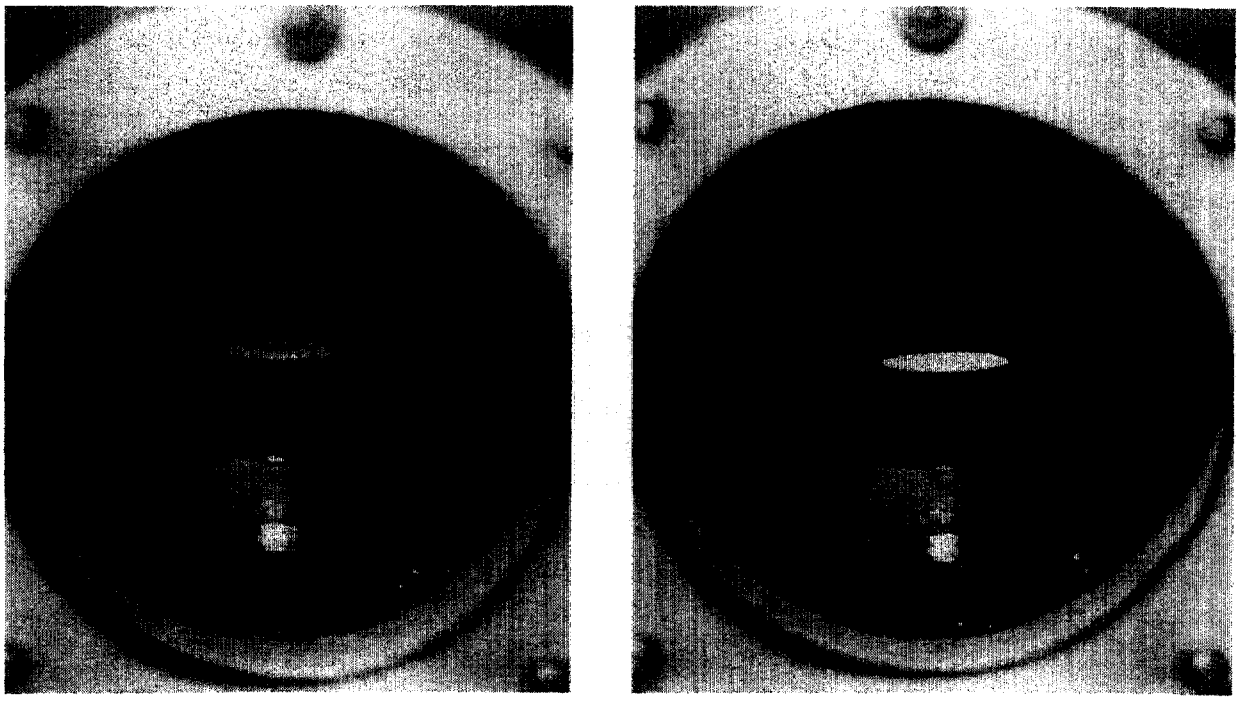
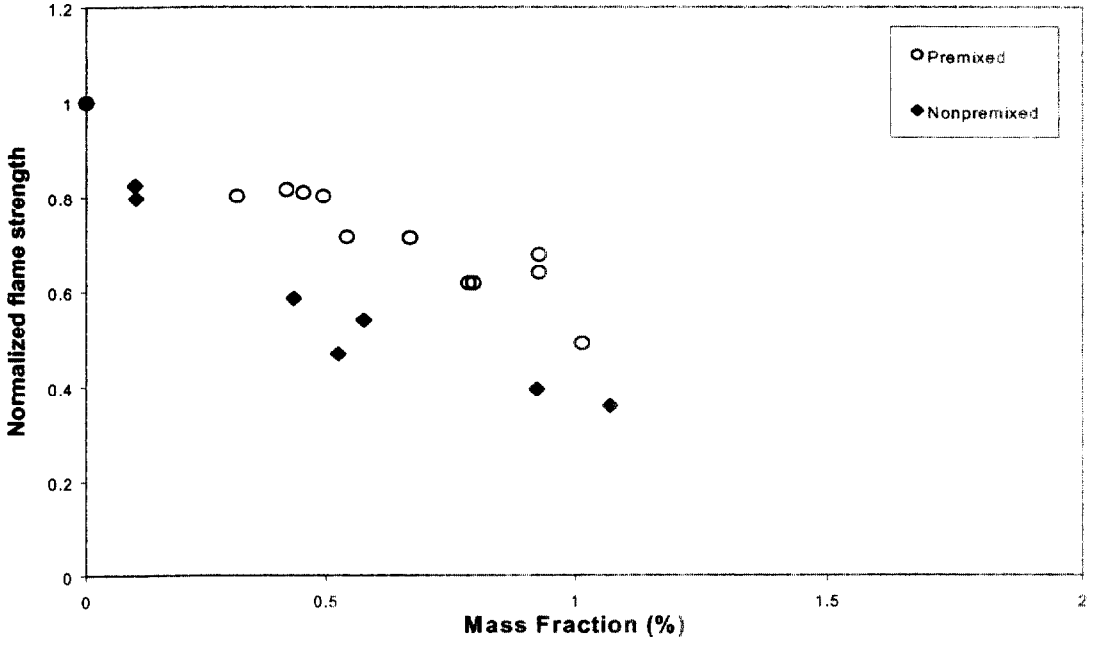


Figure 10. Normalized Flame Strength as a Function of Added $NaHCO_3$ Mass Fraction for Premixed and Counterflow Diffusion Flames.



It appears that the original intent to try $Fe(CO)_5$ as the adsorbed suppressant will not be fulfilled. While zeolite-NaX, zeolite-NaY, porous silica, and aerogel all absorbed significant $Fe(CO)_5$, they also all showed reaction of the absorbed agent when exposed to air. Further, microscope images of zeolite-NaY particles after absorption of $Fe(CO)_5$ and exposure to air showed that nodules of a condensed-phase substance (likely Fe, FeO, or perhaps even Fe_2O_3) formed on the exterior surface. This implies that $Fe(CO)_5$ may not be available from the matrix to provide gas-phase Fe, which is required for efficient flame inhibition. Consideration of $Fe(CO)_5$ and other metal-containing compounds may also be unwarranted if, as noted earlier, they prove ineffective on practical flames. Fortunately, the zeolites can absorb about 25 % by mass of either Br_2 or I_2. The release from these particles will be tested soon.

New and Improve Aerosol Suppressants Publications

Zegers, E.J.P., Williams, B.A., Sheinson, R.S., and Fleming, J.W., "Dynamics and Suppression Effectiveness of Monodisperse Water Droplets in Non-Premixed Counterflow Flames," *Proceedings of the Combustion Institute* **28**, in press (2001).

Zegers, E.J.P., Williams, B.A., Sheinson, R.S., and Fleming, J.W., "Water Mist Suppression of Methane/Air and Propane/Air Counterflow Flames," *Proceedings of the 2000 Halon Options Technical Working Conference*, pp. 251-261, Albuquerque, 2000.

Rumminger, M.D. and Linteris, G.T., "Numerical Modeling of Inhibition of Counterflow Diffusion Flames by Iron Pentacarbonyl," *Proceedings of the Sixth International Symposium on Fire Safety Science*, pp. 289-300, International Association for Fire Safety Science (2001).

Rumminger, M.D. and Linteris, G.T., "Inhibition of Premixed Carbon Monoxide-Hydrogen-Oxygen-Nitrogen Flames by Iron Pentacarbonyl," *Combustion and Flame* **120**, 451-464 (2000).

Linteris, G.T. and Rumminger, M.D., "Premixed Carbon Monoxide/Nitrous Oxide/Hydrogen Flames: Measured and Calculated Burning Velocities with and without $Fe(CO)_5$," *Combustion and Flame* **122**, 58-75 (2000).

Rumminger, M.D. and Linteris, G.T. "The Role of Particles in Flame Inhibition by Iron Pentacarbonyl," *Combustion and Flame* **123**, 82-94 (2000).

Linteris, G.T. and Rumminger, M.D., "Flame Inhibition by Thermal and Catalytic Blends: Synergistic and Antagonistic Effects," *Proceedings of the Combustion Institute* **28**, in press (2001).

Rumminger, M.D. and Linteris, G.T. "An Experimental Study of the Role of Particles in Flame Inhibition by Iron Pentacarbonyl," *Combustion and Flame*, in press (2001).

D. IMPROVED SUPPRESSANT DELIVERY

Improving the efficiency of getting the suppressant to the site of the fire is as important as finding new agents. Last year, NGP research staff completed and validated a new computer code for prediction of two-phase fire suppressant flows during discharge. This will enable appraisal of a new suppressant's compatibility with the existing distribution plumbing. The focus of the research has now progressed to storage and discharge technology and transport once the agent has been dispensed from the storage/distribution hardware.

1. Solid Propellant Gas Generators (SPGGs)

NGP research is developing new types of these suppressant storage devices that have both reduced SPGG combustion temperatures and increased flame suppression efficiency, which in turn will enable freedom of selection of the momentum of the suppressant stream. The approaches include modification of the solid propellant, inclusion of additives in the propellant formulations, and entrainment of a chemically active additive into the gas stream

a. Cooled propellant formulations. A first set of these propellant compositions (Table 4) was based upon novel high-energy, high-nitrogen fuels: 5-aminotetrazole (5AT) and the new high nitrogen compound BTATZ ($C_4H_4N_{14}$) in an attempt to increase efficiency of combustion while keeping oxidizer content to a minimum. They were formulated with oxidizers such as potassium perchlorate and strontium nitrate, and an elastomeric binder added to facilitate pressing of pellets and increase abrasion resistance. The performance benchmark was FS01-40, a state-of-the-art chemically inert formulation.

These formulations represent an important step towards increased efficiency SPGG fire suppression devices. Gas temperatures were reduced in some cases by 10 % to 20 % relative to FS01-40. The increased burn rate compositions while maintaining relatively low gas temperatures provides a means for further increases in agent cooling when these compositions are further modified with endothermic chemical coolants.

Additional high-nitrogen compounds (GAZT, BT, BGT, and TAGN), tested experimentally and by thermochemical calculation, exhibited high combustion temperatures and burn rates. We expect that lower levels of oxidizer or the use of different oxidizers will reduce the combustion temperature while maintaining high nitrogen generation.

b. Chemically active additives. Compositions incorporating combustion inhibitors were demonstrated to burn efficiently and were shown to be effective in fire suppression. Their physical properties are summarized in Table 5. The incorporation of these inhibitors does not prevent combustion of the propellant.

Table 4. Cool, High-Nitrogen Developmental Propellant Compositions

Composition Identifier → / Property ↓	Current SOA	5AT	5AT/BTATZ(1)	5AT/BTATZ(2)
Composition (wt %)	FS01-40	5AT 86 KP 10	5AT 48 BTATZ 48	5AT 43 BTATZ 43 KP 10
Exhaust species (vol % @ T_c)	N_2 45 CO_2 35 H_2O 20	N_2 57.1 H_2 35.4 CO 7.5 KCl (s) 5.3 g	N_2 66.4 H_2 32.1	N_2 61.4 H_2 30.2 CO 8.5 KCl (s) 5.3 g
T_c, °K (°F)	1000 (1400)	874 (1113)	908 (1175)	967 (1281)
Gas Output, mol/100 g (mol/100 cc)	2 (5)	4.41 (7.41)	4.14 (6.87)	4.01 (6.86)
Pressure exponent, n	0.5	0.80	1.6 (500-1000 psi)	0.7 (1000-2750 psi)
BR_{1000}, cm/s (in/s)	1.3 (0.5)	0.43 (0.17)	1.4 (0.55)	3.3 (1.31)

Notes: 5AT= 5-amino-tetrazole; KP= potassium perchlorate; binder = poly(butyl acrylate); C-black = carbon black; BTATZ = $C_4H_4N_{14}$. The balance remaining in each formulation is made up of binder, opacifier and process aid; BR_{1000} is the linear burn rate of a propellant composition when burned at 1000 psi.

Table 5. Properties of Chemically Active Developmental Propellant Compositions

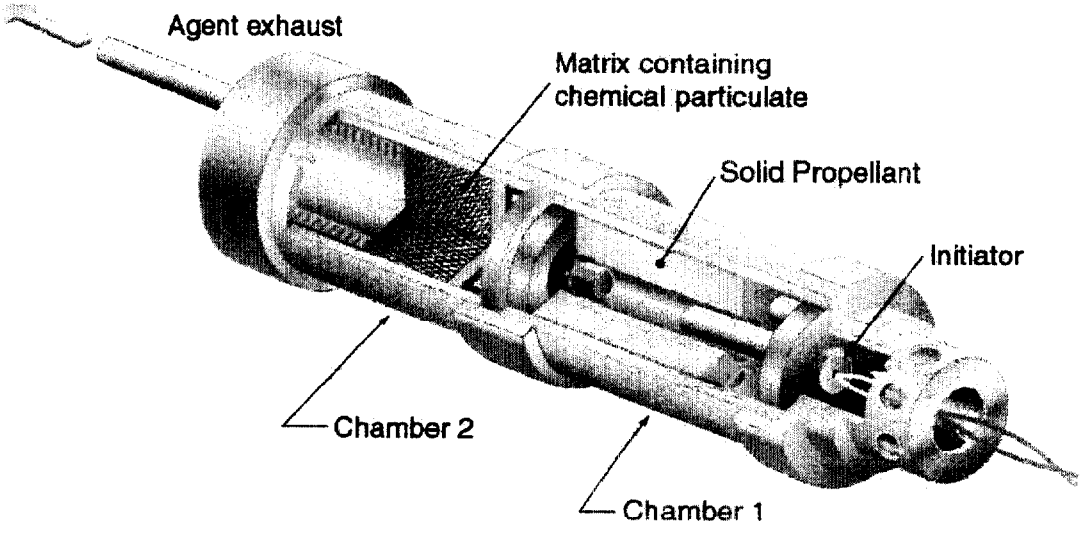
Composition Identifier → / Property ↓	Current SOA	0807-Mod KN	0807-Mod K-Carb	0807-ModD	5AT/DECA Br
Composition (wt %)	FS01-40	5AT 22.13 SrN 24.76 KNO_3 13.11	5AT 19.96 SrN 34.72 K_2CO_3 8.87	5AT 21.90 SrN 38.10 Fe_2O_3 5.00	5AT 81.00 KP 10.00 DBPE 5.00
Exhaust species (vol % @ T_c, or g/100g propellant)	N_2 45 CO_2 35 H_2O 20	N_2 44.1 CO_2 35.2 H_2O 20.7 (K_2CO_3 9.0 g) (0.13 mol K)	N_2 42.6 CO_2 37.6 H_2O 19.9 (K_2CO_3 9.0 g) (0.13 mol K)	N_2 44 CO_2 36 H_2O 20 Fe_2O_3 5 g (0.06 mol Fe)	N_2 56.1 H_2 34.0 CO 7.8 KCl (s) 2.0g KBr(s) 5.4 g
T_{ex}, °K (°F)	1000 (1400)	1102 (1524)	1206 (1711)	1098 (1517)	874 (1113)
Gas Output, mol/100 g (mol/100cc)	2 (5)	1.61	1.78 (4.09)	1.88 (4.87)	4.24 (7.29)
Pressure exponent	0.5	0.66	0.59	0.62	1.0
BR_{1000}, in/s	0.5	0.41	0.52	0.64	0.1

Notes: SrN = Sr(NO3)2; DBPE= decabromodiphenyl ether. The balance remaining in each formulation is made up of binder, coolant, opacifier and process aid.

c. Entrained fire suppressants

Exploratory tests were conducted to bound the mass of fire suppressant needed to suppress a test fire. The selected, chemically active agents were KI, KBr, K_2CO_3, Fe_2O_3, iron oxalate, ferrocene and decabromodiphenyl ether (DBDPO). The fire was a 1 MW JP-8/air spray flame in a test fixture 180 cm in length and a square cross section 3600 cm^2 in area. The agents were loaded inside the discharge section of a neutral-burning SPGG (Figure 11), whose exhaust consisted mainly of CO_2, N_2 and H_2O. During SPGG discharge, the agents were to be vaporized and delivered into the fire zone by the high pressure, high temperature exhaust gases. Fine-grid metallic meshes and porous plates downstream of the agents enhanced the mixing between SPGG exhaust and the agents prior to entering the distribution tube.

Figure 11. Solid Propellant Gas Generator Test Unit



About 40 g of either KI or K_2CO_3 was sufficient to suppress the flames. Flames were not suppressed by the addition of 40 g of iron oxalate, by 60 g of KBr or DBDPO, or by 80 g of Fe_2O_3 or ferrocene. Based on the distinctive colors imparted to the flames by several of the impinging agents, the powders seemed to be ejected out of the SPGG throughout the test duration of about 8 seconds. In the ferrocene tests, needle-shaped ferrocene crystals were deposited on the exit port of the delivery tube.

The similarity in performance between KI and K_2CO_3 is similar to that observed in turbulent spray burner tests. This likely reflects the lead role of the potassium ion in suppression effectiveness rather than the anion. The reduced effectiveness of KBr relative to KI is unexpected, and the cause is unknown. It is also difficult to understand why the bromine-laden DBDPO and the iron compounds appear ineffective. The appearance of ferrocene crystals at the SPGG exit implies that the delivery of the chemicals to the flame is not quantitative. Additional work is planned to quantify the mass of agent reaching the flame and, if appropriate, modify the SPGG design to improve the agent delivery.

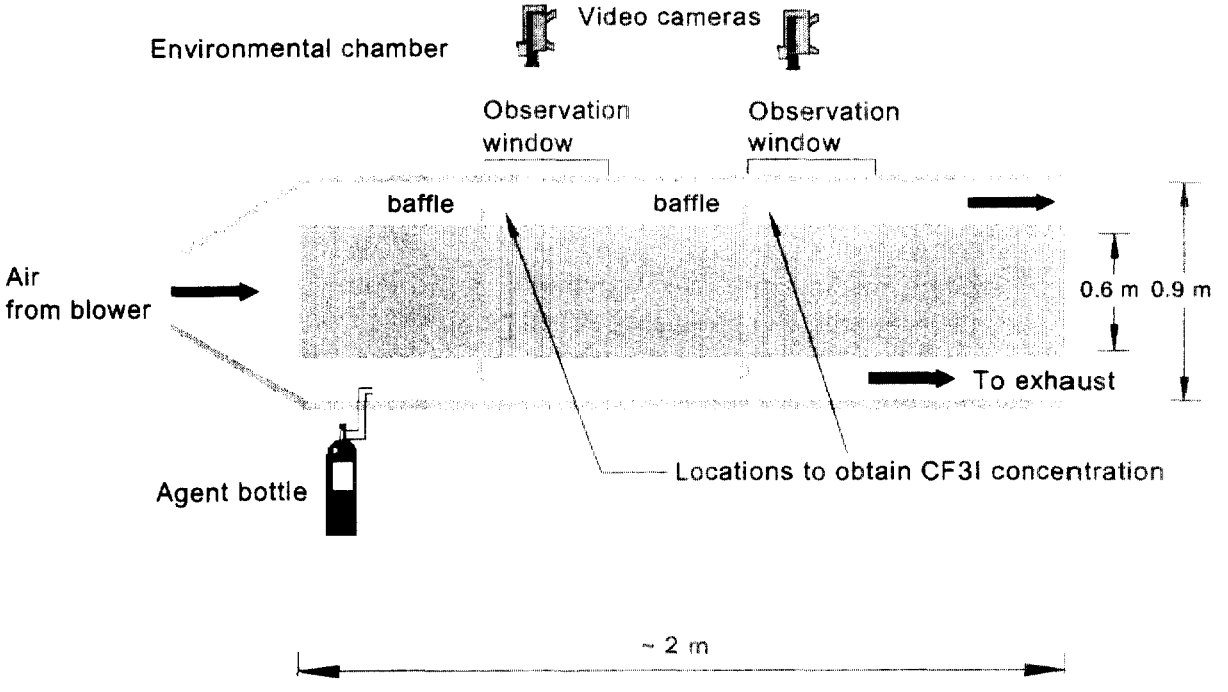
2. Dispersion of Mid-boiling Suppressants at Low Temperature

The above unexpected results indicate the importance of ensuring efficient delivery of the suppressant to the flame. In a space where the fire could be anywhere, this means efficient dispersal of a suppressant throughout the volume. Halon 1301, with a boiling point of -58 °C, flash vaporizes and distributes well, even at the lowest temperatures (*ca.* -40 °C) it experiences in in-flight aircraft. While CF_3I has a flame suppression efficiency and heat of vaporization similar to halon 1301, it has a higher boiling point of -22 °C. Earlier research had indicated that its dispersion at low temperature might be problematic.

Accordingly, an aircraft engine nacelle simulator has been built (Figure 12). The simulator consists of two concentric cylinders, each about 2 m in length. The outer cylinder, simulating an engine casing, has a diameter of 0.9 m; the inner cylinder has a diameter of 0.6 m. Two baffles are attached to the inner cylinder to simulate an engine core; this can readily be varied as desired. A maximum velocity of 7 m/s in the annulus of the simulator can be attained. CF_3I concentrations will be measured during the ca. 0.5 s discharge using a fiber-optic based UV spectrometer. The entire simulator is located in an environmental chamber capable of temperatures as low as -40 °C. Still lower storage bottle temperatures can be achieved.

As needed, the dependence of the dispersion on baffle height, airflow, and ambient temperature can be evaluated. Should CF_3I flood the volume efficiently, the developed test procedures will be used to examine higher boiling chemicals.

Figure 12. Schematic of Low Temperature Engine Nacelle Simulator



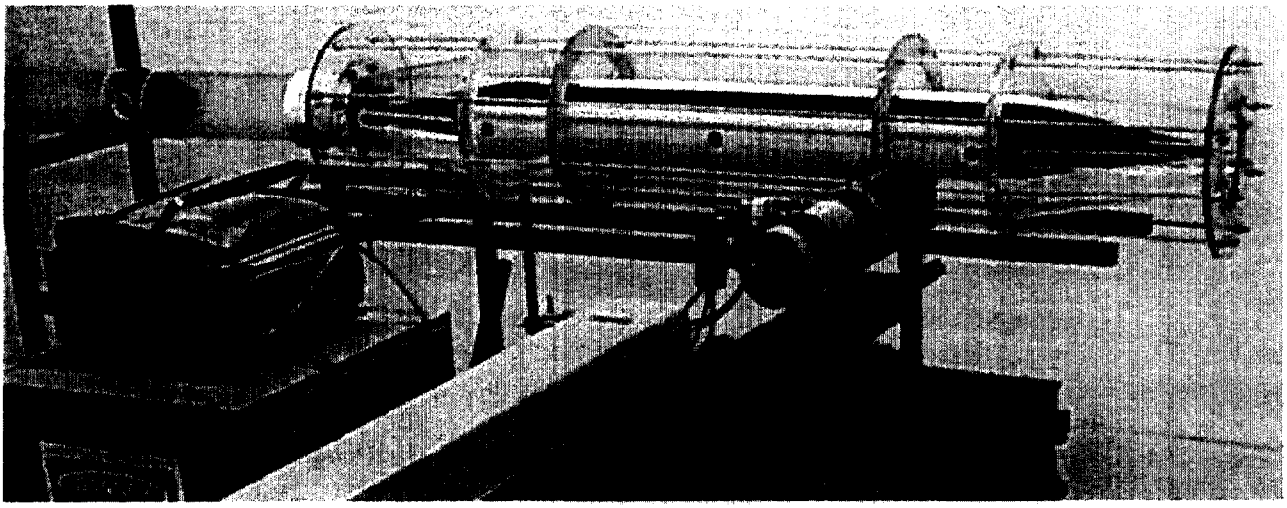
3. Modeling of Fire Suppressant Dynamics in Engine Nacelles

The Navy and Air Force aircraft safety and survivability teams have verified the expectation that improved location and styling of discharge sites can significantly reduce the mass of agent needed to control a fire in an engine nacelle. The NGP intends to develop a systematic approach to support such design modifications for all aircraft nacelles.

A central component of this effort is the development of a validated computational fluid dynamic (CFD) model of suppressant flow, a fire, and fire extinguishment in cluttered environments. This will provide a foundation for optimizing the distribution of suppressants for newly designed or retrofit fire safety systems in aircraft engine nacelles.

To establish a baseline for more complex geometries, CFD predictions were compared with detailed measurements in a quarter-scale, smooth nacelle fixture (Figure 13) under well-controlled conditions. Velocity and turbulent intensity profiles were obtained using hot wire anemometry and Laser Doppler Anemometry (LDA). Two separate models were used for the flow calculations: VULCAN and CFD-ACE. Figure 14 shows good agreement between measurements and numerical predictions of streamwise velocity and turbulence intensity for regions away from the wall. Reasons for discrepancies observed near the wall are being explored. Possible causes are the rectangular mesh in VULCAN and the small velocities near the walls that serve to increase the uncertainty in both the models and the data.

Figure 13. Quarter-Scale Simulator with LDA Test Setup



The second step has been to determine representative forms of clutter (Figure 15) to insert in both the models and the test fixture. The long runs of tubing suggested using cylinders at various angles to the air flow. For the random shaped clutter, it was decided to use body-centered cubes of spheres, with the area blockage factor or the volume percent of the spheres matching that of

Figure 14. Comparison of CFD Predictions of Streamwise Velocity and Turbulence Intensity at the Expansion Inlet of the ¼-Scale Nacelle

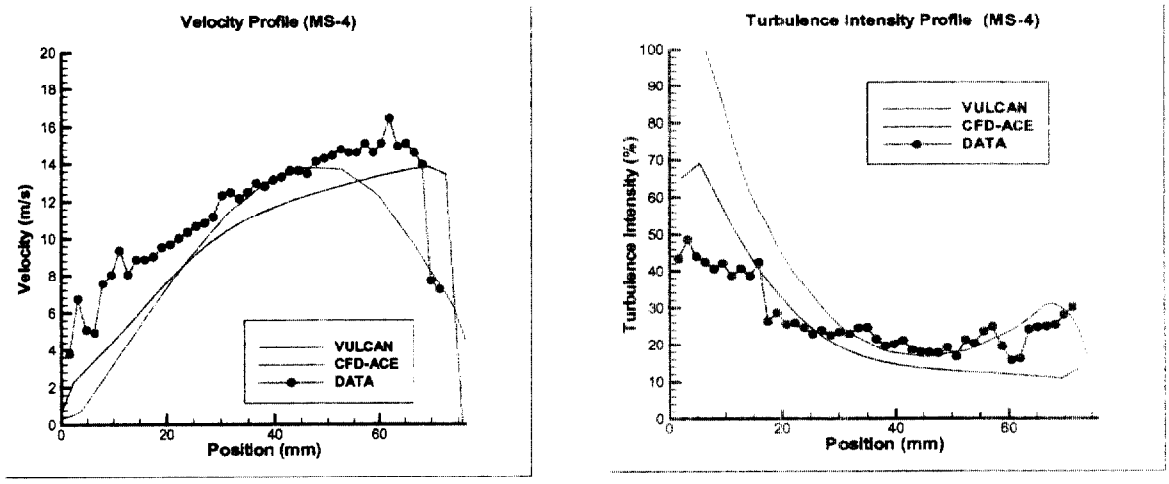
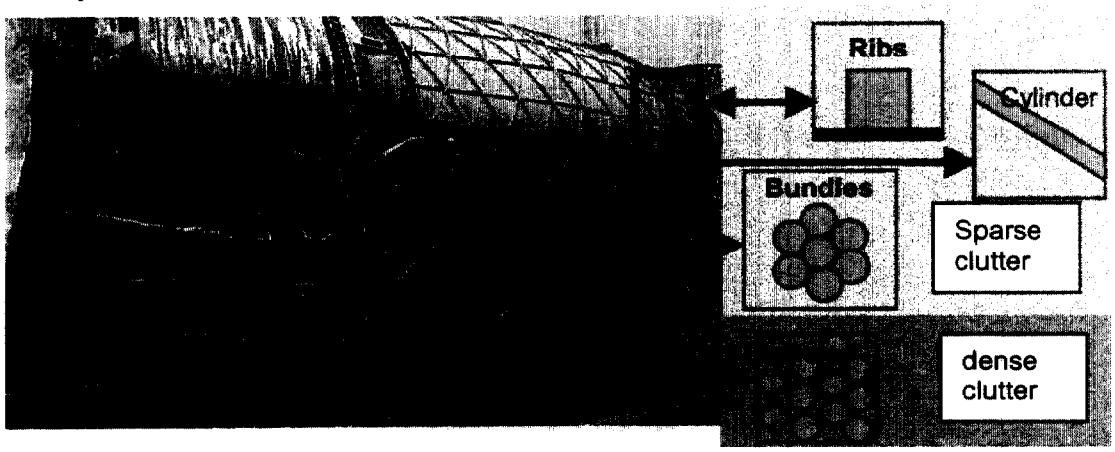


Figure 15. Schematic of Engine Nacelle Clutter Represented by Geometric Description



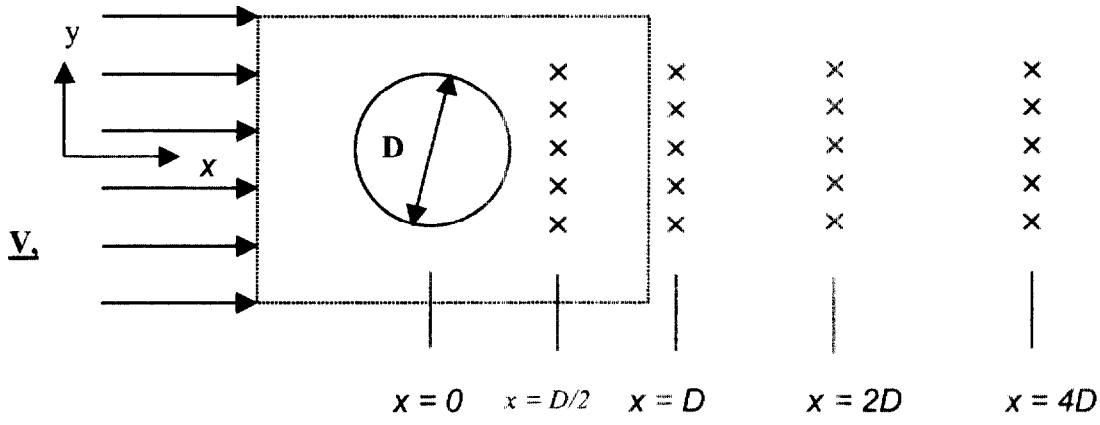
the actual hardware clutter, and the size of the spheres approximating the major dimensions of the clutter being modeled. These hypotheses will be tested and, if needed, refined.

Next, the modeling team has completed subgrid clutter packages, freely adapting concepts from the porous media and large eddy simulation literature. These packages:

- capture the influence of clutter (pressure losses and turbulent kinetic energy increase);
- accommodate a spectrum of clutter sizes ranging from a single object *(i.e.* bluff body drag) to many objects that are randomly placed *(i.e.* porous media limit);
- include asymmetric irregularly spaced clutter shapes;
- address both wall-bounded flows and clutter in free space; and
- allow for grid convergence studies to be performed.

The experimental work will focus on point measurements of velocities using hot-wire anemometry to determine the spatially-averaged drag force per unit volume of clutter and phase- and time-averaged turbulent kinetic energy. The array of sensor locations is shown in Figure 16. The results will be compared with the predictions from the CFD calculations.

Figure 16. Location of Sensors in Phase One Clutter Experiments



Including aerosol agents in such a model requires data on the change in flow behavior as the droplet-laden stream moves around obstacles: measurement of gas mean and turbulent velocity data both upstream and downstream of the obstruction. Accordingly, to an existing spray facility, we have added a flow straightener, an obstacle and an octagonal boundary to enable measurements of a well-characterized, closely isotropic turbulent flow field around a prescribed obstacle (Figure 17). The obstacle is a tube that is stretched across the turbulent flow field downstream of the wire mesh screen. The octagon wall shape accommodates our measurement requirements for planar imaging velocimetry and phase Doppler interferometry. The injectors introduce the liquid agent to the same flow field as prescribed for the gas-only case.

4. Enhancing Engine Nacelle Fire Extinguishment with Intumescent Coatings

Quenching a fire in an engine nacelle requires maintaining a sufficient concentration of agent in the flame zone for a sufficient time interval. This must be accomplished while a forced air flow through the nacelle (to prevent the accumulation of any flammable vapors, and possibly also provide some machinery cooling) serves to sweep the suppressant out the exhaust.

A novel approach to achieving the residence time with a smaller amount of suppressant is to reduce the cross sectional area of the nacelle, in the event of a fire, by strategic placement of an intumescent material (Figure 18). These materials are typically coatings that respond to the impingement of heat by swelling substantially, a factor of 10 or more. Since the width of the (irregular) annular air passage is commonly no more than 3 cm - 10 cm, an appreciable reduction in air flow through the nacelle could be achieved. Such a local fire block would weaken the fire

due to oxygen starvation (by constricting airflow), and reducing the mass of suppressant needed; the constriction could even lead to extinguishment by itself.

Figure 17. Schematic of the Obstructed Spray Facility

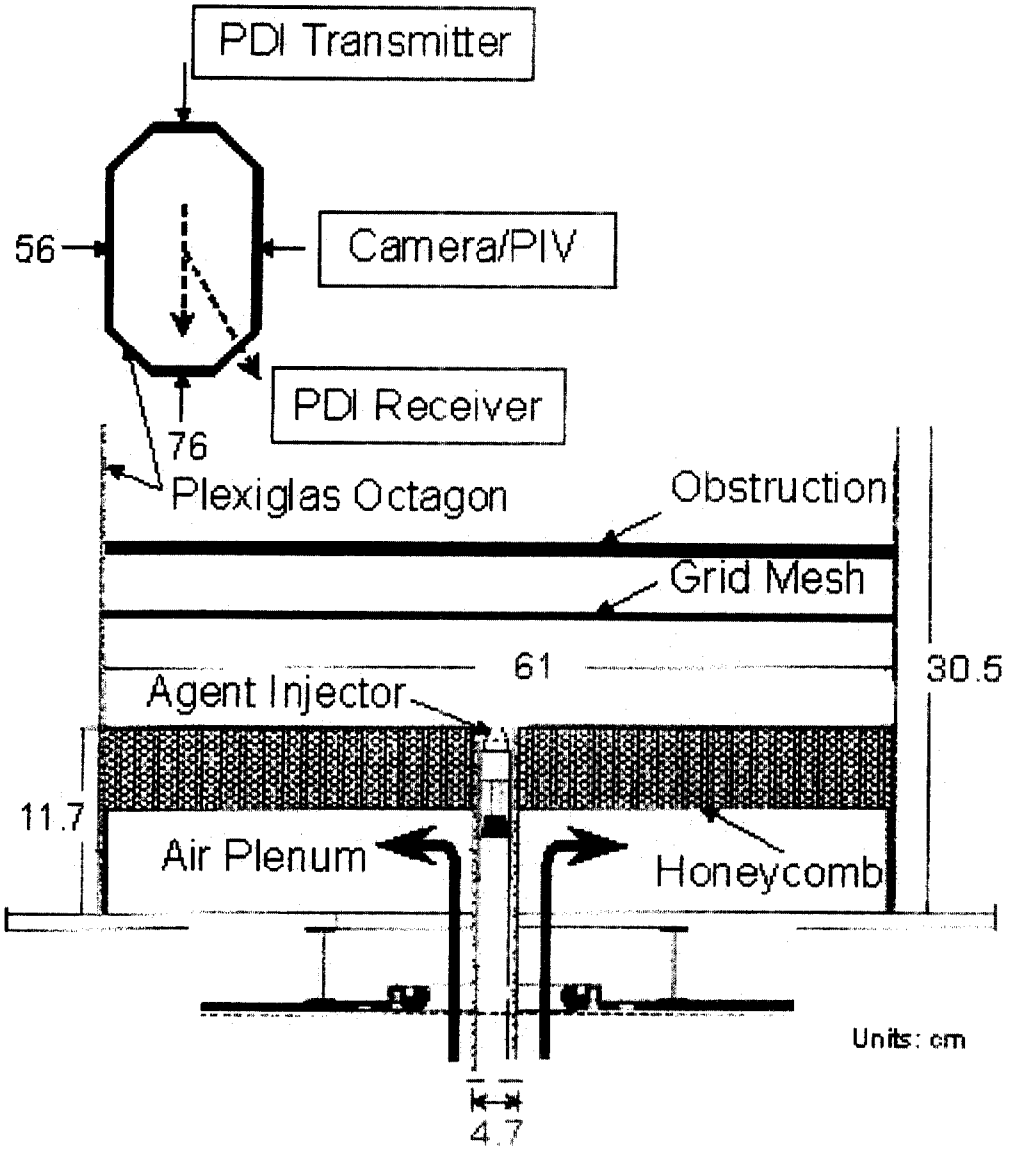
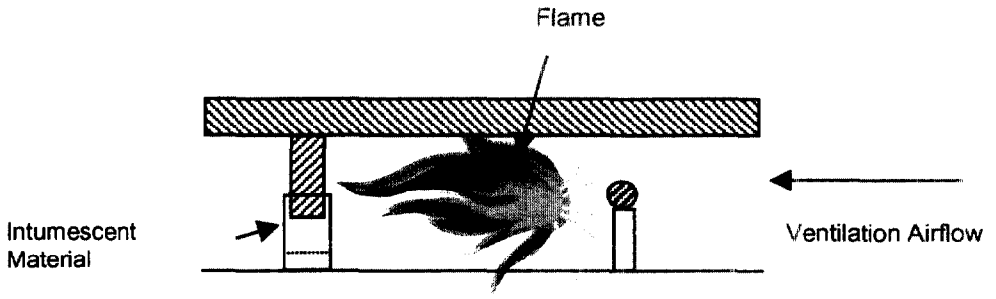


Figure 18. Conceptual Schematic of the Use of an Intumescent Coating to Reduce Engine Nacelle Air Flow



We have identified over 80 companies that manufacture intumescent materials for building construction, shipboard and aircraft fire containment barriers, and other flame stop applications. These products are being reviewed for:

- Durability of the coating during normal flight operations and adhesiveness and vibration-resistance of the expanded char following activation of the paint by a fire,
- Effectiveness of the coatings, including the expected expansion rate and the fraction of the nacelle flow reduced by the coating, and
- Ability to apply the coatings to the nacelle.

Data on current aircraft engine nacelles are being obtained to help determine the specific properties of a successful intumescent coating: areas of minimal clearance, engine materials (to identify potential material compatibility issues), airflow requirements in the engine nacelle, etc. These will enable an estimate of the decreased oxygen and/or increased suppressant residence time that would result from a given constriction in air flow. This will in turn lead to an estimate of the reduction in suppressant needed as a result of using this technology.

Improved Suppressant Delivery Publications

Takahashi, F., Schmoll, W. J., Strader, E., and Belovich, V. M., "Suppression of Step-Stabilized Nonpremixed Flames," *Combustion and Flame,* accepted for publication (1999).

Fallis, S., Reed, R., Lu, Y.C., Wierenga, P.H., and Holland, G.F., "Advanced Propellant/Additive Development for SPGG Fire Suppression Systems," *Proceedings of the 2000 Halon Options Technical Working Conference*, pp. 277-281, Albuquerque, 2000.

Bennett, M.V., A Method For Extinguishing Engine Nacelle Fires By Use Of Intumescent Coatings, *Proceedings of the 2000 Halon Options Technical Working Conference*, pp. 277-281, Albuquerque, 2000.

E. VIABILITY OF NEW SUPPRESSANT TECHNOLOGIES

1. Suppressant Concentration Measurement for Real-scale Tests

Research has been completed on an instrument for measuring agent concentration from 1 % to 25 % by volume with a 10 ms time response, fast enough for quantification of the transient agent concentration during the suppression of the fastest fires involving military systems. Tests of a second-generation version of the Differential Infrared Agent Concentration Sensor (DIRRACS-2) had showed that the device was able to follow HFC-125 discharges with acceptable signal-to-noise ratio and time response. This year a much smaller, portable DIRRACS-2 was fabricated with dimensions *ca.* 22 cm x 31 cm x 18 cm. Figure 19 is a view from the top of the internal components of the instrument. The chopper controller and the power supplies are up to 1 meter outside the box. The data acquisition software was modified to include a third channel so that the pressure pulse could be monitored along with the IR beam intensity and the chopper signal.

A series of HFC-125 discharge tests was carried out in a Bradley armored personnel carrier modified for testing agent release and fire suppression (Figure 20a). All of the releases were from the right, high mounting position just behind the turret. The concentration was monitored either near head height or waist height for an occupant of the vehicle. Figure 20b shows the DIRRACS-II positioned at head height in the left rear of the compartment about halfway back from the turret to the rear of the tank. The instrument is located between two objects at the location and of the approximate size of two vehicle occupants.

Figure 19. Top View of the Portable DIRRACS II

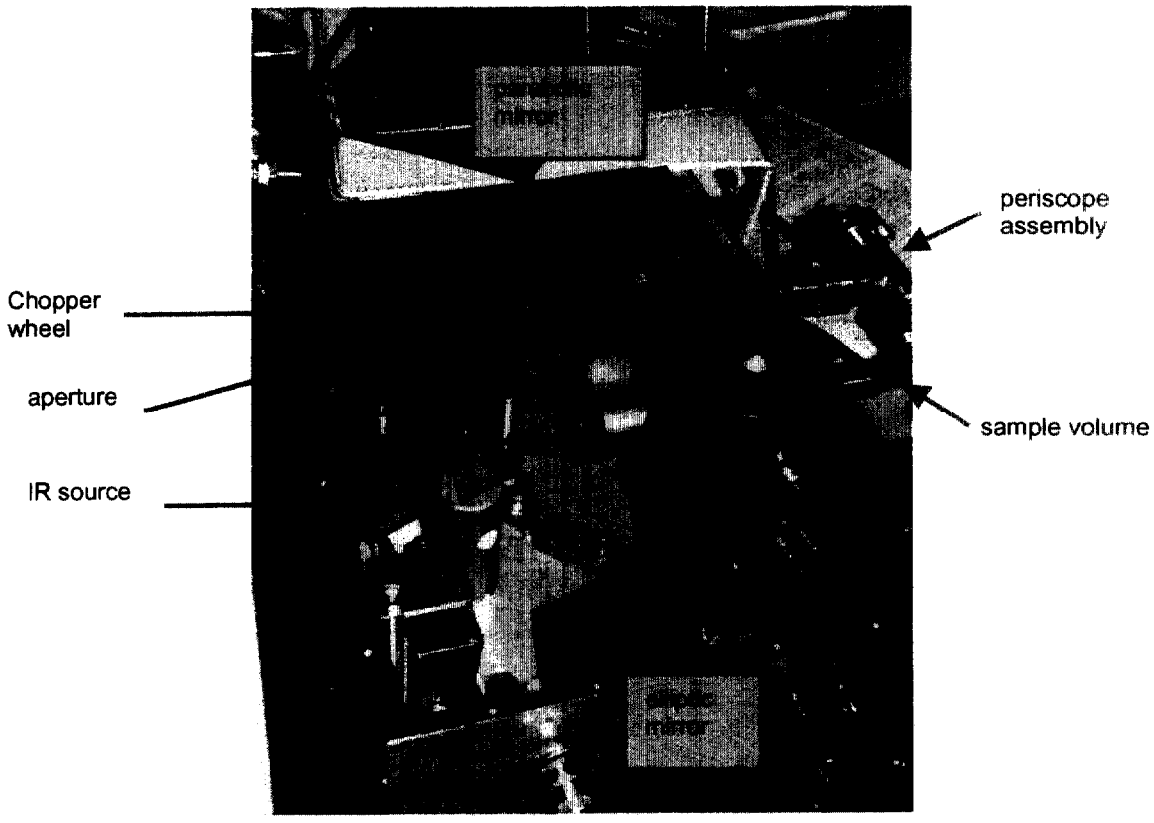
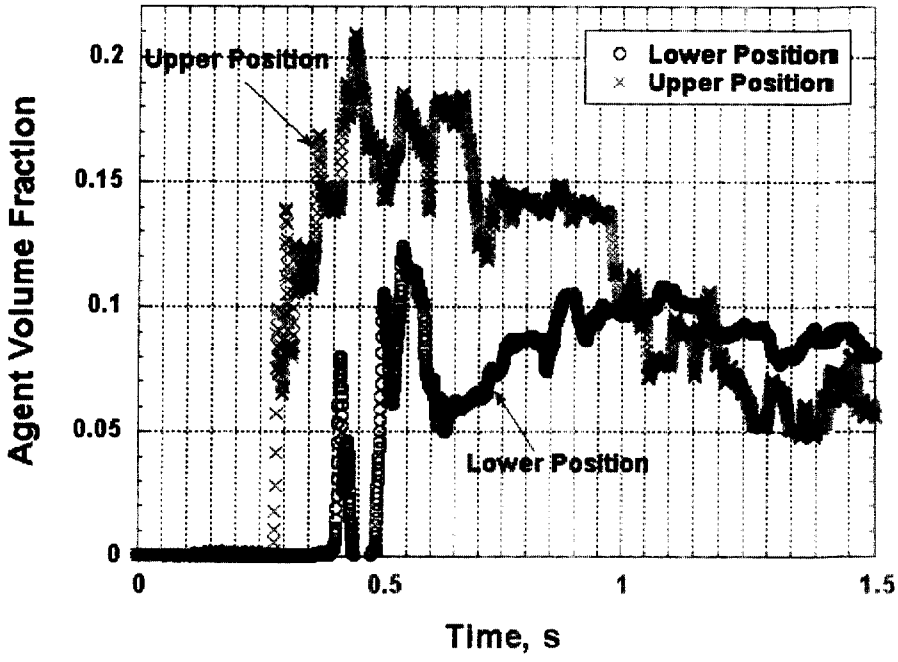


Figure 20. (a) Modified Bradley Armored Personnel Carrier; (b) Head Height Location of the DIRRACS-II, Set Between Two "Occupants"

Figure 21. Agent Concentrations from Two Releases of 3.5 kg of HFC-125

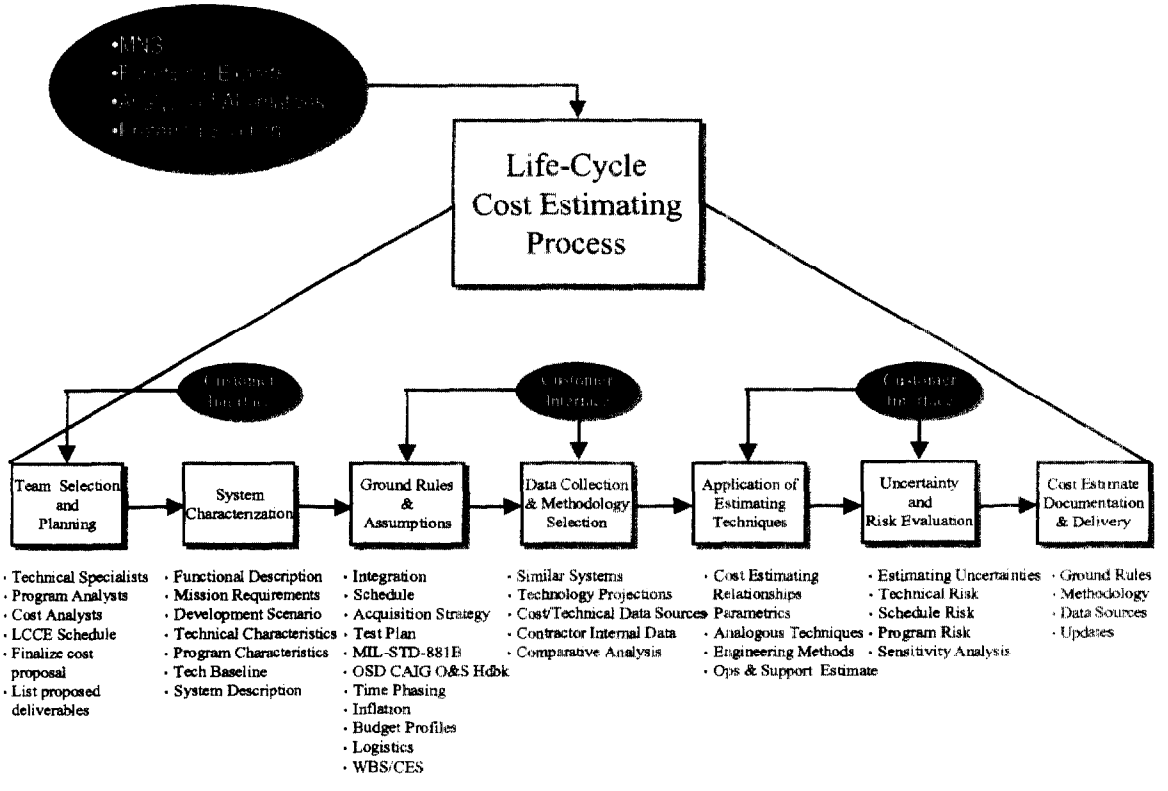


2. Benefit Assessment of Fire Protection System Changes

There are a large number of contributing factors that must be considered when making a decision to retrofit a fire suppression system (or not). These include both objective cost factors and subjective value factors. Accordingly, the NGP has developed a methodology to quantify a fire suppression technology by its total, life cycle cost and to enable superimposing on this a subjective value system.

The methodology determines the net cost of the fire suppression system: the cost of the system (which is a function of system size/weight) minus the cost savings provided by the system (which are a function of extinguishant effectiveness and result in aircraft saved). This methodology was developed for the C-17 aircraft for the existing halon 1301 system and a system of equal performance using an off-the-shelf-alternative, HFC-125. The process shown in Figure 22 was used to determine the fire suppression system costs. The following paragraphs detail this process.

Figure 22. Life-Cycle Cost Estimating Process



Actual data were used to characterize the halon 1301 system on the C-17. It provides protection for its four engines (4 storage bottles, 2-shot potential) and an auxiliary power unit (1 storage bottle, 1-shot potential). The required concentration in the nacelle and the auxiliary power unit (APU) is 6 % for 0.5 seconds. Since there is no fielded C-17 with a HFC-125 system, design

estimates for this agent were based on information developed in real-scale experiments conducted under the DoD *Technology Development Plan For Alternatives to Ozone-Depleting Substances For Weapon Systems Use.* The performance data indicated that the HFC-125 system would require 3.2 times the system mass and 4.1 times the system volume to achieve performance similar to the halon 1301 system. Accommodating this increased volume would require either modification of the aircraft structure or optimization of the distribution plumbing.

The suppression system cost was based on the proprietary data maintained by the Defense Logistics Agency, additional information provided by the C-17 Program Office, and engineering estimates where data were not available. Uncertainties were introduced because of the lack of historical information over the life of the C-17 aircraft and the non-existence of a fielded HFC-125 system. Thus the following figures are indicative, rather than definitive.

In constant FY2000 dollars, the total cost of ownership of the halon 1301 systems in the current fleet of C-17 aircraft is estimated to be $37 M (assuming a 20-year life cycle); the equivalent cost of ownership for a proposed HFC-125 system is estimated to be $43 M. These are each about one tenth of one percent of the total (life cycle) cost of the aircraft. Based on an estimated fire cost per flight hour, the total estimated number of flight hours over the life of the C-17, and a traditional success rate of halon 1301 suppression systems in military aircraft of 60 % to 80 %, it is estimated that the C-17 halon 1301 systems would save the Air Force between $124 M and $165 M in avoided fire losses (in constant FY2000 dollars). Therefore, it appears that the benefit of having either fire suppression system substantially outweighs its cost, and the difference in total cost of the two systems is modest compared to the total cost of owning and operating the aircraft.

The project will continue with extension of the methodology to the F/A-18 E/F and a rotary wing platform. Further work will focus on dry bay applications, in particular the F-18 E/F "belly," the V-22, and the B-1B overwing fairing.

Viability of New Suppressant Technologies Publications

Mulholland, G.W., Johnsson, E.L., Fraser, G.T., Zuban, A.V., and Leonov, I.I., "Performance of Fast response Agent Concentration Meter," *Proceedings of the 2000 Halon Options Technical Working Conference*, pp. 480-491, Albuquerque, 2000.

Bennett, M.V., "Relative Benefit Assessment Of Fire Protection System Changes," *Proceedings of the 2000 Halon Options Technical Working Conference*, pp. 26-31, Albuquerque, 2000.

Bennett, M.V., "Providing the Technical and Business Solutions," SURVIAC Bulletin **XV** (3), Fall 1999.

F. IMPROVED FUEL TANK INERTION

Research in this area has been limited. There are only two aircraft that currently use halon 1301 to inert fuel tanks when entering combat, the F-16 and the F-117. The Air Force is considering

the use of CF_3I for this application. Should this decision be positive, then alternative technologies for fuel tank inerting will not be an NGP task.

As an exploratory measure, the NGP has assessed the current status of alternate systems that had in prior decades shown promise for fuel tank inerting. An extensive literature search identified 25 such systems and characterized, e.g., their latest status, any history of testing or use, and any concerns with their implementation.

The most viable of these are the LFE (Linear Fire Extinguisher) and the PRESS (Parker Hannifin Reactive Explosion Suppression System). Each has advantages that outweigh the disadvantages, and the latter were deemed capable of being overcome with further development.

Improved Fuel Tank Inertion Publication

Bennett, M.V., "Review Of Technologies For Active Suppression For Fuel Tank Explosions," *Proceedings of the 2000 Halon Options Technical Working Conference*, pp. 314-323, Albuquerque, 2000.

III. WHAT LIES AHEAD?

Because of the substantial technical accomplishments in its initial years, the NGP has a solid base from which to develop new fire suppression technology for weapons systems. From this point forward, the NGP will be directed toward two targets.

A. New Flame Suppression Chemicals

NGP research will complete its review of the world of chemicals in looking for alternatives to CF_3Br.

- There appears to be promise remaining in those families of chemicals that contain a bromine or iodine atom and a feature that ensures their degradation before they can have an adverse environmental impact.
- Resolution of why compounds containing phosphorus and certain metals perform poorly at extinguishing some flames will determine whether these families receive further attention.
- A variety of nitrogen-containing compounds will be examined.

Research into each of these chemical families will identify trends in suppression effectiveness, toxicity, etc. using NGP screening methods and quantitative structure-activity relationships from prior work. The optimal candidates will be flagged for further development. However, funding will limit the extent to which individual chemicals can be pursued:

- Extensive and costly testing for a full toxicological examination will not be performed.
- A few real-scale tests will be conducted to demonstrate the reliability of the bench-scale results as a predictor of the success of agents, rather than full characterization of the performance of all candidate agents.

Nonetheless, by the end of the NGP, we will be able to define the world of potential chemicals for fire suppression in aircraft.

B. Improved Suppressant Storage and Delivery

Concurrently, NGP research has developed basic principles for the relationship between suppressant flow properties and the enhanced concentrations needed for the quenching of flames in cluttered spaces. The research has also shown the importance of the location (relative to the flame) where a suppressant fluid vaporizes.

What remains, then, is the development of modeling of the interactions between the suppressant flow and the fire in cluttered spaces. This will serve as a guide for the selection of optimal dispensing conditions, nozzle locations, etc. for effective suppression of fires in the various engine nacelle and dry bay configurations.

Further work will also develop new ways of positioning the suppressant and controlling its discharge properties, approaches complementary to the traditional pressurized fluid bottles. Combined, these will then constitute a set of source terms for the above models and offer flexibility and efficiency to the platform designer.

Again, funding will limit the extent to which concepts for efficient storage and delivery can be examined.

- The NGP will perform a modest number of indicative real-scale experiments to demonstrate the effectiveness of the new distribution principles, rather than rigorously establishing the validity of the models.
- These tests will mainly be monitored using video cameras. The instrumentation to establish model validity will not be developed or adapted.
- These models and technologies will be turned over to the platform managers for optimization testing in their particular configurations.

C. Additional Efforts

Over the past 4 years, the NGP has solicited proposals for "outside the box" approaches to fire suppression. Some of these novel ideas have proven successful at broadening the NGP thinking. A modest continuation of these solicitations is possible.

Much of the innovation in NGP projects has resulted from interactions among a large set of investigators in diverse but related aspects of fire suppression. The number of concurrent projects, which peaked at 23, will decrease to 12 in FY2001 and to about 5 in FY2002. The NGP will continue to co-sponsor and participate actively in the spring Halon Options Technical Working Conference. The NGP will broaden the participation in its autumn Annual Research Meeting, inviting past investigators and other experts. It is hoped that these two meetings will continue to broaden the perspective and stimulate the innovation of the NGP investigators.

The prognosis for successfully meeting the revised NGP goal is excellent, given the technical infrastructure and cadre of experts advanced by the NGP. The Department of Defense will then need to set in place the engineering programs to develop the new technologies for implementation in its fleet of aircraft.

APPENDIX

NGP PROJECTS

A. SUPPRESSANT SCREENING TESTS

3A/1/789. DISPERSED LIQUID AGENT FIRE SUPPRESSION SCREEN
Principal Investigator: Jiann C. Yang, NIST

3A/2/890. TRANSIENT-APPLICATION-RECIRCULATING-POOL-FIRE AGENT EFFECTIVENESS SCREEN
Principal Investigator: William Grosshandler, NIST

3B/1/89. TOXICOLOGICAL ASSESSMENT OF HUMAN HEALTH CONSEQUENCES ASSOCIATED WITH INHALATION OF HALON REPLACEMENT CHEMICALS
Principal Investigator: Darol Dodd, AFRL

3B/2/8. AGENT COMPATIBILITY WITH PEOPLE, MATERIALS AND THE ENVIRONMENT
Principal Investigators: Marc Nyden, NIST;
Stephanie Skaggs, Universal Technical Services

B. NEW FLAME SUPPRESSION CHEMISTRY

2A/1/7890, /2/890. MECHANISMS OF ULTRA-HIGH EFFICIENCY CHEMICAL SUPPRESSANTS
Principal Investigators: James Fleming, NRL; Kevin McNesby, ARL

4D/2/7. IDENTIFICATION AND PROOF TESTING OF NEW TOTAL FLOODING AGENTS
Principal Investigator: Robert E. Tapscott, NMERI
COR: Andrzej Miziolek, ARL

4B/1/8,4D/15/0. TROPODEGRADABLE BROMOCARBON EXTINGUISHANTS
Principal Investigator: J. Douglas Mather, NMERI
COR: Ronald Sheinson, NRL

4B/2/8,4D/3/7. FLAME INHIBITION BY PHOSPHORUS-CONTAINING COMPOUNDS
Principal Investigator: Elizabeth M. Fisher, Cornell University
COR: Andrzej Miziolek, ARL

4D/14/1. FLUOROALKYL PHOSPHOROUS COMPOUNDS
Principal Investigator: Douglas Mather, NMERI

4C/1/890. SUPER-EFFECTIVE THERMAL SUPPRESSANTS
Principal Investigator: William Pitts, NIST

4D/13/1. EFFECTIVE, NON-TOXIC METALLIC FIRE SUPPRESSANTS
Principal Investigator: Gregory Linteris, NIST

4B/3/8901. ENVIRONMENTAL IMPACT OF NEW CHEMICAL AGENTS FOR FIRE SUPPRESSION
Principal Investigators: Robert Huie and Marc Nyden, NIST; Andrzej Miziolek, ARL

4B/4/01. PERFORMANCE DATA ON COLD TEMPERATURE DISPERSION OF CF_3I AND ON MATERIALS COMPATIBILITY WITH CF_3I
Principal Investigator: Jiann Yang, NIST

4B/5/01. ASSESSMENT OF COMPLETENESS OF SEARCH FOR ALTERNATIVE SUPPRESSANT CHEMICALS
Principal Investigator: Richard Gann, NIST

C. NEW AND IMPROVED AEROSOL SUPPRESSANTS

2B/1/78901. SUPPRESSION EFFECTIVENESS OF AEROSOLS AND PARTICLES
Principal Investigator: Ronald Sheinson, NRL

2B/2/89. DROPLET INTERACTIONS WITH HOT SURFACES
Principal Investigator: Yudaya Sivathanu, En'Urga, Inc.
COR: William Grosshandler

2B/3/89. TECHNICAL SUPPORT FOR THE STUDY OF DROPLET INTERACTIONS WITH HOT SURFACES
Principal Investigator: Jiann Yang, NIST

4A/1/890. POWDER-MATRIX SYSTEMS
Principal Investigators: Gregory Linteris, NIST

4D/1/7. ELECTRICALLY CHARGED WATER MISTS FOR EXTINGUISHING FIRES
Principal Investigator: Charles H. Berman, Titan Corp.
COR: Ronald Sheinson, NRL

4D/4/7. DEVELOPMENT OF A SELF ATOMIZING FORM OF WATER
Principal Investigator: Richard K. Lyon, EER, Inc.
COR: William Grosshandler, NIST

4D/7/8. DENDRITIC POLYMERS AS FIRE SUPPRESSANTS
Principal Investigator: Nora Beck Tan, ARL

D. IMPROVED SUPPRESSANT DELIVERY

2C/1/789. STABILIZATION OF FLAMES
Principal Investigator: Vincent Belovich, AFRL

4D/6/8. DUAL AGENT APPROACH TO CREW COMPARTMENT EXPLOSION SUPPRESSION
Principal Investigator: Douglas Dierdorf, ARA Corp.
COR: Andrzej Miziolek

4D/17/0. A METHOD FOR EXTINGUISHING ENGINE NACELLE FIRES BY USE OF INTUMESCENT COATINGS
Principal Investigator: Leonard Truett, Eglin AFB

5A/1/01. PARAMETRIC INVESTIGATION OF DROPLET ATOMIZATION AND DISPERSION OF LIQUID FIRE SUPPRESSANTS
Principal Investigator: Cary Presser, NIST

5D/1/9. ADVANCED PROPELLANT/ADDITIVE DEVELOPMENT FOR GAS GENERATORS
Principal Investigators: Gary Holland, Primex Aerospace; Russell Reed, NAWC-WPNS
COR: Lawrence Ash, NAVAIR

5E/1/1. ENHANCED POWDER PANELS
Principal Investigator: Dan Cypher, Skyward, Inc.
COR: Martin Lentz, Eglin AFB

6A/1/01. FIRE SUPPRESSANT DYNAMICS IN CLUTTERED WEAPONS SYSTEM COMPARTMENTS
Principal Investigator: David Keyser, NAVAIR

6B/1/89. SUPPRESSANT FLOW THROUGH PIPING
Principal Investigator: John Chen, Lehigh University
COR: William Grosshandler, NIST

6C/1/1. MECHANISM OF UNWANTED ACCELERATED BURNING
Principal Investigator: William Pitts, NIST

E. VIABILITY OF NEW SUPPRESSANT TECHNOLOGIES

1A/1/78. DEVELOPMENT OF MODEL FIRES FOR FIRE SUPPRESSION RESEARCH
Principal Investigator: Anthony Finnerty, ARL
Associate Investigators: James Tucker, AFRL and Juan Vitali, ARA; Ronald Sheinson, NRL

1C/1/8901. RELATIVE BENEFIT ASSESSMENT OF FIRE PROTECTION SYSTEM CHANGES
Principal Investigator: Michael Bennett, Eglin AFB

3C/1/789. LASER-BASED INSTRUMENTATION FOR REAL-TIME, IN-SITU MEASUREMENTS OF COMBUSTIBLE GASES, COMBUSTION BY-PRODUCTS, AND SUPPRESSANT CONCENTRATIONS
Principal investigator: Kevin McNesby, ARL

3C/2/890. FAST RESPONSE SPECIES CHARACTERIZATION DURING FLAME SUPPRESSION
Principal Investigator: George Mulholland, NIST

F. FUEL TANK INERTION

5C/1/9. ACTIVE SUPPRESSION FOR FUEL TANK EXPLOSIONS
Principal Investigator: Leonard Truett, Eglin AFB