HALON REPLACEMENT AGENT TESTING: PROCEDURES, PITFALLS, AND INTERPRETATION

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ABSTRACT

There are a large number of factors that need to be considered in experimentally determining the amount of a chemical required to extinguish a fire. Extinguishment is a critical phenomenon; small influences can have large effects. This paper considers the importance of many of these factors in order to guide valid testing of candidate halon replacement agents. It is based on our experiences over the years with small laboratory burners and discharge flooding tests in small compartments on through 650 cubic meter (23,000 cubic feet) spaces, and applies primarily to total flooding agents.

BACKGROUND

Halon 1301, **CF₃Br**, has enjoyed widespread usage as a fire suppression agent, perhaps far wider than justified considering the availability of alternate **fire** protection strategies. While it is a highly efficient, clean, non-conducting and non-toxic suppressant well suited for a total flooding mode, there are some disadvantages.

The low halon agent weight and volume requirement is due to the very efficient chemical catalytic activity of its bromine substituent. Over half its effectiveness in fighting organic fuel-air fires is due to bromine.⁴ The chemical mode of operation acts by inhibiting gas phase combustion. The implications, as studied by the Naval Research Laboratory (NRL) in the 1970s, are that smoldering (surface or deep seated) fires require much more agent. Carbon monoxide concentrations significantly increase when halon 1301 is used to suppress charcoal fires. Surface oxidation generating carbon monoxide is only weakly suppressed, while the oxidation of carbon monoxide to carbon dioxide, a gas phase reaction, is strongly inhibited.

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The chemical activity of halon comes into play only in the flame reaction zone. Inertion - preventing a fire from initiating - is largely a physical process and much higher concentrations of halon are **required.**^{4,5} Also, by definition, a chemical process will yield reaction products. The toxic and corrosive gases hydrogen fluoride (HF) and hydrogen bromide (HBr) **are** products of halon fire suppression.^{5,6} Acid concentrations generated depend on fire intensity and agent addition factors, with HF concentrations over one half percent having been **observed.**⁷

Acid production does not require the presence of bromine or hydrogen on the fluorocarbon species. Studies on perfluorocarbons as suppressants showed the presence of a carbon-carbon bond would likewise allow high HF concentration generation. C_2F_6 and C_3F_8 gave HF product; CF_4 gave little.⁴

The property of halons that now requires their drastic production restriction is their capability of causing reductions in the stratospheric ozone layer. Significant stratospheric ozone depletion from chlorine containing chlorofluorocarbons (CFCs) was proposed in **1974** by Roland and Molina. By 1976, **Dr**. Homer **Catact** had requested a paper study at NRL on the possibility of bromine containing halons causing similar atmospheric reactions. The conclusion was, while much reaction rate data was lacking, it was likely the halons would be at least as potent, if not more **so**, ozone depleters as the CFCs.

Studies were conducted at NRL in the mid and late **1970s on** halon 1301 replacement, fire suppression products, and suppression mechanisms. These involved flow tube kinetics, cup burners, and small, intermediate and full scale total flooding discharge extinguishmenttests. These and more recent work from the mid 1980s form the technology base experience, including errors and lessons leamed, upon which this paper is based. Because fire extinction is a critical phenomenon - the flame can be either barely stable **a** extinguished • very small influences are sufficient to change its state. It is imperative to control, if not understand, parameters and variations that can otherwise change results.

CUP BURNER EVALUATION

Initial testing is usually via small laboratory burners which **are** typically patterned after the liquid fueled **ICI** Cup Burner. such **as** the Factory Mutual Research Corporation version.⁸ Results among laboratories may differ due both to apparatus and operation protocol, as well as specific operator characteristics. Candidate rankings and relative differences compared to a **standard**, such **as** halon 1301, **are** thus more significant than single agent numerical results **run** by the various laboratories. Burner size, shape and rim design, chimney size, fuel feed, agent feed and metering devices, and air-agent mixing (homogeneity)method, all contribute to defining the apparatus.

In particular, the lip of the burner and the device for maintaining the fuel level in the cup **are** critical. If the fuel level can **be** held to the **rim** level, the pool can be said to simulate an infinite size pool. While setting the fuel height is a procedure factor, the apparatus will dictate its stability. Agent metering can also be a variable factor. If rotometers are employed, changing one flow significantly can change the system back pressure, which in turn affects all other flowmeters.

Addition of liquid **or** low volatility agents can be especially prone to fluctuations. Syringe drive devices can have uniformity problems or agent can condense before reaching the flame. Uniform mixing must be maintained.

Cup burner operation protocol includes flow rate, where and how fuel level in the burner cup is set and maintained, preburn standardization, agent addition increment amount and timing protocol, and agent concentration calibration **or** analysis. As pitfall examples, a heated exposed burner rim can act **as** a flame holder or cause fuel boiling. In the former case, the flame will require a higher agent concentration for extinguishment. In the latter case, too rapid evolution of fuel vapors can cause the burner **rim** to "overflow" with fuel rich vapor. This will be manifested by having tongues of flame descend below cup level. The burner rim - flame coupling will be weakened and premature extinguishment can occur.

A similar fuel rich situation occurs with too rapid agent addition. The inhibited flame is **no** longer able to consume the fuel at its former rate, but fuel vaporization rate decrease can lag the oxidation rate decrease.

Too drastic an agent addition increment can cause flame extinguishment while smaller increases may permit flames to exist at higher agent concentrations. Both addition approaches can give reproducible results with their respective addition procedure. Likewise, too slow addition can give more time for fluctuations to act **on** an inhibited flame. Agent or products dissolved in unconsumed fuel can cause decreased agent requirements.

Determination of agent concentration from flowmeter **settings** may be adequate for rapid candidate screening, but errors may be significant. Formula calculated calibrations for 'new' agents may deviate from actual non-ideal properties. If possible, the most reliable agent concentration determination would be actual analysis of the agent-air mixture immediately following extinguishment.

The ultimate responsibility for setting the fuel level rests with the operator. Even with selfleveling reservoirs, this is not a simple procedure for exacting results. A pressure head can be used to hold the fuel level constant, but pressure, not height, is the principle of operation. As fuel in the cup becomes heated, its density decreases. The level would then rise. Operator interaction until steady state conditions **are** reached is required. Only then should extinguishment be determined. Using a large diameter reservoir compared to a **small** diameter cup is an approximation that becomes less satisfactory **as** time to extinguishment increases (past the minimum **required** to achieve steady state conditions).

TOTAL FLOODING DISCHARGE TESTS

In larger scale tests, the fire size is important, as is the fire area/enclosure volume ratio. Pool fires around 10cm are in a transition zone from laminar to turbulent combustion. Turbulent flames can be more difficult to extinguish as the convoluted flame sheet gives higher fuel consumption and energy generation rates. Intermediate size pan fires are more difficult to extinguish if there is induced turbulence, such as from a fan. Fire area/enclosure volume ratio, compartment ventilation, and prebun procedure are important in assuring reproducible conditions with undiminished oxygen concentration immediately prior to agent addition. A key pitfall is that reduced oxygen levels and carbon dioxide accumulation will decrease fire intensity, decreasing agent requirements. A reasonable "wcrse-case" fire threat scenario is needed for safety evaluation.

An additional consideration is that input agent weight is not sufficient to determine enclosure agent concentration. Enclosure leakage of agent and air will **occur**. Which predominates will depend **on** leak location and nozzle pattern. Also, agent weight calculations include **an** assumed enclosure temperature. An intense **fine** will reduce air density, resulting in a higher agent (v/v) concentration. Agent and oxygen concentrations **are** best measured, preferably at several sampling points.

The details of **total** flood rapid dumping, including plumbing, nozzles, pressure, ullage, configuration, and obstacles, can affect results. Two-fluid flow, concentration transients in time and space, discharge time and agent addition rate profile, compartment leakage (short and long term), will differ with agent physical properties. The effects of environmental factors may likewise differ.

Care must be taken to **assure** valid comparisons among agents correctly deconvolutes the influence of their differing physical properties. In other **words**, all candidates should be compared with each optimized for effectiveness. This ideal may not be possible, **so** test results should not be simply compared **as** numbers without some evaluation of system influence evaluation, including for the factors listed above.

A particular fire may be extinguishedrapidly due to transient effects. It is best to attempt reignition to assure safe conditions. Evaluation of conditions and concentrations near the fire from start of agent addition to extinguishment is very helpful. However, the fire in the real world can occur at any location in the entire enclosure. The concentration of agent required near the fire for extinguishment may only be achieved with a suitable safety factor. The minimum agent concentration required must be everywhere guaranteed in the presence of nonuniform agent distributions and fluctuations. Agent penetration into solid fuel fires may require **a** higher concentration safety factor as a concentration gradient may be required to assure timely mass flow.

Valid sampling is not simple. Halogen acid gas sampling is especially difficult. If *in situ* optical techniques9 **are** not practical, the how, when, and where of grab sampling **are** far more important than analysis technique (ion chromatography, ion specific electrode, wet chemistry) in obtaining accurate representative concentration results. A sampling strategy we **are** currently evaluating allows determination of HF on a time scale of seconds so that acid generation and consumption during and immediately following agent discharge can be followed. This minimizes sampling time biasing.

An additional practical consideration is maintaining equipment and facilities in a moist acidic environment is a challenge.

SUMMARY

Becoming aware of agent testing pitfalls and learning how to assure valid test interpretation comparisons among the various halon replacement fine extinguishing agents, and different test situations, **are** the topics of this paper. Decisions should ideally be based on complete knowledge. At the practical level, the identity and form of possible influential factors should be sought, and their significance judged. A firm backing in fire protection, combustion science, and combustion engineering will then allow informed interpretation and use of fire suppression studies.

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