

1. INTRODUCTION

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1.1 Background

1.1.1 Halons and the Ozone Layer. The Montreal Protocol of 1987 identified halon 1301 (CF_3Br) as one of a number of halogenated chemicals that were sufficiently deleterious to stratospheric ozone that their continued production and use required limitation. An amendment to the Protocol caused commercial halon production to cease at the beginning of 1994 (Harrington, 1993). The focus of concern is that the halon molecule is sufficiently stable in the lower atmosphere that it will eventually be transported to the stratosphere unaltered. There the carbon-bromine bond is vulnerable to photodissociation by solar ultraviolet radiation. The liberated bromine atom then enters into a catalytic cycle which has the net effect of consuming the shielding ozone.

Much has been written in the scientific and popular literature on how bromine and chlorine atoms lead to depletion of the ozone layer. Conferences are held annually (*e.g.*, *The 1993 International CFC and Halon Alternatives Conference*, 1993; *Halon Alternatives Technical Working Conference*, 1993) to discuss progress in finding replacements for technologically important ozone depleting chemicals. An exhaustive study of the atmospheric chemistry of fluorinated compounds being considered as alternatives to halons and chlorofluorocarbons (CFCs) was commissioned by the World Meteorological Organization (1989). Background on the halon/ozone issue is also provided by Andersen (1987) and Grant (1989). Additional articles are cited in the report by Pitts *et al.* (1990).

Ford (1975) has traced the development of CF_3Br for firefighting purposes since its original formulation in the 1940s. Halon 1301 has been the agent of choice for fire suppression on board aircraft for decades because of its inherent ability to inhibit flames at low concentrations while exhibiting a number of additional strongly positive attributes, including a high level of stability, high liquid density, low boiling point, low electrical conductivity, low corrosiveness, low toxicity, and low cost. These properties are desirable for many applications, but the penalty placed upon excessive weight or volume on board commercial and military aircraft tightly constrains the choices of suitable alternatives.

The elimination of new production of halon 1301 has forced the manufacturers, owners, and users of aircraft to search for an alternative. Since it may take years to retrofit the large fleet of current aircraft, there is an urgency to identify one or more chemicals soon. The retrofit process will likely be expensive. The bromine atom in halon 1301 which is responsible for the ozone destruction is also largely responsible for the molecule's high fire suppression effectiveness. If the alternative chemicals do not contain a moiety like bromine and are less efficient suppressants, then new, larger agent storage and delivery components will need to be designed. To avoid costly design mistakes, extensive performance data regarding the amount of agent required for flame extinction and the compatibility of the alternatives with the delivery system and aircraft construction materials is essential.

1.1.2 Aircraft Engine Nacelles and Dry Bays. There are a number of distinct areas in need of protection against an in-flight fire in an airplane, including the cockpit, passenger compartment, baggage areas, auxiliary power units, fuel tank ullages, engine nacelles, and dry bays. The research

program described in this publication focussed on the latter two. The requirements and constraints of the engine nacelle and dry bay areas are quite different, and the methods used to arrive at the best choice for an alternative to halon 1301 for each application differ accordingly.

The engine nacelle is the portion of the airframe which surrounds the main jet engines. It varies in shape and size but is typically annular with a length and diameter of the same order as the engine it encases. Fuel and hydraulic lines, pumps and lubrication systems are located within the nacelle volume. Ventilation is provided to prevent the build-up of combustible vapors, and drain holes on the underside are used to reduce the amount of fluid that could pool following a leak. The engine's combustion chamber liner is isolated from the nacelle wall, but surface temperatures up to 700 °C can exist during operational extremes. The firefighting agent can be located directly adjacent to the nacelle or removed by tens of meters and piped to the fire zone, depending upon the availability of space. An example of a nacelle and fire suppression system is shown schematically in Figure 1.

The operational requirements for commercial and military engine nacelle protection are similar. Thermal sensors are used to determine when an abnormal, overheated condition exists in the nacelle region. In such a case, the flight of the airplane is leveled and the designated crew member arms the appropriate halon 1301 bottle and fires the release mechanism. The halon is stored at pressures in the range of 2 to 4 MPa, and the certification process requires that enough agent be available to maintain a minimum concentration (about 6% by volume) throughout the nacelle for a minimum time interval (about 0.5 s) to ensure that the fire will be extinguished and not relight. Many systems have a duplicate bottle to be used as a back-up should the first shot be unsuccessful.

Dry bays refer to normally closed spaces, often adjacent to flammable liquid storage areas and in which a combustible mixture and an ignition source could co-exist following penetration by an anti-aircraft projectile. The fire threat is unique to military aircraft. Dry bays vary considerably in volume, typically being in the range of 0.2 to 3.0 m³. They are located in the wings and fuselage, and their shape is most often irregular, as can be seen in Figure 2. Aspect ratios up to 10:1 are not uncommon. The bays may or may not be ventilated, and are usually cluttered with electronic, hydraulic and mechanical components. Compared to the events leading to engine nacelle fire suppression, the required timing is two orders-of-magnitude faster for dry bay protection. High speed infrared detectors sense the initial penetration of the projectile and automatically arm and fire the halon bottle. The storage bottles are located directly in or adjacent to the protected space to minimize the time needed to flood the volume totally. The entire suppression sequence occurs in less than 100 ms and requires no crew intervention.

1.1.3 Full-scale Simulations. Fire suppression is affected by a combination of the agent's physical properties, chemistry and transport phenomena, making it a highly nonlinear process and difficult to scale. Full-scale tests are needed to extend bench-scale experiments and validate theoretical models before aircraft safety systems can be reliably designed. The Survivability Enhancement Branch of Wright Laboratory, located at Wright-Patterson Air Force Base, Ohio, operates unique full-scale aircraft engine nacelle and dry bay fire test facilities. How these facilities are to be used to identify the best near-term alternative to halon 1301 is outlined by Bennett (1992). The Design of Experiments (DOX) methodology which has been adopted allows the minimum number of full-scale tests to have the maximum impact on identifying the critical parameters which influence an engine nacelle or dry bay fire. The range of parameters chosen was determined by the Air Force after surveying existing military aircraft manufacturers and users (Mascarella, 1993).

The Aircraft Survivability Research Facility (ASRF) at Wright-Patterson AFB consists of a gun range in which an anti-aircraft round can be directed at a precise location in a full-size test article in a repeatable, controlled manner while maintaining the safety of the operating personnel. Rectangular boxes with internal volumes between 0.28 and 2.8 m³ have been used to simulate actual aircraft dry

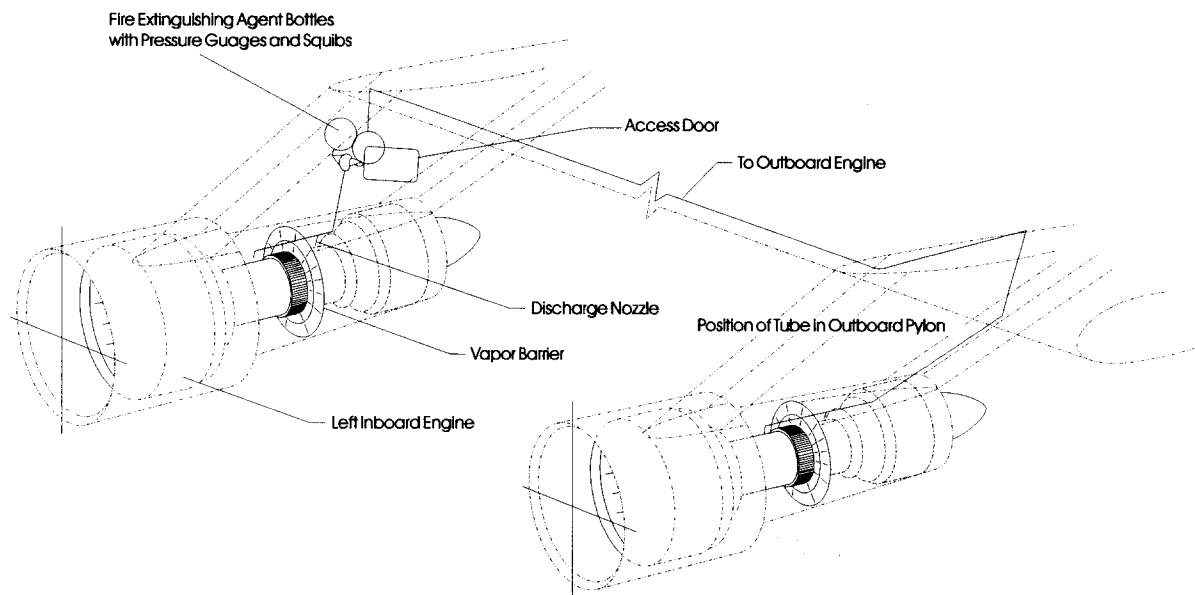


Figure 1. Schematic diagram of wing-mounted engine nacelle and fire extinguishing system (based upon C5-A and provided by M.L. Kelleck, Booz-Allen & Hamilton, Inc.).

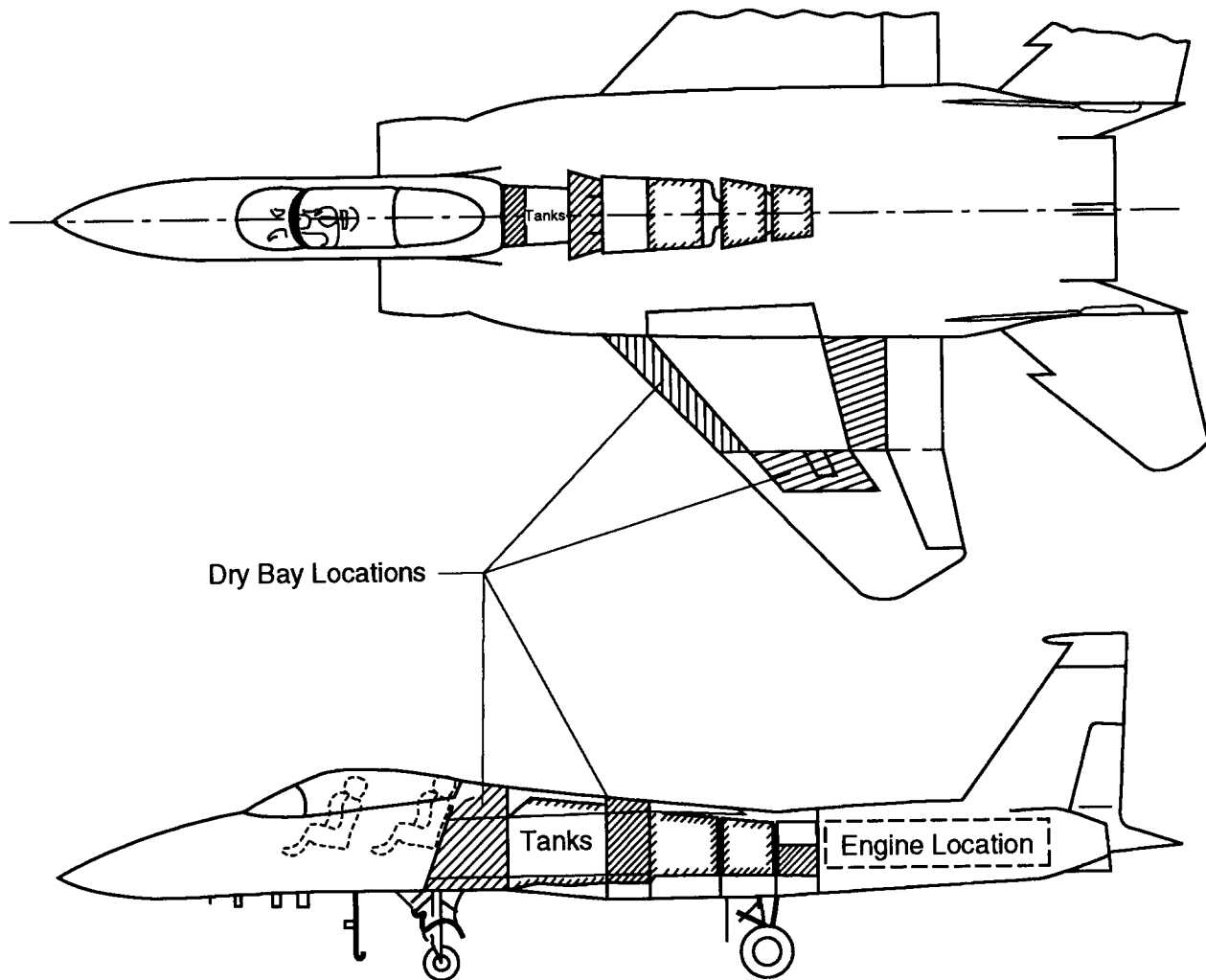


Figure 2. Schematic diagram of typical dry bays in an aircraft (taken from Figure 1 of Heinonen *et al.*, 1990).

bays. A fuel tank is located behind the dry bay so that it will rupture following the impact of a fired projectile. Dry bay geometry (aspect ratio), internal obstructions, location and timing of the release of the firefighting agent, the type and amount of fuel released, and the characteristics of the projectile are some of the parameters which can be varied. Jet engine exhaust streams can be directed past the test article to simulate the high speed flows experienced in flight. A typical test article is shown in Figure 3.

The Aircraft Engine Nacelle (AEN) facility (Figure 4) was designed to simulate a 120° arc segment of a full size engine nacelle. The air flow, air temperature, and air pressure can be varied to cover the range experienced by an actual aircraft in flight. A fire from a fuel spray or ruptured hydraulic fluid line can be simulated, and the amount of clutter, location and timing of agent injection, and hot-surface temperature are some of the parameters which can be precisely controlled. The AEN is used to determine the amount of agent necessary to extinguish a realistic engine nacelle fire, and can compare the relative effectiveness of two different agents in suppressing a nearly identical fire. A full 360° simulated engine nacelle with adjustable diameter core is a new addition to the facility.

1.1.4 Agents Selected for Screening. In a study by Pitts *et al.* (1990), an exploratory list of over 100 possible halon alternatives was constructed. These included both high boiling point and low boiling point compounds for replacements of halon 1211 and halon 1301, respectively. The chemicals embodied a range of chemical and physical principles thought to affect flame suppression capability. Examination of these chemicals, then, provides a basis for the search for alternatives to the current commercial halons. This list included the following classes of compounds:

- saturated and unsaturated halocarbons,
- halogenated hydrocarbons containing single and double-bonded oxygen,
- sulfur halides,
- phosphorous compounds,
- silicon and germanium compounds,
- metallic compounds, and
- inert gases.

Zallen (1992) reviewed past investigations of firefighting agents, starting with the seminal work by Purdue University (1950). In that early investigation, the concentrations necessary to inhibit a mixture of heptane and air from igniting were tabulated for over 50 chemicals. An objective was to identify general purpose agents which were effective, clean, stable and less toxic than CCl₄. A large number of halocarbons were scrutinized, along with a few compounds containing sulfur, phosphorous and silicon. Zallen (1992) summarized the extensive work done by the U.S. Navy (*e.g.*, Sheinson *et al.*, 1989) and the New Mexico Engineering Research Institute (*e.g.*, Tapscott *et al.*, 1990) for ship-board and ground-based aircraft fire suppression, respectively, before arriving at his recommendations to the U.S. Air Force for their in-flight applications. An important consideration was the likely availability of the chemical in large quantities for full-scale testing in 1994, and fleet installation by 1996.

Zallen recommended four perfluorocarbons (FCs), six hydrofluorocarbons (HFCs), and two hydrochlorofluorocarbons (HCFCs). The core candidate compounds actually selected by the Air Force for screening are shown in Table 1. Several compounds in the table were not on Zallen's list: a 60%/40% mixture by mass of HFC-32 and HFC-125, sodium bicarbonate powder, and HFC-236fa. The HFC-32/125 mixture and sodium bicarbonate were added by the Air Force; HFC-236fa was added following a press release soliciting additional chemicals that met the criteria discussed above

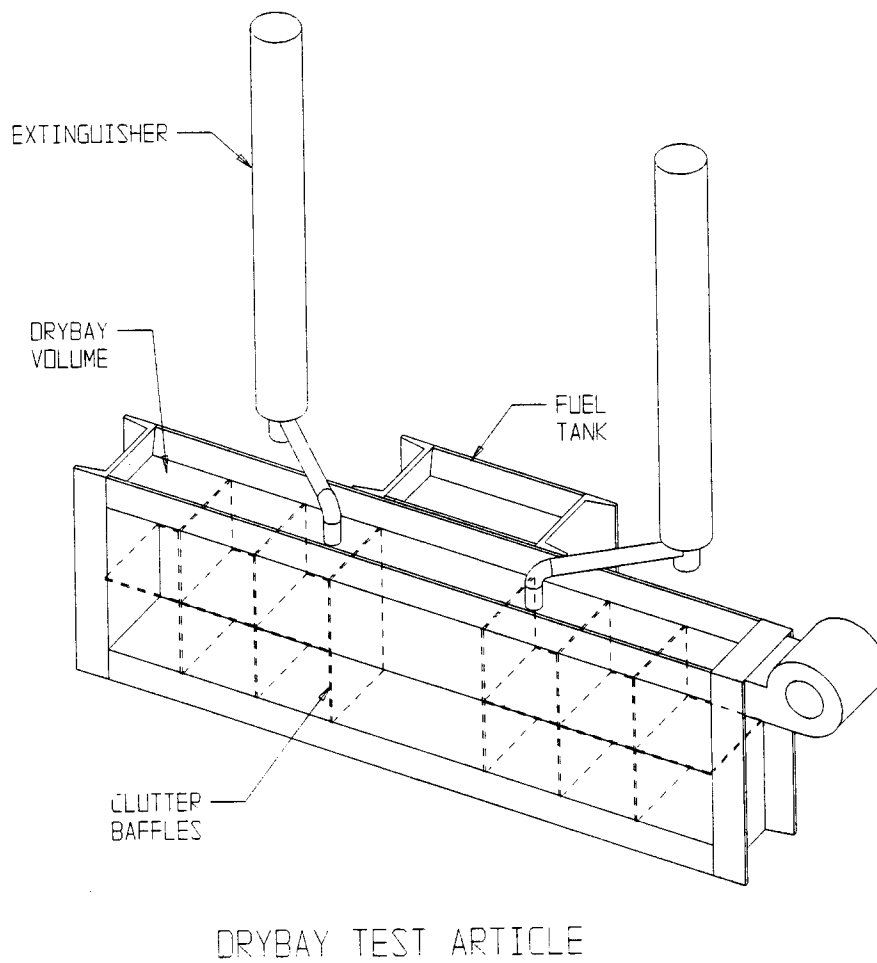
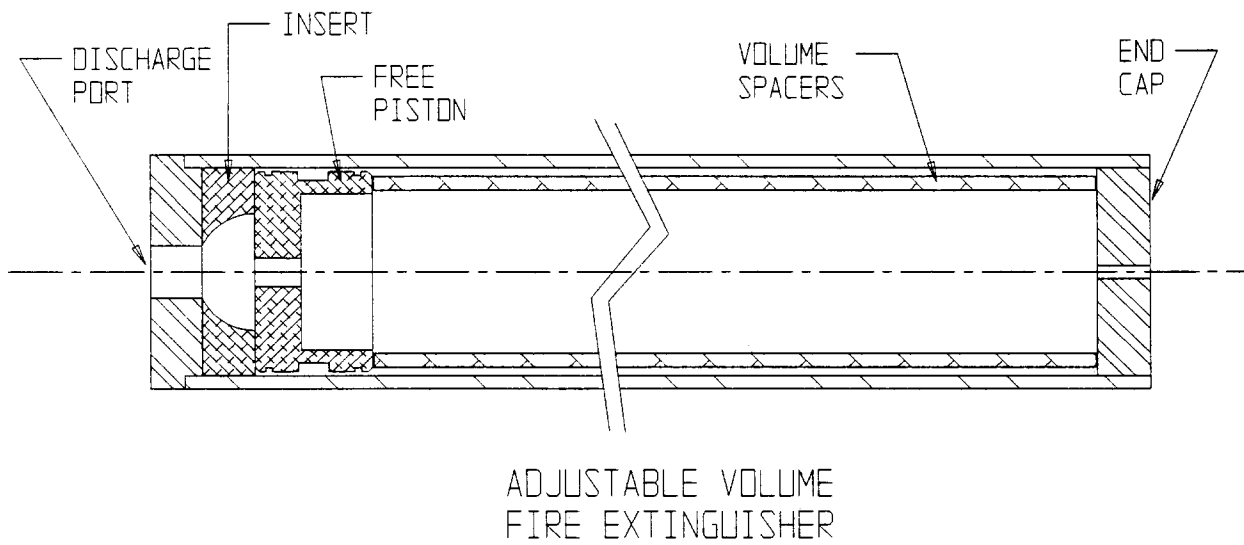


Figure 3. Example of test article used in live-fire dry bay simulator at WPAFB Aircraft Survivability Research Facility (provided by B. Poole, WPAFB).

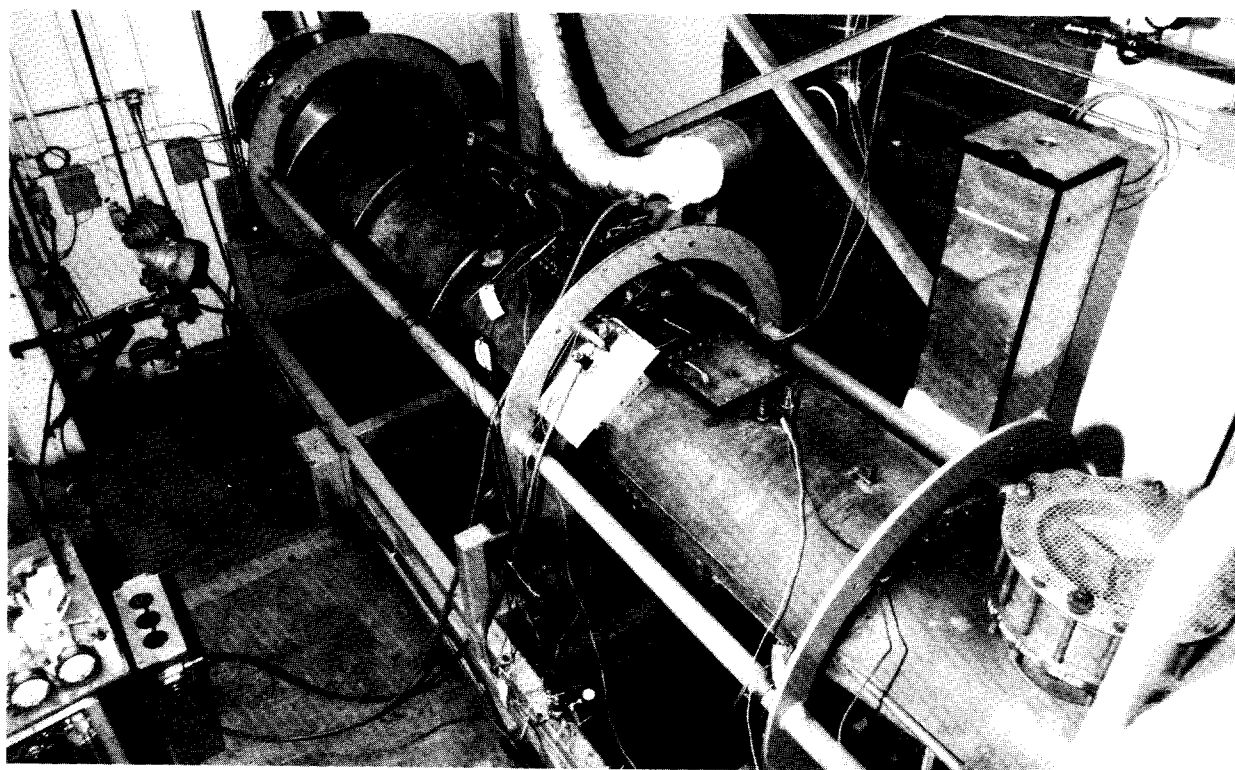
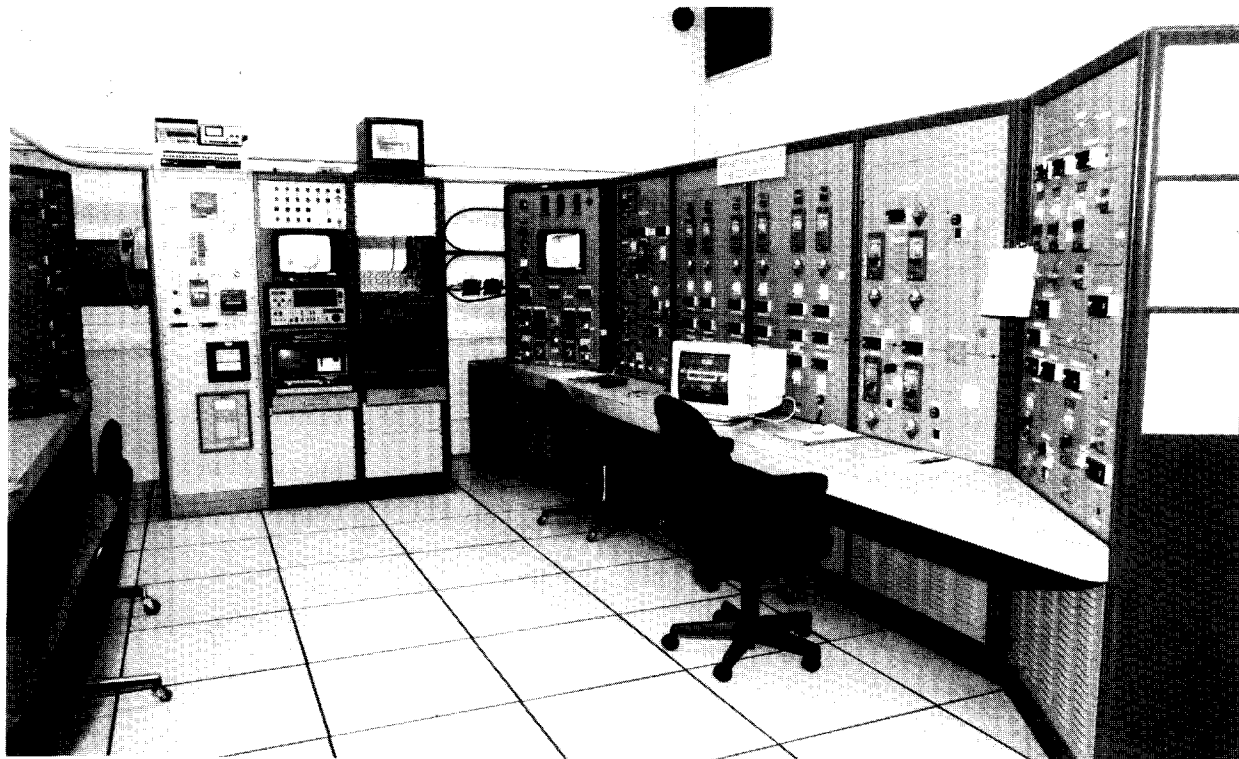


Figure 4. Aircraft Engine Nacelle test facility at WPAFB (provided by G. Caggianelli, WPAFB).

Table 1. Core chemicals examined

Chemical Formula	Designation	IUPAC Name
C_2F_6	FC-116	hexafluoroethane
C_3F_8	FC-218	octafluoropropane
C_4F_{10}	FC-31-10	decafluorobutane
cyclo- C_4F_8	FC-318	octafluorocyclobutane
CH_2F_2	HFC-32	difluoromethane
C_2HF_5	HFC-125	pentafluoroethane
CH_2F_2 (60 %)/ C_2HF_5 (40 %)	HFC-32/125 (60/40)	-
$C_2H_2F_4$	HFC-134a	1,1,1,2-tetrafluoroethane
C_3HF_7	HFC-227ea	1,1,1,2,3,3,3-heptafluoropropane
$C_3H_2F_6$	HFC-236fa	1,1,1,3,3,3-hexafluoropropane
CHF_2Cl	HCFC-22	chlorodifluoromethane
C_2HF_4Cl	HCFC-124	2-chloro-1,1,1,2-tetrafluoroethane
$NaHCO_3/SiO_2$ (1 %)	-	sodium bicarbonate/silicon dioxide

(Kosko, 1993). On Zallen's list but not included among the core candidates were HFC-23 and HFC-143a. HFC-32 was dropped early in the NIST research program because testing confirmed that it was flammable at concentrations likely to be encountered. A full test program was therefore carried out for eleven gaseous potential alternatives and sodium bicarbonate.

1.2 Objectives and Task Summary

This research program began in 1992, funded jointly by the Air Force, Army, Navy and the Federal Aviation Administration because of their mutual interest in aircraft safety. The program entailed:

- establishing a comprehensive experimental program to screen the performance of the agents listed in Table 1, plus other promising chemicals, as a means to identify the best candidates for subsequent full-scale aircraft fire extinguishment evaluation at Wright Laboratory; and
- addressing the compatibility of these agents with flight systems, people, and the environment.

Based on these data, three candidates for each of the two applications (dry bay and engine nacelle) were to be recommended for full-scale evaluation at Wright-Patterson AFB. These did not need to be the same sets. Ideally, each set would include the top two candidates from Table 1.

If the search for additional chemicals uncovered other promising candidates, then the best of these was to be recommended for full-scale testing as well. Otherwise, a third chemical from Table 1 would be identified. These recommendations were to be presented to the sponsors in September, 1993. Following the sponsors' selection of chemicals for full-scale testing, longer-term compatibility experiments to increase confidence in the preliminary results were to continue, with a report on that phase of the research to be delivered by September 30, 1995.

Sections 2-9 of the current report document the research activities related to the fire fighting effectiveness of possible alternatives, and research activities dealing with various aspects of the agents' compatibility with aircraft construction materials and associated systems. Establishing a scientific basis upon which to choose the best alternatives has been an overriding objective of the program. The facilities developed and knowledge gained in meeting this objective go well beyond the specific applications to aircraft, and advance fire suppression technology in general. A summary of the major conclusions are given and significant recommendations are highlighted in Section 10.

In the course of searching for alternative agents and in developing these facilities, certain products were used and are identified by trade name in this report to adequately document the research performed. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply that this commercial equipment is the best available for the purpose intended.

1.2.1 Fire Suppression Effectiveness Screening. Because of storage weight and volume constraints, the new suppressant should demonstrate optimal efficiency for quenching flames. The thermodynamic state, transport properties, and combustion chemistry of an agent are critical to this ability. An experimental design was chosen that allowed these three aspects of the different agents to be examined under conditions which isolated the influence of the many independent parameters. Considerable thought was given to the most appropriate means to relate the results of the individual tests to overall performance criteria. The uncertainty in each experiment was estimated by replication when appropriate. In other cases, analogy to similar experimental procedures, experience with related test methods, and theoretical calculations were used to establish error limits.

The thermodynamic state of a pure substance is defined by its density over a range of pressures and temperatures. In mixtures, the solubility of one material into another influences the state as well. Quantitative thermodynamic state relations are incomplete for many of the pure alternative agents, and very little data on the solubility of pressurizing gases into the liquid agent existed at the start of this investigation. An objective of this task was to measure the pressure of the agent at -60 °C, 25 °C and 150 °C in a constant volume vessel, with the agent pure and in mixtures with CHF₃ and N₂. The temperatures chosen span the maximum anticipated range of exposure of a storage bottle in the field. The solubility of the pressurizing gas was measured at room temperature and 4 MPa, a typical halon 1301 bottle pressure. Section 2 presents the results of the thermodynamic study.

The release and delivery of the agent is particularly critical for dry bay protection, where events leading to a threatening over-pressure occur in less than 50 ms. The behavior of the agent during conditions of vessel blow-down and the characterization of the dispersion, mixing and evaporation of the resulting two-phase turbulent jet are the objects of investigation in Section 3.

Four different flame suppression experimental facilities were designed with the objective of examining the flame extinction properties of the agents over the whole range of conditions likely to be encountered by aircraft in flight. The facilities, briefly mentioned in the following paragraphs, are described and the suppression concentrations are tabulated in Section 4.

The first suppression facility, an opposed-flow diffusion flame (OFDF) burner, is an excellent test-bench for evaluating an agent's extinguishing efficiency over a broad range of flame conditions. The reasons for this are five-fold:

1. the geometry of the flow is eliminated as variables in the system;
2. the flow field strain rate is an independent variable;
3. the system is steady, one-dimensional, and accessible to probing;
4. the reactant flow rates are relatively small, enabling extensive testing with limited quantities of chemicals; and
5. the concentrations and temperatures of the agent, fuel, and oxidizer are easily controlled and repeatable.

Cup burner measurements, which have been relied upon almost exclusively in the past to determine suppression concentrations, were made in the second facility and compared to the OFDF results. The cup burner is also flexible, and was used to assess the impact of multiple fuels on the ability of all the agents, including the sodium bicarbonate powder, to suppress the flames.

In the third facility, a turbulent spray burner was built to simulate a fire created by a ruptured fuel or hydraulic fluid line in an engine nacelle, or the splash of fuel into a dry bay. This is because threatening fires are invariably turbulent, and the turbulence influences the mixing of the fuel and air, the heat released, and the products of combustion. The amount of agent (gaseous or powder) and the rate of injection were independent parameters which could be controlled with this facility.

The speed of an accelerating turbulent flame near the detonation limit can reach magnitudes two orders higher than that of the spray flame. The interaction of the agent with a detonation could not be predicted from the other flame results. Thus, a detonation tube (the fourth facility) was used to simulate the threat posed by an impending explosion. The reduction in velocity and pressure build-up of the high speed, turbulent flame was used as a quantitative measure of the agent's effectiveness in suppressing the detonation.

Significant improvements to suppression performance are likely to occur only if the agent is able to inhibit key chain-branching reactions in the combustion process. It would be beneficial to understand the mechanisms by which alternative agents extinguish a flame. If such chemical intervention were possible with materials that were tailored to degrade before threatening the atmosphere, then additional environmental constraints might be overcome, and opportunities for enhancing the performance of advanced aircraft through the reduction in bulk of the onboard fire suppression system might exist. To assist in gaining the objective of superior chemical inhibition, the elementary reactions of different classes of chemicals were examined, and a partial understanding of how the molecular structure influences the suppression process and the atmospheric reactivity of the neat agent was obtained. Section 5 outlines the progress made to date on the kinetics of fluorine inhibited flames and possible routes to acid gas formation. Alternative chemicals beyond the core list from Table 1 are discussed, with the rationale for choosing them and our current assessment of their potential. The development of an understanding of the acid gas formation process is ongoing, and a method of estimating the amount formed during suppression of a given fire threat will be provided in the September, 1995 report.

1.2.2 Compatibility with Systems and People. A desirable suppressant also needs to have minimal harmful interactions with aircraft materials, people, and the environment. A set of tasks were designed to provide essential data on the stability of the chemicals, compatibility of the chemicals and their by-products with both metallic and polymeric materials, and definition of possible limitations for exposure of people and the environment. The approach followed from an earlier study (Gann *et al.*, 1990), in which preliminary screening procedures and criteria were developed for the **general** evaluation of alternatives to both halons 1211 and 1301. The advanced procedures developed here are more directly applicable to the conditions in engine nacelles and dry bays.

The compatibility studies covered a range of storage conditions. Based on information supplied by the Air Force, it was presumed that the agent storage would be initially at 25 °C and 4.1 MPa. In flight, these could rise to 150 °C and 5.8 MPa. Thus, the stability of a chemical and its potential damage to the storage vessel were examined under these conditions. Lower temperatures and pressures are also possible in service. However, lesser damage would occur under these conditions, and we deemed reduced temperature measurements unnecessary.

At present, the storage times on board aircraft are of the order of five years. In order to enable a selection of the most promising chemicals by the September 30, 1993 deadline, only much shorter exposures were possible. Phenomenological modeling, based on exposures at various time intervals, has been pursued to increase confidence in the extrapolation to longer times. Were severe non-linear effects observed for some chemicals, NIST would recommend against their use or would suggest that shorter storage times be implemented. For those chemicals selected for further testing, longer exposures (*e.g.*, one year) will be performed to improve confidence in the extrapolations. The procedures and data are presented in Section 6. The results of the long-term experiments will be summarized in the September, 1995, report.

During storage under elevated pressure and perhaps temperature, it is desirable that the agent not harm the storage container. This could result in leakage of the chemical over time or even in-flight rupture of the bottle. With the assistance of the sponsors, a list of current and potential materials for storage bottles was compiled. This included eight metal alloys, six elastomer o-rings, and three lubricants. Approximately one-month exposures at *ca.* 150 °C and 5.8 MPa provided data on the potential for affecting the storage materials. The metals corrosion research is discussed in Section 7. Section 8 details the study of the compatibility of polymeric materials which could be in contact with the agent under the above range of conditions.

Following dispensing, the suppressant chemical spends time in and near the flames, leading to some decomposition and the production of potentially harmful by-products. It is known that the fluids in Table 1 produce HF and, in two cases, HCl. To a first order, it was presumed that the yields of HF from the various chemicals would pose the same threat to aircraft materials, thus providing little differentiation among the chemicals. Testing of this will be reported in the September, 1995 report. Pilot examination of the potential for NaHCO₃ and its by-products was performed, since there was reason to expect a serious interaction with the aluminum used in aircraft bodies. This is presented in Section 7.

There are two other key components affecting the selection of alternative suppressants. First, one must be able to predict the potential exposure of people during an accidental discharge. The simplest assumption is that the distribution of the chemical in a confined space is uniform. Experiments were conducted to verify the validity of this hypothesis. Second, with the rapidly-changing regulations for protecting the earth's environment, it is necessary to know the pertinent requirements for testing of these families of chemicals. Both of these topics are discussed in Section 9.

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10. SUMMARY AND RECOMMENDATIONS

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The main objective of this research program was to provide guidance to the sponsors on which materials to evaluate in the full-scale fire suppression test plan at Wright-Patterson AFB. Specifically, the recommendations were to include the following:

1. the best two agents from the core list of twelve FCs, HFCs and HCFCs provided by the Air Force when NIST began the project in 1992,
2. the best practical alternative from among materials not on the list of twelve, and
3. whether or not sodium bicarbonate powder was a viable option.

New metrics have been developed along the way which can be used to rate other fire fighting compounds for a variety of applications.

The methodology for combining the results of literally hundreds of tests for the purpose of defining an overall performance rating of the chemicals is described in this section. A justification for each agent recommended using the methodology and the ranking of all of the agents evaluated by these methods are included. The report ends with a summary of the continuing investigation into the formation of by-products during the suppression process and long-term materials compatibility for the agents selected by the sponsors for full-scale testing. A list of recommendations for further research is provided.

10.1 Rationale for Selection

The agents have been rated using the criteria given below. The desirable magnitude of each variable is given in parentheses.

- saturation liquid density at 25 °C (high)
- temperature at which storage vessel reaches liquid-filled condition (high)
- boiling point at 101 kPa (low)
- discharge rate from vessel (high)
- dispersion and mixing with air (high)
- distance required for agent vaporization during sudden discharge (short)
- concentration required to extinguish laminar flame in opposed-flow diffusion (OFDF) burner for two air temperatures, multiple fuels, and variable strain rates (low)
- concentration required to suppress cup burner flame for multiple fuels (low)
- concentration required to extinguish turbulent spray flame for two temperatures and fuels, and variable injection rates (low)
- concentration required to suppress a high-speed turbulent flame in detonation tube for two equivalence ratios (low)

- agent residue (low)
- corrosion of metals by neat agent for multiple materials (low)
- swelling of polymers by neat agent for multiple materials (low)
- durability of elastomers and greases by neat agent for multiple materials (high)
- decomposition during storage (low)
- concentration of corrosive byproducts during suppression (low)
- ozone depletion potential (low)
- atmospheric lifetime (short)
- relative potential human exposure (low)
- availability (high)
- price of chemical (low)

Many of the above criteria did not lead to differentiation among the alternative agents to a statistically significant degree. The discriminating factors could be lumped into four categories: agent dispersion and evaporation characteristics, required storage volume, environmental factors, and operational issues.

10.1.1 Dispersion and Evaporation. The rate of agent discharge from the storage vessel was discussed in Section 3.4 for different initial conditions. The average volume flow rate, V_d , of the liquid agent from a 2/3-filled vessel initially at room temperature and 4.1 MPa is summarized here in Table 1. All of the alternative agents leave the vessel at about the same volume flow rate, 10.5 ± 0.6 l/s, which is significantly faster than the discharge rate of halon 1301. Once leaving the bottle, more of an agent is required aboard an aircraft if it disperses and evaporates slowly to ensure that a fire anywhere within the protected space can be extinguished. Measurements taken during a discharge under conditions similar to a large open bay were discussed in Section 3.5. From those measurements, the dispersion, mixing and evaporation behaviors of the alternative agents were evaluated. The rankings from that study are also listed in Table 1.

Unlike the dry bay discharge which is limited to the heat contained in the stored liquid for vaporization of the agent, more opportunity is available for evaporating the liquid droplets in engine nacelle applications. Heat transferred from the piping system and air can provide the additional energy for the vaporization process as long as the surrounding temperature is sufficiently above the agent boiling point. The minimum temperature required to ensure that enough agent is in a fully gaseous state, T_{min} , can be estimated from an energy balance on the protected volume assuming the mass fraction of agent, Y_i , is the amount required to suppress a JP-8 cup burner flame. It can be shown that

$$T_{min} = T_b + \frac{Y_i \Delta H_{vap}(T_b)}{(1 - Y_i) C_{p,air} + Y_i C_{p,i}} \quad (1)$$

where the specific heats are for the liquid agent, $C_{p,i}$, and air, $C_{p,air}$, and ΔH_{vap} is the enthalpy of vaporization at the boiling point, T_b . Values of T_{min} are listed in Table 1 for each of the agents. HFC-134a, FC-318, FC-31-10, HCFC-124 and HFC-236fa require temperatures greater than 25 °C to vaporize fully, making them suspect for low temperature operation. The FC-116 is stored above its critical point, but if one were interested primarily in low temperature operation, its T_{min} value equal to -43 °C would make FC-116 a strong candidate. FC-218, HFC-125 and CF₃I are the only other compounds with T_{min} less than 0 °C.

Table 1. Agent discharge, dispersion and evaporation parameters

Agent	Sect. 3.5 Rank	T_{min} , °C	V'_d , l/s
CF ₃ Br	n.r.	-42	7.6
FC-116	n.r.	-43	a
FC-218	1	-7	10.8
HFC-125	1	-6	9.8
HFC-32/HFC-125	3	+20	10.0
HCFC-22	4	+21	10.2
HFC-134a	5	+29	10.7
HFC-227ea	6	+19	11.1
HCFC-124	7	+28	10.9
FC-318	8	+28	10.8
FC-31-10	9	+29	10.3
HFC-236fa	10	+37	10.8
CF ₃ I	n.r.	-1	a

a data not taken

n.r. not ranked

The Jakob number, Ja, was defined in Section 3 as the amount of heat available from cooling the liquid agent from ambient temperature to its normal boiling point, divided by the agent's heat of vaporization. A high value for Ja and a low value for T_{min} are both desirable attributes which often, but not always, go hand-in-hand. For example, the Jakob numbers for FC-218 and CF₃Br are 0.59 and 0.51, respectively, while T_{min} for CF₃Br is 35 °C less than the minimum temperature for FC-218. The implication is that the perfluorocarbon will flash more completely from a storage vessel at room temperature than halon 1301 in a dry bay application, but FC-218 will vaporize less efficiently in the engine nacelle at lower operating temperatures.

10.1.2 Storage Volume. The required storage volume is estimated from the measured suppression concentration and the density of the agent within the storage vessel at ambient temperature. The fuel type and temperature of the air were found to be of secondary importance in the measurements of the relative mass of the agents. While the absolute amount of agent necessary to quench the flames varied with the apparatus, the strain rate, the rate of injection, and the equivalence ratio, a single parameter called the volume factor, VF, is useful in comparing the relative suppression performance of the various agents. VF is a measure of the liquid agent volume in the storage vessel normalized by the liquid volume of halon 1301 required to suppress a flame under identical conditions; *i.e.*,

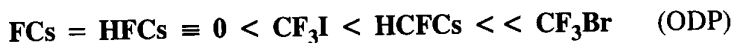
$$VF \equiv \left(\frac{\rho_{1301}}{\rho_i} \right) \left(\frac{Y_i}{Y_{1301}} \right) \left(\frac{1 - Y_{1301}}{1 - Y_i} \right) \quad (2)$$

The saturation liquid densities at 25 °C, ρ_i , were taken from Section 2 of this report. Table 2 lists the values of VF for each apparatus. The OFDF values were found from the ambient temperature experiments with JP-8, taken at a strain rate of 100 s⁻¹. The cup burner values were measured with heptane as the fuel. For the spray burner, the VF was calculated from the mass of agent injected in the ambient temperature JP-8 experiments. The performance in the detonation tube was based upon the average of the mass of agent required to reduce the pressure ratio by one half and to 10% of the maximum increase, with data restricted to the lean experiments. The uncertainty in the values of VF is estimated to be $\pm 10\%$.

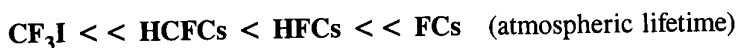
Independent of the apparatus, the volume factors for FC-116 and the HFC-32/125 mixture are the highest (*i.e.*, the poorest performers). The best performer in the table is sodium bicarbonate. (Note that the flame suppression number, FSN, is used to rate the powder rather than VF. The direct comparison is valid as long as the powder density is close to the density of liquid halon.) Iodotri-fluoromethane is the most effective of the gaseous agents in suppressing the cup and spray burner flames, and HCFC-124 is the best of the core alternatives. FC-218 stands out as the best agent in suppressing the high-speed deflagration. Except for the high value of VF for HCFC-22 in the deflagration tube, there is little basis upon which to say that any one of the remaining agents is better than another in suppressing the flames using this metric.

10.1.3 Environmental Factors. Primary environmental concerns include acute toxicity, ozone depletion potential, and atmospheric lifetime of the alternative agents. None of the core chemicals have been identified as presenting an acute toxicity hazard, so that consideration of application to normally unoccupied spaces like the engine nacelle and dry bay does not lead to any discrimination among them. Toxicity data on CF₃I is incomplete, but preliminary studies (as of this writing) have not uncovered any major health hazards which would prevent its application to unoccupied spaces.

All but two of the core agents have an ODP of zero. The two chlorinated compounds, HCFC-22 and HCFC-124, have an ODP less than one tenth of the present EPA limit. Iodides are not currently regulated, but preliminary estimates indicate that the ODP for CF₃I released in the lower troposphere is small because it easily photodissociates. Any of the chemical released directly into the stratosphere, however, would react efficiently with the local concentration of ozone. The general ranking (from best to worst) based upon ODP is as follows:



Short atmospheric lifetime is considered a positive attribute in an alternative agent, but as of this writing it is not mandated by governmental regulations nor international agreements. The estimated tropospheric lifetime varies by over four orders-of-magnitude, with CF₃I having the shortest (weeks) and the perfluorocarbons having the longest (1000s of years). Among the remaining compounds, the HCFCs have a shorter lifetime than the HFCs, which are less long-lasting than CF₃Br (estimated lifetime is 66 years). The following ranking applies, from best to worst:



Because sodium bicarbonate is a powder, atmospheric chemistry is a non-issue. The powder is also considered to be non-toxic.

Table 2. Volume factors for flame suppression in different apparatus

Agent	OFDF	Cup Burner	Spray Burner	Deflag. Tube
NaHCO ₃	0.23 ^b	0.45 ^b	0.85 ^b	a
CF ₃ I	a	0.9	0.8	1.4
HCFC-124	2.5	2.2	1.8	1.5
HCFC-22	3.0	2.8	1.8	2.5
HFC-236fa	3.1	2.3	1.8	1.4
HFC-227	3.2	2.4	1.8	1.4
FC-218	3.6	2.8	2.1	1.2
FC-31-10	3.9	2.6	2.1	1.4
HFC-134a	4.0	2.8	2.0	1.8
HFC-125	4.1	2.8	2.0	1.7
FC-318	4.1	2.6	2.0	1.4
HFC-32/125	5.3	3.5	2.5	2.5
FC-116	7.1	6.0	4.0	2.5

^a data not taken^b FSN for powder

10.1.4 Operational Issues. Factors which involve maintenance or logistics can be evaluated separately from fire suppression performance and environmental impact. These include agent residue, stability under storage, accidental discharge under storage, corrosion from combustion byproducts, compatibility of the agent with metals and seals, and availability of the chemical. Table 3 compares the agents on operational issues. A rating of "B" in the table implies the compound has no significant shortcomings nor advantages over the other agents in that particular performance criteria. A "C" indicates a weakness or below average performance, but not necessarily a fatal flaw. An "A" rating means above average performance or a particular operational advantage demonstrated by the compound.

None of the core agents left an undesirable residue when discharged, none segregated in space to a significant degree during a simulated leak, and little decomposition was observed during one-month, high temperature storage. All produced a considerable amount of undesirable HF during suppression. There was some variation in the interaction of the core compounds with metals and polymers, but storage material combinations do exist which are compatible with most of the agents. Industrial sources exist for the core agents, so that neither lack of availability nor price of the agent were issues of major concern.

Iodotrifluoromethane from the initial batch received was observed to be slightly more aggressive than the core agents in attacking some metals and polymers, but the limited amount of short-term testing which was completed did not uncover insurmountable materials compatibility issues. Iodine

Table 3. Rating of agents on various operational issues: A, above average performance or particular advantage; B, average performance or neutral; C, below average, or particular disadvantage.

Agent	Avail- ability	Cost	Stability in Storage	Metals Compati- bility	Polymers Compati- bility	Combustion Byproducts	Residue
FC-116	B	B	A	A	A	B	A
FC-218	B	B	A	B	B	B	A
FC-318	B	B	A	C	A	B	A
FC-31-10	B	B	A	C	B	B	A
HFC-125	B	B	*	A	A	B	A
HFC-32/125	A	B	B	B	A	C	A
HFC-134a	A	B	A	A	B	C	A
HFC-227ea	B	B	A	A	A	B	A
HFC-236fa	B	B	*	B	A	B	A
HCFC-22	A	A	A	C	B	B	A
HCFC-124	B	B	A	B	A	A	A
CF ₃ I	C	C	B/C	*	*	*	#
NaHCO ₃	A	A	B	C	*	C	C

* insufficient data for rating

highly acidic impurity present in some samples

was observed as a decomposition product when the CF₃I was subjected to the high temperature storage test. No other significant decomposition products were identified. (However, noticeable acidic residue was present in batches of CF₃I received later from a second supplier.) U.S. production of CF₃I, as of September 30, 1993, was of the order of 50 kg/yr, and bulk quantities sufficient for full-scale testing were unavailable. The renewed interest generated in iodofluorocarbons could cause industrial production to increase substantially. However, as of this report, bulk production of sufficiently pure chemical has not been demonstrated.

All of the NaHCO₃ which is not carried away from a fire remains as an undesirable residue. Instability of the carbonate under high temperature storage was not fully explored, but some metal corrosion was evident. A major product of combustion from the powder is NaOH, which interacts aggressively with aluminum.

10.2 Ranking of Agents

10.2.1 Agents Recommended *Against* Full-Scale Engine Nacelle and Dry Bay Testing. Cup burner tests with HFC-32 confirmed previous reports that the compound is flammable. The decision was made, in consultation with the sponsors, to replace HFC-32 with HFC-236fa in the test matrix.

During the course of the evaluation, seven chemicals were identified which either performed unimpressively or were deficient in other ways. Considering the available alternatives, we do not recommend these for full-scale testing. These chemicals are listed below with the major reasons for our non-recommendation:

<u>Agent</u>	<u>Major Deficiencies</u>
FC-116	highest volume factor in all flame configurations; critical temperature below 20 °C leading to uncertainty in design of storage vessel and speed of discharge
HFC-32/HFC-125	high volume factor in all flame configurations; highest over-pressures in detonation tube; high acid gas levels in combustion products
HFC-236fa	highest vaporization temperature; lowest Jakob number
FC-318	high vaporization temperature; low Jakob number; below average metals compatibility; long atmospheric lifetime
FC-31-10	high vaporization temperature; low Jakob number; below average metals compatibility; long atmospheric lifetime
HCFC-22	highest ODP; poorest compatibility with metals
HFC-134a	overall mediocre performance; higher levels of HF in combustion products

10.2.1 Ranking of Remaining Agents. The performance of all the candidates regarding environmental and operational issues was judged to be sufficient enough that those criteria, alone, were inadequate to disqualify any of the remaining agents. The relative weighting of the suppression and dispersion criteria depended upon the application; *i.e.*, full-scale engine nacelle or dry bay testing.

10.2.1.1 For Full-scale Simulated Engine Nacelle Testing. The release of the agent into the engine nacelle is crew-initiated, and the agent is normally distributed to different engines or regions of a single nacelle via piping manifolds. The fire is relatively slowly growing, and conditions which favor the transition to a detonation are unlikely to be present. The highest premium is placed upon fire suppression efficiency (low VF) for the three atmospheric pressure test flames. The time for dispersion is relatively long, so that heat is transferred from the air to the spray to assist vaporization. Thus, T_{min} is more appropriate than Ja as a measure of dispersion effectiveness. Table 4 summarizes these parameters and the recommended action for each agent regarding full-scale engine nacelle

Table 4. Ranking of agents for full-scale engine nacelle test matrix

Agent	Average VF	T _{min}	Environmental Factors	Operational Issues	Recommendation
HCFC-124	2.2	+ 28 °C	-	+	test
HFC-125	3.0	- 6 °C	+	+	test
FC-218	2.8	- 7 °C	-	+	1st back-up
HFC-227ea	2.5	+ 19 °C	+	+	2nd back-up
NaHCO ₃	0.5	powder	+	-	partial test matrix
CF ₃ I	0.8	- 1 °C	0	-	partial test matrix

testing. A "+" indicates overall positive attributes in that category and a "-" indicates that there is at least one serious concern in applying the agent.

The volume factor for the HCFC-124 is the lowest of all the core agents evaluated. Full-scale testing at low temperatures is required to ascertain if a T_{min} of + 28 °C might hamper the agent's effectiveness. The negative environmental factor is the non-zero ODP of the chlorine-containing compound. Nonetheless, HCFC-124 is recommended for full-scale testing, especially to see if the low volume factor is validated.

HFC-125 and FC-218 have similar values for T_{min} and only slightly different values for VF. The HFC-125 is a more conservative choice for full-scale testing because the FC-218 has a much longer atmospheric lifetime. HFC-227ea is a logical back-up because it has the second best volume factor.

Sodium bicarbonate has a volume factor half the size of halon 1301, and less than 1/4 the best of the core agents. There are three concerns with using sodium bicarbonate:

1. powders do not disperse as effectively as gases; hence, the performance of NaHCO₃ is likely to be lower in an engine nacelle than is indicated by the bench-scale tests;
2. NaOH, a by-product of the suppression process, reacts strongly with aluminum, which leads to the corrosion of exposed aluminum surfaces; and
3. high temperature storage leads to a deterioration of the flow properties of the powder.

Full-scale engine nacelle tests could determine if the first concern is warranted. In connection with the second concern, it should be ascertained whether the nacelle exhaust would put decomposition products in contact with aluminum. If so, aluminum test coupons strategically placed in the engine nacelle test fixture could be used to assess the significance of corrosion. The third problem

requires additional research to determine the best solution, but it is unlikely, by itself, to be a cause for rejecting sodium bicarbonate.

Iodotrifluoromethane also has a volume factor less than halon 1301. It leaves little residue (if it is pure) and appears to have a short tropospheric lifetime. Only a limited full-scale test matrix is recommended because:

1. greatly increased production levels are required to meet the full-scale test program and fleet needs;
2. toxicity, stability and corrosion test results are incomplete, and
3. detailed atmospheric chemistry and the implications of stratospheric release need to be further investigated.

10.2.1.2 For Full-scale Simulated Dry Bay Testing. Different criteria apply to the performance of an agent in dry bay fire suppression. Here, time is of the essence. Agent release is initiated automatically within milliseconds of a sensed threat. Following ignition, the heat release can create increases in pressure if expansion is restricted, leading to flame acceleration, the generation of turbulence due to high speed flow over obstructions, and the possibility of a strong shock wave. Effectiveness in damping the pressure build-up in the detonation/deflagration tube, averaged with the results in the spray burner, was used to determine an appropriate volume factor for the dry bay. Because the discharge occurs so quickly, there is no time for heat transfer from the surrounding air to vaporize the liquid agent; hence, the rankings on dispersion from Section 3.5 apply. The environmental factors and operational issues are identical to the engine nacelle application, but differences in the amount of agent released in a year and the cleanup procedure following a false discharge affect the way this information is factored into the recommendations. Table 5 gives the ranking of the remaining agents for full-scale simulated dry bay fire testing.

FC-218 and HFC-125 are recommended for testing because they have the highest Jakob numbers. None of the core agents has a volume factor below FC-218. The negative associated with long atmospheric life is of less concern for dry bay applications because the total annual release is much lower than in engine nacelle applications. HFC-125 had a slightly higher VF than FC-218, and produced high over-pressures in the detonation/deflagration tube at concentrations below the suppression level. Testing is recommended, but should similar over-pressures be observed in the simulated dry bay, then HFC-227 is the recommended back-up. The VF for HCFC-124 is the same as for FC-218, but the HCFC is difficult to vaporize. Considering that it has a non-zero ODP, FC-218 remains the better choice.

The CF_3I has a VF only 10% greater than halon 1301, but a very low Jakob number. A unique pressure/concentration behavior was observed with this agent in the detonation/deflagration tube which needs further investigation. If sufficient supplies of CF_3I can be arranged, full-scale testing in the simulated dry bay is recommended, especially at low temperatures. The ongoing toxicity, stability, corrosion and atmospheric chemistry studies should be closely monitored. When one compares VF in the engine nacelle and dry bay applications, the difference in performance between CF_3I and the best core agent is much greater in the engine nacelle application. Adding in the low Ja number makes CF_3I somewhat less attractive for the dry bay application.

The recommendation against sodium bicarbonate in the dry bay program is based upon the much higher premium placed on dispersion to counter the fire threat. A destructive fire can develop in tens of milliseconds, requiring that the fire suppressing agent be distributed throughout the volume in an equivalent time. The gasified agents can easily penetrate a reasonable amount of clutter in the dry

Table 5. Ranking of agents for full-scale dry bay test matrix

Agent	Average VF	Sect 3.5 Rank	Environmental Factors	Operational Issues	Recommendation
FC-218	1.6	1	-	+	test
HFC-125	1.8	1	+	+	test
HFC-227ea	1.6	6	+	+	1st back-up
HCFC-124	1.6	7	-	+	do not test
CF ₃ I	1.1	not ranked	0	-	partial test matrix
NaHCO ₃	incomplete data	powder	+	-	do not test

bay, but powders can impact and stick on surfaces and do not follow the carrier gas streamlines, greatly reducing the mass of material which actually is delivered to the fire zone. Clean-up could be more difficult in the dry bay, and since exposed aluminum surfaces are likely to be plentiful, they would be susceptible to NaOH corrosion.

A summary of the recommendations for all of the core agents, CF₃I and NaHCO₃ is given in Table 6. The inter-governmental technology transition team will weight the NIST recommendations with other practical concerns to arrive at the final set of chemicals for full-scale testing.

10.3 Ongoing Studies

The original research program begun in 1992 contained several projects which were to continue beyond September 30, 1993. These tasks were designed to enhance the selection and use of the optimal suppressant(s). Intermediate data will be available late in 1994 to assist the sponsors in evaluating the three candidate suppressants for each application. Knowledge developed during the continuation period will guide optimal use of agents selected for deployment.

10.3.1 By-Product Formation.

10.3.1.1 Instability Under Storage. In the one-month exposures, HFC-125, FC-218 and HCFC-227 showed no decomposition at 150 °C in the presence of any of the eight metals. By contrast, CF₃I did show some iodine formation and metals discoloration at 150 °C. During the next two years, the four selected chemicals will be exposed for about 18 months at three temperatures (22, 125, and 150 °C) to three metals: Nitronic-40 (21-6-9 stainless steel), 304 austenitic stainless steel, and titanium 15-3-3-3.

Table 6. Summary of recommended actions by agent

Agent	Recommended Actions	Cautions
HFC-125	Perform full-scale test matrix in nacelle. Screen for high pressures in dry bay, and complete matrix if pressure is not a problem.	Over-pressures may occur in dry bay tests.
HCFC-124	Perform full test matrix in engine nacelle simulator.	Note high T_{min} and non-zero ODP. Care needed when choosing elastomers to reduce chance of swelling.
FC-218	Perform full test matrix in dry bay simulator. Use as a back-up for engine nacelle.	Long atmospheric lifetime, properties of greases affected at high temps.
HFC-227ea	Consider it as a back-up to HFC-125 in engine nacelle and dry bay test program.	Relatively high T_{min} may limit dispersion
$NaHCO_3$	Test in engine nacelle simulator. Truncate test matrix if mass concentrations consistently exceed HFC-125.	Complications associated with powders (particle dispersion, corrosive by-products of combustion, high temperature storage) need to be off-set by superior full-scale fire suppression effectiveness to warrant fleet adoption.
CF_3I	Perform reduced test matrix in engine nacelle simulator to verify superior performance. Perform tests in dry bay consistent with availability of chemical.	Supply for testing limited; pilot scale production capability for 1995 not proven; toxicity, atmospheric chemistry, stability, and materials compatibility not fully documented
HFC-134a	Not recommended for full-scale testing.	Mediocre performance compared to alternative HFCs, higher HF levels
FC-116	Not recommended for full-scale testing.	Critical temperature below ambient limits storage
HFC-236fa	Not recommended for full-scale testing.	High T_{min} limits dispersion
HCFC-22	Not recommended for full-scale testing.	Incompatible with many materials, non-zero ODP
FC-31-10	Not recommended for full-scale testing.	High T_{min} , some materials incompatibility
FC-318	Not recommended for full-scale testing.	High T_{min} , materials issues
HFC-32/125	Not recommended for full-scale testing.	High over-pressure, high VF
HFC-32	Not recommended for full-scale testing.	Flammable

These were selected in conjunction with the sponsors and the manufacturers of suppression storage containers and systems. Samples will be analyzed for decomposition every 1 to 2 months using FTIR, with stretched intervals if no decomposition is observed.

CF_3I will be exposed to the same three metals, with and without the presence of metallic copper, a suggested inhibitor of the agent's decomposition, and perhaps at a fourth temperature. We expect that FTIR analyses will need to be supplemented by gas chromatography, mass spectroscopy or a combination of the two.

Should there be any decomposition of any of the chemicals in the presence of any of the metals, approximate first-order decomposition rate constants will be determined. These results will enable

evaluation of the viability of storing this chemical for extended periods. Alternatively, the results can be used to determine how often cylinders will need to be refilled. The work will be completed by September, 1995.

10.3.1.2 Combustion By-Products. The objective of this project is to develop an understanding of acid gas formation in hydrocarbon flames suppressed by three halon 1301 replacements, HFC-125, HFC-227 and HFC-218. This will provide the basis for a predictive capability for the amount of acid gas formed during the suppression of dry bay and engine nacelle fires, allowing the rank ordering of the three agents with respect to by-product production for these situations. CF_3I will be tested to verify that the amounts of HF formed are comparable to that formed with CF_3Br .

The general approach is to obtain global information on the final products in simple burners which permit operation over a range of conditions imitating those of dry bay and engine nacelle fires. This will allow examination of the effects of fuel and inhibitor structure and concentration. Fluid dynamic effects will be examined through a comparison of diffusion and premixed flames under laminar and turbulent conditions. Since the characteristic time for chemistry is on the order of one millisecond, and fluid dynamic times are usually longer, the chemistry important in HF formation can be studied under steady-state configurations more amenable to species sampling and variation of the individual operating parameters over a range of conditions which simulate those estimated for the dry bay and engine nacelle fires. The results from the steady-state measurements will then be used to predict the HF formed in flames suppressed under transient conditions. To test these predictions, experiments will be conducted where the agent is added rapidly to a flame so that the flame extinguishes, and the HF formed will be measured. These results will be compared to the predictions based on the steady-state measurements.

A second component will develop correlations, based on experimental results and global properties, of acid gas formation in inhibited flames based on inhibitor chemical formula and concentration, fuel type and consumption rate and flame type. The extent of the correlations will depend upon the importance of the chemical kinetic rates of inhibitor and inhibitor fragment decomposition. Measuring the concentration of acid gases formed in the flames described above and comparing these with the estimated concentrations from a simple global model will help elucidate the degree of kinetic control in the acid gas formation process.

Third, we will develop understanding of the chemical mechanism of acid gas formation in hydrocarbon flames to provide a fundamental basis for a true predictive capability. This entails (a) detailed numerical calculations of flame structure using a chemical kinetic code and (b) validation of the mechanism through comparison of model predictions and experimental measurements of temperature and species concentrations in the flame. The latter will be obtained in a laboratory flame using micro-probe gas sampling with mass spectrometry.

10.3.2 Metals Corrosion. The recent data show that a selection of metals are compatible with the down-selected chemicals over a one-month period. Additional testing will be conducted to enable judgments concerning relative performance of the chemicals over their storage lives in the suppression system.

Samples of the three metals will be exposed to the four chemicals plus halon 1301 at both ambient temperature and 150 °C at 5.4 MPa. Periodic (initially monthly) examination will provide a time history of the advancing of any corrosive effects. Slow strain rate tensile tests will be performed at ambient conditions and 150 °C and 5.4 MPa to provide information relating to liquid phase interactions.

Electrochemical experiments of the three metals and four chemicals will be conducted to:

- improve the quality of corrosion ratings by helping to resolve the scientific uncertainties inherent in short-term exposure tests;
- enable assessment of the effects of variations in the exposure conditions that could cause rapid runaway corrosion that would otherwise be missed by the exposure test matrix due to the time limitations; and
- enable assessment of the potential for galvanic attack and local breakdown of protective films to a level not possible with exposure tests.

It is also important to assess the potential for damage from the combustion by-products of the suppressants. Thirty-day surface exposures of key metals (identified by the sponsors) will be conducted in aqueous solutions of HF. Up to three concentrations will be used, depending upon the magnitude of the predicted difference in acid production for the four chemicals. The studies will be conducted at ambient temperature and pressure.

10.3.3 Compatibility with Seals and Elastomers. The recent research showed some differentiation among the chemicals in their interactions with the selected elastomers and greases, and these were factored into the down-selection process. It was also observed that the 150 °C exposures resulted in degradation of many of the seal materials by some of the chemicals. Subsequent information from the Air Force indicated that all-metal storage is used for exposures above about 70 °C.

In the continuing research, mechanical property measurements and additional short-term exposures will be performed at 50, 75, and 100 °C for the four agents and seven elastomers, the original six plus an ethylene-propylene-diene terpolymer (EPDM). These will enable a valid activation energy analysis over the full temperature range of interest. Compression set measurements and tensile testing (ultimate elongation, tensile strength, and modulus at 100% elongation) will be conducted after exposure times of 1, 2, and 4 weeks. The analysis of these measurements using an activated process model will provide reliable estimates of the elastomer resistance to the fluid exposure in service conditions.

Since CF₃I was not included in the initial experimental plan, swelling measurements will be conducted at 35, 70, 105, and 150 °C for all elastomers (crosslinked/uncrosslinked sets of fluorocarbon, standard and low temperature nitrile, silicone, fluorosilicone, and neoprene) and greases (Braycote 600, Krytox 240AC, Braycote 807) at four different vapor pressures. Swelling measurements on a crosslinked/uncrosslinked set of EPDM rubber will also be performed.

Following completion of the above studies, samples of seven elastomers will be exposed for about 18 months to the four fluids at 75 °C. Tensile testing and compression set measurements will be made after 8, 16, 32, 48 and 78 weeks.

10.4 Complementary Research Underway

There are additional projects now beginning at NIST that will provide knowledge important to the implementation of an agent selection decision. The objectives are summarized in this section.

10.4.1 Discharge Optimization. The research documented above shows that the effectiveness of a fire-fighting agent can depend as much on how the material is delivered to the fire zone as it does on its molecular composition. A particular chemical which leads to flame extinction in a laboratory

burner at very low concentrations may, in fact, be a poorer choice than one which exhibits no chemical activity if the inert material can be transported to the critical portions of an actual fire in a much more efficient manner. This project will develop the understanding needed to ensure that the agents chosen by the inter-governmental technology transition team for full-scale testing are delivered to the fire in an efficient manner so that an unbiased evaluation of system effectiveness can be made. The generic scientific data will also aid fire suppression system suppliers and airframe manufacturers in their efforts to design protective systems for existing and future aircraft. To accomplish this, NIST will:

- determine the practical limits to the design of system hardware which constrain what can be done;
- expand temperature-pressure data on the recommended fluids, pure and in mixtures with nitrogen, to enable the development of correlations for total pressure as a function of fill density and temperature for pressures up to 40 MPa;
- for dry bay applications, determine how the initial conditions in the storage bottle and the design of the release mechanism and exit orifice can be modified to enhance the discharge rate of the recommended fluid agents directly into an unconfined space; and
- for engine nacelle applications, determine the performance of the recommended fluid agents flowing through various piping geometries and components in transient operation.

10.4.2 Alternative Agent Concentration Monitors. It is essential to know that the fire suppression system will deliver an appropriate concentration of suppressant to the regions where a fire might occur. This requires a probe capable of extremely fast (milliseconds) measurements at many points. Our research has indicated that the initial flows may be either liquid or two-phase and that the mixing patterns are extremely complex.

The objective of this effort is to evaluate possible methods for real-time measurements of concentrations of alternative fire fighting agents for dry bay and nacelle fire applications. No analytical measurement techniques have yet been applied to such a complex problem. It will therefore be necessary to extend current measurement techniques or to develop completely new approaches. If one or more feasible approaches are identified early in the investigation, a demonstration system will be developed for characterization under actual test situations. This will be accomplished as follows:

- search the concentration measurement literature to identify measurement techniques for the required concentration measurements and two-phase flow characterization and recommend approaches for further research;
- test and evaluate an infrared sensing instrument recently developed by a company under contract to the Air Force for measuring alternative agent concentrations; and
- conduct theoretical and experimental feasibility evaluation of aspirated hot-film probes, recommending whether to pursue further development of this measurement technique.

10.4.3 Engine Nacelle Simulations. There are a number of different aircraft and operating conditions for which a new suppressant for nacelle fires is needed. Because testing cannot be performed

for all possible aircraft and conditions, knowledge is needed which will provide guidance in the extension of the Wright Patterson AFB full-scale data to untested systems and conditions.

Extinguishment occurs when a critical amount of agent is transported to the flame, where it is entrained into the primary reaction zone. The extinction process is affected by a number of parameters, including the velocity of the air flow, the type and quantity of fuel, the system temperature, agent properties and concentration, and the flow field geometry (*e.g.*, the location of obstacles in the flow field). Re-ignition is also dependent on these system parameters and should be considered independently from the extinction phenomena.

The objective of this research is to produce organized guidance for adjusting the needed concentration of candidate fire suppressants over a range of engine nacelle fire conditions. This will include

- review of the range of parameters which characterize the temperature and flow field in various engine nacelle types in an effort to understand better the possible fire scenarios and to develop an appropriate test program;
- use of the coaxial spray burner described earlier to measure (in a well-controlled and reduced-scale environment) the effects of air flow, air temperature, fuel flow, pre-burn time, system pressure, agent type (CF₃I, HFC-125, and HFC-227ea), rate of application, and the flow field geometry (*e.g.*, effect of an obstacle in the flow field) on the amount of chemical needed to suppress a fuel-spray fire;
- measurement of the impact of increased agent temperature on flame stability;
- computational modeling and optimizing the agent concentration as a function of location, rate, and orientation of agent injection, including possible multiple-location injection and differences in nacelle geometry, with wind tunnel validation; and
- compilation of the knowledge and data gained through the study into tools to assist suppression system designers, including information regarding concentration/duration requirements as a function of fire zone conditions.

The engine nacelle simulations will complement and provide guidance to the ongoing full-scale effort at Wright-Patterson.

10.5 Recommendations for Further Research

A significant amount of resources, effort, and science have gone into selecting the best candidates for full-scale evaluation, and it is expected that the additional testing at Wright-Patterson AFB will be successful in identifying one or two chemicals which will be suitable for replacing halon 1301 for in-flight suppression of engine nacelle and dry bay fires. It is equally likely that some inconsistencies will be revealed in scaling up one hundred-fold from the laboratory apparatus to the actual test articles.

More understanding is required of the fundamental principles controlling the suppression of a turbulent flame, the dispersion of a vaporizing spray in an enclosure, the chemistry of halogenated species in the flame and in the atmosphere, and modeling the interaction of all these phenomena to

increase the generality of the laboratory results and suggest improvements in the full-scale test protocol. Specifically, pursuit of the following topics is recommended:

- Inhibition mechanisms by both halocarbons and non-halogenated entities, including chemical kinetics measurements, studies of flame chemistry and dynamics, and computer modeling of chemically perturbed combustion.
- Innovative suppression, such as by non-intrusive flame perturbations or species chemically generated *in situ*.
- Atmospheric chemistry of flame extinguishants other than chlorinated and brominated species, including laboratory measurements of the rate processes and computer modeling of the atmospheric impacts.
- Turbulent two-phase flow, both experimental characterization and numerical modeling of the dynamics.
- Standardized suppression test methods at both small and medium scale, including the appropriate instrumentation.

True understanding of a phenomenon requires a sustained effort, and the flexibility to allow research to explore multiple paths. In the environment of continuously changing regulations and evolving technologies, the understanding which would be generated by the above research is essential so that optimal agents and suppression strategies can be developed in a rational and efficient manner.