Modes *of* Chemical Suppression Action: Guidance for Agent Evaluation

Ronald S. Sheinson' and Samuel P. Baldwin,

NAVAL RESEARCH LABORATORY
Navy Technology Center for Safety and Survivability
Code 6180, Washington, DC 20375-5342 USA
(202) 404-8101, Fax (202) 767-1716

INTRODUCTION

Due to recent national and international legislation, the brominated halocarbons that the US Navy uses for fire fighting applications face a world wide production halt by 1 January 1994. Halon 1301 (CF_3Br) and halon 1211 (CF_2BrCl) are clean, effective, as well as non-conducting fire suppression agents, characteristics which have led to their widespread use. The atmospheric lifetimes of the completely halogenated halons unfortunately are quite long and the bromine atom on the molecule undergoes a catalytic chain reaction in the upper atmosphere, degrading the earth's ozone layer. It is this characteristic of the halons which has come under fire from legislation such as the Montreal Protocol.

In order to ensure continued system performance, as well as to guarantee safety of life and property, suitable alternatives must be developed. In order to aid in the search for a(n) suitable alternative(s), a predicative algorithm for calculating minimum agent concentrations required for flame extinguishment has been developed at NRL. The model may also be used to predict if a compound is flammable. This model is based on the data from the NRL Cup Burner tests. This data is listed in Tables II to IV.

Determination of the 'optimum' halon replacement is dependent on the specific fire challenge as well as the scenario. There are different 'best' solutions which are dependent on the circumstances involved.

---

* Author to whom correspondence should be addressed.

Supported in part by the U.S. Office of Naval Technology and Naval Sea Systems Command.

EXPERIMENTAL

The liquid hydrocarbon cup burner used by NRL is described elsewhere'. The fuel used was n-heptane. In order to ensure repeatable and accurate results for the modeling, great care was taken in the maintenance of the fuel level in the burner, and with the overall system operation[2]. The concentrations of the agents required for extinguishment were obtained through the use of a Foxboro/Wilks Model 80 infrared spectrophotometer, as opposed to interpretation from flowmeter readings. Sierra mass flow controllers were used to give stable and reproducible gas flow rates.

EXTINGUISHMENT PATHWAYS

There are two main pathways through which a flame may be extinguished; Physical and Chemical. Physical extinguishment is a combination of spatial and energetic disturbances, but chemical extinguishment includes reactive interference mechanisms. Physical agents work solely through physical means, while chemical agents work through a combination of the two pathways.

The spatial contribution to the physical effect arises from the dilution of the reactants, as well as the separation of the fuel and the oxidizer, and the decoupling of the flame reaction zone from the fuel. For monatomic molecules, the dilution effects play a major role, with the heat capacity contributing only 20% to the extinguishing nature of helium[3]. Examples of separation would be a blanket or a foam layer. This prevents fuel vaporization and degradation. Decoupling the energy and the radical rich zone occurs in the blowing out of a candle, or the blasting of an oil well fire.

The energetic component of the physical pathway refers to the abstraction of energy from the flame by the agent. The removal of energy is dependent on the heat capacity of the agent, the thermal conductivity of the agent, and the decomposition reactions of the agent. For polyatomic agents such as CF_4 and SF_6, the heat capacity is responsible for greater than 70% of the effect[3]. The decomposition of the agent requires an input of energy to break bonds. This set of reactions, but not the reactions of the decomposition products, is considered to be a physical process.

The chemical pathway is dependent on the reactive nature of the agent. The radical scavenging nature of the halogens is responsible for the removal of reactive radical intermediates from the flame, primarily through hydrogen atom reaction. (The key H·, OH·, and O: radicals are in quasi-equilibrium. Removing any one decreases the radical pool concentration). In addition, bromine, as well as iodine, undergoes a series of catalytic reactions, whereby the halogen radical is regenerated after causing the combination of two hydrogen radicals.

$$Br\cdot + H\cdot + M \rightarrow HBr + M$$
$$HBr + H\cdot \rightarrow Br\cdot + H_2 \qquad \text{Equation 1}$$

In this manner, bromine and iodine are able to remove many more radicals from the

flame than is fluorine. Chlorine shares this catalytic nature, but to a lesser extent', while fluorine is not able to regenerate itself after the first step in the reaction series, due to the strong HF chemical bond formed.

The order of decreasing radical scavenging ability is Br≥I»F > Cl. This has been shown through the cup burner testing of the appropriate mono-substituted trifluoromethane molecules (Table II). Radical chain lengths for specific agents can be calculated from cup burner results from different gas composition mixtures. Bromine and iodine have been shown to have approximately the same radical chain lengths[4].

In order for flame propagation to be maintained, the minimum flame reaction temperature rises to replace the lost radicals. That is, a higher temperature is required to allow for faster radical production via endothermic reactions. When the temperature required exceeds the maximum temperature possible from the fuel combustion, (ie., the adiabatic flame temperature) the flame is extinguished.

MODELING EFFORTS

The physically predicative model is used to experimentally determine energy losses required to cause flame extinction. It is based on the integral of the heat capacity from room temperature to the minimum flame propagation temperature', as well as the relative concentrations of the various suppressant agents, normalized to the concentration of oxygen. The equation is shown below.

$$\Delta H' = \sum_i \left(\frac{X_i}{X_{O_2}}\right) \int_{298}^{1600} C_{pi}^T dT \qquad \text{Equation 2}$$

The inversion of this equation allows for the determination of the concentration required for extinguishment from the agent's enthalpy of heating. This equation is used to determine the physical contribution to suppression from an agent.

$$X(A) = \frac{\mathbf{AH'(0.21)\ -7.9}}{\int C_{PA}\,dT + \mathbf{AH'(0.21)\ -7.9}} \qquad \text{Equation 3}$$

There are several different extended chemical models used to determine the extinguishment concentration requirements of the proposed replacements. The Linear Model is the addition of the contribution from the chemical action to the physical predicative model. The experimental values for the agents will lie in the interval between the concentrations for the purely physical and the concentration required for the combined chemical and physical predictions.

The Modified Chemical Model is based in the Linear Model and incorporates both the bond energy of the agent, as well as the ligand reactivity considerations. It is able to make specific extinguishment predictions. **As** the intramolecular bond strength varies for each agent, so does the extent of the chemical interaction with the flame. The

rates for unimolecular decomposition and abstraction are such that significant quantities of some agents are able to pass through the flame without ever chemically interacting with the combustion processes. Weighing factors have been incorporated into the model to adjust for the non-interacting agent.

This Modified Chemical Model is structured around Group Factors. A molecule is composed of several 'Groups' of atoms, with each group contributing to the chemistry of flame suppression. A molecule such as halon 1211 (CF_2BrCl), is composed of **4** separate groups, C, CF_2, Br, and Cl. A factor is assigned to each group based on the relative effect the group has on the chemistry of suppression. The factors for inhibiting groups are positive numbers, corresponding to the removal of energy and radicals from the flame. The factors for fuels (i.e., the hydrogen in CF_3H) are negative numbers, corresponding to the addition of energy to the flame. Bromine is the strongest inhibitor and hydrogen is the strongest fuel. The incorporation of the Group Factors into the expression for agent requirements is shown in Equation **4.**

$$Ext\% = \frac{1}{\frac{1}{Phys\%} + \sum Group * Group\ Factor} \qquad \text{Equation 4}$$

The Empirical Model (Free Oxygen), has been based on Tucker, et al.[5], and further developed using the experimental data obtained from our Cup Burner. It is a combination of the physical prediction from the linear model with the experimental mixture data to calculate the effective, or 'Free', oxygen concentrations required for neutralization. The efficiency of halon **1301** is a non-linear function of its concentration. At **low** concentrations, its effectiveness increases. This model can predict non-linear agent requirements for agent mixtures and for different oxygen concentration environments.

DATA AND DISCUSSION

As the following table shows', the experimental concentration of halon 1301 required for flame extinction is dependent on the calculated value for Free Oxygen, not the actual oxygen concentration. These results counter the idea that more agent would always be required for an enriched oxygen atmosphere, but is amply supported by our extensive experimental agent mixture extinguishment data.

TABLE **I**: FREE OXYGEN DEPENDENCE OF 1301 REQUIREMENTS

O_2 Conc.	**N_2 Conc.**	**SF_6 Conc.**	Free Oxygen	**1301** Required
19.7%	**80.8%**	0%	5.37%	2.00%
26.9%	50.8%	**21.2%**	5.40%	2.03%

Figures **1-4** show the strong non-linear concentration dependence of CF_3Br and CF_3I, as well as the increasing efficiency with decreasing concentration. With data such as

AGENT	PHYSICAL PREDICTION	MODIFIED PREDICTION
CF_2H_2	19	40
CFH_2Cl	18	80
$CH_2ClCHCl_2$	11	180
$CFCl_2CH_3$	11	280

CONCLUSIONS

Several different models have been developed in an effort to better describe the chemistry of suppression. The Modified Chemical Model predicts agent, extinguishment concentration requirements with only the chemical formula and an estimate of the enthalpy of heating. The Free Oxygen model predicts agent requirements for complex mixtures, including for oxygen depleted and oxygen enriched environments. It requires only our prediction for purely physical agents or one cup burner data set for each chemically acting agent. The predicted agent concentration values can be used to calculate weight and storage space volume requirements, as shown in Table III for currently considered total flooding agents.

An understanding of the importance for the different modes of fire suppression action allows for insight into the behavior of candidate agents. This understanding will aid in the selection of suitable replacements that are appropriate for their individual applications and evaluating the magnitude of their fire scenario HF production. In addition to predicting suppression capabilities of halogen containing hydrocarbons, the proposed CFC and HCFC replacement candidates can also be evaluated for flammability.

AGENT	FORMULA	CONC %	REL WT	REL OL
Halon 1301	CF_3Br	3.1	1X	1X
3M PFC-410	C_4F_{10}	5.2	2.7	2.7
Great Lakes FM-200	CF_3CFHCF_3	*6.6*	2.4	2.7
Du Pont FE-25	C_2F_5H	8.8	2.3	2.8
Sulphur Hexafluoride	SF_6	10.6	**3.3**	**3.0**
Du Pont FE-13	CF_3H	12	1.8	3* +
Carbon Dioxide	CO_2	21	2.0	4.1

ssure.

Table IV: EXTINCTION CONCENTRATIONS (Per Cent)

AGENT	PREDICTION	EXPERIMENTAL	% ERROR
CF_3Br	3.3	3.1	8
CF_3H	13.2	12	10
CF_3Cl	7.9	6.9	14
CF_3I	3.4	3.2	7
CF_2BrCl	3.4	3.6	6
CF_2BrH	4.2	4.1	2
C_2F_5Br	2.9	3.1	5
C_2F_5H	8.6	8.8	2
C_2F_5I	3.0	3.5	15
C_3F_7H	6.4	6.6	3

Figure #1

MIXTURE EFFECT
CF3Br - SF6 EXTINGUISHMENT

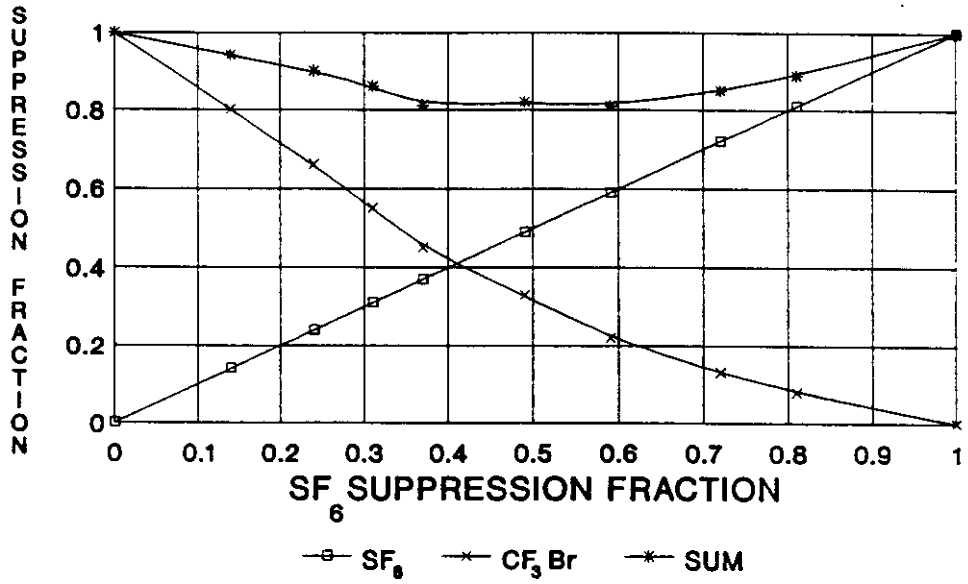


Figure #2

CHEMICAL SUPPRESSION EFFICIENCY

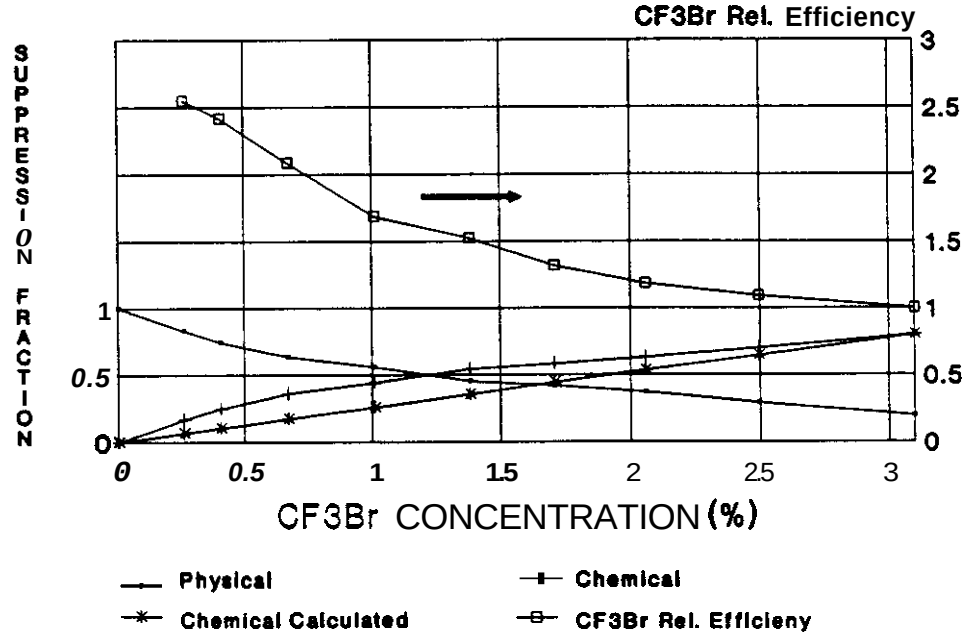


Figure #3

CF3I
MIXTURE EFFECT

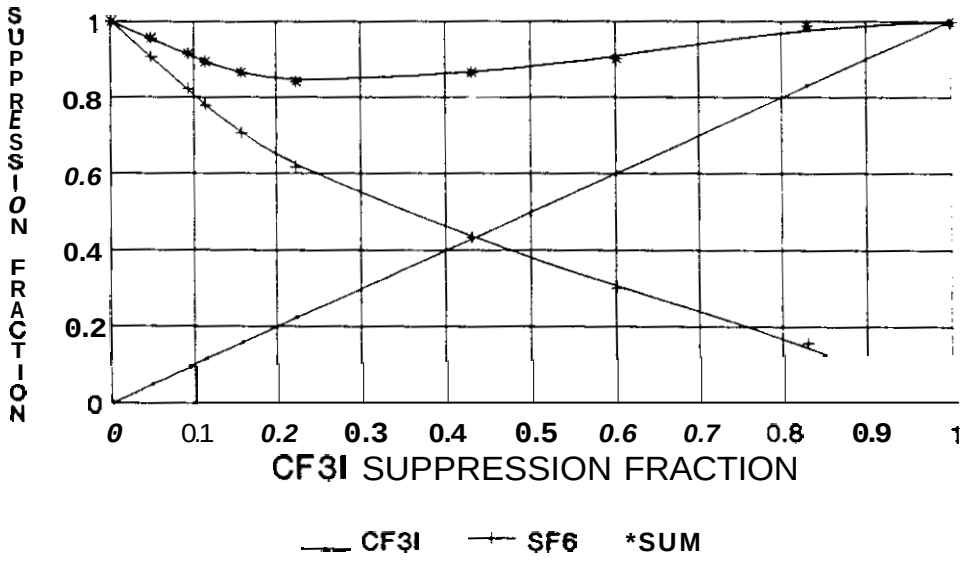
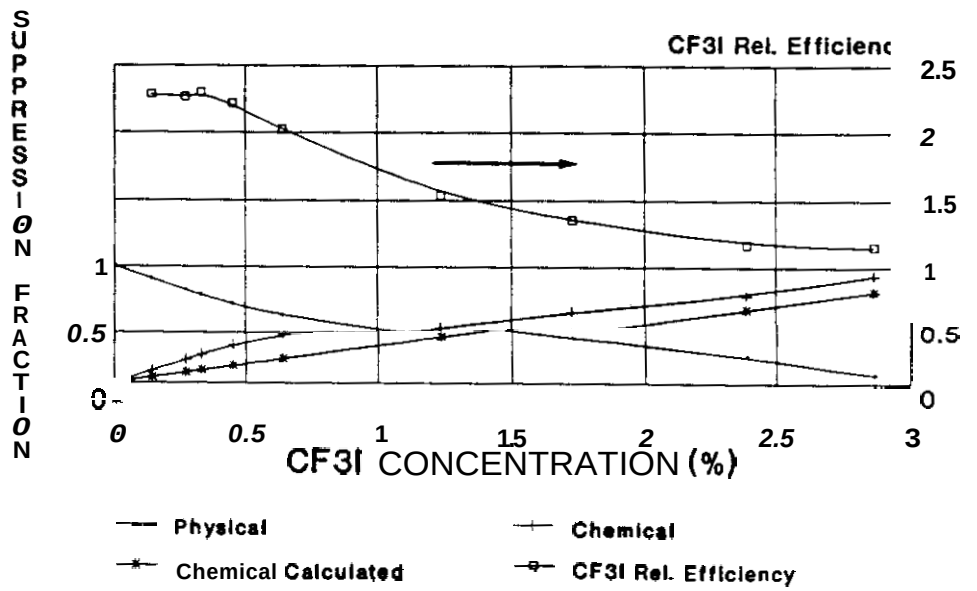


Figure #4

CHEMICAL SUPPRESSION EFFICIENCY



References

1. Sheinson, R.S., Penner-Hahn, J.E., and Indritz, D., "The Physical and Chemical Action of Fire Suppressants," Fire Safety Journal, Vol. 15, pp 437-450, 1989.

2. Baldwin, S.P, Brown, R., Burchell, H., Driscoll, D.C., Eaton, H.C., Salamon, G., St. Aubin, J., Sheinson, **R.S.,** and Smith, W.D., "Halon Replacement Agent Testing: Procedures, Pitfalls, and Interpretation," Proceedings of the Halon Alternatives Technical Working Conference 1992, May 12-14, Albuquerque, NM, pp 207-212.

3. Indri, D. Boris, J. Oran, E., Sheinson, R., Williams, F. and Young, T. Calculation of Physical Effects of Diluents on Flames," Paper Presented at the 178th National American Chemical Society Meeting. Washington, DC, USA, September 1979.

4. Sheinson, **R.S.,** Baldwin, **S.P.,** and Driscoll, D.C., "Halogenated Fire Suppressant Action," Paper presented at the 203rd American Chemical Society Meeting, Atmospheric Science and Combustion Symposium, San Francisco, CA, April 5-10, 1992.

5. Tucker, D.M., Drysdale, D.D., and Rasbash, D.J., Combustion & Flame, Vol. 41, p. 293, 1981.

6. Sheinson, **R.S.,** and Driscoll, D.C., "Fire Suppressant Concentration Requirements: Agent Mixtures and Depleted/Enriched Oxygen Concentrations," 23rd International Symposium on Combustion, Abstracts **Book,** Orleans, France, The Combustion Institute, July 1990, p.204.

7. Sheinson, **R.S.,** Gellene, G.I., Williams, F.W., and Hahn. J.E., "Quantification of Fire Suppressant Action on Liquid Pool Fires," Paper 18, 1978 Combustion Institute, Eastern Section Meeting, Proceedings. Miami Beach, FL. USA, November 29-December 1, 1978.

8. Sheinson, **R.S.,** and Driscoll, D.C, "Fire Suppression Mechanisms: Agent Testing by Cup Burner," Proceedings *of* the International Conference on CFC & Halon Alternatives, October 10-11, 1989 Washington, DC.