See: NIST SP861, W. L. Grosshandler, et al., Editors

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

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

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 CF_3I 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_3Br	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_3I	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 CF_3Br are 0.59 and 0.51, respectively, while T_{min} for CF_3Br 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 ± 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.) Iodotrifluoromethane 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 CF_3I 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 CF_3I 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:

$$\mathbf{FCs = HFCs \equiv 0 < CF_3I < HCFCs << CF_3Br} \quad \text{(ODP)}$$

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 CF_3I 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 CF_3Br (estimated lifetime is 66 years). The following ranking applies, from best to worst:

$$\mathbf{CF_3I << HCFCs < HFCs << FCs} \quad \text{(atmospheric lifetime)}$$

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_3I	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	Availability	Cost	Stability in Storage	Metals Compatibility	Polymers Compatibility	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_3I	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 CF_3I was subjected to the high temperature storage test. No other significant decomposition products were identified. (However, noticeable acidic residue was present in batches of CF_3I received later from a second supplier.) U.S. production of CF_3I, 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 $NaHCO_3$ 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:

Agent	Major Deficiencies
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_3I	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 $NaHCO_3$ 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_3I	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, CF_3I and $NaHCO_3$ 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, CF_3I 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 CF_3I 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 (CF_3I, 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.