

**John F. Kennedy Space Center**  
Kennedy Space Center, Florida 32899

# **Technical Support Package**

---

## **Perfluorocarbons as Fire-Suppression Agents**

NASA Tech Briefs  
KSC-11573

**NASA**  
National  
Aeronautics and  
Space  
Administration

Technical Support Package

For

PERFLUOROCARBONS AS FIRE-SUPPRESSION AGENTS

KSC-11573

NASA Tech Briefs

The information in this Technical Support Package comprises the documentation referenced in KSC-11573 of NASA Tech Briefs. It is provided under the Technology Utilization Program of the National Aeronautics and Space Administration to make available the results of aerospace-related developments considered to have wider technological, scientific, or commercial applications.

Additional information regarding research and technology in this general area may be found in Scientific and Technical Aerospace Reports (STAR) which is a comprehensive abstracting and indexing journal covering worldwide report literature on the science and technology of space and aeronautics. STAR is available to the public on subscription from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

---

NOTICE: This document was prepared under the sponsorship of the National Aeronautics and Space Administration. Neither the United States Government nor any person acting on behalf of the United States Government assumes any liability resulting from the use of the information contained in this document or warrants that such use will be free from privately owned rights.

INVESTIGATION OF THE USE OF  
PERFLUOROCARBONS AS FIRE SUPPRESSION AGENTS

Prepared By:

Philip J. DiNenno, P.E., and Eric Forssell

Hughes Associates, Inc.  
2730 University Boulevard, West  
Suite 902  
Wheaton, MD 20902  
(301) 949-0505

August 8, 1991

## Table of Contents

|   | <u>Page</u> |
|---|-------------|
| ABSTRACT .....  | vi          |
| INTRODUCTION .....                                    | 1           |
| BACKGROUND .....                                      | 3           |
| Attributes of Halons as Fire Suppression Agents ..... | 3           |
| Effectiveness .....                                   | 3           |
| Agent Cleanup/Collateral Damage .....                 | 4           |
| Toxicology/Material Compatibility .....               | 5           |
| Halons and Stratospheric Ozone Depletion .....        | 5           |
| PERFLUOROCARBONS .....                                | 7           |
| Fire Suppression Effectiveness .....                  | 7           |
| Chemical and Physical Properties .....                | 8           |
| Toxicology .....                                      | 10          |
| Environmental Properties .....                        | 11          |
| Ozone Depletion Potential .....                       | 11          |
| Global Warming Potential .....                        | 11          |
| CUP BURNER TESTS .....                                | 13          |
| Objectives .....                                      | 13          |
| Apparatus .....                                       | 13          |
| Procedure .....                                       | 15          |
| Test Sequence .....                                   | 15          |
| Results and Discussion .....                          | 15          |
| Minimum Extinguishing Concentrations .....            | 15          |
| Mechanism of Extinguishing (Physical/Chemical) .....  | 18          |
| Physical Mechanism .....                              | 19          |
| Vitiated and Enhanced Oxygen Atmosphere .....         | 21          |
| FEASIBILITY .....                                     | 24          |
| Agent Requirements .....                              | 24          |
| Leakage Rates .....                                   | 25          |
| Flow Characteristics .....                            | 27          |
| System Modifications .....                            | 31          |
| Thermal Decomposition Products .....                  | 32          |
| Commercialization .....                               | 32          |

Table of Contents (continued)

|   | <u>Page</u> |
|---|-------------|
| CONCLUSIONS .....                                       | 34          |
| RECOMMENDATIONS FOR FURTHER INVESTIGATION .....         | 35          |
| Flow Characteristics .....                              | 35          |
| Material Compatibility .....                            | 35          |
| Toxicology .....  | 35          |
| Thermal Decomposition .....                             | 36          |
| Full Scale Testing .....                                | 36          |
| Comparison With Other Proposed Halon Alternatives ..... | 37          |
| REFERENCES .....  | 38          |

## List of Figures

|   | <u>Page</u> |
|---|-------------|
| Fig. 1 - Cup Burner Apparatus . . . . .   | 14          |
| Fig. 2 - Extinguishing Concentration Dependence on Flow Rate . .  | 17          |
| Fig. 3 - Extinguishing Concentrations as a Function of Free<br>Oxygen Concentration . . . . .                               | 23          |
| Fig. 4 - Predicted Interface Recession with 6.4 cm (2.5 in.)<br>Diameter Leaks in a 3.1 m (10 ft) Cubic Enclosure . . . . . | 28          |

## List of Tables

|  | <u>Page</u> |
|--|-------------|
| Table 1 - Vaporous Agent Requirements [4] . . . . .                              | 4           |
| Table 2 - Results of Moderate Scale Compartment Tests . . . . .                  | 8           |
| Table 3 - Chemical and Physical Properties . . . . .                             | 9           |
| Table 4 - Cup Burner Extinguishing Concentrations<br>(% by Volume) . . . . .     | 16          |
| Table 5 - Halon 1301 Extinguishing Concentrations<br>(% by Volume) . . . . .     | 18          |
| Table 6 - Agent Concentration Required for Physical<br>Mechanism Alone . . . . . | 20          |

## Abstract

Three perfluoroalkane compounds have been evaluated as candidate Halon 1301 replacements. Perfluorobutane ( $C_4F_{10}$ ) and Perfluoropropane ( $C_3F_8$ ) show significant promise for both new and retrofit applications.

Small scale cup burner tests have shown these compounds to be effective fire suppressants in relatively low (6-8%) volumetric concentrations. The literature demonstrates that these compounds are clean, stable, non-toxic, and non-ozone depleting. Hydraulic performance and mixing characteristics pose no unusual problems although there is inadequate data to develop engineering methods for design purposes.

The only unresolved technical question related to the use of these compounds as fire suppressants is the quantity and character of thermal decomposition products. Evaluation of decomposition behavior would require additional testing. There are unresolved regulatory issues associated with these compounds, most notably global warming potential. It is expected, however, that the use quantities of these compounds will be such that this question is largely irrelevant.

It is recommended that additional work be undertaken to (1) compare the perfluorocarbons to other proposed alternatives, (2) develop engineering methods and data to enable system design and retrofit evaluation, and (3) perform tests to evaluate the thermal decomposition products of these compounds. Accomplishment of this work will expedite regulatory approvals, user-community acceptance, and general commercialization of these compounds.

# INVESTIGATION OF THE USE OF PERFLUOROCARBONS AS FIRE SUPPRESSION AGENTS

## INTRODUCTION.

The objective of this work is to evaluate the feasibility of using perfluorocarbons as Halon 1301 alternatives. This effort was intended to evaluate the feasibility of using perfluorocarbon agents against the range of required characteristics of a gaseous, clean fire suppression agent. Such characteristics include ozone depletion potential, fire suppression effectiveness, material compatibility, flow/discharge characteristics, mixing, decomposition behavior (during flame extinguishment), and toxicity. If the research demonstrates feasibility, which is further proven, an effective and environmentally acceptable alternative which can be produced in commercial quantities in the near term will be available.

The primary technical objective of this Phase I research was to evaluate the feasibility of using perfluorocarbons as a replacement for Halon 1301 fire suppression agents. Hence, the efficacy of a Halon 1301 replacement must be evaluated. This invokes accomplishing the following technical objectives.

1. Evaluate in small diffusion flames the extinguishing capabilities of perfluorocarbons.
2. Establish baseline minimum extinguishing thresholds for a range of typical gaseous and liquid fuels.
3. Evaluate the toxicity of undecomposed perfluorocarbons using available toxicity studies. Identify required toxicity testing.
4. Evaluate required storage pressure and flow characteristics.

5. Identify additional work required to develop the application of perfluorinated compounds as extinguishing agents.
6. Evaluate material compatibility relative to engineering materials.
7. Evaluate "drop in" potential of agents relative to existing Halon 1301 systems.

Halon 1301 has been used as fire suppressant for over forty years [1]. It was used primarily in applications that required a clean agent that would not cause collateral damage upon discharge and could be used in normally occupied spaces. It also was very effective in low concentrations resulting in a low space/weight requirement.

The search for alternatives to the use of Halon 1301 was initiated when its link to stratospheric ozone depletion became generally accepted. This acceptance has manifest itself in the 1987 Montreal Protocol which calls for a cap on Halon 1301 production at 1986 levels beginning in 1992 and in 1990 amendments to the Protocol that require a phase-out of production by 2000 [2].

An alternative suppressant to Halon 1301 would have to retain many of the same attributes as Halon 1301 in order to fill the same application niche. Hence, one must identify a relatively low toxicity, clean, and effective fire suppression agent.

## BACKGROUND.

### Attributes of Halons as Fire Suppression Agents

The origin of the use of Halon 1301 (bromotrifluoromethane) can be traced to a 1948 U.S. Army study conducted to find alternatives to methyl bromide and chlorobromomethane for use in military vehicles [1]. By 1986, the global use of Halon 1301 had grown to 10,000 metric tons per year (22.2 million pounds per year) and its use was continuing to grow at approximately 4.5% per year [3]. This growth was due to significant advantages over other fire suppressants in terms of effectiveness, collateral damage, toxicology, etc. and occurred in spite of higher system and agent cost.

#### Effectiveness.

Halon 1301 is particularly effective against fires involving either liquid or vapor fuels. It is also effective against fires involving solid fuels but fuels tend to develop deep-seated fires (cellulosic materials for example) often require higher concentrations and prolonged soaking times. When employed by a total flooding system, Halon 1301 is able to extinguish guarded or otherwise inaccessible fires that would either require prolonged application of liquid suppressants or could not be extinguished at all by liquid suppressants.

Halon 1301 has lower agent requirements than most other vaporous agents. The percent by volume Halon 1301 concentration required to extinguish most hydrocarbon fuels ranges from approximately 3% to 7.5% as shown in Table 1 [4]. For comparison, the percent by volume concentration of carbon dioxide is approximately 4 to 6 times greater for these same fuels with a range of 18% to 26% as shown in Table 1 [4]. On a mass basis, the difference is not as great, as Halon 1301 is approximately 3 times heavier than carbon dioxide.

Table 1 - Vaporous Agent Requirements [4]

| Fuel     | Halon 1301 |       |         | CO <sub>2</sub> |       |         | N <sub>2</sub> ** |       |         |
|----------|------------|-------|---------|-----------------|-------|---------|-------------------|-------|---------|
|          | Vol. %     | Mass* |         | Vol. %          | Mass* |         | Vol. %            | Mass* |         |
|          |            | kg    | (lb)    |                 | kg    | (lb)    |                   | kg    | (lb)    |
| Heptane  | 3.50       | 6.33  | (13.97) | 20.50           | 13.30 | (29.35) | 30.20             | 14.19 | (31.34) |
| Acetone  | 3.50       | 6.33  | (13.97) | 18.30           | 11.55 | (25.50) | 29.20             | 13.53 | (29.87) |
| Ethanol  | 3.90       | 7.08  | (15.63) | 21.80           | 14.38 | (31.73) | 33.30             | 16.38 | (36.16) |
| Methanol | 7.30       | 13.74 | (30.33) | 26.20           | 18.31 | (40.41) | 39.00             | 20.98 | (46.30) |
| Benzene  | 2.90       | 5.21  | (11.50) | 20.10           | 12.97 | (28.64) | 29.70             | 13.86 | (30.60) |
| Hexane   | 3.30       | 5.95  | (13.14) | 19.50           | 12.49 | (27.57) | 31.00             | 14.74 | (32.54) |
| Pentane  | 3.30       | 5.95  | (13.14) | 19.00           | 12.10 | (26.70) | 31.50             | 15.09 | (33.30) |

\* Mass required to protect a 28.3 m<sup>3</sup> (1000 ft<sup>3</sup>) space.

\*\* N<sub>2</sub> added to air.

This effectiveness is due to several mechanisms. First, the addition of Halon 1301 to air results in an increased heat capacity causing an increased heat loss in the combustion zone. This addition also displaces oxygen resulting in a reduced burning rate of the fuel. Second, Halon 1301 absorbs heat in the decomposition reaction which liberates CF<sub>3</sub>• and Br• radicals. Halon also absorbs heat to a small extent by the phase change. Third, Halon 1301 interrupts the combustion process by the removal of activated intermediates. One explanation of this is the following cycle beginning with the bromine radical liberated as Halon 1301 decomposes:



where R-H represents the fuel vapor [5].

Agent Cleanup/Collateral Damage.

The most significant advantage Halon 1301 has over liquid and solid (powder) agents is in the area of collateral damage and clean up after application. Water and to a lesser extent foam agents, cause a great deal of collateral damage even though

the fire involved maybe small [6,7]. This is particularly true when protecting electrical equipment as they are particularly vulnerable to damage caused by shorting in the presence of water [6,7]. Even if the equipment is de-energized prior to water application, electrical equipment must be washed (generally rinsed with de-ionized water) and dried before restarting. With foam agents, the extent of damage is generally tied to the water content of the foam.

#### Toxicology/Material Compatibility.

Halon 1301 is inert, stable and nontoxic. At high concentrations, Halon 1301 can act as a simple asphyxiant through oxygen displacement. Cardiac sensitization has been observed to a limited extent in dogs for Halon 1301 concentrations above 7.5% by volume in conjunction with adrenaline [5]. This is a distinct advantage over carbon dioxide which displaces enough oxygen at its required extinguishing concentrations to cause asphyxiation [8].

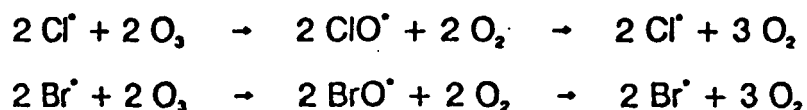
Halon 1301 is compatible with most material of construction. It has been shown to swell some elastomers and plastics, notably Viton, silicone, and ethyl cellulose [5].

#### Halons and Stratospheric Ozone Depletion.

The link between CFCs, chlorinated fluorocarbons, and ozone depletion was first proposed around 1974 [9]. This link is based upon the ability of these highly stable compounds to deliver an active species to the stratosphere. In the case of CFCs, the active species is chlorine which is suspected of participating in a catalytic cycle that increases the rate of ozone destruction. At first, the halons were not suspected of significantly affecting the rate of ozone depletion due to the relatively small amount of halons that are produced compared to the more basic CFCs (R-12, R-114, etc). Closer investigation revealed that due to the longer atmospheric lifespan of the halons, their ozone depletion potential per pound emitted was greater than that

of the more basic CFCs [10]. Halon 1301 was found to have an ozone depletion potential of 11.43-(relative to R-11, trichlorofluoromethane) and on this weighted basis, represented approximately 12% of the total ozone depletion potential generated in the U.S.A. in 1985 [10].

There are several mechanisms proposed to explain the role of CFCs and halons in ozone depletion. All of which involve the emission of the compound and as these compounds do not breakdown in the lower atmosphere, an eventual migration to the stratosphere occurs. Once in the stratosphere, the higher energy ultraviolet radiation present in the stratosphere causes the breakdown of the compound with the emission of the active bromine or chlorine radical. One mechanism involves the formation of the hypohalite radical from the released halogen radical and ozone. The hypohalite radical in turn decomposes to form the original radical and oxygen.



Other cycles involve the formation of the hypohalous acids (HOCl and HOBr) or the nitrates of the halogens (ClNO<sub>3</sub> and BrNO<sub>3</sub>) in addition to the hypohalite radical [9].

## PERFLUOROCARBONS.

### Fire Suppression Effectiveness.

Several perfluorocarbons were investigated by Huggett and McHale of Atlantic Research Corporation [11-14] in the early seventies for use in the creation of inhabitable atmospheres that would not support combustion. The emphasis of this investigation was on the lower molecular weight straight chain perfluoroalkanes, i.e., perfluoromethane ( $\text{CF}_4$ ), perfluoroethane ( $\text{C}_2\text{F}_6$ ), perfluoropropane ( $\text{C}_3\text{F}_8$ ), etc. These same compounds would appear to have significant potential as Halon 1301 alternatives.

Limited cup burner data are available on some perfluorocarbons. 3M Company internal data gives extinguishing concentrations of approximately 8.9% for  $\text{C}_2\text{F}_6$ , 6.3% for  $\text{C}_3\text{F}_8$ , and 5.5% for  $\text{C}_4\text{F}_{10}$ , for heptane. Sheinson et al. [15] report extinguishing concentration values of 7.9 for  $\text{C}_2\text{F}_6$  and 4.1% for  $\text{C}_3\text{F}_8$  for heptane fuels. A full discussion of cup burner tests conducted for this study are given in the next section of this report. These small scale cup burner values indicate that these perfluorocarbons are quite effective extinguishing agents in low volumetric concentrations.

In addition to these small scale cup burner screening tests, the 3M Company conducted a series of experiments involving moderate scale (50-500 kw) diffusion flames on a variety of fuels in a small 2.4 x 2.4 x 2.4 m (8 x 8 x 8 ft) cube. The results of these experiments are summarized in Table 2. These data verify the small scale cup burner results and demonstrate the effectiveness of  $\text{C}_3\text{F}_8$  and  $\text{C}_4\text{F}_{10}$ , on a range of fuel types including heptane, methanol, and wood cribs.

Table 2 - Summary of Moderate Scale Compartment Tests

| <u>Agent</u>                   | <u>Fuel Type</u> | <u>Fire Size (kW)</u> | <u>Agent Concentration (%)</u> | <u>Discharge Time (sec)</u> | <u>Extinguishment Time (sec)</u> |
|--------------------------------|------------------|-----------------------|--------------------------------|-----------------------------|----------------------------------|
| C <sub>4</sub> F <sub>10</sub> | Heptane          | 50                    | 6.6                            | 3.3                         | 3.8                              |
| C <sub>3</sub> F <sub>8</sub>  | Heptane          | 50                    | 7.6                            | 3.5                         | 4.8                              |
| C <sub>4</sub> F <sub>10</sub> | Heptane          | 50                    | 3.3                            | 3.6                         | 6.6                              |
| 1301                           | Heptane          | 50                    | 5.0                            | 4.2                         | 3.2                              |
| C <sub>4</sub> F <sub>10</sub> | Heptane          | 100                   | 6.6                            | 5.6                         | 4.1                              |
| 1301                           | Heptane          | 100                   | 5.0                            | 4.0                         | 2.3                              |
| C <sub>4</sub> F <sub>10</sub> | Wood Crib        | 250                   | 6.6                            | 3.8                         | 7.0                              |
| C <sub>3</sub> F <sub>8</sub>  | Wood Crib        | 250                   | 7.6                            | 4.3                         | 6.0                              |
| 1301                           | Wood Crib        | 250                   | 5.0                            | 3.9                         | 1.9                              |
| C <sub>4</sub> F <sub>10</sub> | Heptane          | 250                   | 6.6                            | 3.3                         | 2.3                              |
| 1301                           | Heptane          | 250                   | 5.0                            | 4.2                         | 2.4                              |
| C <sub>4</sub> F <sub>10</sub> | Heptane          | 500                   | 6.6                            | 3.6                         | 2.2                              |
| 1301                           | Heptane          | 500                   | 5.0                            | 4.1                         | 1.7                              |
| C <sub>4</sub> F <sub>10</sub> | Methanol         | 50                    | 10.9                           | 4.8                         | 3.2                              |
| 1301                           | Methanol         | 50                    | 9.4                            | 5.8                         | 4.5                              |

#### Chemical and Physical Properties.

The lower molecular weight perfluorocarbons have found limited use as either special use refrigerants, i.e., low temperature refrigeration for perfluoromethane (CF<sub>4</sub>), or as electrical insulating gases [16]. As a group, they are odorless, colorless, stable, inert, and are not suspected of contributing to ozone depletion.

The perfluoroalkanes selected for consideration as Halon 1301 alternatives were those in the progression between perfluoroethane (C<sub>2</sub>F<sub>6</sub>) and perfluorobutane (C<sub>4</sub>F<sub>10</sub>). CF<sub>4</sub> was not included as it is supercritical at room temperature and atmospheric pressure which would result in high agent storage pressures [16]. Higher molecular weight perfluorocarbons are liquids at room temperature and atmospheric pressure.

Physical and chemical properties of the selected perfluoroalkanes and Halon 1301 are given in Table 3 [5,16].

Table3-ChemicalandPhysicalProperties

| <u>Agent</u>   | <u>Halon 1301</u>  | <u>Perfluoroethane</u>        | <u>Perfluoropropane</u>       | <u>Perfluorobutane</u>         |
|--|--------------------|-------------------------------|-------------------------------|--------------------------------|
| Chemical Formula   | CF <sub>3</sub> Br | C <sub>2</sub> F <sub>6</sub> | C <sub>3</sub> F <sub>8</sub> | C <sub>4</sub> F <sub>10</sub> |
| Molecular Weight   | 148.91             | 138                           | 188                           | 238                            |
| Heat of Vaporization<br>kJ/gmol (Btu/lbmol)<br>at 21°C (70°F)  | 12.3 (5292)        | -                             | 15.1 (6492)                   | 21.2 (9093)                    |
| Normal Boiling Point<br>°C (°F)  | -57.8 (-72)        | -78.2 (-56)                   | -36.7 (-34)                   | -2.2 (28)                      |
| Vapor Pressure MPa<br>(psi) at 21°C (70°F)   | 1.47 (213.7)       | -                             | 0.792 (114.8)                 | 0.240 (34.8)                   |
| Critical Temperature<br>°C (°F)  | 67 (152.6)         | 19.7 (67.5)                   | 72 (161.4)                    | 113.2 (235.8)                  |
| Critical Pressure<br>MPa (psi)   | 3.97 (575)         | 2.98 (432)                    | 2.68 (389)                    | 2.32 (337)                     |
| Vapor Density<br>kg/m <sup>3</sup> (lb/ft <sup>3</sup> )<br>at 21°C and 0.101 MPa<br>(70°F and 14.7 psi) | 6.26 (0.391)       | 5.72 (0.357)                  | 7.79 (0.486)                  | 9.86 (0.615)                   |
| Liquid Density<br>kg/m <sup>3</sup> (lb/ft <sup>3</sup> )<br>at 21°C (70°F)                              | 1567 (97.8)        | -                             | 1352 (84.3)                   | 1517 (94.6)                    |

## Toxicology.

In general, perfluorocarbons, by virtue of their stability and inertness, are considered nontoxic. In high concentrations, they can act as simple asphyxiants by displacing oxygen.

In their studies of inhabitable atmospheres that would not support combustion, McHale and Huggett performed inhalation tests of perfluorocarbon/air and perfluorocarbon/oxygen atmospheres without finding physiological damage [11,14]. Huggett used a four hour exposure to 80% by volume perfluorocarbon ( $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , or  $\text{C}_4\text{F}_{10}$ ) and 20% by volume oxygen [11]. McHale used a ten day exposure to 21% by volume  $\text{CF}_4$  in air or to 12% by volume  $\text{C}_2\text{F}_6$  in air [14].

McHale also did cardiac sensitization tests with dogs,  $\text{CF}_4$  at two concentrations (20% by volume in air and 60% by volume in air), and epinephrine at a 8  $\mu\text{g}/\text{kg}$  dose level [14]. The cardiac arrhythmias, found at lower concentrations when testing with Halon 1301, were not found in these tests [14].

Both acute and sub-chronic inhalation tests performed by 3M on their Fluorinert Brand Electronic Liquid FC-72 which is a mixture of higher molecular weight perfluoroalkanes ( $\text{C}_5\text{F}_{12}$  and higher) attests to the nontoxic nature of perfluoroalkanes. Both studies exposed rats to near saturated perfluorocarbon/air mixtures (approximately 30% by volume perfluorocarbon) [17]. In the acute inhalation tests the exposure was for 1 hour while in the sub-chronic the exposure was for 7 hours per day, 5 days per week, over a 6 week period. In either test series, no significant adverse effects were noted [17].

Given the existing toxicology data on these compounds as well as their excellent chemical stability, no toxicological problems are expected. Additional toxicological work that may be required by the EPA in order to permit the manufacture and sale of perfluorocarbons as fire suppression agents is a regulatory issue that will be resolved

by the manufacturer(s) and EPA. Further toxicological evaluations other than those required by the EPA are needed. The perfluorocarbons appear to have excellent toxicological properties, representing a substantial improvement over Halon 1301.

Environmental Properties.

### Ozone Depletion Potential

The perfluorocarbons evaluated in this report are non-ozone depleting compounds. Hence, they eliminate the major environmental drawback of Halon 1301.

### Global Warming Potential

An emerging environmental issue is that of global warming. A partial indicator of the behavior of a compound relative to global warming is the Global Warming Potential (GWP) of a material. The GWP is a function of the ability of a compound to absorb radiation in the 7 and 13  $\mu$  window and the atmospheric lifetime of the compound. The GWP number only represents the potential for global warming. The degree of warming is a function of the amount of material released.

While specific data on the perfluorocarbons evaluated in this report are not available, these compounds will have relatively high global warming potential values due to an expected long atmospheric lifetime associated with these very stable compounds. (This stability is also responsible for their nontoxicity.) The larger question is whether the use of these compounds will cause unacceptable environmental problems. A key difference between ozone depletion and global warming is the relative quantities of compounds required to cause an environmental impact. At use levels exceeding those associated with the peak production of Halon 1301, it is expected that releases of perfluorocarbons for use as fire suppressants will result in insignificant impact on global warming.

Hence, while further information on the GWP and associated warming effects is necessary for any candidate fire suppressant it appears that the global warming impact of the perfluorocarbon materials for use as fire suppressants is negligible.

## CUP BURNER TESTS.

### Objectives.

The purpose of these tests was to evaluate the perfluoroalkanes of the progression between perfluoroethane ( $C_2F_8$ ) and perfluorobutane ( $C_4F_{10}$ ) as alternatives to Halon 1301 in total flooding fire protection systems. These tests would determine minimum extinguishing concentrations and provide an insight into the mechanism of extinguishment for these alternative agents.

### Apparatus.

The apparatus used in these tests was a cup burner similar to that used by Hirst and Booth [4] and is shown in Figure 1. The burner itself was a 0.9 cm (0.38 in.) O.D. tube opened up to 2.8 cm (1.1 in.) O.D. 2.5 cm (1 in.) from the top end. The edge of the burner was beveled to help maintain fuel level at the top of the burner. The burner was axially mounted in a 8.5 cm (3.25 in.) I.D. glass chimney. The fuel was fed from a 1 L separatory funnel, mounted on a jack to allow for the adjustment of the fuel level, to the base of the burner tube via 0.9 cm (0.38 in.) O.D. tubing. A 0.9 cm (0.38 in.) O.D. tube was teed off the fuel line to act as both a vent and drain. The flow of both agent and air was controlled by Manostat Calcuflow Flowmeters size Numbers 4 and 5, respectively. Air and agent flows are combined in a tee prior to introduction at the base of the burner chimney below a 7.5 cm (3 in.) section of glass ball packing. Two water manometers and two thermometers monitor the air and agent temperature and pressure.

A third Manostat flowmeter size number 5 was used in performance of the tests involving synthetic air ( $O_2/N_2$  mixtures).

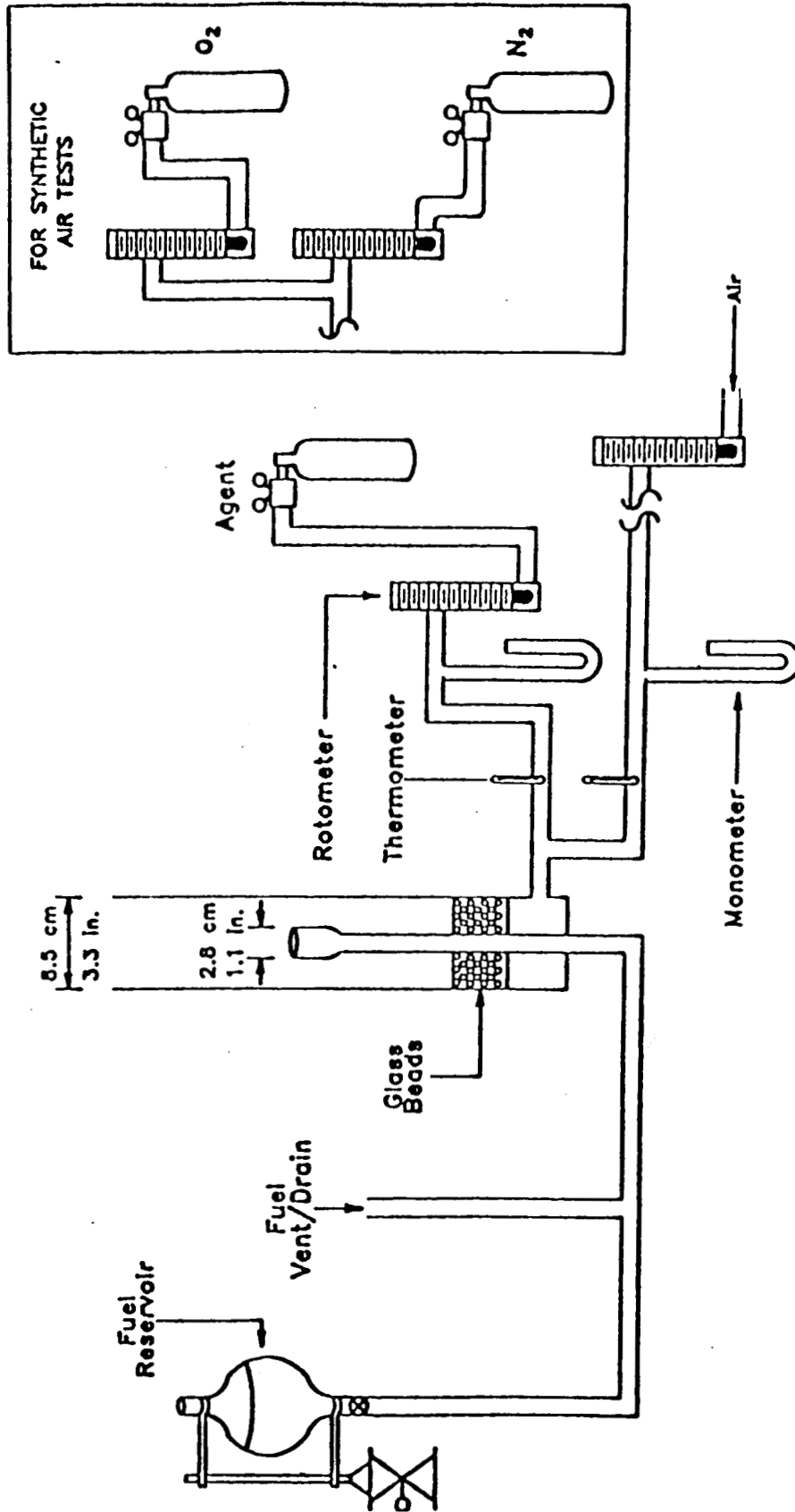


Fig. 1 - Cup burner apparatus

## Procedure.

Two tests series were conducted. The first involved the determination of the minimum extinguishing concentration for each candidate alternative agent and Halon 1301 for a variety of fuels. The fuels used were n-heptane, acetone, ethanol, and methanol. The second series concerned the use of synthetic air in order to investigate the mechanism(s) of extinguishment of the candidate alternative agents. Each test was repeated at least three times with the results averaged.

## Test Sequence.

- A. Fill fuel reservoir with desired fuel and set air flow rate (set both O<sub>2</sub>, and N<sub>2</sub> flow rates if synthetic air test).
- B. Ignite fuel.
- C. Place chimney over burner and adjust fuel level to even with top of burner.
- D. Slowly increase agent flow rate until flame is extinguished.
- E. Remove chimney and clean burner by removing top layer of fuel if same fuel is to be used in next test. If not, then drain fuel and rinse tubing with new fuel.

## Results and Discussion.

A series of calibration tests were performed in regards to the total flow rate past the burner due to the lack of agreement found in the literature. Hirst and Booth [5] report an operating air flow range defined by a Halon 1211 extinguishing concentration plateau above a total flow rate of approximately 12 cm/s (corresponds to 38 L/min in their 8.5 cm I.D. chimney) lasting until the blow out velocity is achieved.

Moore et al. [18] report an operating range defined by a minimum Halon 121 1 extinguishing concentration over a range of 9 to 15 L/min. Sheinson et al. [15] and Tucker et al. [19] report an insensitivity to total flow rate over ranges of 5 to 50 L/min (10.5 cm I.D. chimney) and 15 to 20 L/min (9.3 cm I.D. chimney), respectively.

The results of this series of tests are presented in Figure 2. The range of extinguishing concentration determined for Halon 1301 is from a low of 3.67% by volume to a high of 3.94% by volume with the total flow rate varying from 17.8 to 50.4 L/min. This variation represents the error in determining the extinguishing concentration as well as a dependence upon the total air flow rate.

#### Minimum Extinguishing Concentrations.

The determined extinguishing concentrations for the perfluorocarbon series and Halon 1301 for n-heptane, methanol, acetone, and ethanol are given in Table 4. In the perfluorocarbon series, the required extinguishing concentration decreased with increasing molecular weight.

Table 4 - Cup Burner Extinguishing Concentrations (% by Volume)

| <u>Agent</u>                   | <u>Heptane</u> | <u>Methanol</u> | <u>Ethanol</u> | <u>Acetone</u> |
|--------------------------------|----------------|-----------------|----------------|----------------|
| 1301                           | 3.07           | 7.73            | 4.74           | 3.74           |
| C <sub>2</sub> F <sub>6</sub>  | 8.67           | 11.95           | 9.84           | 8.38           |
| C <sub>3</sub> F <sub>8</sub>  | 6.83           | 10.14           | 8.02           | 6.98           |
| C <sub>4</sub> F <sub>10</sub> | 5.76           | 8.40            | 7.06           | 5.73           |

The air flow rate was held constant during these tests at 38.4 L/min  $\pm$  0.3 L/min. This caused the total air flow rate in these tests to vary with the determined extinguishing concentration from a low of 39.6 L/min to a high of 43.25 L/min. A

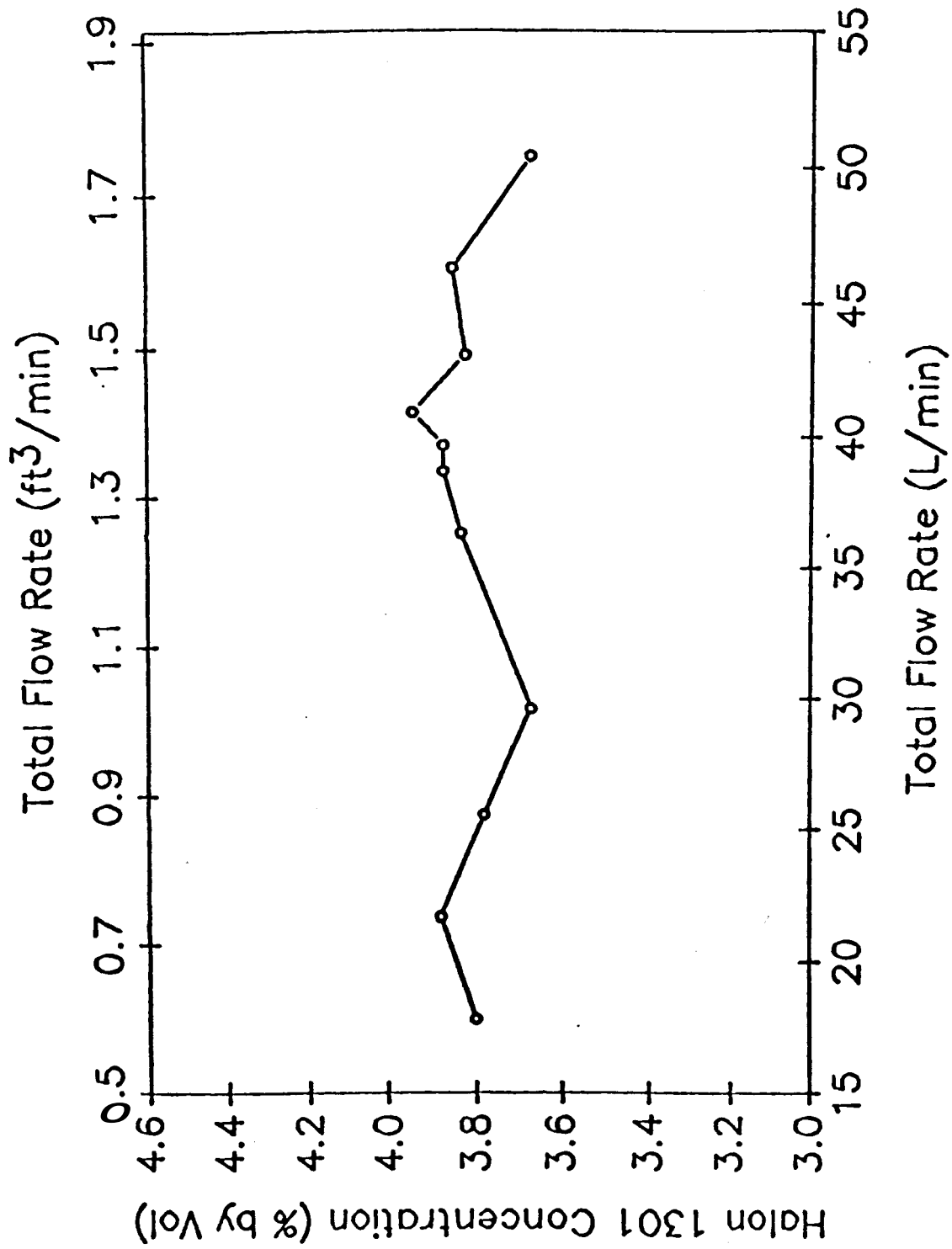


Fig. 2 - Extinguishing concentration dependence on flow rate

comparison of the determined required Halon 1301 concentrations and those determined in similar apparatus are given in Table 5 [1,4]. The concentrations determined in this series are higher than those given for comparison. This could be due to differences in the apparatus, flow operating range, and experimental error.

Table 5 - Halon 1301 Extinguishing Concentrations (% by Volume)

|                       | Fuel             |                |                 |                |
|-----------------------|------------------|----------------|-----------------|----------------|
|                       | <u>n-Heptane</u> | <u>Acetone</u> | <u>Methanol</u> | <u>Ethanol</u> |
| This Study Determined | 3.9              | 3.7            | 7.7             | 4.7            |
| Hirst & Booth [4]     | 3.5              | 3.5            | 7.3             | 3.9            |
| FMRC [1]              | 3.3              | 3.3            | 7.1             | 3.7            |
| Sheinson et al. [18]  | 3.1              |                |                 |                |
| NFPA 12a [20]         | 4.1              | 3.3            |                 | 3.8            |

#### Mechanism of Extinguishment (Physical/Chemical).

Fire suppression agents are classified by the primary mechanism of extinguishment. For vaporous agents, there are three classifications. If the agent works only by displacing oxygen and by increasing the heat capacity of the environment around the fire, then the agent is classified as a physical agent. The prototypical physical agent is carbon dioxide. If the agent works in a manner similar to Halon 1301, invoking a reaction or reaction cycle to remove radicals, then it is classified as a chemical agent. The third classification is an in-between class. These agents do not participate in the type of reactions or cycles that chemical agents do, but increase the heat losses in the reaction zone by more than can be explained by oxygen displacement or increased heat capacity. The primary mechanisms employed by this group are endothermic disassociation reactions.

Physical Mechanism.

A physical agent effectively lowers the flame temperature below that necessary to maintain the combustion process. This temperature is referred to as the critical flame and is approximately 1600°K [18,21]. The flame temperature can be determined through an energy balance in the combustion zone as follows:

$$X_{O_2} \Delta H'_c = M_R \sum X_i \int_{T_a}^{T_f} C_{p,i} dt + L \quad (1)$$

where  $X_{O_2}$  is the mole fraction of oxygen available for combustion,  $\Delta H'_c$  is the heat of combustion of the fuel per mole of oxygen,  $X_i$  is the mole fraction of combustion product/inert species  $i$  ( $H_2O$ ,  $CO_2$ ,  $N_2$ , etc.),  $C_{p,i}$  is the constant pressure heat capacity of species  $i$ ,  $T_a$  is the ambient temperature,  $T_f$  is the flame temperature,  $M_R$  is the moles of inerts and combustion products formed per mole of air consumed, and  $L$  is the heat losses out of the combustion zone per mole of air consumed. The effects of the addition of a physical agent on the flame temperature can be shown by the following modifications of equation 1:

$$(1 - X_A) X'_{O_2} \Delta H'_c = (1 - X_A) M_R \sum X'_i \int_{T_a}^{T_f} C_{p,i} dt + X_A \int_{T_a}^{T_f} C_{p,A} dt + (1 - X_A) L \quad (2)$$

where  $X_A$  is the resulting mole fraction of agent  $A$ ,  $X'_{O_2}$  and  $X'_i$ , oxygen and species  $i$ , respectively, prior to addition of agent  $A$ , and  $C_{p,A}$  is the constant pressure heat capacity of the agent.

In order to estimate the concentration of agent required to cause extinguishment, equation 2 is rearranged and the critical flame temperature is substituted for  $T_f$ , as follows:

$$X_A = \frac{\left( X'_{O_2} \Delta H'_c - M_R \sum X'_i \int_{T_0}^{T_i} C_{p,i} dt - L \right) / \int_{T_0}^{T_i} C_{p,A} dt}{1 + \left( X'_{O_2} \Delta H'_c - M_R \sum X'_i \int_{T_0}^{T_i} C_{p,i} dt - L \right) / \int_{T_0}^{T_i} C_{p,A} dt} \quad (3)$$

Table 5 gives the predicted concentrations determined from equation 3 for Halon 1301, nitrogen, carbon dioxide, and the perfluorocarbon series CF<sub>4</sub> through C<sub>4</sub>F<sub>10</sub>. Comparison of the concentrations given in Table 6 with those determined experimentally in Table 4 illustrates the extent to which these agents utilize mechanisms in addition to these physical mechanisms. The loss term in equation 3 for each fuel was determined by forcing the predicted CO<sub>2</sub> concentrations to match those given in reference 3. As some of these predicted concentrations are less than those determined experimentally, the determination of the loss term in this manner seems questionable. The loss term maybe altered by the presence of a different agent, i.e., C<sub>4</sub>F<sub>10</sub> might be a better absorber of the infrared radiation given off by a particular flame than CO<sub>2</sub>. Ewing et al. [22] in predicting their physical mechanism alone concentrations, use a loss term that varies with both the fuel and the agent applied. Table 6 also gives the predicted concentrations with a loss term of zero as an upper bound on the predicted concentration for comparison.

Table 6 - Agent Concentration Required for Physical Mechanism Alone

|                                | <u>n-Heptane</u> |       | <u>Methanol</u> |       | <u>Ethanol</u> |       | <u>Acetone</u> |       |
|--------------------------------|------------------|-------|-----------------|-------|----------------|-------|----------------|-------|
| L [kJ/gmol]                    | 18.02            | 0.00  | 7.74            | 0.00  | 14.38          | 0.00  | 27.23          | 0.00  |
| CO <sub>2</sub>                | 20.50            | 34.24 | 26.20           | 31.88 | 21.80          | 32.82 | 18.30          | 38.32 |
| N <sub>2</sub>                 | 30.12            | 46.54 | 37.25           | 43.90 | 31.79          | 44.96 | 27.25          | 50.95 |
| CF <sub>3</sub> Br             | 12.14            | 21.83 | 15.99           | 20.06 | 13.00          | 20.76 | 10.72          | 24.99 |
| CF <sub>4</sub>                | 1248             | 22.37 | 16.42           | 20.57 | 13.36          | 21.28 | 11.03          | 25.58 |
| C <sub>2</sub> F <sub>6</sub>  | 7.80             | 14.59 | 10.44           | 13.31 | 8.38           | 13.82 | 6.85           | 16.93 |
| C <sub>3</sub> F <sub>8</sub>  | 5.67             | 10.83 | 7.65            | 9.84  | 6.10           | 10.23 | 4.97           | 1266  |
| C <sub>4</sub> F <sub>10</sub> | 4.46             | 8.61  | 6.04            | 7.81  | 4.80           | 8.12  | 3.89           | 10.10 |

Vitiated and Enhanced Oxygen Atmospheres.

A more definitive approach to the physical/chemical mechanisms is that suggested by Tucker, Drysdale and Rasbash [19]. In this approach, equation 2 is simplified by subtracting the heat absorbed by the products of combustion and heat loss term from the heat of combustion per mole of oxygen.

$$X_{O_2} \Delta H'_{bc} = X_{N_2} \int_{T_a}^{T_f} C_{pN_2} dt + X_A \int_{T_a}^{T_f} C_{pA} dt \quad (4)$$

where  $\Delta H'$  is the heat of combustion per mole of oxygen minus the heat absorbed by the products of combustion and the heat loss term.  $\Delta H'_{bc}$  is assumed to be a constant for each fuel. If nitrogen by itself is used to extinguish the fire, equation 4 becomes the following:

$$X_{O_2} \Delta H'_{bc} = X_{N_2} \int_{T_a}^{T_f} C_{pN_2} dt = k_x X_{N_2} \Delta H'_{bc} \quad (5)$$

where  $k_x$  is the ratio of the oxygen concentration to that of nitrogen at extinguishment or the molar amount of oxygen "inerted" per mole of nitrogen. If this is substituted back into equation 4, then with some rearrangement, the following expression is arrived at:

$$(X_{O_2} - k_x X_{N_2}) \Delta H'_{bc} = X_A \int_{T_a}^{T_f} C_{pA} dt \quad (6)$$

The expression in parenthesis is referred to as the free oxygen concentration and if the agent is purely physical, then the relationship between the agent concentration and the free oxygen concentration should be linear.

Figure 3 gives the results of using carbon dioxide, Halon 1301, or one of the perfluorocarbons to extinguish a n-Heptane fire in various vitiated and enhanced atmospheres. Carbon dioxide gives the expected straight line in Figure 3. Halon 1301 generated a curve instead of a straight line as expected. The three perfluorocarbons give curves that suggest dependence on a mechanism in addition to the physical mechanism.

The curve generated by Halon 1301 has an increasing slope with increasing free oxygen concentration which is consistent with the results of Tucker et al. [19], but is the opposite trend of that observed for the perfluorocarbons. As most endothermic (heat absorbing) reactions increase in rate exponentially with increasing temperature, it would be expected that an agent that depends on this type of reaction would become more efficient with the increasing temperature associated with an increasing oxygen concentration. The reverse trend in the Halon 1301 curve may well be the result of a competing reaction requiring the increased temperature to provide its required activation energy. The fairly sharp increase in the required Halon 1301 concentration above 10% by volume free oxygen would seem to support this assumption.

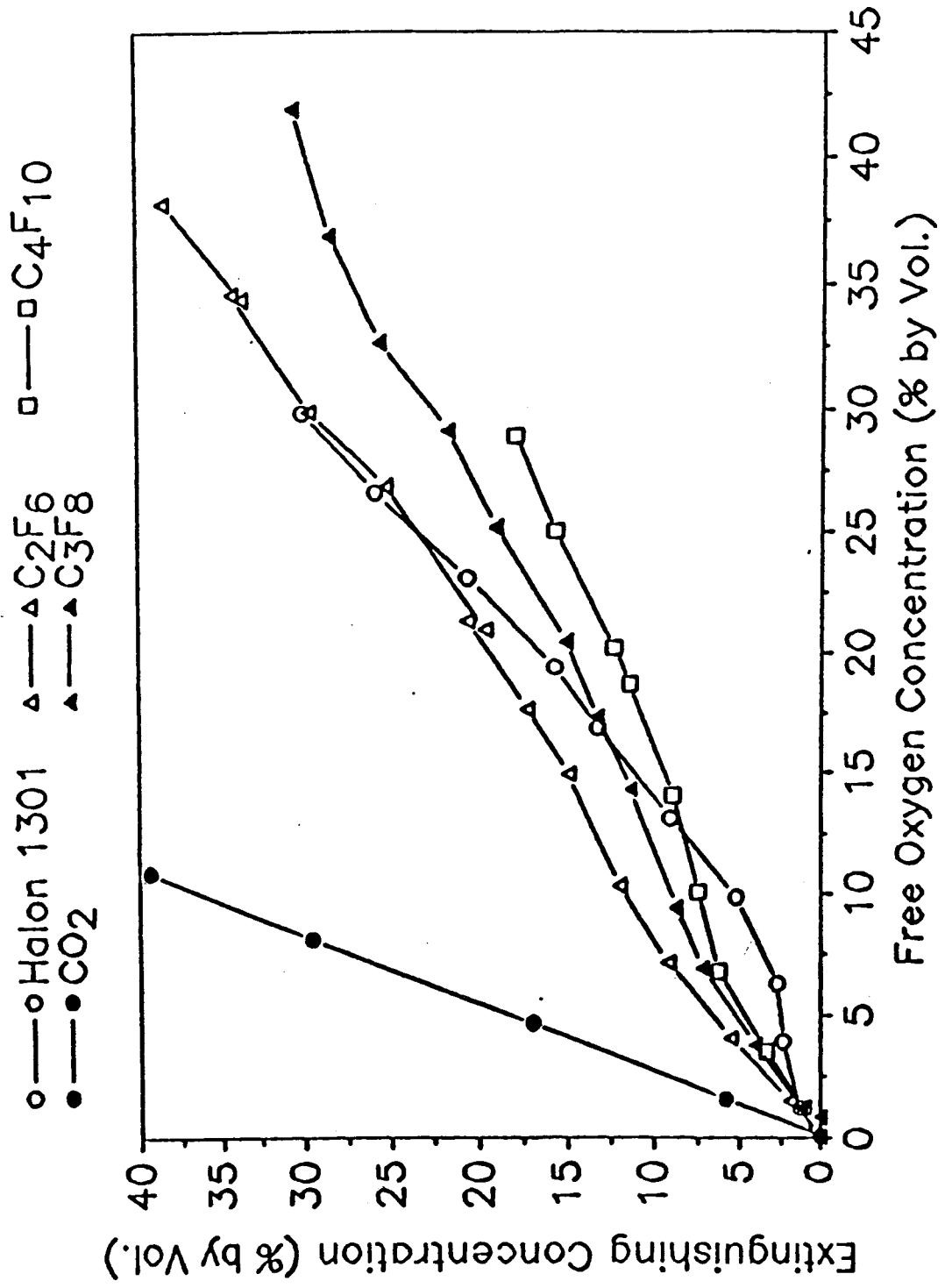


Fig. 3 - Extinguishing concentrations as a function of free oxygen concentration

## FEASIBILITY.

### Agent Requirements.

A comparison of the amount of agent and cylinder volume required to store the agent is given for Halon 1301 and the three perfluorocarbons in Table 7. The concentration of agent in Table 7 is 20% higher than that determined in the cup burner tests described previously for n-Heptane. This follows the recommendation in NFPA 12A; it is uncertain whether this 20% safety factor is required in practice. The cylinder volume is based on a 72% liquid fill which corresponds to a 1,121 kg/m<sup>3</sup> (70 lbm/ft<sup>3</sup>) fill density for Halon 1301 with the exception of that determined for perfluoroethane which is supercritical. The cylinder volume for perfluoroethane is the volume required to contain the agent at 2.48 MPag (360 psig).

Table 7 - Agent requirements to protect 1000 ft<sup>3</sup> space

| <u>Agent</u>                     | <u>Conc. *</u><br><u>(Vol. %)</u> | <u>Mass Req.</u><br><u>(lbm)</u> | <u>Cylinder</u><br><u>Volume</u><br><u>(ft<sup>3</sup>)</u> | <u>Mass Rel.</u><br><u>to 1301</u> | <u>Cylinder</u><br><u>Vol. Rel.</u><br><u>to 1301</u> |
|----------------------------------|-----------------------------------|----------------------------------|---|------------------------------------|---|
| Halon 1301                       | 4.680                             | 18.923                           | 0.270   | 1.000                              | 1.000   |
| C <sub>2</sub> F <sub>6</sub> ** | 10.440                            | 41.640                           | 4.573   | 2.200                              | 16.917  |
| C <sub>3</sub> F <sub>8</sub>    | 8.160                             | 43.238                           | 0.716   | 2.285                              | 2.649   |
| C <sub>4</sub> F <sub>10</sub>   | 6.960                             | 46.086                           | 0.680   | 2435                               | 251 5   |

\* 12 times determined cup burner concentration for n-Heptane.

\*\* Cylinder volume requirement based on 2.48 MPag storage pressure.

A little more than twice the mass of agent relative to Halon 1301 is required to protect the same volume enclosure with one of the perfluorocarbons. With the exception of perfluoroethane (C<sub>2</sub>F<sub>6</sub>), it takes approximately 25 times the cylinder

volume to contain the agent required relative to Halon 1301.  $C_2F_6$  is supercritical at 21.1 °C (70°F) and therefore requires either much higher pressure cylinders, greater cylinder volumes, or both.

#### Leakage Rates.

The leakage rate from an enclosure in a total flooding fire protection system can be predicted using the methods derived by DiNunno and Forssell [23]. In this method a distribution of the leakage area over the enclosure is assumed to be divided between two leaks, one in the ceiling and the other in the floor, after the total effective leakage has been determined by a door fan test or other method. The separation of the flows in and out of the enclosure, and low degree of mixing, makes this a descending interface phenomenon. This situation is then modeled by extending the concepts of Yao and Smith [24] as follows:

$$A_L = F_A K_d A_T / K_{dL} \quad (7)$$

$$A_U = (1 - F_A) K_d A_T / K_{dU} \quad (8)$$

$$\Delta P_L - \Delta P_U = (p_m - p_{air}) gh \quad (9)$$

$$Q_U = -Q_L \quad (10)$$

$$(1 - F_A) C (2 \Delta P_U / p_{air})^N = -F_A C (2 \Delta P_L / p_m)^N \quad (11)$$

where  $A_L$  and  $A_U$  are the lower and upper leakage areas, respectively,  $F_A$  is the fraction of the total effective leakage area represented by the lower leak,  $K_d$  and  $A_T$  is the flow coefficient and total leakage area determined by the door fan testing  $K_{dL}$  and  $K_{dU}$  are the flow coefficients of the lower and upper leaks,  $\Delta P_L$  and  $\Delta P_U$  are the pressure differences across the lower and upper leaks,  $p_m$  is the density of the agent-air mixture,  $p_{air}$  is the density of air,  $h$  is the height of the interface,  $Q_L$  and  $Q_U$  are the

volume flow rates through the lower and upper leaks, N is the door fan flow exponent, and C is the door fan correlation coefficient equal to the product of  $K_{dL}$   $A_T$  and a constant based on the value of N and the units used.

An expression for the flow rate through the lower leak is determined by solving equation 12 for  $\Delta P_U$ :

$$\Delta P_U = -[F_A / (1 - F_A)]^{\frac{1}{N}} (\rho_{air} / \rho_m) \Delta P_L \quad (12)$$

then substituting in equation 10, solving for  $\Delta P_L$ , and finally substituting back in equation 12:

$$\Delta P_L = [(\rho_m - \rho_{air}) gh] / \left[ 1 + [F_A / (1 - F_A)]^{\frac{1}{N}} (\rho_{air} / \rho_m) \right] \quad (13)$$

$$Q_L = F_A C [2 (\rho_m - \rho_{air}) gh] / \left[ \rho_m + [F_A / (1 - F_A)]^{\frac{1}{N}} \rho_{air} \right]^N \quad (14)$$

As the rate of descent of the interface is related to the volume flow rate a differential equation is arrived at:

$$dh / dt = -Q_L / A_r \quad (15)$$

where  $A_r$  is the horizontal cross-sectional area of the enclosure. This equation is then integrated to yield the following expression for the time required for the interface to descend from an initial height,  $h_i$ , to a height  $h$ :

$$t = [h_i^{(1-M)} - h^{(1-M)}] / [(1-M) K_1] \quad (16)$$

where

$$K_1 = (F_A C / A_f) [2 (\rho_m - \rho_{air}) g] / \left[ \rho_m + [F_A / (1 - F_A)]^{1/N} \rho_{air} \right]^N \quad (17)$$

Figure 4 gives the interface recessions predicted for Halon 1301, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, and C<sub>4</sub>F<sub>10</sub>, of the concentrations given in Table 6 for an enclosure with a height of 3.1 m (10 ft) and a cross-sectional area of 9.3 m<sup>2</sup> (100 ft<sup>2</sup>). Two circular leaks, 6.1 cm (2.5 in.) in diameter with flow coefficients of 0.61 were assumed in the enclosure, one in the roof and one in the floor. A flow exponent of 0.5 was used.

As can be seen in Figure 4, the greater mass required for the perfluorocarbons resulted in approximately 30% shorter time predicted for the interface to descend the same distance as the Halon 1301-air interface.

#### Flow Characteristics.

Phenomenologically, the discharge and pipe flows of the perfluorocarbons are similar to that of Halon 1301, with the exception of perfluoroethane. All these flows are two phase-two component flows with the exception of perfluoroethane which experiences single phase (most likely single component also) vapor flow. These flow phenomena are extremely complex and difficult to predict, however, several computer schemes have been developed for the discharge of Halon 1301 and could be modified for use with the perfluorocarbons. Notably among these computer schemes are the Jet Propulsion Laboratories HFLOW (simplified Halon 1301 algorithm) and their modifications of Los Alamos National Laboratories SOIA-LOOP program (finite difference, drift flux algorithm) [25].

In these programs, the discharge is divided into two segments. The first segment is the bottle pressure recession. In this segment, the pressure is incrementally decreased from its initial value to ambient, with the amount of agent and nitrogen leaving the bottle determined for each increment as follows:

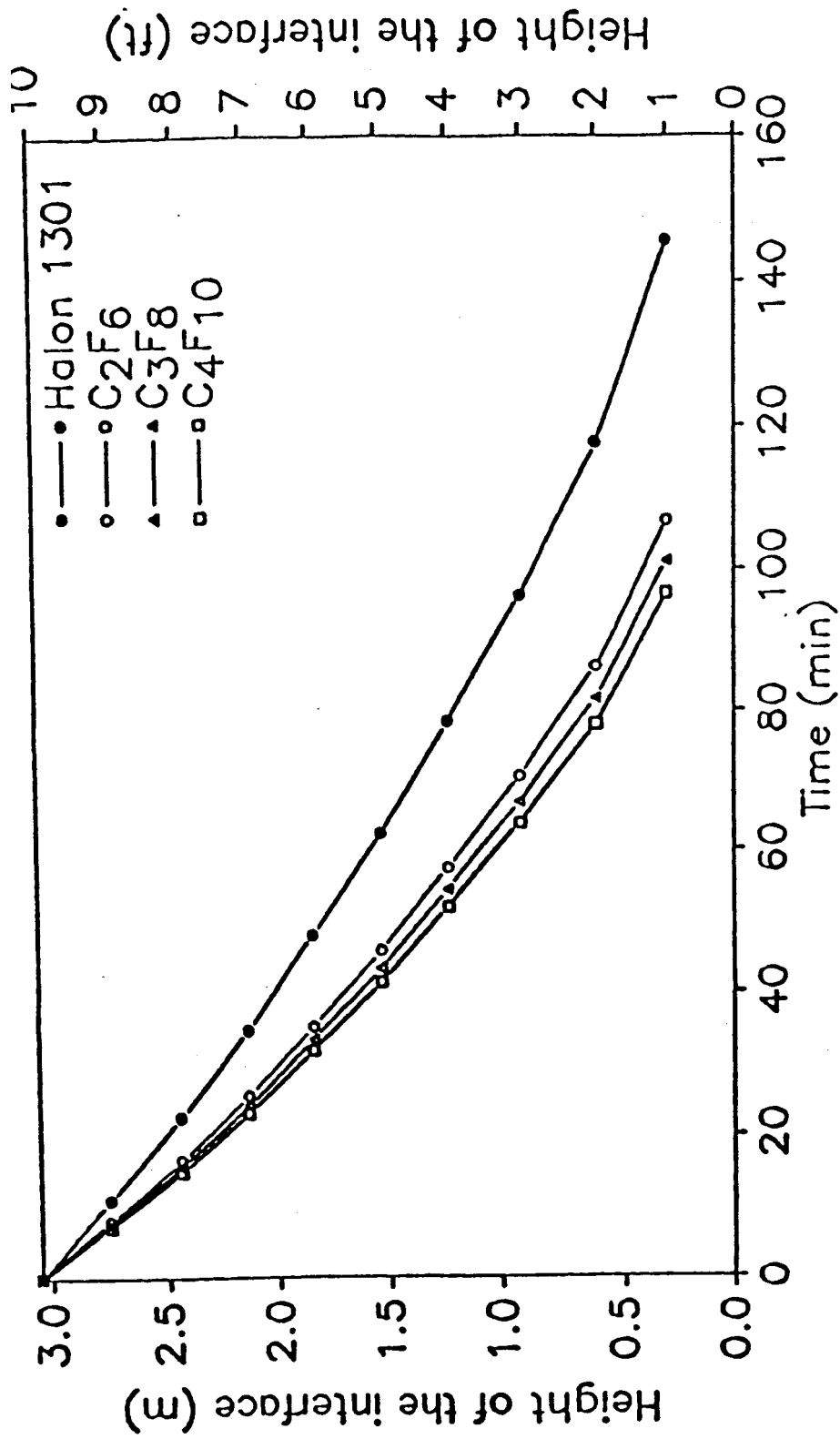


Fig. 4 - Predicted interface recession with 6.4 cm (2.5 in.) diameter leaks in a 3.1 m (10 ft) cubic enclosure

$$V_{out} = (m_1/\rho_2) - V_{cyl} \quad (18)$$

Where  $V_{out}$  is the volume of the agent and nitrogen that leaves the cylinder in the pressure increment,  $m$ , is the mass in the cylinder at the beginning of the increment,  $\rho_2$  is the average density in the cylinder at the end of the increment, and  $V_{cyl}$  is the volume of the cylinder. The portion of this volume that is agent, nitrogen, or liquid is determined from the average conditions in the lower section of the cylinder. Some vapor is included in the discharge as only a fraction of the vapor generated in an increment actually joins the ullage. The temperature at the end of the pressure increment is determined from an energy balance:

$$U_1 - U_2 = m_{out} H_{out} \quad (19)$$

where  $U_1$  and  $U_2$  are the internal energies of the contents of the cylinder at the beginning and end of the increment, respectively,  $m_{out}$  is the mass leaving the cylinder, and  $H_{out}$  is the specific enthalpy of that mass. Note that for the assumed adiabatic bottle segment there is no time dependence.

The pipe/nozzle segment of these programs determines the flow rate through the pipe network. The elapsed time is determined from the determined flow rate and the mass that must be discharged in each bottle pressure increment (determined in the previous segment). In each pipe section, the force opposing flow causes a reduction in pressure and an increase in momentum (the average velocity is increased due to the reduction in average density at the lower pressure).

$$0.125 \rho_m V_m^2 f \pi DL = A_p (P_1 - P_2) - m (V_2 - V_1) \quad (20)$$

where  $\rho_m$  is the average density in the section,  $V_m$  is the average velocity in the section,  $f$  is the pipe flow friction factor,  $D$  is the pipe diameter,  $L$  is the section length,  $A_p$ , is the cross-sectional area of the pipe,  $m$  is the mass flow rate,  $V_2$  and  $V_1$  are the

average velocities at the end and beginning of the section, respectively. The friction factor can be determined from a Moody diagram [26] or from the Colebrook equation [26] which is good for the highly turbulent flows involved ( $Re > 4000$ ):

$$f^{-0.5} = -2 \log \left[ \left( \frac{k_s}{3.7D} \right) + \frac{2.51}{Re f^{0.5}} \right] \quad (21)$$

where  $k_s$  is the equivalent sand roughness and  $Re$  is the Reynolds number based upon average fluid properties at the mid-point of the pressure increment. The contribution of the Reynolds number term is insignificant for the majority of the flows involved in the discharge of a total flood system and can be ignored. This friction factor is valid for homogeneous flow with no slip, i.e. one phase evenly dispersed in the other with no difference in velocity between phases. If either conditions are untrue then the friction factor must be modified accordingly [27,28]. The temperature at the end of the pressure increment is determined by an energy balance where the decrease in enthalpy is equal to the increase in kinetic energy:

$$H_1 - H_2 = (V_2^2 - V_1^2) / 2 \quad (22)$$

The nozzle flow is determined by stepping down the nozzle pressure until atmospheric pressure is reached. The increase in velocity is determined for each pressure step as follow:

$$V_2^2 - V_1^2 = 2 \int_{P_2}^{P_1} dP / \rho_m \quad (23)$$

The temperature at the end of each step is determined in the same manner as in pipe flow. At the end of each step the required flow area is determined as follows:

$$A_2 = m / (\rho_2 V_2) \quad (24)$$

The lowest value for  $A_2$  is the required throat area for the nozzle to accommodate the mass flow rate  $m$ . This is compared to the actual effective nozzle throat area and the  $m$  flow rate in the piping and nozzle are then adjusted accordingly.

Qualitatively, the flow of either perfluoropropane,  $C_3F_8$ , or perfluorobutane,  $C_4F_{10}$ , superpressurized with nitrogen from a cylinder filled similarly to that done with Halon 1301 (same percent liquid fill), would have lower nozzle pressures and flow more like a liquid with a resulting higher average density due to their lower vapor pressure. Both of these effects tend to reduce the volumetric flow rate of the agent but the effect on the mass flow rate is slight due to the higher density offsetting the change in volumetric flow.

Perfluoroethane,  $C_2F_6$ , would be a vapor phase discharge with a higher volumetric flow rate offset by the lower density, and a quicker drop in cylinder pressure per unit mass discharged.

The bottom line in any case is an increase in discharge time due to the increase in mass that must be discharged unless nozzle sizes and/or pipe sizes are increased.

#### System Modifications.

The larger agent storage volume, faster leakage rate from the protected space, and longer discharge times require modifications to an installed Halon 1301 fire protection system in order to use any of these perfluorocarbons. These modifications can be as minor as adding additional cylinders and switching out nozzles. However, increased pipe sizes maybe required in some systems in order to obtain a 10 second discharge time. Additional modification may also be necessary to reduce the leakage rate from the space protected.

In order to use perfluoroethane,  $C_2F_6$ , higher agent storage pressures than the normal commercial 2.48 MPag (360 psig) storage pressure or possibly cold storage may be necessary to reduce the required storage volume to practical levels.

## Thermal Decomposition Products.

There is evidence that the perfluorocarbons (as well as other proposed alternatives) will produce higher levels of thermal decomposition products than Halon 1301. This is a natural consequence of eliminating the highly effective chemical suppressant Bromine from the molecule in order to preclude ozone depletion. The amount of decomposition products produced is a function of the fire size at time of discharge and the discharge time. Decomposition products of HF and HBr associated with Halon 1301 varied between <5 and >5000 ppm, a thousand fold difference by varying the fire size and discharge time. No reliable data is available on the decomposition products of the perfluorocarbons hence testing specifically designed to measure HF production as a function of fire size and discharge time would be required.

The degree of acceptable decomposition is a function of the facility being protected relative to collateral damage associated with the decomposition products. The range of "acceptable" decomposition associated with Halon 1301 indicates that this problem is not critical to the acceptability of the perfluorocarbons. Furthermore, decomposition product production can be reduced by applying the agent while the fire is small or decreasing the discharge time.

## Commercialization

Several chemical manufacturers are known to have the ability to produce the perfluoroalkanes in commercial quantities. Barriers to the commercialization of these compounds as fire suppressants can be categorized broadly as those associated with the technical aspects of the compounds as fire suppressants (for example, effectiveness, flow characteristics, decomposition products, hardware compatibility, etc.), those problems associated with regulatory approvals (EPA, UL, FM, NFPA, etc.) and production issues.

This study has indicated that relative to the technical aspects of the proposed agents, feasibility has been demonstrated. Regulatory approvals including associated toxicological and environmental studies will be undertaken by interested manufacturers. Production capacity currently exists; the size of the market as well as other resource allocation issues will determine whether additional production capacity is warranted.

The value of this and future work lies in the ability to remove technical barriers and to provide independent data and analysis for use in the regulatory approval process. Interest has been shown in this work, and possible Phase I effort by 3M Company, the most probable manufacturer of commercial quantities of  $C_4F_{10}$  and/or  $C_3F_8$  is also possible.

## CONCLUSIONS.

This investigation has demonstrated the feasibility of using the perfluorocarbons of the straight chain series from perfluoroethane,  $C_2F_6$ , to perfluorobutane,  $C_4F_{10}$  as alternatives for Halon 1301 in total flooding fire protection system. They are non toxic, clean, and effective at relatively low volumetric concentrations. They have been shown to have mass requirements of a little over twice that for Halon 1301 based on n-heptane extinguishing concentrations. Assuming the 10 second discharge time requirement remains constant, the degree of system modification required to retrofit either  $C_3F_8$  or  $C_4F_{10}$  in lieu of Halon 1301 is variable. Some systems would only require nozzle changes while others may require additional piping changes.

The major uncertainty is the degree of thermal decomposition. This could readily be evaluated through a moderate and large scale testing program. In addition, the development of engineering data for flow calculations and pipe and nozzle sizing would be required for both retrofit and new applications. The major regulatory uncertainty is the global warming potential of the compound. This will be driven by the expected use quantities, additional scientific information, and the regulatory position of the EPA.

The potential of perfluoroethane is limited ( $C_2F_6$ ) by the high cylinder volume requirement caused by its low critical temperature and pressure. Hence, it should not be considered further.

## RECOMMENDATIONS FOR FURTHER INVESTIGATION.

Further investigation in the areas of flow characteristics, larger scale fires, initial mixing, material compatibility, toxicology, and thermal decomposition products of perfluoropropane, and perfluorobutane is required.

### Flow Characteristics.

Additional investigation is needed into the discharge of these perfluorocarbons. This investigation would involve two parts. The first would involve the adaptation of a program like HFLOW and SOIA-LOOP to the prediction of the two phase-two component flow of these perfluorocarbons in a total flooding fire protection system.

The second part would involve a series of tests with differing flow parameters, flow splits, nozzle sizing, etc. These tests would also serve as a confirmation of the program adaptations.

### Material Compatibility.

While there is no reason to expect compatibility problems with the materials of construction, sealing materials, or lubricants commonly used in Halon 1301 equipment, this will need to be confirmed. The primary test method for material compatibility is the sealed tube test where a sample of the material in question is sealed in a tube with the liquid perfluorocarbon with any change in appearance of the sample material or liquid noted.

### Toxicology.

While these perfluorocarbons are considered non-toxic, it is likely that the acute inhalation toxicology tests will have to be run at exposures that are greater than those

expected from any discharge of agent. These tests would also be required prior to EPA regulatory approval and are best performed by the gas manufacturer(s).

#### Thermal Decomposition.

A series of tests would need to be run that would quantify the amount of thermal decomposition products produced in extinguishing a fire. The primary variables affecting thermal decomposition products evolution are the size of fire at the time of discharge and the time required for discharge. Halon 1301 is known to produce quantities of hydrobromic and hydrofluoric acids at levels that are considered of minor significance. The quantity of hydrofluoric acid produced from these perfluorocarbons will need to be evaluated in terms of its significance in the context of a fire-induced environment.

The initial evaluation of thermal decomposition product production is best accomplished in small scale enclosures (1 x 1 x 1 m). This enables the relevant physics and chemistry to be preserved while allowing for more precise gas sampling. The scaled relationships between fire size, enclosure volume, and decomposition products should be verified against more realistic scales (minimum of 3 x 3 x 3 m).

#### Full Scale Testing.

The development of engineering data and models on the hydraulic performance of perfluorocarbons and the small scale thermal decomposition work should be validated in larger scale tests. A series of large scale tests which evaluates fire suppression effectiveness, hydraulic flow characteristics, agents mixing, and thermal decomposition should be conducted.

## Comparison With Other Proposed Halon Alternatives

The proposed use of  $C_3F_8$  and  $C_4F_{10}$  as fire suppression alternatives should also be evaluated against the other leading halon alternative pentafluoroethane ( $CF_3CHF_2$ ) proposed by DuPont. Specifically the agents should be compared relative to toxicity, effectiveness, and production of thermal decomposition.

## REFERENCES.

1. Ford, Charles L., "An Overview of Halon 1301 Systems," ACS Symposium Series, Number 16, "Halogenated Fire Suppressants," American Chemical Society, Washington, D.C., 1975.
2. Dunn, Robert M., "Update 1990 on the Montreal Protocol 1987," Halon and Environment '90-2nd Conference on the Fire Protecting Halons and the Environment, National Fire Protection Association, Canberra, Australia, 1990.
3. McCulloch, Archie, "Past and Future of Halons, an Industry Perspective," Halon and Environment '90-2nd Conference on the Fire Protecting Halons and the Environment, National Fire Protection Association, Canberra, Australia, 1990.
4. Hirst, R. and Booth, K., "Measurement of Flame-Extinguishing Concentrations," Fire Technology, Vol. 13, No. 4, November 1977.
5. "DuPont Halon 1301 Fire Extinguishant," Bulletin B-29D, E.I. DuPont de Nemours & Company, Wilmington, DE, 1977.
6. Poulsen, Ole and Wollemann, P., "Fire and Water Damage to Albertslund Trunk Exchange," Teleteknik (English Version), Vol. 26, No. 1, 1982.
7. Sielert, Vern A., "Modern Fire Protection: An Application," in Proceedings of the Second Annual Fire Engineering Conference: Fire Protection Engineering and Design for Special Hazards, Manhattan College, Riverdale, NY, 1984.
8. "Standard on Carbon Dioxide Extinguishing Systems," NFPA Standard 12, National Fire Protection Association, Batterymarch Park, Quincy, MA, 1985.
9. Ember, L.R., Layman, P.L, Lepkowski, W., and Zurer, P.S., "The Changing Atmosphere," Chemical and Engineering News, Vol. 64, No. 47, 1986.
10. Anderson, Stephen O., "Halon and the Stratospheric Ozone Issue," Fire Journal, May/June 1987.
11. Huggett, Clayton, "Habitable Atmospheres Which Do Not Support Combustion," Combustion and flame, Vol. 20, 1973.
12. Huggett, Clayton, "Oxygen-Containing Atmospheres," U.S. Patent 3,840,667, October 8, 1974.
13. Huggett, Clayton, "Habitable Combustion-Suppressant Atmosphere Comprising Air, A Pedluoroalkane, and Optionally Make-up Oxygen," U.S. Patent 3,715,438, February 6, 1973.

14. McHale, Edward. T., "Life Support without Combustion Hazards," *Fire Technology*, Vol. 10, No. 1, February 1974.
15. Sheinson, Ronald S., Penner-Hahn, James E., and Indritz, Doren, "The Physical and Chemical Action of Fire Suppressants," *Fire Safety Journal*, Vol 15, 1991.
16. Braker, William, and Mossman, Allen L., *Matheson Gas Data Book*, Matheson, Lyndhurst, NJ, 1980.
17. "Product Toxicity Summary Sheet: FLUORINERT Brand Electronic Liquid FC-72," 3M, St. Paul, MN, 1990.
18. Moore, Joanne P., Moore, Ted A., Salgado, Dan, and Tapscott, Robert E., "Halon Alternatives Extinguishment Testing," Presented at the International Conference on CFC & Halon Alternatives, Washington, D.C., October 10-11, 1990.
19. Tucker, D.M., Drysdale, D.D., and Rasbash, D.J., "The Extinction of Diffusion Flames Burning in Various Oxygen Concentrations by Inert Gases and Bromotrifluoromethane," *Combustion and Flame*, Vol. 41, 1981.
20. "Standard on Halon 1301 Extinguishing Systems," NFPA Standard 12A, National Fire Protection Association, Batterymarch Park, Quincy, MA, 1985.
21. Drysdale, Dougal, *An Introduction to Fire Dynamics*, John Wiley and Sons, Chichester, 1985.
22. Ewing, Curtis T., Hughes, J. Thomas, and Carhart, Homer W., "The Extinction of Hydrocarbon Flames based on the Heat-absorption Processes which Occur in them," *Fire and Materials*, Vol. 8, No. 3, 1984.
23. DiNenno, P.J., and Forssell, E.W., "Evaluation of the Door Fan Pressurization Leakage Test Method Applied to Halon 1301 Total Flooding Systems," *Journal of Fire Protection Engineering*, Vol. 1, No. 4, 1989.
24. Yao, C. and Smith, H.F., "Convective Mass Exchange between a 'FREON' FE 1301 - Air Mixture in an Enclosure and Surrounding Air Through Openings in Vertical Walls," Factory Mutual Research Corporation, Report 16234.1, Norwood, MA, January 1968.
25. Elliot, D.G., Garrison, P.W., Klein, G.A., Moran, K.M. and Zydowicz, M.P., "Flow of Nitrogen-Pressurized Halon 1301 in Fire Extinguishing Systems," JPL Publication 84-62, Jet Propulsion Laboratory, Pasadena, CA, Nov. 1984.
26. Baumeister, Theodore, Editor-in-Chief, Marks' *Standard Handbook for Mechanical Engineers*, McGraw-Hill Book Company, New York, NY, 1978.

27. Hirt, C.W. and Romero, N.C., "Application of a Drift-Flux Model to Flashing in Straight Pipes," Los Alamos Scientific Laboratory, Los Alamos, NM, 1976.
28. Lockhart, R.W. and Martinelli, R.C., "Proposed Correlation of Data for Isothermal Two-Phase, Two-Component Flow in Pipes," Chemical Engineering Progress, Vol. 45, No. 1, 1949.