

Technology for Fire Suppression in Aircraft: Findings of the Next Generation Fire Suppression Technology Program

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I. Introduction

The U.S. Department of Defense (DoD) Next Generation Fire Suppression Program (NGP) was born of necessity. A viable alternative to halon 1301 (CF_3Br) was needed. Atmospheric science had made it clear that fully halogenated compounds containing chlorine or bromine posed a threat to the earth's ozone layer. The large number of countries signing the Montreal Protocol indicated that this was a concern to the international community. An extensive, multi-year search by the DoD found that the best commercially available alternative to the ozone depleting chemicals used for fighting in-flight fires was HFC-125 ($\text{C}_2\text{F}_5\text{H}$). The high weight and storage volume penalties of this compound spoke to the need for further research. In 1997, the Next Generation Fire Suppression Technology Program (NGP) began, with an objective that evolved 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."

Ten years later, the NGP has revitalized the science of fire suppression. While the research focused on the extreme conditions operative in in-flight fires in aircraft engine nacelles and dry bays, much of the science and understanding is applicable to a broader range of civilian and military fire scenarios.

The final report of the NGP will be available in book form and on CD this autumn. See the NGP web site (www.bfrl.nist.gov/866/NGP) for ordering information later this year.

II. Complexity of In-flight Fires and Their Suppression

The roughly annular interior of an aircraft engine nacelle is bounded by the engine core on the inside and the aerodynamic skin on the outside. To cool the engine and to mitigate the buildup of flammable fuel/air mixtures, air flows through this space, with a typical residence time of the order of tenths of a second. The surfaces are irregular, and the air flow is highly turbulent. The exterior shell of the nacelle can be as low as -40°C at high altitudes. The interior of the annulus is somewhat warmer.

Spray and pool fires can arise in numerous locations within the nacelle due to a fuel leak or, during combat, an incoming round. The fire suppressant must get from the storage bottle to the nacelle, and then fill the entire space with a sufficient concentration of agent for sufficient time duration to quench the flames before the air flow flushes the agent out the nacelle exhaust. Because mass and storage volume are at a premium, the mass of the agent and its hardware must be kept to the minimum to do the job.

In dry bays, most peacetime fires are due to equipment failure or failure of the engine or starter. Combat dry bay fires are usually initiated by a round penetrating the dry bay wall and an adjacent fuel cell. The interiors of dry bays are irregular in shape and highly cluttered. The nature and magnitude of air flow depends critically on the location and extent of breach of the outer wall. The rapid pressure buildup following an ignition can result in an explosion as air mixes with the released fuel. Thus, dry bay fires must typically be suppressed within a few tenths of a second.

Such considerations led to guidance for the search for alternatives to the current halon 1301 systems:

- Efficient and rapid distribution of the suppressant is essential. Halon 1301 accomplishes this with little assistance, because its boiling point (T_b) is below even the lowest ambient temperatures, which leads to flashing. Other suppressants must have similarly low boiling points or be dispersed by other means (see below). A mist of a high boiling chemical will condense on the inside of the cold exterior surface of the aircraft.
- There are significant weight and storage volume penalties for an inefficient or inefficiently distributed agent that affect the relative cost of alternative fire suppressant technologies.
- Despite the complexity of the flames in in-flight fires, existing laboratory burners can be used to extract the properties of chemicals that effect fire suppression.

Fuel tank fires during combat are also a major cause of aircraft losses. However, the Military had decided to vintage the existing systems in the only two U.S. aircraft that use halon 1301 to inert the fuel tanks, and no NGP examination of the dynamics of inerting against this type of fire was performed.

The suppression requirements for fires in military ground vehicle crew compartments are similar to those for dry bay fires. The flames must be quenched within 250 ms to prevent incapacitation of the crew.

III. NEW UNDERSTANDING OF THE FIRE SUPPRESSION PROCESS

A. Overview of Fire Suppression

The quenching of flames can be accomplished by removing the fuel or separating the fuel from an air supply, reducing the available oxygen supply, reducing the time in which the fuel and oxygen are mixed and available to react, cooling the fuel/air mixture below a temperature that supports sufficiently rapid chemical reaction for flame propagation, or adding a combustion inhibiting chemical at a concentration sufficient to reduce the rate of fuel oxidation below that needed for flame propagation.

Conversely, flame extinguishment will not occur, or be less efficient, if too little of the flame suppressant reaches the fire zone in a timely manner, the flame suppressant passes through the flames too quickly to effect its role, or the flame suppressant is released so slowly, or disperses so broadly, that the fire is not exposed to an extinguishing concentration.

B. Control of the Air Supply to the Fire

An annular band of intumescent material applied to the inside of an engine nacelle can significantly reduce the flow of air through the nacelle. The material would be applied to the downstream end of the housing so that the heat from an upstream fire would activate the chemical expansion of the material. This decreasing the mass of agent needed for an extinguishing concentration, increase the residence time of the chemical in the flame zone, and allowing the flames to deplete the local oxygen concentration.

C. Delivery of the Fire Suppressant to the Fire

1. Dispensing from a Storage Bottle

In the absence of extensive distribution piping, the discharge rate of a suppressant fluid from its storage bottle depends on the prevailing internal pressure within the bottle ullage. The pressure in the ullage of the storage bottle is a function of the fluid vapor pressure, the partial pressure of pressurizing gas added to the ullage for rapid discharge, and the solubility of the pressurizing gas in the fluid. The computer code PROFISSY predicts the pressure to within 10 % using only the agent mass, the bottle volume, the fill temperature, and either the nitrogen mass needed to pressurize the vessel or the fill pressure of the vessel.

2. Fluid Flow through Distribution Plumbing

Upon the opening of the storage bottle, the fluid enters the distribution piping as a two-phase mixture of superheated liquid and vapor. These phases are not in thermodynamic and thermal non-equilibrium. Due to the large pressure drop in the piping, continuous flashing can occur as the fluid travels through the piping, and choked flow can result. This can severely reduce the discharge rate of the fluid.

The computer code FSP estimates the pressure history and discharge flow from a pipe run of arbitrary design (e.g., bends, tees and elbows). The code is also able to replicate the qualitative behavior associated with the release of dissolved gas as the delivery system undergoes rapid depressurization during the discharge of the suppressant agent. The shapes of the calculated pressure histories are similar to experimental curves, and the predicted discharge times are accurate to within 15 %. Because of these characteristics, the code is a viable tool for the analysis or design of suppressant delivery systems.

3. Effective Fluid Dispersion

Coordinated experiments and fluid dynamics modeling added the following knowledge enhancements to the general expectations that (a) clutter retards the flow of suppressant and can reduce the mass available to reach the site of a fire and (b) fires stabilized behind obstructions are the most difficult to extinguish.

- Agent concentrations in the recirculation zone near a fire can be estimated from concentration measurements made under the same nacelle operating conditions, but without the fire.
- A fire suppression system design based on room temperature test data may well fail to provide adequate fire protection when activated at low temperatures.
 - Low temperatures (below the boiling point of the agent) of the agent storage bottle, airflow, or nacelle surfaces can adversely affect agent dispersion. Condensation will result in pooling at low points, and evaporation is likely too slow to generate an extinguishing concentration.
 - High clutter density and low air velocity synergistically reduce the mass of agent convected downstream by increasing the likelihood of agent contact with cold surfaces.
 - Discharging additional suppressant can result in an extinguishing concentration throughout the nacelle, but at an attendant increase in system weight and volume.
- The speed of suppressant injection is more important than the total mass of agent deployed. If a “wave” of sufficiently high agent concentration reaches all the potential zones of fire for even a fraction of a second, the fire will be extinguished.
- The transport of liquid droplets downstream is dependent on the droplet size. Large (> 30 μm to 50 μm) droplets tend to impinge on clutter surfaces. Smaller droplets entrain into the gas stream and transport around the clutter into the recirculation region behind an obstacle. Droplets with low boiling points tend to vaporize, resulting in decreased droplet size or complete evaporation.
- Rapid lateral distribution of the suppressant in an engine nacelle is enhanced by multiple injection ports, as contrasted with the single port that is sufficient for halon 1301. Three well-located ports is a reasonable starting point for suppression system design.
- The time to mix agent into the flame-stabilizing recirculation zone behind *isolated* clutter is proportional to the size of the clutter divided by the velocity past the clutter.
- Interaction between *multiple* clutter objects can reduce or extend the time to mix agents into recirculation zones behind obstructions. A nearby (second) piece of clutter that is the same distance from the agent injection port as a flame-stabilizing piece of clutter *reduces* the mixing rate of agent into the flame stabilization region. The second object pulls the streamlines away

from the recirculation zone. A nearby (second) piece of clutter that is behind (downstream of) a flame-stabilizing piece of clutter *increases* the mixing rate of agent into the flame stabilization region. The downstream object pushes the streamlines into the recirculation zone. Larger clutter drag coefficients tend to influence the mixing process more strongly.

- Three fire simulation programs (VULCAN, FDS, and FPM) used in the NGP research captured much of the physical knowledge summarized above. Any of the three can help design a fire suppression system in practically any space inside an aircraft. There is no conceptual impediment to their use in other spaces. Any of the three can be used to guide the optimization of the design of tests for acceptance of a fire suppression system for an aircraft or ground vehicle.

Each of these programs incorporates a different set of assumptions. If two or more programs agree in the outcome, the tests likely will confirm. Disagreement among programs shows that the conditions are near the edge of the extinguishment envelope. In NGP full-scale nacelle testing, almost all the predictions of borderline extinguishment outcomes were, in fact, extinguished.

- As demonstrated in live-fire testing, improved powder panels, as weight efficient as halon 1301 systems, can provide excellent quenching of ballistically initiated explosions in aircraft dry bays. Compared to conventional designs, these new designs provide greater powder release into the dry bay, better dispersion of the powder to prevent ignition off the shotline, longer powder suspension to prevent fire ignition for a longer time, and greater flexibility of design to effect application-specific objectives. Front face crack growth, which promotes more and better powder dispersion, can be optimized through the use of particular front face materials, thicknesses, rib designs, attachment methods to the ribs, and even surface scoring. Additional benefit can be obtained by back face improvement and taking advantage of the strong synergism between the rib structure and the front face design. Accidental leakage can be prevented by proper choice of materials and adhesives. While these improvements were demonstrated using Al_2O_3 , an inert powder, additional enhancements can be obtained with chemically active powders that are also lighter. There is logical extension of this technology to fire suppression in ground vehicles.
- A new generation of solid propellant fire extinguishers offers effective fire suppression for both engine nacelles and dry bays. Lower effluent temperature, obtained by incorporating the new high nitrogen propellant BTATZ and by the introduction of a coolant to the propellant formulation, reduce the potential for thermal damage. Enhanced fire suppression efficiency was obtained by the introduction of chemically active compounds to the formulation. (Adding K_2CO_3 to the propellant reduced the mass needed for fire suppression by a factor of 3.) Hybrid fire extinguishers (HFEs), in which a chemically active suppressant is added to the propellant effluent, offer the potential for even larger gains in fire suppression efficiency. Prototype units have shown *system* weight reductions by over a factor of two, with still greater reductions possible by optimizing the findings. This technology was effective in the quenching of automotive gasoline tank fires.
- Significant masses of some suppressants can be adsorbed onto inorganic particles, at mass fractions of 0.2 or higher. This might be a delivery option for a compound whose fire suppression efficiency is about a factor of five or more higher than that of halon 1301 and which poses environmental or toxicological threats.

D. Effectiveness of a Fire Suppressant at Quenching Flames

1. Required Agent Residence Time

Extinguishment of an open flame occurs when the concentration of suppressant exceeds some minimal value long enough for the chemical kinetics to quench the flame chemistry. There are two stabilization conditions for occluded flames. In one, the flame detaches and goes out as soon as the agent arrives. In

the other, the shear layer first becomes unstable, followed by flame extinguishment in the recirculation zone. There, the agent residence time needed for extinguishment depends on the concentration of the agent in the free stream and the time interval over which the agent has been injected into the free stream.

The minimum volume fraction of CF_3Br for suppression at different injection time intervals, normalized by its value for continuous application, correlates with $[1 - \exp(-\Delta t/\tau)]^{-1}$, where Δt is the injection time interval and τ characterizes the mixing time behind the obstacle in the flow. The agent mass needed for suppression can be minimized by injecting the agent for a period near the characteristic mixing time, which scales with the obstacle height divided by the velocity of the flow. The minimum volume fraction of an agent required to suppress these flames is similar to the value determined in cup burner tests.

To make use of the full mass of suppressant stored in and released from the bottle, a chemical must be:

- Released as a gas, a condition virtually impossible for a volume-efficient fluid;
- Prone to flashing upon release, requiring a boiling point below the design ambient temperature, a condition satisfied for very few fluids; or
- Dispensed as fine droplets, a condition requiring fine nozzles on the distribution piping and a high backing pressure. This will be difficult to achieve with a sufficiently high discharge rate.

2. Chemistry of Fire Suppression

Intensive NGP efforts have generated more detailed understanding of the interaction of inhibiting chemicals with flames and culminated in a unified model of fire suppression. This included effectiveness by both physical and chemical processes, each of which affects the rates of the chemical reactions that must proceed sufficiently fast to sustain fuel combustion.

Flame extinguishment without any chemical activity entails making it harder for the flame-generated enthalpy to maintain the fuel/air “bath” at a temperature high enough for these reactions to continue. For a gaseous agent, the enthalpy needed to raise the suppressant from the ambient temperature to flame temperature is determined by its heat capacity. A high heat capacity results from a molecule having a large number of atoms, with the associated large number of thermally excitable vibronic modes, and possibly from dissociation of one or more weak chemical. For aerosol agents, the liquid phase heat capacity and the heat of vaporization also contribute. For a constant mass of an aerosol, there is a monotonic increase in the flame extinction efficiency with decreasing droplet size. Aerosols delivered to the hot surfaces in the vicinity of a fire can assist in quenching the flames and preventing relight by cooling surfaces. Effectiveness is enhanced by high values of the mass delivered, the droplet diameter, and the droplet velocity.

Efficient chemical extinguishment of flames results from depletion of the H, OH and O radicals that drive flame propagation. The process can be simple removal or catalysis of radical combination to less reactive compounds. In either case, the suppressant also functions as a thermal suppressant. For agents that are comparable in flame suppression efficiency to halon 1301, this thermal component is smaller than the chemical component.

Many of the pre-NGP (and some NGP) studies of the effects of additives on flames addressed flame *inhibition*, measuring decreases in burning velocity, free radical concentrations, etc. for small quantities of additive. From these studies emerged insights into the chemical and physical processes that degraded the flames. Additional processes contribute to the *extinguishment* of actual fires.

A unified view of the suppression of flames by chemically active agents is 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 decompose in the flame to

generate the entities that catalytically reduce the radical concentrations toward equilibrium levels. While this catalytic process slows the flame, it does not necessarily extinguish it. Both chemically active and physically active suppressants increase the heat capacity of the fuel/air mixture, reducing the flame temperature and thus, along with the decreased concentrations of radical reactants, decrease the flame reaction rates below the level needed to sustain combustion. These two effects are synergistic. Thus, if weight limitations allow, the effectiveness of a chemical agent can be enhanced by combination with a high heat capacity chemical.

Among compounds containing non-metallic elements, catalytic activity has only been determined for the halogen atoms and for phosphorus.

- Halogenated compounds are more effective at inhibiting flames when added to the air than when added to the fuel. Their effectiveness is not sensitive to the form of the non-catalytic moiety. However, any included hydrogen acts as fuel, which offsets the flame suppression effectiveness. The relative efficiency of halogen atoms in inhibiting flames is $\text{Cl} < \text{Br} = \text{I}$. This reflects the ratio of the forward to reverse rates of the $\text{HCl} + \text{H} = \text{H}_2 + \text{Cl}$ reaction, which causes Cl to be less effective at flame temperatures. The H-F chemical bond is sufficiently strong (570 kJ/mol) that the H atom no longer participates in the flame propagation chemistry. Thus, there is no catalytic activity from the F atom.
- Compounds containing a single phosphorus atom are at least as effective as halon 1301 on a molar basis. Their effectiveness is independent of the structure of the non-phosphorus moiety, as long as the phosphorus is fully in the gas phase in the flame zone. This requires vaporization or decomposition with sufficient residence time. Chemical kinetic flame modeling showed that the active phosphorus-containing species concentrations reached plateaus at levels below those required for flame extinguishment, indicating contribution of thermal effects.

From a detailed examination of the published literature, compounds containing 21 transition metallic elements demonstrated inhibitory effects in flame systems and/or on engine knock. Of these, five (P, Cr, Pb, Fe, and Mn) have a high potential for flame inhibition and three (Ni, W, and Mo) a medium potential, in the absence of condensation of the active species to form inactive particles.

Iron-containing compounds were studied as examples of highly efficient flame inhibitors. $\text{Fe}(\text{CO})_5$ and ferrocene are 10 times more effective as flame velocity inhibitors as halon 1301. The mechanism for their effectiveness of iron-containing compounds primarily results in H atom recombination. A secondary catalytic cycle results in O atom recombination. Gas phase transport of the active iron-containing species to the region of high H atom concentration is necessary for efficient inhibition. Particle formation near the location of peak H atom concentration can act as a sink for the iron-containing intermediate species and reduce the catalytic effect. Ferrocene was ineffective at suppressing a spray burner flame, presumably due to extensive condensation of the iron-containing species into particles.

This loss of fire suppression potential due to particle formation in some flame systems has been observed for Cr, Pb, Mn, Sn, Co, and Sb, as well. Were this condensation to occur in practical fires, as was observed for ferrocene, compounds of these metals would likely not demonstrate fire suppression capabilities commensurate with their high flame velocity inhibition efficiency that was observed when added at low concentration to laboratory premixed flames. There are no data to indicate the potential for particle formation for compounds containing Ni, W, and Mo. The vapor pressures of the suggested flame-quenching species (for which data are available) are reasonably high.

Prediction of the potential loss of effectiveness due to condensation is presently difficult. The potential depends upon the local supersaturation ratio in the inhibited flame. Calculation of this 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.

Emerging from these studies is the principle that the effectiveness of a catalytically acting agent can be temperature dependent. For a higher temperature flame, the radical pool will be larger, so that a fixed amount of inhibitor will have a smaller relative effect on the radical pool. The higher temperature also leads to a smaller difference between the superequilibrium radical concentrations and the equilibrium concentrations, further decreasing the effectiveness of the additive. A higher temperature can also lead to a shifting of the equilibrium of the key intermediate species (for example, to the right in the $\text{HBr} + \text{HX} \rightleftharpoons \text{H}_2 + \text{BrX}$ reaction), leading to a lower effectiveness. A higher flame temperature can decrease the condensation rate (or increase the vapor pressure) of the particles, increasing their effectiveness.

IV. EVALUATION OF CANDIDATE FIRE SUPPRESSANT TECHNOLOGIES

A. Screening Measures

The NGP anticipated the need to evaluate thousands of chemicals in its search for alternative fluids to halon 1301. While full-scale testing of chemicals is eventually necessary to demonstrate acceptability, it was impractical to use such tests to narrow that large a list of candidates. Moreover, many of the chemicals would need to be custom synthesized and/or would be of unknown toxicity. Thus, a protocol for rapid and inexpensive screening was developed to identify those relatively few agents worthy of further examination. For each property to be screened, the first result from a three-step process was used: literature search for a published value, estimation of the value based on analogous compounds, and performance using the selected screening test. The screening tests determined to be most critical were for fire suppression effectiveness, volatility, atmospheric impact, and toxicity.

The criterion for fire suppression effectiveness was a cup burner flame extinguishment value below 5 % by volume, comparable to halon 1301 and superior to the HFCs.

- For thermally active compounds, the first step sufficed. The NGP developed a figure of merit based on the total enthalpy absorbed by the compound as it was heated from room temperature to flame temperature, represented by 1400 K. Enthalpy data were available for thousands of compounds, and thousands more were eliminated by analogy.
- For chemically active compounds, the cup burner was the main tool. Some compounds had already been tested, enabling additional appraisals by analogy. Others were measured here.
- Two other laboratory flame suppression devices were developed to examine specialized aspects. The Dispersed Liquid Agent Fire Suppression Screen was used to appraise the differences between a chemical being applied as a gas or a liquid. The Transient Application Recirculating Pool Fire Agent Effectiveness Screen was used to identify differences in effectiveness that might arise from impulsive (rather than steady state) injection of the suppressant, such as from a solid propellant fire extinguisher. Experiments indicated that reignition of flames could occur at hot surface temperatures as low as 400 °C. The knowledge gained was used in evaluating chemicals in general, but neither was used as a routine screen.

Volatility was reflected in a compound's boiling point. Compounds with boiling points above 20 °C were eliminated from further consideration. Including compounds with boiling points up to 20 °C was liberal, in that this allowed consideration of compounds that could only achieve an extinguishing concentration at equilibrium. The evaporation process would likely be overtaken by flushing of the chemical from an engine nacelle unless a large excess of the chemical were dispensed. However, if the *surface* temperatures within in-flight engine nacelles were as high as the predicted nacelle interior *air* temperatures, (about 10 °C to 30 °C), then some of the compounds with boiling points near 20 °C would flash and disperse effectively.

No screening measurements were made of the molecular properties that determine atmospheric lifetime. A chemical continued under consideration if it had a feature that rendered it tropodegradable, i.e., likely

to have a short atmospheric lifetime. However, a chemical that has such a feature was likely to have a high molecular weight and thus a high boiling point.

The screening criterion for toxicity was the absence of data indicating that serious effects on people could occur at a concentration lower than that needed to extinguish flames. The focus was on acute toxicity, in particular cardiotoxicity.

- No effective screen was found for the cardiac sensitization of dogs, the standard test. (Dog tests of chemicals, conducted in parallel with the NGP, revealed unexpectedly high toxicity.) In vitro tests are in their infancy, especially for cardiac arrhythmia. The use of octanol/water partition coefficients showed promise as a screen for cardiotoxicity.
- Research was performed to extend and apply a realistic human exposure model (whose input was animal exposure data). This has the potential for more accurate assessment of the hazard from a short exposure to a discharged suppressant.
- Literature values were obtained for some appealing compounds. However, no new compounds survived screening for all four properties. Thus, the NGP performed no animal tests for candidate agents for in-flight fire suppression.

The cost and availability of a compound were not initial screening criteria. However, it was recognized that, for a non-commercial chemical, the difficulty (or non-existence) of a synthetic approach and the cost of the starting materials could prove problematic in obtaining operational quantities of the chemical.

B. Measurements during Fire Tests

Conventional real-scale testing of fire suppression effectiveness involved little instrumentation, typically limited to the time of fire extinguishment and the concentration of suppressant that lead to extinguishment. To learn more about the fire extinguishment process and to pave the way for improved qualification testing, the NGP developed additional measurement technology for real-time, in situ monitoring of the suppression event.

- Time-resolved measurement of the concentration of a suppressant, C_2F_5H , in a single location was performed using infrared absorption. The combined standard uncertainty was about 0.005 volume fraction. The technique can be extended to other agents with discrete infrared absorption.
- Steady state concentrations of CF_3I were measured using ultraviolet (UV) absorption. The repeatability was $\pm 15\%$. The technique can be extended to other UV-absorbing agents.
- Time-resolved concentrations of O_2 during live fire testing were measured using four-location laser absorption. The minimum detection limit was 3000 $\mu L/L$.
- Fuel vapor concentrations were obtained using a novel two-laser, infrared absorption probe. The limit of detection was about 200 ($\mu L/L$)-m. The unit had not yet been tested at real scale.
- Time resolved concentrations of HF, a principal combustion product generated during fire suppression by fluorinated agents, were measured using infrared absorption at 1.31 μm .

C. Life-cycle Cost Assessment

The NGP adapted a life cycle cost model to estimate the cost benefits of carrying fire protection systems for engine nacelles and dry bays on board military aircraft, and developed a methodology for estimating the total cost of either retrofitting existing aircraft or configuring future aircraft with new systems based on a non-ozone-depleting fire suppressant. Calculations were performed for cargo, fighter, and rotary wing aircraft. The current agent baseline was for halon 1301; the modeled replacement agent was HFC-

125. These estimates showed that additional investment in optimizing fire suppression system performance pays off in assets saved. Specifically:

- It is highly cost effective for aircraft to carry fire protection systems, despite their life cycle costs and the infrequency of their use. Based on historical data, the return on investment in halon 1301 fire protection systems (in terms of the cost of aircraft assets saved by their use and their historical extinguishing success rate) was estimated to be over five-fold.
- It would also have been highly cost effective for larger HFC-125 systems (of fire suppression effectiveness comparable to these halon 1301 systems) to have been installed on military aircraft. The return on investment would have been at least two-thirds that of the halon 1301 systems.
- For comparable fire suppression effectiveness, the net cost of a system using HFC-125 installed in a future aircraft is comparable to the net cost of a conventional halon 1301 system as a ratio of the overall fire protection system cost of ownership to the total aircraft platform cost.
- Additional investment in developing systems with superior fire suppression performance (as indicated by higher extinguishing success rates in the field) to systems exhibiting historical levels of performance was observed to be cost effective and beneficial.

The methodologies were fashioned to serve as a stand-alone product, to provide the framework to build modified models for future halon replacements, and to serve as analysis tools to identify key indicators of desirable halon replacement properties to consider in later research on new technologies. Since their formulation, this approach has been used on some developmental aircraft. This methodology can be expanded to meet the additional challenges of new aircraft, new fire suppression technologies, and additional applications, such as fuel tank inerting.

V. POTENTIAL FOR NEW, VIABLE SUPPRESSANTS

Over the course of the NGP, virtually the entire world of chemistry was reviewed, screened, and, if warranted, tested against the criteria described earlier.

No inorganic compounds were identified that met the screening criteria. The findings for specific families of inorganic compounds are as follows:

- Compounds of radioactive elements were toxicological unsuitable.
- Aqueous solutions of some of the salts mentioned below were highly efficient flame suppressants. However, the freezing points of these solutions are above the lower agent storage temperatures for in-flight aircraft.
- Compounds of Group I elements in the periodic table (Li, Na, K, Rb, Cs, and Fr) are flammable or are solids at room temperature. Alkali metal compounds applied as dry powders or liquid solutions are extremely effective fire extinguishants. Since these have not already been accepted for use on in-flight aircraft fires, due to corrosion problems, alternative compounds were not screened. K-based powders are more effective than the corresponding Na-based powders, consistent with the easier decomposition of the former to generate vapor phase K atoms.
- The compounds of Group II elements (Be, Mg, Ca, Sr, and Ba) are solids or low volatility liquids and have not shown the needed fire suppression effectiveness.
- The compounds of Group III elements (B, Al, Ga, In, and Tl) showed no promise, due to flammability, toxicity, or absence of catalytic flame suppressant capability.

- In Group IV (C, Si, Ge, Sn and Pb), carbon compounds are discussed below as organic chemicals. Si- or Ge-based compounds offer no flame suppression advantages over the similar C-based compounds. Compounds of Sn and Pb are environmentally unacceptable.
- Within Group V (N, P, As, Sb, and Bi), As, Sb, and Bi compounds are too toxic and/or environmentally unacceptable. Phosphorus compounds are very efficient at fire suppression, but not sufficiently volatile for total flooding, and some are toxic. Inorganic nitrogen compounds were not efficient fire suppressants.
- Of the compounds of Group VI elements (O, S, Se, Te, and Po), oxygen has no fire suppression function itself, and inorganic oxides are too low in volatility. S and Se compounds have not shown good fire suppression efficiency, and they or their combustion byproducts are generally toxic. Te and Po compounds are unlikely to be more efficient suppressants than S compounds.
- Compounds of several of the transition metals are far more efficient flame inhibitors than halon 1301. However, these compounds are insufficiently volatile for flooding applications, and most are ineffective due to condensation of the active species into relatively inert particles.
- Compounds containing four of the halogen atoms in Group VII (F, Cl, Br, and I) have been studied extensively. These are discussed further under the organic compounds.
- The Group VIII gases (He, Ne, Ar, Kr, and Xe) are inefficient fire suppressants.

Examination of organic compounds was barely more successful:

- There were no available compounds that did not contain a halogen or phosphorus atom that met all the screening criteria, especially fire suppression efficiency and volatility. $N(CF_3)_3$ was reported to have a boiling point of $-10\text{ }^\circ\text{C}$ and should have fire suppression efficiency superior to HFC-125. However, since the compound is fully fluorinated and since the compound could give rise to nitrogen oxides (potent ozone depleters) in the stratosphere, there was caution about its environmental acceptability. Attempts to synthesize this compound were unsuccessful.
- Some organophosphorus compounds had fire suppression efficiencies comparable to halon 1301. However, even with extensive fluorination, their volatility was too low, and some reacted in air.
- The replacement of hydrogen atoms with fluorine atoms and fluoroalkyl groups generally decreased the combustibility and increased the volatility of a wide range of organic chemical families. For the most volatile of these, the atmospheric lifetimes were too long and/or they were not superior to HFC-125 in fire suppression efficiency.
- For halogenated compounds, most attention focused on those containing bromine. Chlorinated compounds are less efficient at flame suppression. The iodinated compounds are no more effective fire suppressants, and there were concerns regarding stability and toxicity. Nearly all the brominated compounds tested, or for which literature data were available, showed cup burner flame extinguishment values comparable to halon 1301. The presence of multiple hydrogen atoms tended to offset this efficiency.
- To have a negligible ozone depletion potential, a compound containing Br (or I or Cl) must have a second feature that leads to rapid decay in the troposphere. The heavily, but not fully, fluorinated bromoalkenes have sufficiently high fire suppression efficiency and short atmospheric lifetimes, but high boiling points. The bromofluoroethers show good fire suppression efficiency, but high boiling points. Unless somewhat protonated, they are insufficiently reactive in the troposphere. CF_2BrCN has a boiling point of $3\text{ }^\circ\text{C}$, the lowest of any tropodegradable brominated compound. It extinguished cup burner flames at under 4 % by volume.

In summary, HFC-125 (C_2F_5H) remains the best choice for fire suppression in aircraft. Despite its weight and volume penalty over halon 1301, it has high volatility, acceptable toxicity and (in quantities limited to this purpose) a minor effect on global warming, with no ozone depletion potential. $N(CF_3)_3$ and CF_2BrCN would have sufficient volatility if the low temperature requirement were relaxed. However, for the former, a synthesis path is needed, along with an assessment of whether the nitrogen oxides formed following decomposition pose an ozone threat comparable to halon 1301. For the latter, toxicity and atmospheric lifetime data are lacking. Some bromofluoroalkenes would be eligible if the low temperature requirement were relaxed substantially and toxicity data were developed.