A Comparison of Thermal Decomposition Product Testing of Halon 1301 Alternative Agents

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Introduction

As a result of the ban on Halon 1301 production, much research effort has been devoted toward developing a suitable replacement. It has been documented that gaseous halocarbon Halon 1301 alternative agents produce a significantly higher concentration of decomposition products than Halon 1301 [1-4]. Previous work has shown the level of decomposition products (primarily HF) is dependent on fire size, room volume, agent design concentration, and discharge time [1-3]. This paper examines the maximum and average decomposition product trends for several data sets. Data ranging from small scale tests to large scale tests were incorporated. Laboratory tests for NASA used room volumes of 1.2 m^3 and 29 m^3 and shipboard tests, for the U.S. Coast Guard (USCG) and the U.S. Naval Research Laboratory (NRL). used room volumes of 526 and 756 m^3, respectively. Fire sizes ranged from 0.8 kW to 8.5 MW. Agents evaluated include C_3HF_7 (manufactured by Great Lakes Chemical Corporation as FM-200™), CHF, (manufactured by DuPont Chemical Corporation as FE-I3), and C_4F_{10} (manufactured by 3M™ as CEA-410). Baseline tests with Halon 1301 were also performed. For simplicity purposes, these agents will be referred to by their trade names.

In order to provide some insight on the hazards associated with these HF trends, a HF toxicity assessment of these scenarios is also presented. Data from animal studies have been incorporated to predict how the HF exposure over time may affect humans.

Description of Experiments

Small scale tests were conducted for NASA in two separate enclosures. The first of these enclosures was constructed from 1.2 cm (0.5 in.) thick polycarbonate sheet reinforced with an angle iron frame. Access to the enclosure was gained by four 23 cm (9 in.) square openings that were sealed during testing with an overlapping polycarbonate panel. The second enclosure was constructed with two layers of 1.2 cm (0.5 in) gypsum wallboard over 5 x 10 cm wood framing. There were three 60 x 90 cm polycarbonate windows, and access was gained through a steel door with magnetized seals.

In both of these compartments, all fires were heptane pan fires. In the 1.2 m^3 enclosure, three fire sizes consisting of 0.8, 1.9 and 4 kW were used. Fire sizes were increased in the larger enclosure and included 25, 78, and 250 kW. The agent was discharged after a 60 second prebum time. A more detailed explanation of these tests can be found in Reference 2.

Large scale tests were performed on two separate research ships both located at Little Sand Island in Mobile, AL. The first of these efforts was conducted on the United States Coast Guard test vessel Mayo Lykes. A cargo bay was modified to simulate a "typical" machinery space. Overall dimensions were 6.9 m wide x 11.1 m long x 7.3 m high (526 m^3) bounded by steel bulkheads. A diesel engine mockup was situated approximately in the center of the space. The agent discharge system consisted of two discharge nozzles located in the overhead of the space. The manufacturer's recommended concentration for each agent was used as the design concentration in all tests (7% for FM-200™, 16% for FE-13, 6% for CEA-410, and 5% for Halon 1301). There were three fire scenarios which each consisted of combinations of pan and spray fires. Total fire sizes were either 1, 2.5 or 5.5 MW and they were fueled with either diesel fuel or heptane. Additional information regarding these tests can be found in Reference 3.

The second set of large scale tests was performed for the Naval Research Laboratory aboard the **ex-USS** SHADWELL. The approximate dimensions of this space were 17 m long x 6.1 high x 8.5 m wide (840 m^3). Mockups simulating diesel engines and reduction gear, a gas turbine engine, and ventilation ducts were installed in the space to simulate a typical machinery space found onboard U.S. Navy ships. The volume occupied by these mockups reduced the floodable room volume to 756 m^3. A two-tier agent discharge system was used with 9 nozzles, 5 of which were located on the upper level and the remaining 4 on the lower level. Two fire scenarios were considered with total heat release rates of either 2.4 or 8.5 MW. Each consisted of a combination of pan and spray fires. In most tests, the fuel used was heptane and the prebum time was 45 seconds. A further description of setup can be found in Reference 4.

In all of these tests, a KVB/Analect FTIR spectrometer was used to monitor agent and decomposition product concentration in situ. This was done by using a light pipe system and calcium fluoride windows.

Discussion of Results

A comparison of the maximum HF concentrations as a function of the tire size normalized by the room volume is shown in Figure 1 for all data sets. In order work to eliminate the variable of agent discharge time, only tests in which the discharge time was nominally 10 seconds are included. The linear fit suggested by DiNenno (1) is included for comparison to previously published data. There is good agreement with this line, however, some scatter for the large scale data is apparent. Some of this variation may he attributed to differences in agent design concentrations used thus causing longer fire extinguishment times. More variation in the large scale data is not surprising since the room geometries were more complex than those in the small rooms and obstructions were present. This may have inhibited agent mixing thus increasing the amount of time required for the extinguishment concentration to be achieved.

Since each agent may not necessarily exhibit the same HF production trends, only the data for the FM-200™ tests is provided in Figure 2. The linear trend seen in Figure 1 appears *to* hold true and the scatter noted for larger fire sizes is still evident. Comments have been added to the graph regarding the agent design concentration and the fire extinguishment times. In the large scale tests, this extinguishment time corresponds to the time when visible flames disappeared at the largest pan fire location. Some of this scatter can be explained by these comments. In some cases, such as the points at a tire size to room volume ratio of about 3, longer extinguishment times do indicate higher HF production. However, at a fire size to room volume ratio of about 10, some inconsistencies are noticed. Although one test (526 m^3) had a low agent design concentration, it appears that the time to extinguishment was short and the HF production was very large. Furthermore, the 756 m^3 tests with the two lowest HF concentrations were nearly identical tests in terms of agent design concentration and fire extinguishment time, but their peak HF concentrations varied by 2000 ppm. In the test which used diesel fuel and added a wood crib, the HF concentration is even higher despite the quicker extinguishment time. It is uncertain how the wood crib contributed to the total heat release rate and its effect on the HF production is not known. When the maximum HF concentration trends for CEA-410 and FE-13 were examined, some of these same inconsistencies were again noted. However. the same linear trend for HF production was evident for each agent.

It should be understood that fire extinguishment times are subject to vary due to the interpretation of test protocol. For some of these tests, fire extinguishment times were determined from fire temperature measurements due to the lack of visual data. Also, sometimes there was only a small flamelet present for as long as 10 seconds. Since the fire extinguishment criteria required that no visible flame was present, this could make a substantial difference in the extinguishment time. In tests where temperature data was used to determine extinguishment times, flamelets may not have been accounted for.

Figure 3 shows a typical HF concentration-time history for the NRL tests. The HF reaches its peak concentration very quickly and immediately begins to decay. In approximately five minutes, the concentration has decayed to half of the peak value. At 10 minutes, the concentration is just above 1000 ppm. The agent concentration (FM-200™ in this test) as a function of time has also been included on the graph. Since the concentration is steady throughout the time duration, it is apparent that this decay in HF concentration does not occur due to compartment leakage. This rapid decrease in HF concentration makes the toxicity and corrosion hazards look less ominous than if based on the peak value.

Taking these trends into consideration, a more representative approach to viewing this data may be to consider five minute averages, using the beginning of this 5 minutes as the beginning of agent discharge. This 5 minute average HF concentration is plotted in Figure 4 against the same fire size to room volume ratio as in Figure 1. Average HF concentrations level off as you move to higher fire size to room volume ratios (i.e. ratios of approximately 5). This indicates that while the HF concentration peaks at larger values for large fire size to room volume ratios, it decays more quickly. In Figure 5, the average concentration data for only FM-200™ is presented. It shows the same asymptotic trend as do the other agents. It is uncertain why this trend occurs. Room parameters which could affect the decay rate include wall materials, wall surface area to room volume ratio, and the presence of obstructions. The large scale test compartments had steel walls while the small scale compartments did not. Since HF has a great affinity for metals, this could enhance HF concentration decay. In addition, the large rooms had obstructions while the small compartments did not. Hydrogen fluoride decay may also be a function of the available surface area it can plate onto.

In a study published by Meldrum, toxicity data for HF has been compiled [5}. Based on his study, a dangerous toxic load (DTL) of 12000 ppm-minutes is recommended. This means that if the time (in minutes) integrated exposure of HF (in ppm) exceeds 12000, it can be dangerous. This recommendation is based on mice. Another term used in toxicity studies is LC,, which, for a particular time, represents the concentration which would be fatal to 50% of the population. LC,, studies with some larger mammals, such as monkeys and guinea pigs, have been conducted and are also included in Meldrum's article. These data indicate that a higher HF exposure than the DTL is needed for toxic effects. however the recommended DTL was derived on an LC, not an LC,, (LC, represents the concentration which would be fatal to 1% of the population for a specified time). Also of interest is that animal data indicates that pathological damage to the eyes, internal organs, respiratory tract and skin occurs only around the concentrations causing fatality. Prior to this damage. the animals only experience severe irritation of the eyes, nose, skin, and respiratory tract. This is important to note. since HF exposures may not inhibit a person to the point that they could not move to an uncontaminated environment. Depending on the level of exposure, it is possible that the person may experience sensory irritation for a number of minutes without becoming incapacitated.

Figure 6 shows the recommended DTL line on a plot of HF concentration as a function of time. Various LC,, data from mammal studies are also shown with an approximate curve fit. Typical hydrogen fluoride concentration data from three of the experiment sets has been added for evaluation purposes. In all cases, except the 1 MW USCG fire, the HF exposure reaches the DTL of 12000 ppm-minutes, thereby indicating that these large fires would be a toxicity threat.

Analysis of temperature and carbon monoxide (CO) concentration data can lend some insight into the HF hazard relative to that of the fire. Typical CO concentrations throughout the compartment ranged from 2000 ppm for the 1 MW fire to 4000 ppm for the 8.5 MW fire and did not decay following agent discharge. A person may become unconscious after a CO exposure of 2000-2500 ppm for 30 minutes and concentrations of 4000 ppm and greater are fatal in exposures less than an hour [6]. Since the presence of CO cannot he detected by the senses (unlike HF), a person may become incapacitated and fall unconscious without warning. Thermal exposure considerations are also important. The temperatures in the large scale tests varied greatly but in limited cases, they reached values as high as 300°C. At temperatures of 193°C, a person will immediately be incapacitated and can die in 15 minutes [7]. Immediate death can result from exposure to air which is 343°C. This data is meaningful because it may be unlikely that a person would survive large fires such as these irrespective of the HF exposure.

Also included in Figure 6 are alternative agent data from typical computer room fires [8]. Class **A** materials, such as computer tapes and paper, were tested and the suppression system was activated by smoke detectors. From the examination of these HF exposures, it is evident that this type of fire does not pose a toxic threat. This scenario is more representative of the types of exposures humans may encounter with the use ofthese alternative agents. Due to the growth time required to reach a Class A fire size of 1 MW. it is unlikely that these fire sizes could be achieved prior to the activation of the suppression system. 'The time needed to reach these fire sizes with Class B fuels can be almost instantaneous. However, the number of scenarios where these agents may be used in large spaces with Class B fuels is limited.

Conclusions

These results show that there is a linear relationship between peak HF production and fire size to room volume ratio even with larger scale data incorporated. However, more scatter is introduced by the addition of tests with larger fire sizes and larger room volumes. This may be attributed partially to the long extinguishment times encountered in large scale tests. In contrast, the five minute average HF concentrations appear to be asymptotic as the fire size to room volume ratio increases. A study of toxicity data suggests that fires such as these large Class B fires may pose a toxic hazard. In a more common situation such as a computer room fire, the HF exposure does not appear to be dangerous.

References

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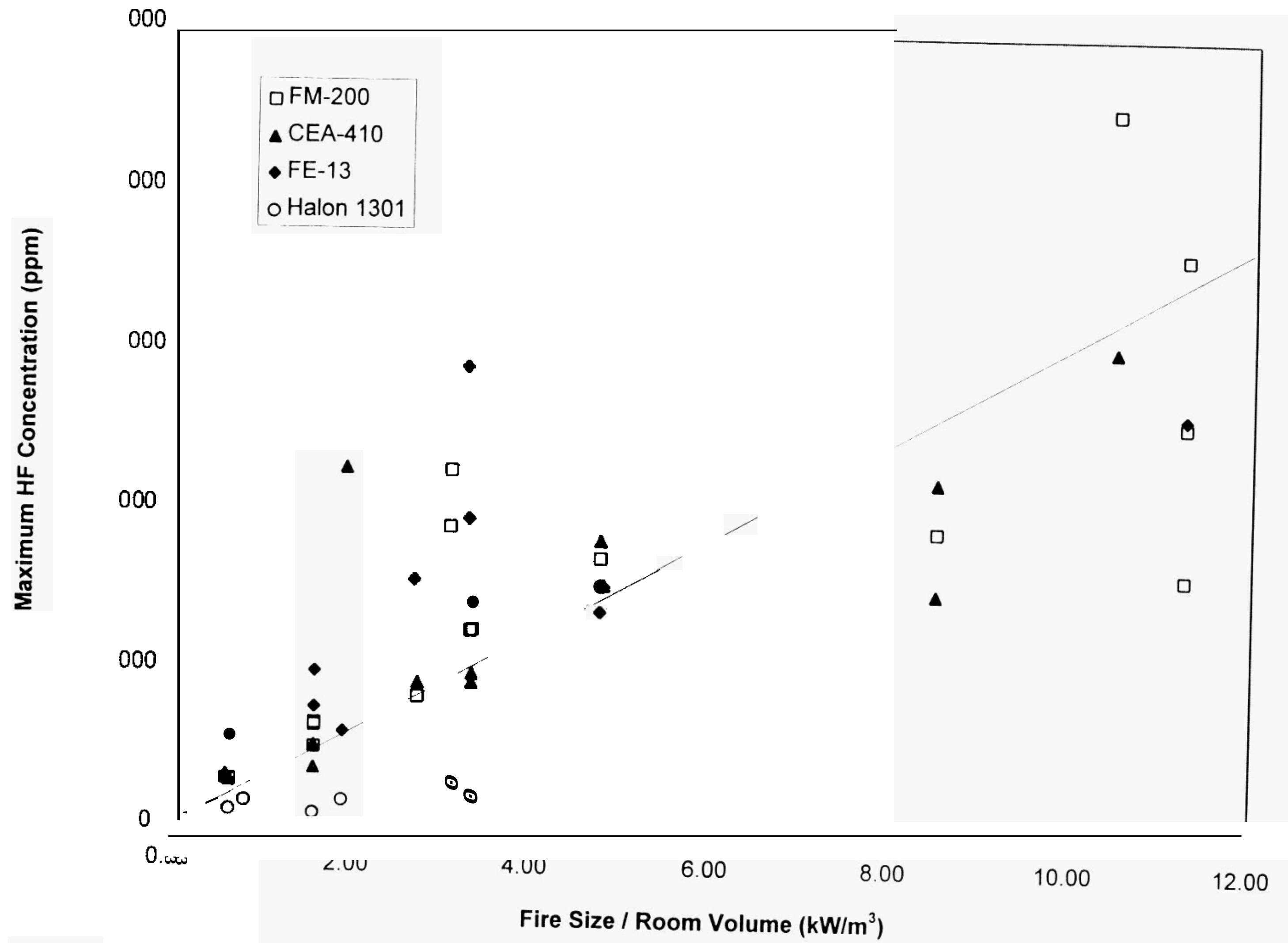

Figure Maximum HF concentration vs. fire size normalized by room volume (nominal 10 sec. discharge time)

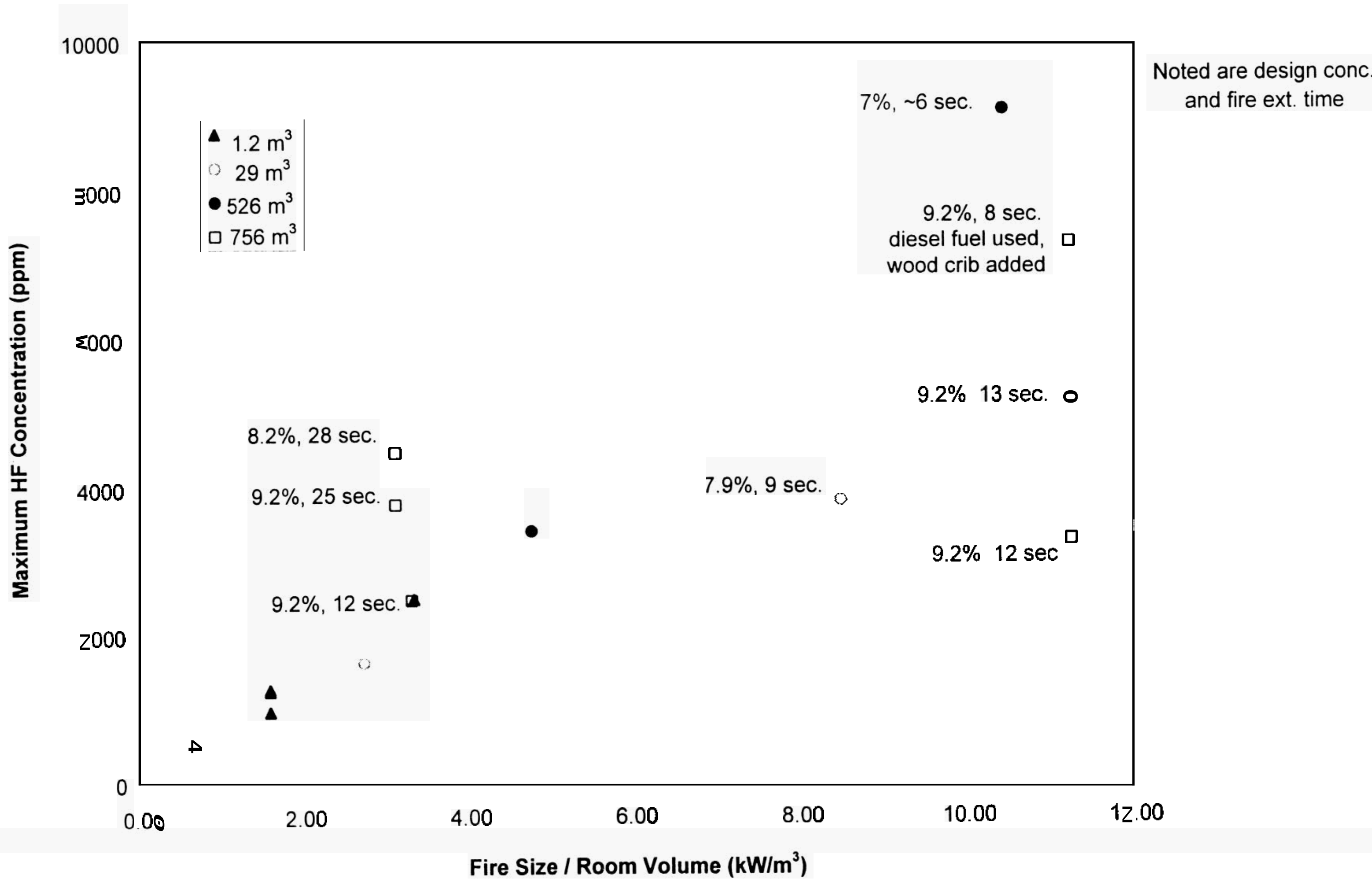

Figure 2. Maximum HF concentration vs. fire size normalized by room volume for FM-200™ tests (nominal 10 sec. discharge time)

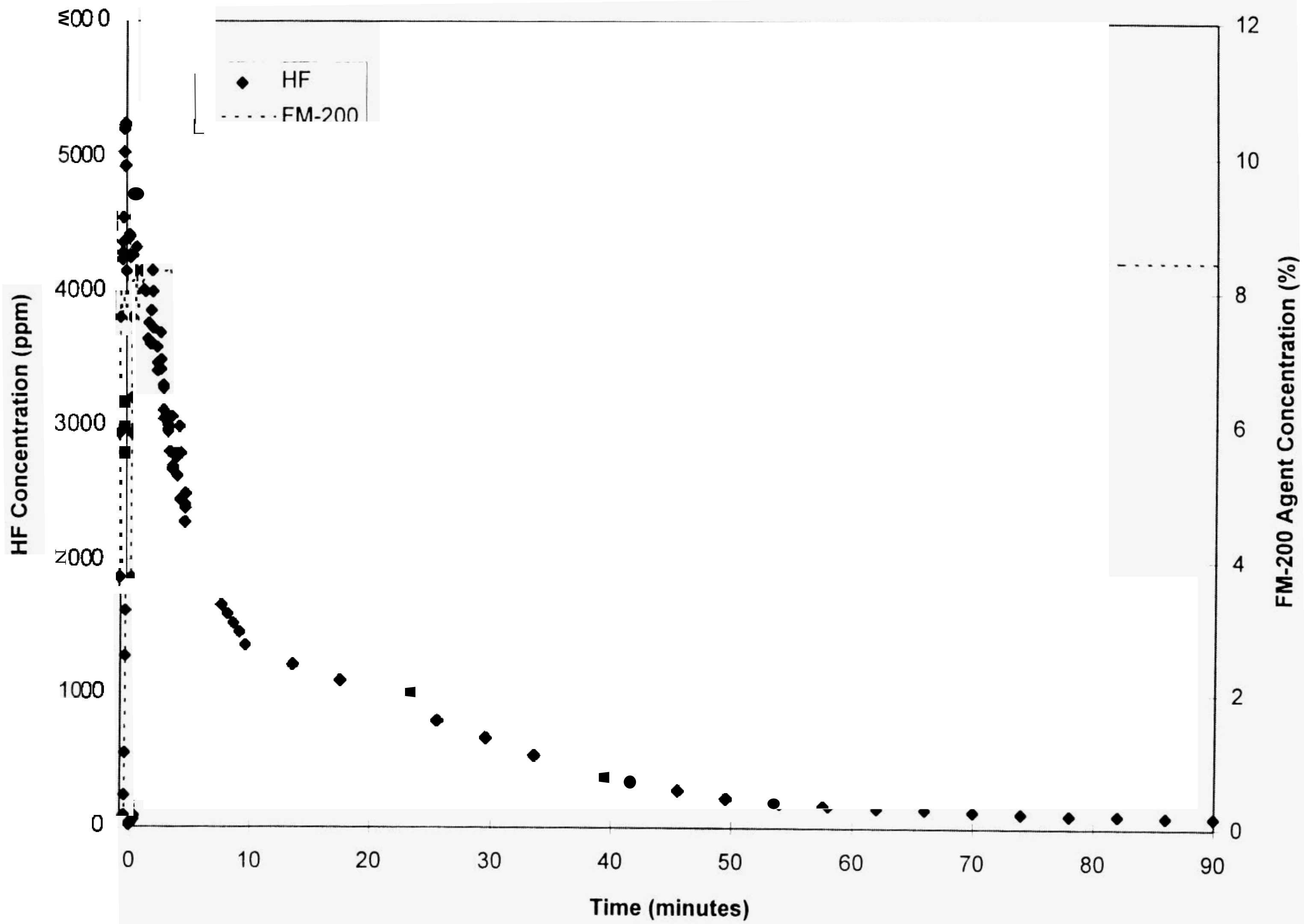

Figure 3. Typical HF concentration-time history for NRL tests

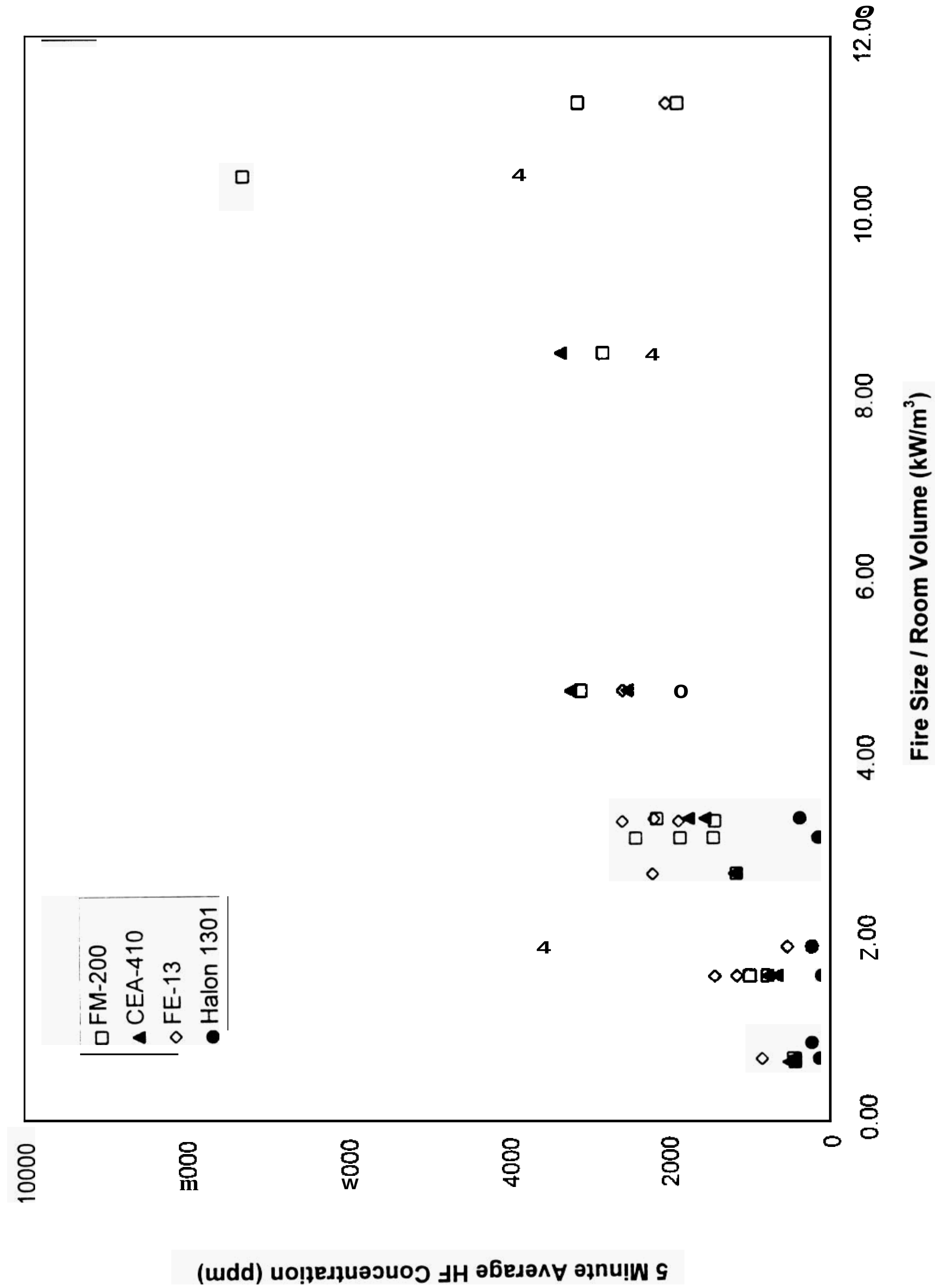

Figure 4. Five minute average HF concentration vs. fire size normalized by room volume (nominal 10 sec. discharge time)

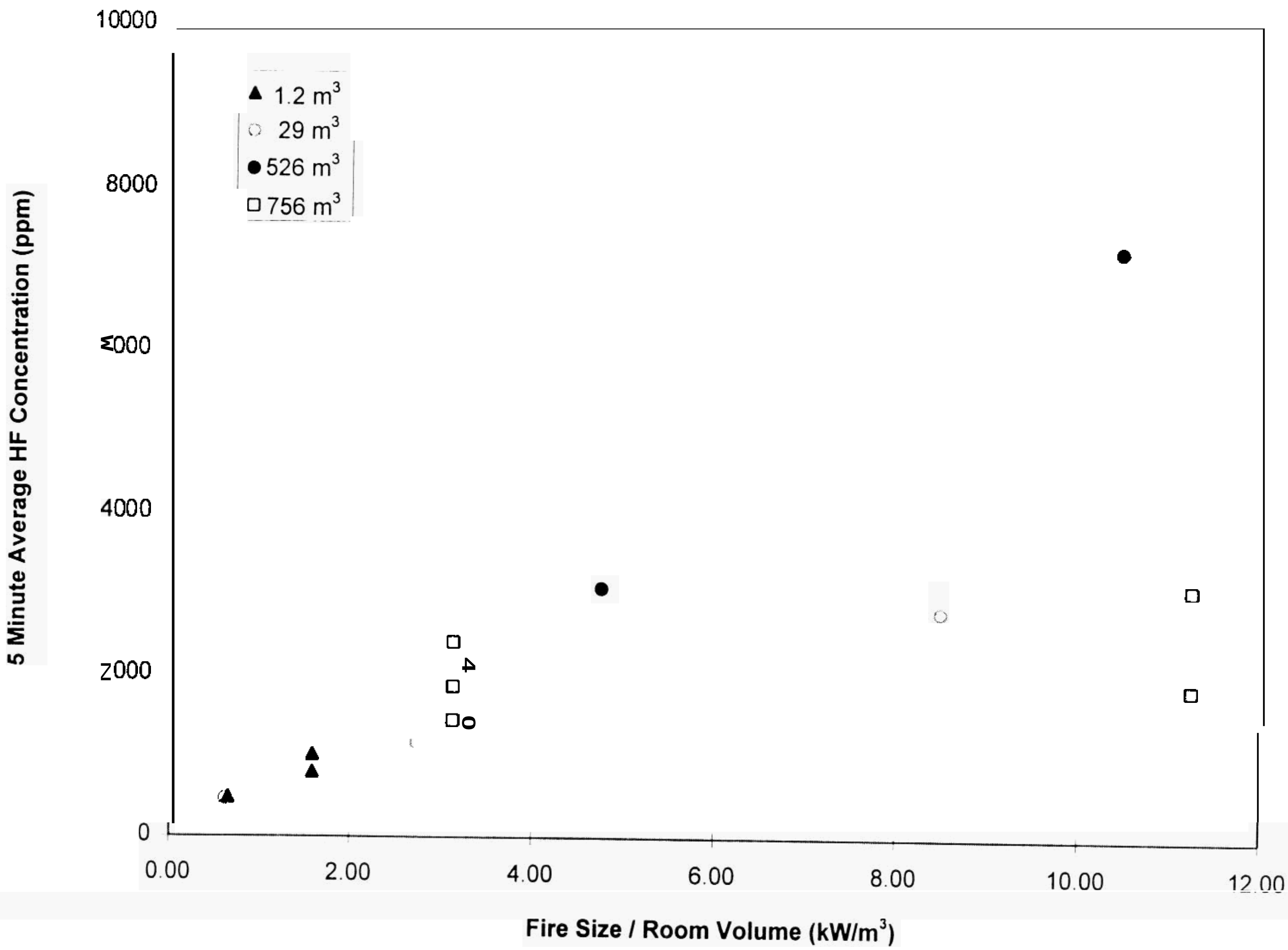

Figure 5. Five minute avg. HF concentration vs. fire size normalized by room volume for FM-200™ (nominal 10 sec. discharge time)

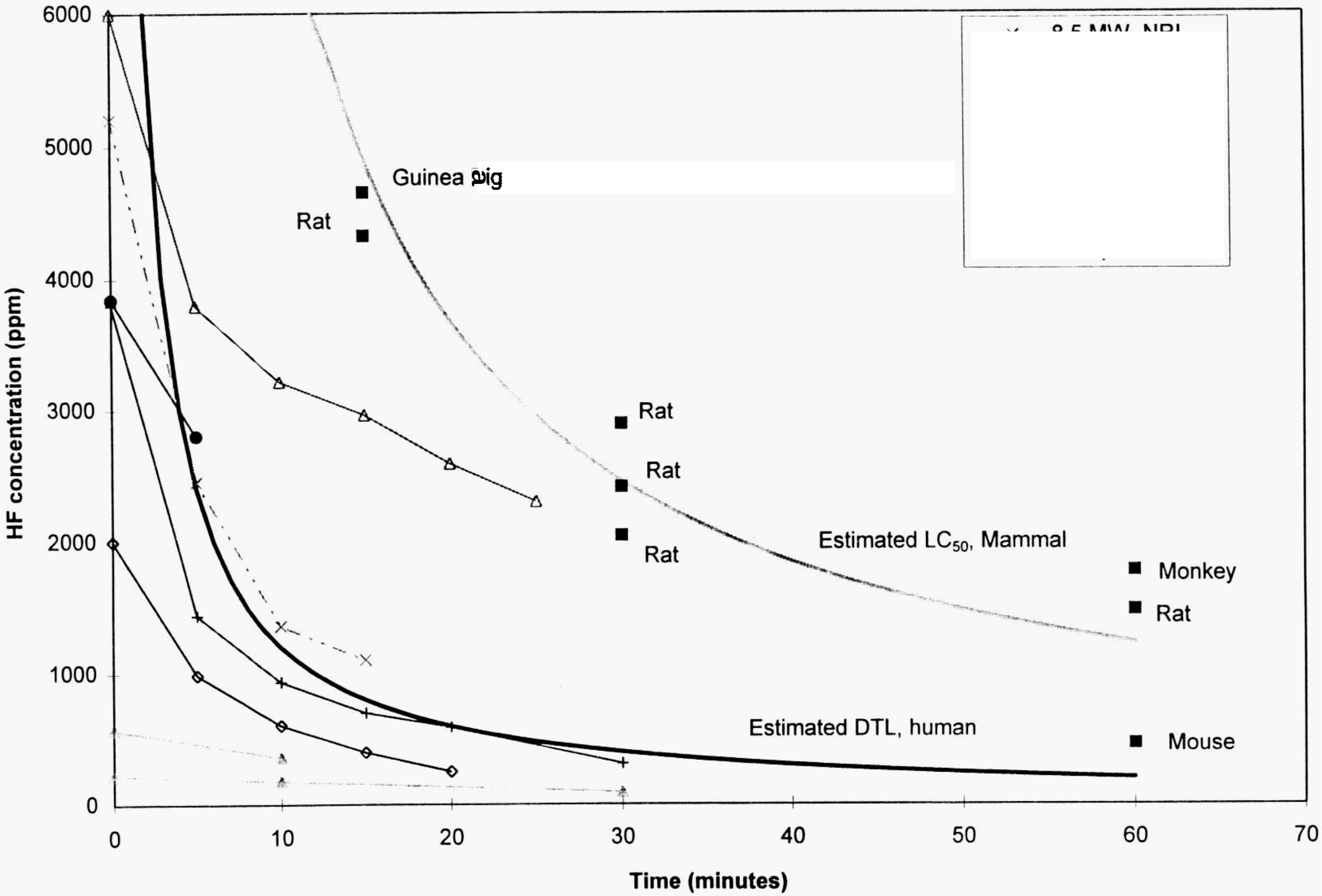

Figure 6. Hazard assessment of HF concentrations in Halon 1301 alternative agent tests