A REVIEW OF THERMAL DECOMPOSITION PRODUCT TESTING OF HALOCARBON FIRE SUPPRESSION AGENTS

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INTRODUCTION

During the past decade, an extensive amount of research has been conducted to develop a suitable replacement for Halon 1301. One objective of this research has been to quantify the thermal decomposition products generated when halogenated replacement agents are broken down at high temperatures and combine with combustion products. The decomposition product of greatest concern with fluorinated agents is hydrogen fluoride (HF). HF is a highly corrosive gas that causes severe sensory irritation in humans [1]. Tests that quantified HF production have been conducted for a large range of fire sizes, room volumes, discharge times, fuels, and agent concentrations. This paper provides an overview of this research.

Most research has shown that HF concentrations generated with fluorinated agents are 2-10 times higher than with Halon 1301. Also, it has been shown that the formation of HF is dependent on fire size, compartment volume, and fire extinguishment time. Fire extinguishment time is directly linked to agent design concentration and system discharge time. Two primary techniques, wet chemistry methods and Fourier Transform Infrared Spectroscopy (FTIR), have been used to measure HF concentrations. Comparison studies have been performed for these techniques [2], however, this type of comparison is beyond the scope of this paper.

SMALL-SCALE TESTS

One of the first published decomposition product studies was performed at 3M using PFC-410 (CEA-410, perfluorobutane) [3]. These experiments were conducted in an enclosure constructed with overall dimensions of 0.91 by 0.91 by 1.7 m (3 by 3 by 5 ft). The floodable volume of the compartment was 1.3 m^3 (45 ft^3). Hydrogen fluoride concentrations were measured using a wet chemistry technique. Plastic gas sampling tubes were evacuated and coated with a thin layer of sodium hydroxide. After the sample was taken, the bottles were rinsed with water and the solution was analyzed using fluoride ion specific electrodes. Tests were conducted first to examine the effect of discharge time on the extinguishment time and the amount of HF formed. These tests were followed by tests that had a fixed discharge time and a variable heat release rate. The agent design concentration was 6.5% for all tests and the fire source was a heptane pan fire. The results from these tests are shown in Table 1 [3].

Agent discharge times ranged from 5.0 to 27.4 sec, fire extinguishment times ranged from 5.8 to 24.4 sec, and HF concentrations ranged from 90 to 3500 ppm. Results from tests where the discharge time was varied show a direct relationship between discharge time and both extinguishment time and HF concentration. Results from tests that varied only the fire size show a direct relationship between fire size and HF concentration. The extinguishment time was not a function of fire size.

Table 1. Summary of total fluorine decomposition products measured during 3M tests with PFC-410.

Discharge Time (sec)	Fire Size (kW)	Extinguishment Time (ppm)	HF Concentration (ppm)
27.4	3.2	24.4	3358
20.3	3.2	20.8	2724
11.0	3.2	8.8	1289
11.1	3.2	11.8	1507
10.8	3.2	11.0	1780
8.4	3.2	10.1	999
8.1	3.2	8.2	1128
8.2	3.2	8.0	1089
6.5	3.2	7.3	1035
5.0	3.2	7.5	944
5.3	3.2	5.8	890
8.2	0.3	6.1	98
8.3	0.3	7.2	90
8.1	1.4	11.6	275
8.2	1.4	7.6	336
8.2	3.2	8.4	999
8.2	3.2	8.5	1071
8.2	7.7	7.9	3540
			2723

In a test program sponsored by NASA, two compartment sizes (1.2 m^3 and 29 m^3) were used to perform tests with CEA-410, FM-200, NAFS-III, E-13, and Halon 1301 [4]. All tests were conducted with agent concentrations that were 1.2 times a cup-burner concentration. This corresponded to agent concentrations of 6.2% for CEA-410, 7.9% for FM-200, 14.4% for FE-13, 13.2% for **NAF-SIII,** and 3.7% for Halon 1301. Parameters that were varied during these tests were agent discharge rate and fire size. **Fire** sizes ranged from 0.8 to 4.0 kW in the small Compartment and 18 to 246 kW in the large compartment. All tests were conducted using heptane pan **fires.** Selected results from these tests are shown in Tables 2 and 3 [4]. HF concentrations nominally ranged between 100 and 3800 ppm in the 1.2 m^3 compartment and between 600 and 4400 ppm in the 29 m^3 compartment.

Chattaway et al. of Kidde International performed experiments using heptane pool fires in a 0.2-m^3 cubic test compartment [5]. A combination of three pool fires was used, one with **a** 70-mm diameter and two with **a** 20-mm diameter. The total energy release rate for these pan fires was 1.5 kW. Agents tested included FE-13, FE-25, HFC-134a, FM-200, E-36, CEA-410, CEA-614, Triodide, and Halon 1301.

Tests conducted with Halon 1301 used agent design concentrations ranging from 2.9 to 4.8%. Corresponding fire extinguishment times ranged from 13 sec to less than **8** sec (before the end of system discharge). When the agent design concentration was increased from 2.9 to 4.8%, the peak HF concentration decreased from 1900 ppm to less than 50 ppm.

Table 2. Summary of HF concentrations measured during 1.2 m^3 NASA tests.

Agent	Fire Size (kW)	Discharge Time (sec)	Extinguishment Time (sec)	Peak HF Concentration (ppm)
Halon 1301	0.8	5.0	11.0	195
Halon 1301	1.9	4.8	3.0	161
Halon 1301	4.0	5.0	6.5	434
Halon 1301	0.8	3.0	2.9	88
Halon 1301	1.9	3.3	2.5	161
Halon 1301	4.0	2.8	3.2	322
CEA-410	0.8	8.0	7.7	563
CEA-410	1.9	8.0	8.0	738
CEA-410	4.0	7.5	9.4	1849
CEA-410	0.8	14.5	20.7	727
CEA-410	1.9	14.5	14.5	1692
CEA-410	4.0	14.2	13.8	3020
FM-200	0.9	8.5	5.8	572
FM-200	1.9	7.7	7.0	1001
FM-200	4.0	8.7	6.1	2520
FM-200	0.8	5.3	3.2	408
FM-200	1.9	5.0	3.5	762
FM-200	4.0	5.0	4.3	1962
FE-13	0.8	Not available	11.3	1121
FE-13	1.9	Not available	5.1	1504
FE-13	4.0	Not available	5.7	2850
FE-13	0.8	Not available	9.6	1416
FE-13	1.9	Not available	24.4	3760
FE-13	4.0	Not available	14.0	4271

Table 3. Summary of HF concentrations measured during 29 m^3 NASA tests.

Agent	Fire Size (kW)	Discharge Time (sec)	Extinguishment Time (sec)	Peak HF Concentration (ppm)
CEA-410	18	7.8	4.6	636
CEA-410	79	7.8	9.7	1828
CEA-410	246	7.5	9.1	3068
FM-200	18	8.3	8.1	602
FM-200	79	8.3	9.0	2358
FM-200	246	8.3	8.5	4378
FE-13	18	Not available	9.4	579
FE-13	79	Not available	10.9	3121

Tests conducted with FM-200 used agent design concentrations ranging from 4.7 to 8.2%. Corresponding fire extinguishment times ranged from 43 to 5.5 sec. Peak HF concentrations ranged from 32000 ppm (agent design concentration **of** 4.7%) to 250 ppm (agent design concentration of 8.2%).

Agent design concentrations ranged from 9.0 to 14.3% for tests with HFC-134a. Corresponding fire extinguishment times ranged from 8.5 to 3.5 sec. Peak HF concentrations were as large as 10500 ppm when the agent concentration **was** 9.0% and as low as 3500 ppm when the agent design concentration was 14.3%.

Agent design concentrations ranged from 9.9 to 11.0% for tests with FE-25. Corresponding fire extinguishment times ranged from 10 to 8 sec. Peak HF concentrations ranged from 4800 ppm for an agent design concentration of 9.9% to 4000 ppm for a concentration of 11.0%.

Tests that were conducted with CEA-614 used agent design concentrations ranging from 3.3 to 5.0%. Corresponding fire extinguishment times ranged from 39 to 6.5 sec. Peak HF concentrations were **as** large as 29000 ppm when the agent design concentration was 3.3% and as low as 3500 ppm when the agent design concentration was 5.0%.

A comparison of thermal decomposition products was also performed for each agent at a design concentration 1.1 times a heptane cup-burner concentration. The results are shown in Table 4 [5].

Table 4. Summary of HF concentrations measured in Kidde International tests.

Agent	Agent Design Concentration (%)	Discharge Time (sec)	Extinguishment Time for Main Fire (sec)	Peak HF Concentration (ppm)
FE-13	12.7	5.3	11.0	8400
FE-25	9.9	4.1	10.0	5000
HFC-134a	11.1	3.2	5.0	5500
FM-200	7.1	3.0	5.5	4100
FE-36	6.0	2.2	7.0	6400
CEA-410[a]	6.2	3.0	6.0	3700
CEA-614	5.0	2.8	6.5	3600
Triodide	3.3	2.3	7.0	1000

[a] Test conducted with agent design concentration approximately 1.2 times the heptane cup-burner concentration.

INTERMEDIATE SCALE

As part of the United States Navy's halon replacement program, the Naval Research Laboratory (NRL) conducted intermediate scale (compartment volume 56 m^3) experiments [6]. The purpose of these tests was to investigate the effect of agent design concentration on fire extinguishment times and thermal decomposition products. The results of these tests were used as a basis for the design of full-scale tests (discussed below). Agents tested during this evaluation included FE-13, FM-200, CEA-410, and Halon 1301. HF concentrations were measured using a wet chemistry technique where teflon tubes coated with sodium bicarbonate were filled with a volume of gas. The tubes were then rinsed with distilled water and analyzed using an Ion Chromatograph.

The dimensions of the test compartment were 4.0 by 3.4 by 4.3 m (13 by 11 by 14 ft). The majority of the tests were conducted with a 0.23 m^2 heptane pan fire; however, several **were** conducted with **a** 1.12 m^2 heptane pan fire. Selected HF concentrations measurements obtained during these tests are included in Tables 5-7 [6].

Table 5. Summary of HF concentrations measured during NRL intermediate scale tests with FE-13.

Design Concentration (%)	Fire Pan Area (m^2)	Discharge Time (sec)	Extinguishment Time (sec)	Peak HF Concentration (ppm)
11.5	0.23	7.5	40.0	34000
14.4	0.23	5.0	13.0	8300
15.3	0.23	5.6	10.0	4700
18.2	0.23	5.0	6.0	3400
20.9	0.23	5.9	4.0	3000
18.1	0.23	17.3	17.3	9700
19.7	0.23	19.1	19.1	7500
18.2	0.23	17.3	19	9700
18.2	0.23	43.8	32	9400 (missing sample)
23.7	1.12	5	3	11000

Table 6. Summary of HF concentrations measured during NRL intermediate scale tests with FM-200.

Design Concentration (%)	Fire Pan Area (m^2)	Discharge Time (sec)	Extinguishment Time (sec)	Peak HF Concentration (ppm)
8	0.23	- 5	10	8000
8.2	0.23	- 5	12	6300
8.3	0.23	- 5	11	5100
9.8	0.23	- 5	7	2500
10.8	0.23	10.5	10.5	2800
9.7	0.23	19.2	19.2	6000
8.6	0.23	15.7	19	12000
8.3	1.12	4.3	3	26000

Table 7. Summary of HF concentrations measured during NRL intermediate scale tests with Halon 1301.

Design Concentration (%)	Fire Pan Area (m^2)	Discharge Time (sec)	Extinguishment Time (sec)	Peak HF Concentration (ppm)
4.7	0.23	3.1	8	600 @ 5 sec
4.7	1.12	2.4	3	1700 @ 5 sec 7200 @ 10 sec

LARGE-SCALE TESTS

Large-scale tests have been conducted by both the US Coast Guard (USCG) [7,8] and the US Navy (USN) [9,10]. Both organizations began performing these experiments in 1994 and their overall objective was to evaluate gaseous halon alternatives for protection of machinery spaces.

The USCG has conducted two phases of testing. The first phase was conducted onboard the USCG Test Vessel Mayo Lykes **[7]**. Four agents were evaluated during these tests: FM-200, FE-13, CEA-410, and a hydrochlorofluorocarbon blend (NAF-HCFC Blend **A).** Also, several tests with Halon 1301 were conducted for comparison.

The machinery space mockup used during this phase had overall dimensions of 6.9 by 11.1 by 7.3 m, which resulted in a volume of 526 m^3. A diesel engine mockup was situated in the center of the space. Three fire scenarios were used during these tests:

(1) Baseline scenario with a 1 MW combination fire (500-kW heptane spray fire in bilge and 500-kW heptane pan fire in bilge)

(2) 2.5 MW combination fire (2 MW heptane spray fire next to engine and 500-kW heptane pan fire in bilge)

(3) 5.5 MW combination fire (two 2.5-MW diesel pan fires in bilge and 500-kW PVC cable fire)

HF concentrations were measured using two FTIRs. The first FTIR was located in a comer of the compartment 1.0 m above the deck and measured the concentrations in-situ. A summary of these measurements is provided in Table 8 [7]. The second FTIR analyzed a sample that was drawn from the test compartment.

Table 8. Summary of HF concentrations measured during first phase of USCG machinery space testing.

Agent	Agent Design Concentration (%)	Total Fire Size (kW)	Discharge Time (sec)	Peak HF Concentration (ppm) (measured in-situ)	Peak HF Concentration (ppm) (measured externally)
Halon 1301	5.0	1000	10	300	390
FE-13	16.0	1000	10	1200	Not available
FE-13	16.0	2500	10	2600	2900
FE-13	16.0	2500	7	3000	2300
FE-13	16.0	5500	10	**7000**	4800
FM-200	7.0	1000	10	2000	2500
FM-200	7.0	2500	10	3500	3200
FM-200	7.0	2500	7	4500	3500
FM-200	7.0	5500	10	9000	6900
CEA-410	6.0	1000	10	4500	4600
CEA-410	6.0	2500	10	3500	4100
CEA-410	6.0	*2500*	**7**	3000	**4700**
CEA-410	6.0	5500	10	6000	5800
NAF-SIII	8.6	2500	12	11000	15000
NAF-SIII	8.6	2500	10	15000	23000

Extinguishment times were generally less than 20 sec except for tests with NAF-SIII where the extinguishment times ranged from 30 to 110 sec. Because of these long extinguishment times, the HF concentrations were much higher than those measured using other agents. HF concentrations measured using alternative agents ranged from 1200 ppm for a fire size of 1000 kW to 9000 ppm for a fire size of 5500 kW.

The second phase of USCG testing was performed to evaluate the proposed International Maritime Organization (IMO) test protocol for determine the extinguishing effectiveness of fixed gaseous halon alternative fire suppression systems [8]. Variables under consideration during these tests included the test compartment configuration, fire scenario, and discharge system parameters. These tests were conducted on the USCG Test Vessel State of Maine. As with the first phase of tests, four agents were evaluated during these tests: FM-200, FE-13, CEA-410, and NAF-SIII. Also, several tests with Halon 1301 were conducted for comparison.

As specified in the draft IMO protocol, the compartment volume was 500 m^3 with overall dimensions of 10 by 10 by 5 m. A diesel engine mockup was positioned in the center of the room. HF concentrations were measured in-situ using a FTIR. A summary of these measurements is included in Table 9 [8].

Tests for the USN were conducted onboard the ex-USS SHADWELL, the Navy's test ship. A compartment volume of 755 m^3 was used for the first phase of tests [9]. Fire scenarios consisted of a combination of pan and spray fires and fuels with either heptane or F-76 (Navy diesel). Several tests were also conducted with a wood crib. HF measurements were recorded real-time using an FTIR and via grab samples (located at multiple locations) that were analyzed using an ion chromatograph. Table 10 [9] includes a summary of the peak measurements obtained using the FTIR.

It was noted that the spray fire took longer to extinguish than the other fires [9]. Extinguishment times for this fire were as high as 28 sec. HF concentrations ranged from 600 ppm for tests with Halon 1301 to 7300 ppm for tests with alternative agents.

The second phase of full-scale testing was performed in a machinery space mockup with a floodable volume of 370 m^3 [10,11]. The only agent evaluated was FM-200 since it was identified as the Navy's clean agent of choice for the Navy's next ship. One purpose of these tests was to investigate the use of a water spray cooling system in conjunction with FM-200. This water spray cooling system served the dual purpose of reducing the compartment temperature and scrubbing acid gases from the air. HF concentrations were measured at multiple locations using a combination of continuous acid analyzers [12], FTIR, and ion chromatography. Limited data has been published at this time, however, general results showed that the water spray cooling system reduced HF concentrations substantially.

Table 9. Summary of HF concentrations measured during second phase of USCG machinery space testing (IMO evaluations).

Agent	Design Concentration (%)	Total Fire Size (kW)	Discharge Time (sec)	Peak HF Concentration (ppm)
Halon 1301	5	7950	9.5	100
Halon 1301	5	3400	9.5	300
Halon 1301	5	6000	9	400
NAF-SIU	12	7950	9.5	2500
NAF-SIU	12	3400	9.5	2300
NAF-SIII	12	6000	9.5	1000
NAF-SIU	12	7950	9.2	4400
NAF-SIU	12	3400	9.0	3400
NAF-SIU	12	6000	9.0	9000
NAF-SIII	12	2400	10.0	1600
NAF-SIU	12	3400	10.5	5100
NAF-SIII	12	4750	10.5	1900
CEA-410	8.2	7950	11.0	2300
CEA-410	8.2	6000	10.0	1400
CEA-410	8.2	4400	10.0	3200
CEA-410	8.2	2400	10.0	1200
CEA-410	8.2	4750	10.0	4500
CEA-410	8.2	3400	10.0	4300
CEA-410	8.2	3400	10.0	2600
FM-200	8.7	7950	11.0	8100
FM-200	8.7	2400	10.0	1500
FM-200	8.7	4750	10.0	3700
FM-200	8.7	6000	10.0	2400
FM-200	8.7	3400	10.0	5000
FM-200	8.7	3400	10.0	3900
FM-200	8.7	4400	10.0	3900
FM-200	8.7	7950	9.6	3600

Table 10. Summary of first phase of NRL full-scale machinery space testing.

Agent	Design Concentration (%)	Total Fire Size (kW)	Discharge Time (sec)	Peak HF Concentration (ppm)
Halon 1301	5.7	2360	11	600
Halon 1301	4.6	2360	10	600*
FM-200	10.0	2360	11	3800
FM-200	9.2	2860	6	2400
FM-200	8.2	2360	10	4500
FM-200	9.2	2360	11	3800
FM-200	9.2	8460	11	5200
FM-200	9.2	2860	10	2500
FM-200	9.2	8460 + wood crib	10	7300
FE-13	17.0	2860 + wood crib	10	3900
FE-13	15.7	2860	10	5800
FE-13	17.0	8460 + wood crib	10	5300
FM-200	9.2	8460	10	3300

SUMMARY

Thermal decomposition product testing has shown that substantial concentrations of HF can be generated when fluorinated halon replacement agents are used for fire suppression. In general, HF concentrations are between **2** and 10 times higher for these agents than for Halon 1301. It is worthwhile to note that these peak HF concentrations generally decay rapidly. Tests have shown that HF concentrations can decay to half of the peak concentration within 5 min after agent discharge [7]. **It** may be more appropriate to consider 5-min average concentrations; however, peak concentrations have been reported in this study to be conservative. Tests have shown that the amount of HF generated is directly related to the fire size to room volume ratio [4,7]. **As** a result, it is critical that reliable, state of the art detection systems are integrated with these suppression systems. HF concentrations will be minimized if the fire size at the time of agent application is minimized.

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