Halon Replacement Decomposition Product Studies

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1   Introduction

A number of laboratories have previously reported results of test programs on Halon replacement agents carried out at laboratory [1], intermediate [2,3] or full-scale [4,5]. However, due to their inherent cost, full-scale tests are usually limited, both in the cross section of agents studied, and the range of test parameters varied. Halon 1301 baseline tests are not always included. Although it is possible to compare results from different organisations, care has to be taken, as test fixtures and methodologies vary considerably from one organisation to another. A further complication arises when decomposition product levels from different studies are compared because there are several methods for measuring the concentrations of acid gases such as HF, HBr and HI. These include *in-situ* FTIR[6], external FTIR/heated sample lines [7] and several aqueous trapping methods followed by either ion chromatography [8] or ion selective electrode analysis'''. Therefore, it was decided to test a wide range of currently available agents under, as near as possible, equivalent conditions. To keep *costs* down a laboratory scale test chamber, suitable for realistic total-flood testing, was chosen.

Parameters that merit examination include test chamber size, fire size, fuel type, **length** of pre-bum, and the extent to which the suppression system is optimised. During this test work these Parameters will all be investigated to try to gain a fundamental understanding of the complex issue of acid gas production. A wide range of currently available agents is being tested, giving a multi-dimensional baseline, against which potential second generation chemically acting agents are currently being evaluated.

2   Experimental

2.1   The Test Chamber and Procedure

A diagram of the 200 **L** cubic test chamber is given in Figure 1. The chamber can be scaled and is equipped **with** a transparent door for observation and access. The fire threats arc three small **pans** containing heptane floated **on** water. The main fire (heptane volume 30 cm^3 and diameter 70 mm) is positioned in the centre of the base of the chamber. Two satellite fires (heptane volume 1 cm^3 and diameter 20 mm) arc positioned at the bottom right front comer and the top left rear comer. This gives a value of 7.3 kWm^{-3} for the fire size to chamber volume parameter (FSRV). **All** fires arc obscured with baffles as shown. Known masses of agents arc contained in a 0.3 L pressure vessel at 23 ± 3 °C. With HFC-134a, HFC-227ea, HFC-236fa, FC-3.1.10, FC-5.1.14 and IFC-13I1 the vessel is pressurised minutes before discharge to 10 bar with nitrogen. Halon 1301, HFC-23 and HFC-125 have a room temperature vapour pressure above 10 bar. Therefore, these agents are propelled by their intrinsic vapour pressure.

Figure 1: The **200 L** Test Chamber

70 mm diameter heptane fire
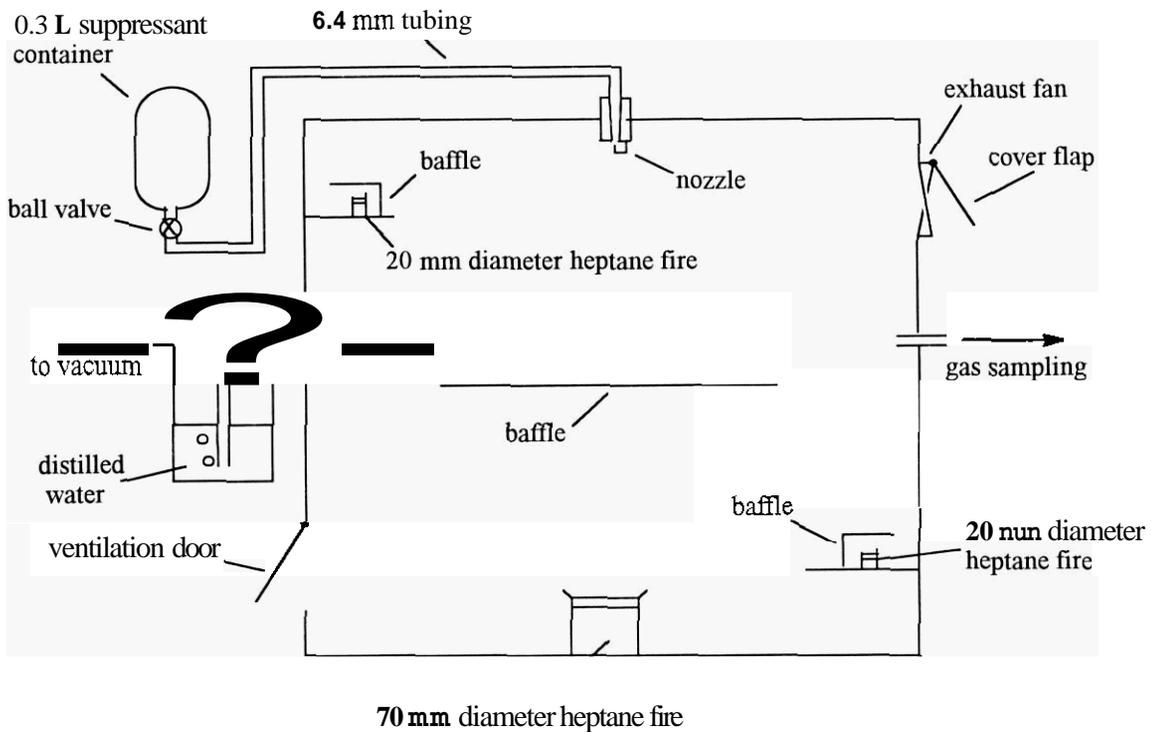
In each test the three fires are lit and allowed to bum under ventilated conditions with the door open and the exhaust fan running. The ventilation rate is sufficient to prevent oxygen depletion in the chamber. **After** 45 seconds the fan is stopped and the doors sealed. The fires continue to bum for a further 15 seconds, after which the agent is discharged through a nozzle which gives fine atomisation. The oxygen concentration is about 20.8 and 20.5 volume % at the end of the 45 second ventilated prebum and the beginning of the agent discharge, respectively. If the fires are allowed to bum in the sealed chamber the main fire self-extinguishes due to oxygen starvation after about 140 seconds.

2.2   **Acid** Gas Determination

During and after the suppression, fixed sample volumes of the chamber gases are drawn through distilled water to trap acid gases. Six independent polythene sample bottles are used to obtain time resolved plots of acid gas concentrations. Each sample bottle has a 3 second sampling time. The trapping efficiency for hydrogen fluoride is greater than 95%, **as** tested with known concentrations of hydrogen fluoride in nitrogen. Polytetrafluoroethene tubing is used throughout for gas sampling. **The** tubing is rinsed through after each test, and the rinsings added to the water, to ensure complete acid gas trapping.

Hydrogen fluoride (HF) and hydrogen bromide (HBr) concentrations generated during the suppression are calculated from fluoride and bromide ion concentration measurements with ion selective electrodes. The iodine generated is trapped in distilled water, reduced with zinc powder and analysed **as** iodide with an ion selective electrode. Zinc reduction is not required for bromide analysis. Acid gas concentrations are quoted to the nearest 100 ppm in this paper. The limit of detection with the current apparatus is about **50** ppm.

2.3   Evaluation **of** Suppressants

Suppressants are evaluated both in terms of the speed at which they extinguish the fires and of their degree of decomposition, particularly regarding acid gas production. The three dimensional (total flood) suppression properties of the agents are evaluated by the use of satellite fires. Salient features of the agents tested are given in Table 1

Table **1:** Agents Tested

Fluorocarbon Number	Trade Name and Manufacturer	Chemical Formula	Boiling Point $/\,^{\circ}C$	Cupburner Concentration[A] $/$ volume %
HFC-23	FE-13, DuPont	CHF_3	-82	12.3
HFC-125	FE-25, DuPont	CF_3CHF_2	-49	9.2
HFC-134a	(various)	CF_3CH_2F	-27	10.5^{B}
HFC-227ea	FM-200™, Great Lakes	CF_3CHFCF_3	-17	6.4
HFC-236fa	FE-36. DuPont	$CF_3CH_2CF_3$	-2	5.3^{C}
FC-3 110	CEA-410, 3M	C_4F_{10}	-2	5.2
FC-5 1 14	CEA-614, 3M	C_6F_{14}	+58	4 4
IFC-I311	Triodide™, Pacific Scientific	CF_3I	-23	$3\ 1^{D}$
13B1	Halon 1301, (none)	CF_3Br	-58	3 1

[A] - Data from Centre for Global Environmental Technologies, CGET1, Sept23, 1994, unless otherwise stated
[B] - Data from NMERI.
[C] - Data from Fenwal Safety Systems Combustion Research Center, Holliston.
[D] - Data from Pacific Scientific.

3   Results

3.1   Halon **1301** Baseline

It is very well established that Halon 1301 **is** an effective fire suppressant. Therefore, Halon 1301 was used to determine a baseline of suppression performance in the 200 L test chamber. The results are summarised in Table 2.

When concentrations above the heptane cupbumer of 3.1 volume % for Halon 1301 were tested, all fires were extinguished before the end of the agent discharge (about 8 seconds). Measured HF concentrations were low. With concentrations of Halon 1301 of 4.1 volume % and 4.8 volume %, measured HF concentrations were below 700 ppm and less than SO ppm, respectively.

The fires were extinguished between 9.5 and 13.0 seconds when a Halon 1301 concentration of 2.9 volume % was used. HF concentrations were correspondingly higher; up to 1900 ppm of HF was measured. HBr concentrations were about one quarter of the HF concentrations.

Agent Concentration / volume %	Time of Extinguishment of Main Fire I s	Maximum HF Concentration I ppm	Maximum HBr Concentration I ppm
2.9	12.5	1900	—
2.9	9.5	700†	200†
4.1	8.0	600	—
4.8	6.0	<50#	<50#

† Final value recorded　　　# Below limit of detection

The time resolved data is presented in Figure 2. Initially, the HF concentration rises steeply, reaching a maximum which corresponds approximately to the moment of fire extinction. After this the HF concentration starts to fall due to absorption in condensed water vapour on the chamber surfaces.

Figure 2:　HF Concentration *vs* Time for Halon 1301
(7.3 kWm^{-3} Heptane Fire in 200 L Chamber)
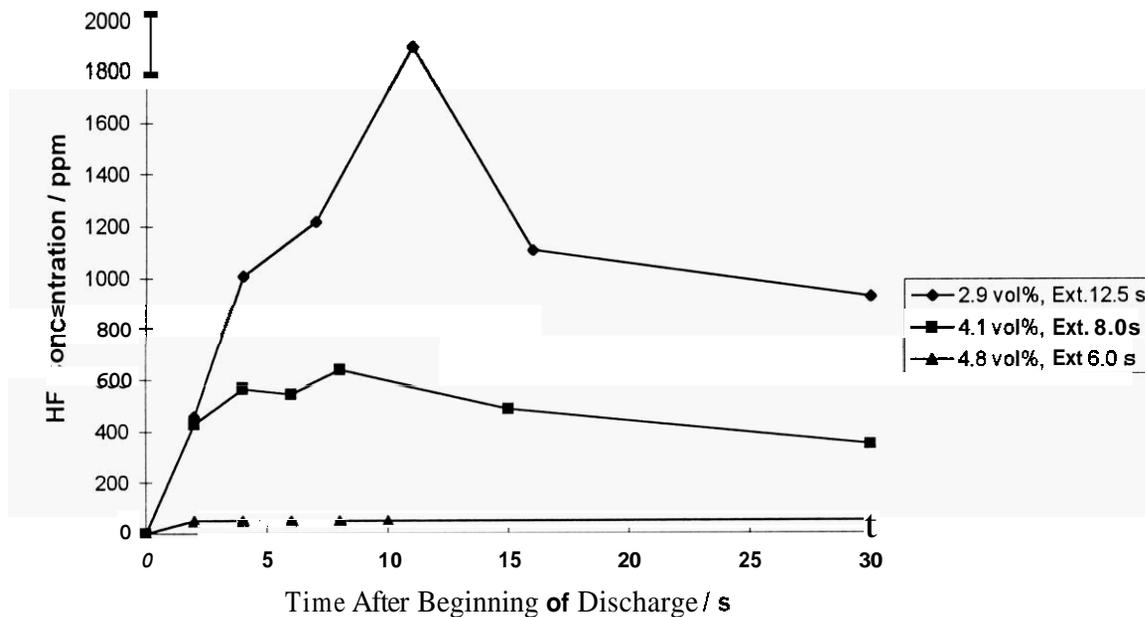
3.2　Halon Replacement Agents

Figures 3 to 6 give the time-resolved HF results obtained with various concentrations of HFC-227ea, HFC-134a, HFC-125 and FC-5.1.14 respectively. The other agents have as yet only been tested at one concentration, and the results are given in Table 3 and Figure 7, which are summaries of all agents tested at approximately the same relative concentration (1.1 x heptane cupbumer concentration).

Figure 3: HF Concentration *vs* Time for HFC-227ea
(7.3 kWm⁻³ Heptane Fire in 200 L Chamber)
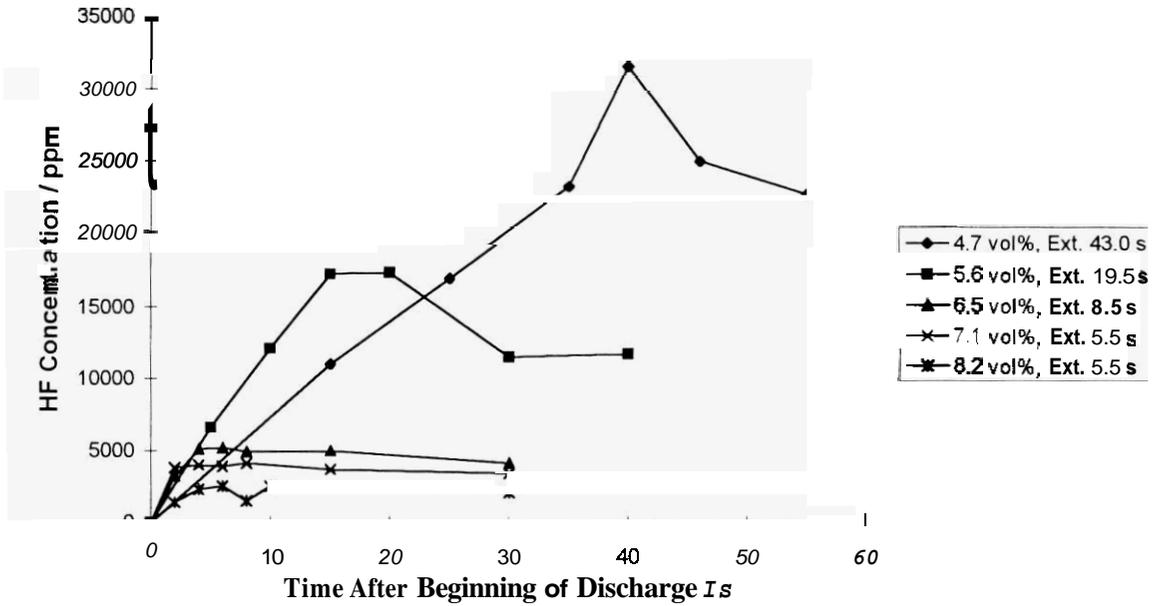
Figure 4: HF Concentration *vs* Time for HFC-134a
(7.3 kWm⁻³ Heptane Fire in 200 L Chamber)
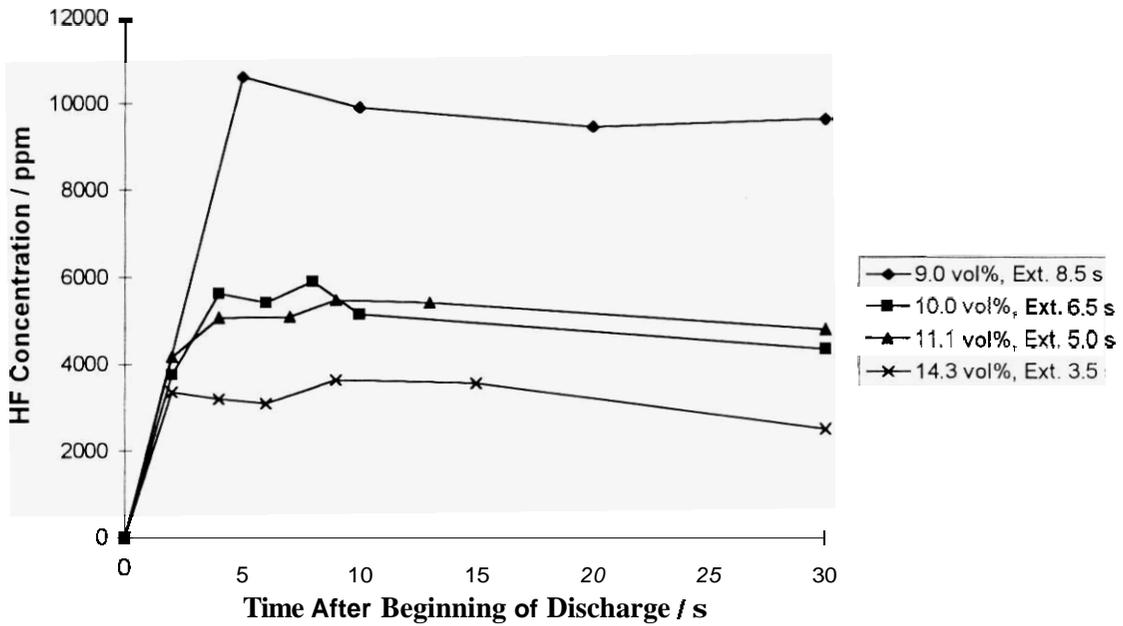
Figure 5: HF Concentration *vs* Time for HFC-125
(7.3 kWm⁻³ heptane tire in 200 L Chamber)
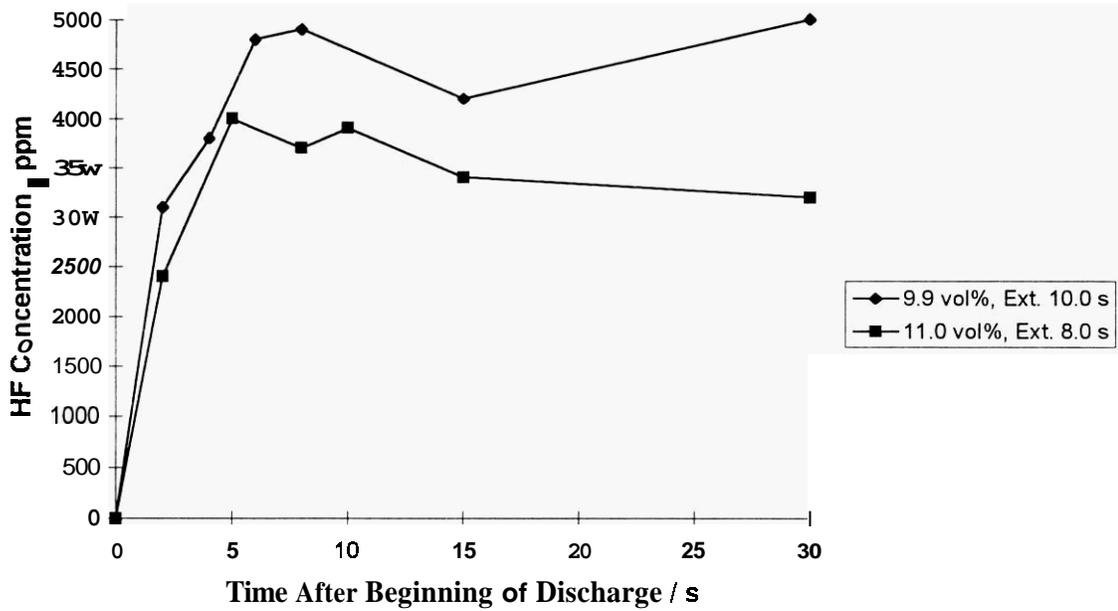
Figure 6: HF Concentration *vs* Time for FC-5.1.14
(7.3 kWm⁻³ Heptane Fire in 200 L Chamber)
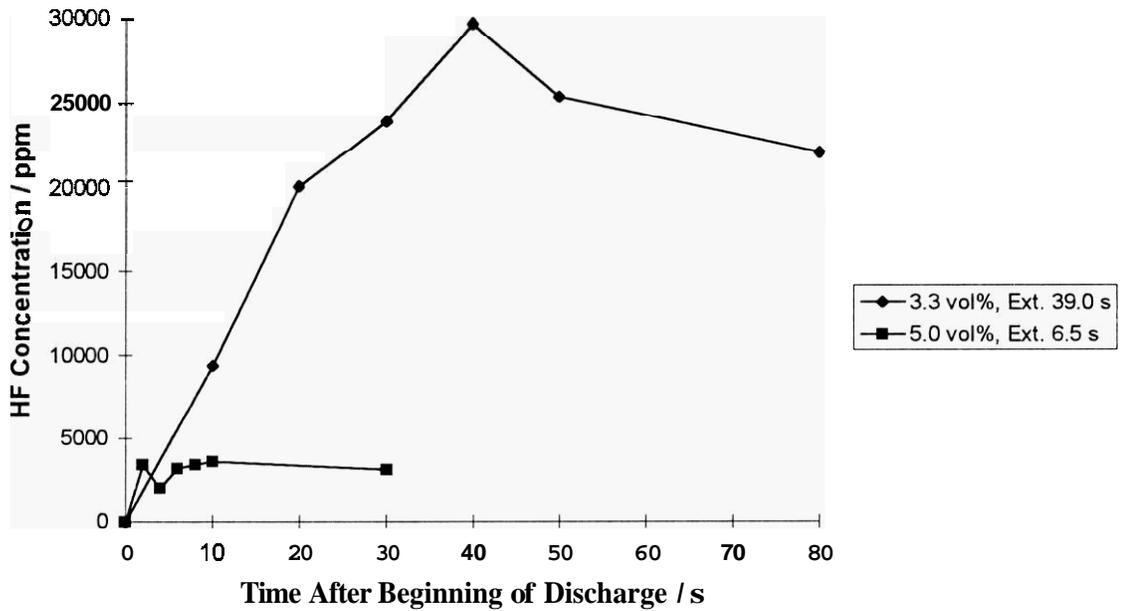
Agent	Agent Concentration / volume %	Discharge Time / s	Time of Ext. of Main Fire / s	Maximum HF Conc. / ppm	Maximum I_2 Conc. / ppm
HFC-23	12.7	5.3	11.0	8400	N/A
HFC-125	9.9	4.1	10.0	5000	N/A
HFC-134a	11.1	3.2	5.0	5500	N/A
HFC-227ea	7.1	3.0	5.5	4100	N/A
HFC-236fa	6.0	2.2	7.0	6400	N/A
FC-3.1.10[#]	6.2	3.0	6.0	3700	N/A
FC-5.1.14	5.0	2.8	6.5	3600	N/A
IFC-13I1	3.3	2.3	7.0	1000	500

[#] FC-3.1.10 tested at approx. 1.2 **x** heptane cupburner concentration

Figure 7: Comparative HF Concentrations vs Time for all Replacement Agents Tested (7.3 kWm^{-3} Heptane Fire in 200 L Chamber)
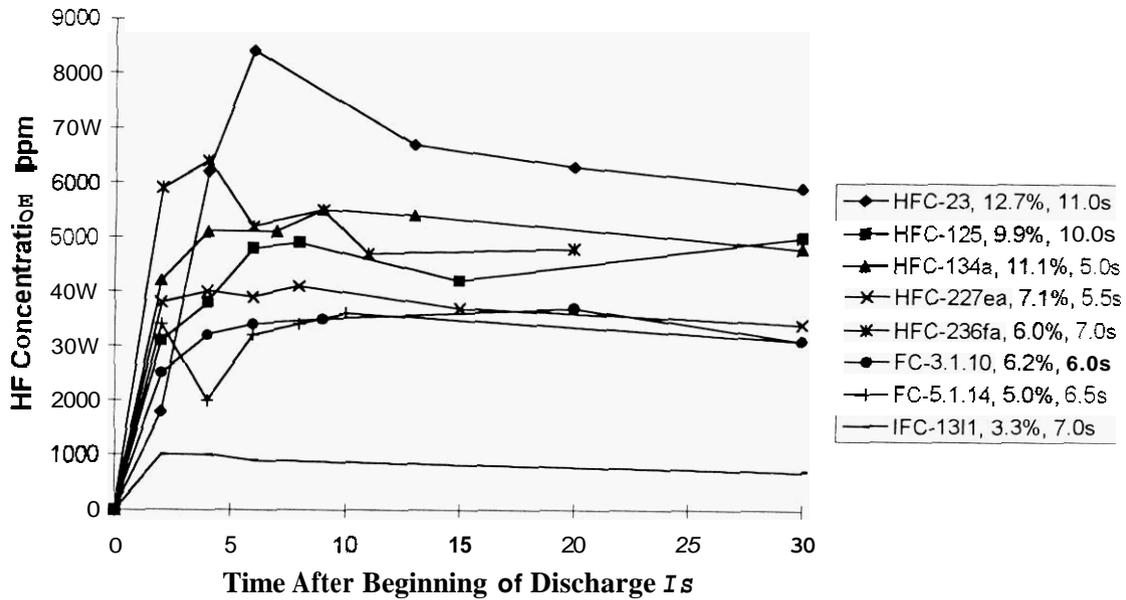
4   Discussion

4.1   Factors Influencing HF **Formation**

There are many **factors** which are known to influence the degree of HF formation when fluorinated f i e **suppressants,** including both Halons and the non-ozone depleting replacement agents, **are** used to extinguish fires:-

1.   Fire Size to Room Volume (FSRV)
      The importance of this factor has been clearly demonstrated in many studies, particularly the work of Robin *et al.*[10] *Agents* are only decomposed when they come in contact with the fire. Therefore, the larger the **fire,** and the more intense it is, the greater the amount of HF formed. The concentration of HF obtained from a given amount of decomposition will naturally be inversely related to the volume of the room. In Robin's study with HFC-227ea, with all other factors held constant, a direct relationship is observed between the FSRV and the measured HF concentration. **A** *similar* **type** of relationship may be expected for other agents and conditions, although with a different proportionality constant. It should be noted that the FSRV used in our study is relatively high, both as fire tests go, and in comparison to real world fires. Modem fire detection systems are designed to detect fires whilst they are relatively **small.** For example, the EN54 *standard* [11] calls for detection of *a* $0.11 \ m^2$ *heptane* fire in a 205-370 m^3 chamber. This equates to FSRV in the range 0.4 to **0.7** kWm^{-3}, and to possible HF concentrations, according to Robin's correlation for HFC-227ea, of 300-500 ppm. Furthermore, the heptane fire is one of 6 fires called up by the **EN54** standard. **A** number of smouldering fires *are* of very much lower heat output and ought therefore to generate lower concentrations of breakdown products.

2.   *Agent* Concentration
      The importance of agent concentration relative to the minimum suppressing concentration (for the particular fuel in **question)** also **has** a very major influence on breakdown product formation. This is shown clearly in Figure 8 where, **as** the agent concentration relative to the heptane cupburner concentration **is** decreased below about a factor of 1.1, the HF concentrations start to **rise** rapidly. This **is** to be *expected* since in such cases inhomogeneities in distribution start to play a part and the agent is *struggling* to extinguish the flame. This effect has also been noted before in large scale tests, e.g. by Sheinson *et al.* [2,5]. Figure 8 also includes data for cases where the amount of agent discharged resulted in a concentration below the suppressing concentration. Now, suppression **is** only achieved after a relatively long time and is clearly aided by oxygen depletion. The long contact times arising from such circumstances enhance the amount of agent brought into contact with the flame and high concentrations of HF **ensue.**

Figure 8: The Maximum **HF** Concentration *vs* Agent Concentration to Heptane Cupburner Ratio (**7.3 kWm^{-3}** Heptane Fire in 200 L Chamber)

3. Flame - Agent Contact Time

The total time for which the agent, at below suppression concentrations, is in contact with the flame plays a significant role, as is shown by Figure **3.** In some of these tests, long contact times are deliberately brought about by choosing a maximum agent concentration below the cupburner concentration. This contact time is a combination of the time required to discharge the agent from the nozzle into the room and the time required to transport the agent (by jet momentum, turbulent diffusion *and* mixing) from the nozzle to the fire and to achieve a suppressing concentration at the fire. **A** slow build up of the agent concentration, or too low an agent concentration will result in long contact times and high concentrations of breakdown products. Agents such **as** HFC-23, which are not superpressurised with nitrogen, but rely on their vapour pressure, exhibit slightly longer discharge times in this apparatus. This is due to the greater pressure decay during the discharge. The effect of **varying** discharge time (or more correctly, mass flow rate) will be examined in the near future. In practical applications, it is the **task** of the fire suppression engineer to design the system such that these contact times are minimised by short discharge times (10 seconds or less) and with nozzles designed and positioned such **as** to get the agent to the fire **as** rapidly as possible. It should also be noted that this has the added benefit of suppressing the fire quickly and reducing the toxic gases arising from the fire itself

4. The Chemical Nature of the Agent

The relative proportion of hydrogen and fluorine atom in the agent molecule influences the amount of HF formed, since it requires a sufficient source of both fluorine and hydrogen atom to produce it. The only source of fluorine is the agent, whereas hydrogen *can* derive from the heptane fuel, water vapour in the air and also from the agent itself (if the agent contains hydrogen atoms). Calculations were performed with the STANJAN Chemical Thermodynamics

program[12] for adiabatic stoichiometric heptane air flames containing increasing proportions of various *agents*. A humidity level of 50% was assumed. Figure **9** shows some of the results. As can be seen, for some *agents* the mole fraction of HF in the flame increases continuously with increasing *agent* concentration; with *other agents* a limiting concentration is reached where the flame essentially runs out of hydrogen and a plateau is reached. For *agents* with a relatively low H F atom ratio in the molecule, such as the perfluorocarbons, HFC-125 and HFC-227ea, this limiting *agent* concentration is reached at concentrations below the suppressing concentration, and thus there is a limit on the rate of HF generation by the flame. For other *agents,* (HFC-23, HFC-134a and HFC-236fa) with a relatively higher H:F atom ratio in the molecule, this limiting concentration is actually above the suppressing concentration and there will *not* be a similar limit on the rate of HF generation by the flame. This effect has been noted before"". The calculations indicate *that* when HF formation is limiting, other fluorine-containing decomposition products, such as carbonyl fluoride and tetrafluoromethane are formed. Carbonyl fluoride is rapidly hydrolysed to HF and carbon dioxide in the atmosphere [14] and thus contributes to the measured concentration of HF. However, STANJAN calculations indicate the mole fraction of carbonyl fluoride is up to an order of magnitude less than HF, which is in accord with previous experimental results [7].

Figure 9: **Calculated HF Mole Fraction in a Stoichiometric Heptane/Air Flame using the STANJAN Program**
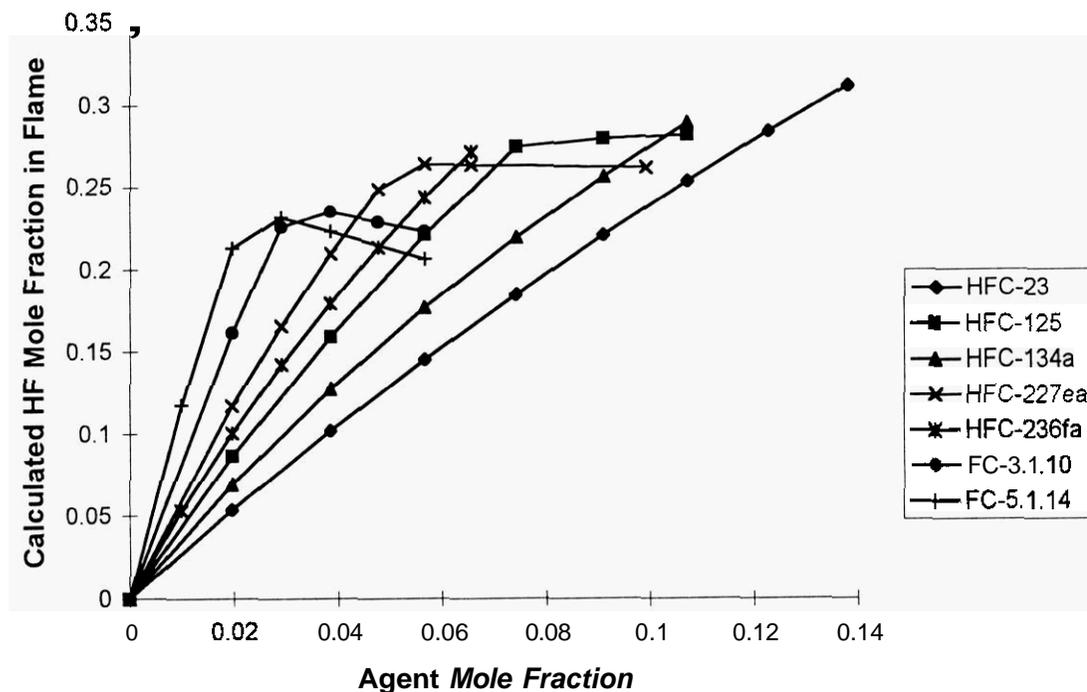
5.   Chemical Nature of the Fuel
Following on from point 4 above, whether or not the flame becomes hydrogen limited will also depend on the chemical nature of the fuel. All of test data refers to heptane as fuel. Very different fuels, e.g. wood or other Class A materials, or gaseous fuels such as methane might be expected to cause different behaviour with some of the *agents*. This is another area of study.

4.2 Modelling of HF Formation

Incorporation of all of the above factors into a model to predict HF formation is, in theory, possible given sufficient knowledge of the agent concentration at the fire as a function of time and the rate at which air is drawn into the flame, also as a function of time. However, even a simplified model can give useful insights into acid gas production. For example, assuming the air consumption rate of the fire stays constant, that all the fluorine in the suppressant molecule is available for HF formation, and that the contact time of the agent with the flame is given by the extinction time, then a crude HF concentration can be calculated and compared with the measured HF concentration, as shown in Figure 10. As can be seen, this very simple model appears to work well for agents with a high H F ratio, hut overestimates the HF concentration for those agents with a relatively low H:F ratio, further illustrating the arguments presented above. Refinements to the model to allow for agents with various H:F ratios are in progress.

Figure 10: Calculated vs Measured HF Concentration
(7.3 kWm^{-3} Heptane Fire in 200 L Chamber)
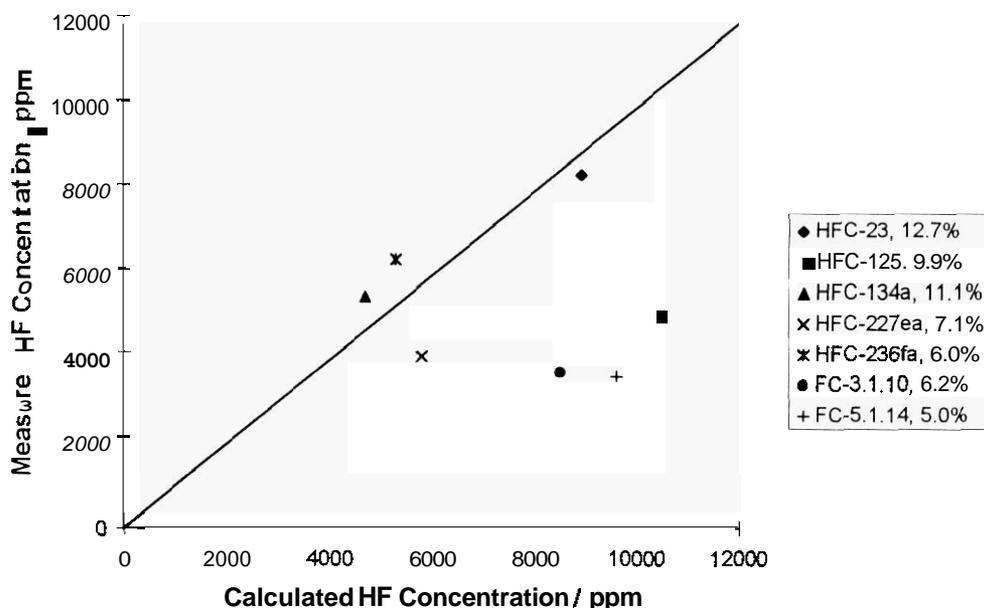
5 Conclusions

The formation of acid gases from the use of halogenated fire suppressants is a complex issue and many factors play a role in determining the concentrations produced. Factors known for some time include the size and intensity of the fire up to the moment of suppression, the size of the enclosure, the concentration of the agent employed relative to the minimum suppression concentration, the speed of the discharge and how efficiently the system gets the agent to the fire. To this we can now add further variables: the nature of the agent (H:F ratio), the nature of the fuel (H content) and to a lesser extent ambient conditions, including temperature and relative humidity

HF formation will be minimised by an efficient fire protection system able to detect the fire whilst it is still small, by well designed suppression systems able to deliver the right quantity of agent to the fire as quickly as possible, or by the choice of an agent with a relatively low hydrogen:fluorine ratio.

6   References

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