

# Application of Detailed Chemical Kinetic Modelling to Predict the Formation of Toxic Compounds in Enclosure Fires under Suppression

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## ABSTRACT

This paper presents the results of a theoretical investigation designed to characterise the formation of toxic compounds in enclosure fires under suppression. The present work was primarily motivated by the need to gain insight into the mechanism of formation of those toxic compounds which are originated from the interaction between fires and gaseous suppression agents. For this purpose, detailed chemical kinetic modelling techniques were used to predict the generation of combustion products within the upper-layer of typical enclosure fires. Effects of the mixing phenomenon were investigated by considering two possible extremes using infinitely fast and infinitely slow mixing models. The heat loss variation was also studied under isothermal and adiabatic conditions. It is demonstrated that, the production of toxic compounds in the upper-layer is kinetically controlled. This is quite consistent with the production of other major species (eg CO) in the upper-layer. Calculations presented here show that the concentration of toxic compounds originated from halon extinguishing agents are much lower than those of halon replacement agents. For such agents due to the lack of significant chemical reaction inhibition, higher extinguishing concentration are required. As a result halon replacement agents produce higher levels of toxic compounds.

## INTRODUCTION

CF<sub>3</sub>Br (halon 1301) is perhaps the most common fire extinguishing agent and has been used extensively all around the world. Unfortunately, despite its high suppression effectiveness, halon 1301 contributes significantly to stratospheric ozone depletion and as of January 1, 1994, the commercial production has ceased by law. This elimination of new production of halon 1301 has initiated tremendous efforts across the world in a search for replacements and alternatives. While no agent with all of the desirable properties of halon 1301 has been clearly identified, over the last few years, several new agents have been proposed and subsequently

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commercialised. The agents which are currently being considered as replacement for CF<sub>3</sub>Br are mostly halocarbons [1] which include compounds containing carbon, hydrogen, bromine, chlorine, fluorine and iodine (see Table 1).

**Table 1:** New technology halocarbon gaseous agents<sup>†</sup>.

Category	Trade Name	Designation	Chemical Formula
Halocarbon	CEA-410	FC-3-1-10	C <sub>4</sub> F <sub>10</sub>
	FM-200	HFC-227ea	C <sub>3</sub> F <sub>7</sub> H
	FE-13	HFC-23	CF <sub>3</sub> H
	FE-24	HCFC-124	C <sub>2</sub> F <sub>4</sub> HCl
	FE-25	HFC-125	C <sub>2</sub> F <sub>5</sub> H
	Triiodide	Halon 13001	CF <sub>3</sub> I
	NAF-SIII	HCFC Blend A	C <sub>2</sub> F <sub>3</sub> HCl <sub>2</sub> (4.75%) CF <sub>2</sub> HCl (82%) C <sub>2</sub> F <sub>4</sub> HCl (9.5%)

<sup>†</sup>Extracted from reference [1].

Like CF<sub>3</sub>Br, new technology halocarbon gaseous (NTHG) agents decompose in flames to form halides and other toxic and corrosive products [2-4]. However, these new agents generally suffer from the lack of significant chemical reaction inhibition in the flame zone. As a result, for such agents significantly higher concentrations are required to extinguish fires (see Table 2). Consequently, the decomposition products generated from NTHG agents may have higher concentrations of undesirable toxic by-products, such as hydrogen fluoride (HF), hydrogen chloride (HCl), and hydrogen bromide (HBr).

**Table 2:** Minimum Design Concentration for halon 1301 and new NTHG agents<sup>‡</sup>.

Chemical Formula	Minimum Design Concentration <sup>#</sup> (% V <sub>ag</sub> /V <sub>air</sub> ) <sup>*</sup>
CF <sub>3</sub> Br	5
C <sub>4</sub> F <sub>10</sub>	6
C <sub>3</sub> F <sub>7</sub> H	7
CF <sub>3</sub> H	16
C <sub>2</sub> F <sub>5</sub> H	10.9
C <sub>2</sub> F <sub>3</sub> HCl <sub>2</sub> (4.75%), CF <sub>2</sub> HCl (82%), C <sub>2</sub> F <sub>4</sub> HCl (9.5%)	8.6
CF <sub>3</sub> I	5

<sup>#</sup> 120% of minimum extinguishing concentration based on the cup-burner test.

<sup>\*</sup> The ratio (in percent) of the volume of the extinguishing agent to the volume of the oxidiser.

<sup>‡</sup>Extracted from reference [1].

A number of experimental and theoretical studies has been recently conducted [5-7] by research organisations, such as NIST<sup>†</sup>, and manufacturers of fire suppressants in order to understand the mechanism of formation of toxic by-products generated from the decomposition of NTHG agents. Most of these studies, however, concentrated on the formation of toxic compounds generated from the interaction of various extinguishing agents

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with laboratory-scale premixed and diffusion flames. While these kinds of studies are quite essential to understand the mechanism of formation of toxic by-product, their application to large-scale enclosure fires needs more research.

Generally the quantities of toxic compounds formed in a large-scale enclosure fire under suppression, will depend upon the properties of the fire itself, characteristics of the agent delivery system (eg agent type, location and number of discharge nozzles, the rate of application of the agent, etc) and the fate of the toxic species after their formation. Since high temperatures are required for rapid agent decomposition, in a typical room fire, toxic by-products are essentially formed in the vicinity of fire itself (flame zone) and in the hot ceiling layer. The latter is of great practical importance because, for instance, the extinguishing agent may not be directly applied to the flame (eg because of the distance between the fire source and the discharge nozzle) but released in the hot layer. It is also possible that some of the unreacted molecules of the extinguishing agent may migrate to the hot layer and decompose there. Thus, for such conditions, there exists a need to understand and predict the mechanism of formation of toxic by-products.

The present work is our preliminary attempt to address this need and for this purpose we employ detailed chemical kinetic techniques. The recent investigations at NIST [5, 6] have demonstrated that experimentally measured acid gas concentrations in cup burner tests are generally lower than those predicted on the basis of thermodynamic considerations. This finding suggests that, the formation of toxic by-products is kinetically controlled.

## CHEMICAL KINETIC MODELLING

A series of Fortran-based computer codes known as CHEMKIN (version II) provided by the Combustion Research Facility of the Sandia National Laboratory [8] were used to perform the calculations presented here. The CHEMKIN library of computer codes is essentially a chemical species database and retrieval system which allows the user to perform an efficient kinetic analysis of the gas phase chemical reactions.

In this study calculations were performed over a range of temperatures between 700 to 1200 K at different levels of global equivalence ratio<sup>†</sup> ( $\phi_g$ ). In order to properly simulate the conditions of hot layers in typical enclosure fires, initial concentrations of gaseous species were taken from the experimental measurements reported by Morehart [10] of combustion products in the upper layers of natural gas fires in the so-called hood tests.

Due to difficulties associated with the modelling of the mixing behaviour and heat loss processes in hot layers, idealised cases corresponding to extreme conditions were studied. The real case would lie between these extreme conditions. Consequently, mixing within the hot layer was assumed to be either infinitely slow (plug-flow reactor "PFR" model) or infinitely fast (perfectly-stirred reactor "PSR" model). Similarly, the heat loss to or from the walls was assumed to be either zero (adiabatic condition) or such that the temperature of the hot layer remains constant (isothermal condition). The transient behaviour of each case for a chosen set of initial conditions was then calculated for a range of 0-20 sec. Modelling of PFR and PSR cases were performed using SENKIN [11] and PSR [12] programs of the CHEMKIN library of codes. Table 3 summarises the ranges of conditions over which calculations were performed.

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<sup>†</sup> Refers to the mass ratio of combustion products in the hot layer derived from the fuel divided by that introduced by air normalised by the stoichiometric fuel to air mass ratio [9].

**Table 3:** The summary of parameters and conditions used in the chemical kinetic modelling.

Parameter	Conditions
Temperature	700-1200 K in steps of 100 K
Equivalence ratio ( $\phi_g$ )	0.5-2 in steps of 0.25
Residence time	0-20 s
Mixing	Plug-flow reactor (infinitely slow) and perfectly stirred reactor (infinitely fast)
Heat transfer mechanism	Adiabatic and isothermal

Apart from  $\text{CF}_3\text{Br}$ , four other extinguishing agents ( $\text{CF}_3\text{H}$ ,  $\text{C}_2\text{F}_5\text{H}$ ,  $\text{C}_3\text{F}_7\text{H}$ ,  $\text{CF}_3\text{I}$ ) were studied and their characteristics were compared with those of  $\text{CF}_3\text{Br}$ . The initial concentrations of extinguishing agents, for all cases studied in this work, were set to their minimum design concentrations given in Table 2. This was done to improve the consistency of the numerical simulations and real enclosure fires.

Three reaction mechanisms were chosen for use in the modelling. The first two mechanism, provided to us by NIST [13], contain reactions involving species with C, H, N, Ar, O, F, Br and I atoms. These two mechanisms are quite suitable for modelling the reactions of  $\text{CF}_3\text{Br}$ ,  $\text{CF}_3\text{H}$ ,  $\text{C}_2\text{F}_5\text{H}$ ,  $\text{CF}_3\text{I}$  agents. However, they incorporate only  $\text{C}_1$  and  $\text{C}_2$  chemistry and therefore cannot be used for the modelling of  $\text{C}_3\text{F}_7\text{H}$ . For this purpose, a third reaction mechanism obtained from the literature [14], was employed. This mechanism is in fact a modified version of NIST mechanisms which also incorporates  $\text{C}_3$  chemistry. This model has been recently developed and needs more experimental validation. Table 4 gives a summary of the major features of the reaction mechanisms used in this study. More details about these three mechanisms including reaction rates and thermodynamic data can be found in the given references.

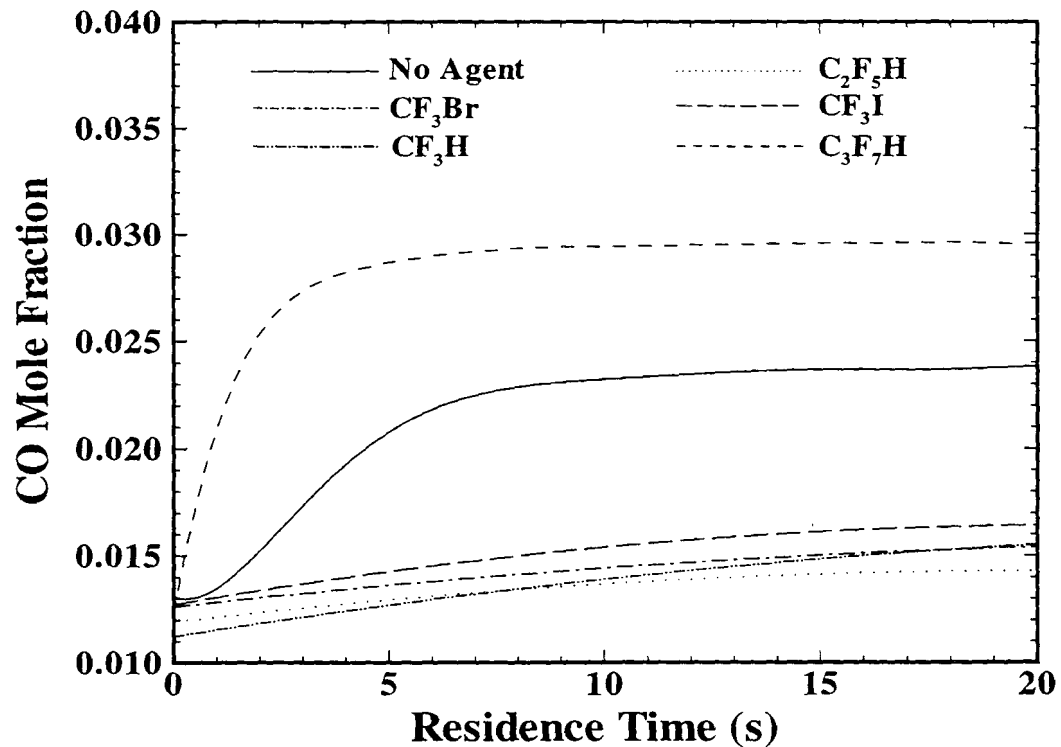
**Table 4:** Main features of the reaction mechanisms.

Mechanism	Source	Atoms considered	No. of species	No. of reactions	Agents Modelled
1	[13]	H/C/O/N/F/Ar/Br	70	595	$\text{CF}_3\text{Br}$ , $\text{CF}_3\text{H}$ , $\text{C}_2\text{F}_5\text{H}$
2	[13]	H/C/O/N/F/Ar/I	70	593	$\text{CF}_3\text{I}$
3	[14]	H/C/O/N/F	91	807	$\text{C}_3\text{F}_7\text{H}$

## RESULTS AND DISCUSSION

One of the principle aims of this investigation was to determine under what conditions toxic compounds (from extinguishing agents) are formed in a hot layer. We were also interested to make a comparison between the concentrations of toxic by-products generated from different agents under the same conditions. A discussion of the major findings for the detailed chemical kinetic calculations is presented in this section.

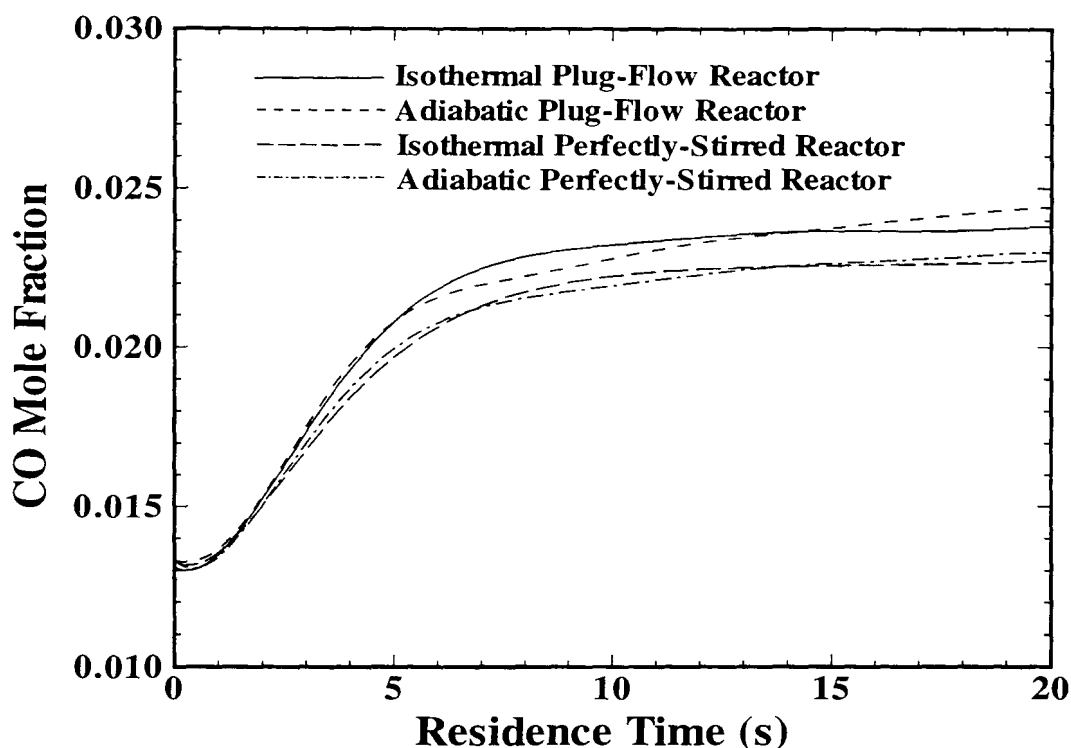
It has been well established [9, 15] that roughly two-thirds of all deaths resulting from enclosure fires can be attributed to the presence of CO. However, this may not be true for an enclosure fire under suppression. To investigate this hypothesis, the CO productions with and without extinguishing agents were compared to each other under a variety of conditions. Figure 1, which describes one of such comparisons, illustrates the calculated CO concentrations as a function of residence time for a rich ( $\phi_g = 1.5$ ) mixture of hood gases in an isothermal plug-flow reactor at a temperature of 900K. As this figure shows, except for  $C_3F_7H$ , other extinguishing agents reduce the level of CO production. This can be partly attributed to the diluent effects of the extinguishing agents which lower the CO mole fraction. However, there must be a chemical effect too. If this phenomenon was only due to the diluent effect, one would expect similar shapes for all cases illustrated in Figure 1. Therefore, in terms of the toxic combustion products, enclosure fires with and without suppression behave differently.



**Figure 1:** Calculated CO mole fraction as a function of residence time for different extinguishing agents in an isothermal plug-flow reactor at a temperature of 900 K and  $\phi_g = 1.5$ .

Figure 2 compares the calculated CO production resulting from the interaction between  $CF_3Br$  and hood gases ( $\phi_g = 1.5$ ) as a function of residence time assuming different mixing conditions and heat loss processes. For all sets of calculations shown in Figure 2, the initial temperatures were set to 900 K. While there are minor differences in the transient behaviour and the ultimate levels of CO produced, all four sets of curves are in good agreement, indicating that predictions are relatively insensitive to mixing conditions and heat loss processes. Therefore, even a simple isothermal plug-flow reactor (PFR) model is quite sufficient for modelling purposes. This is a reasonable conclusion since recent experimental studies [10] have shown that the concentrations of the gaseous species in hot layers of

enclosure fires are generally uniform especially for regions outside of the fire plume. On the basis of the above conclusion, in the present work, PFR model was used as the main modelling tool.

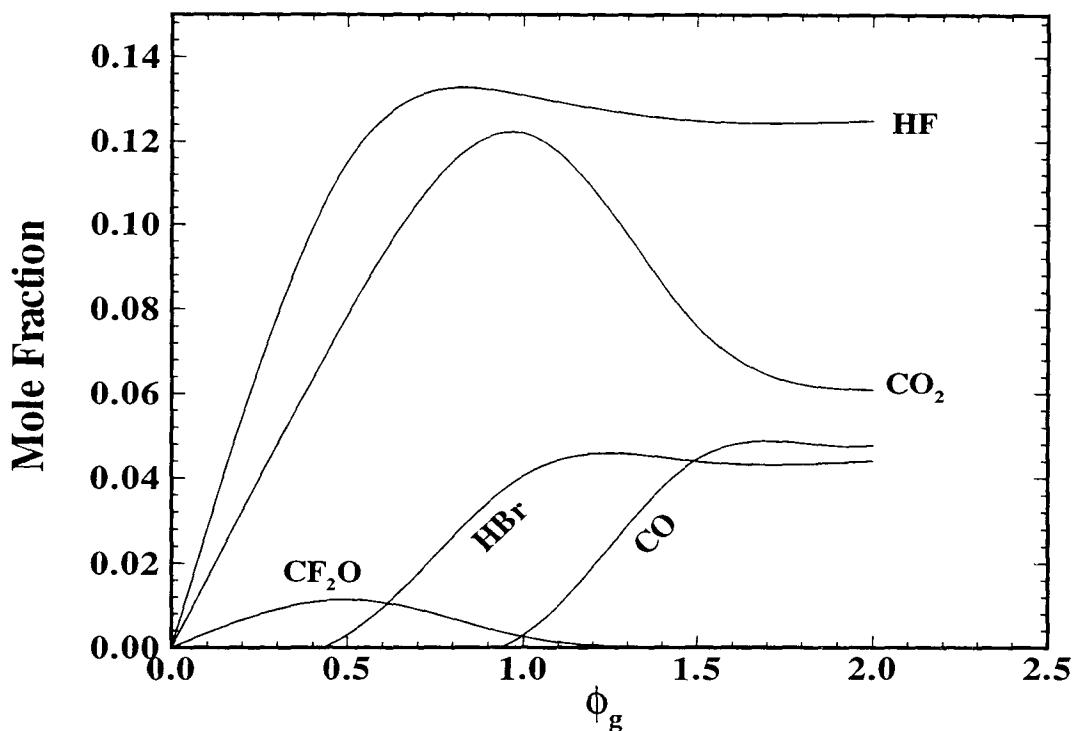


**Figure 2:** CO mole fraction as a function of residence time for different mixing conditions and heat transfer processes. For all calculations  $\text{CF}_3\text{Br}$  was used as the extinguishing agent.

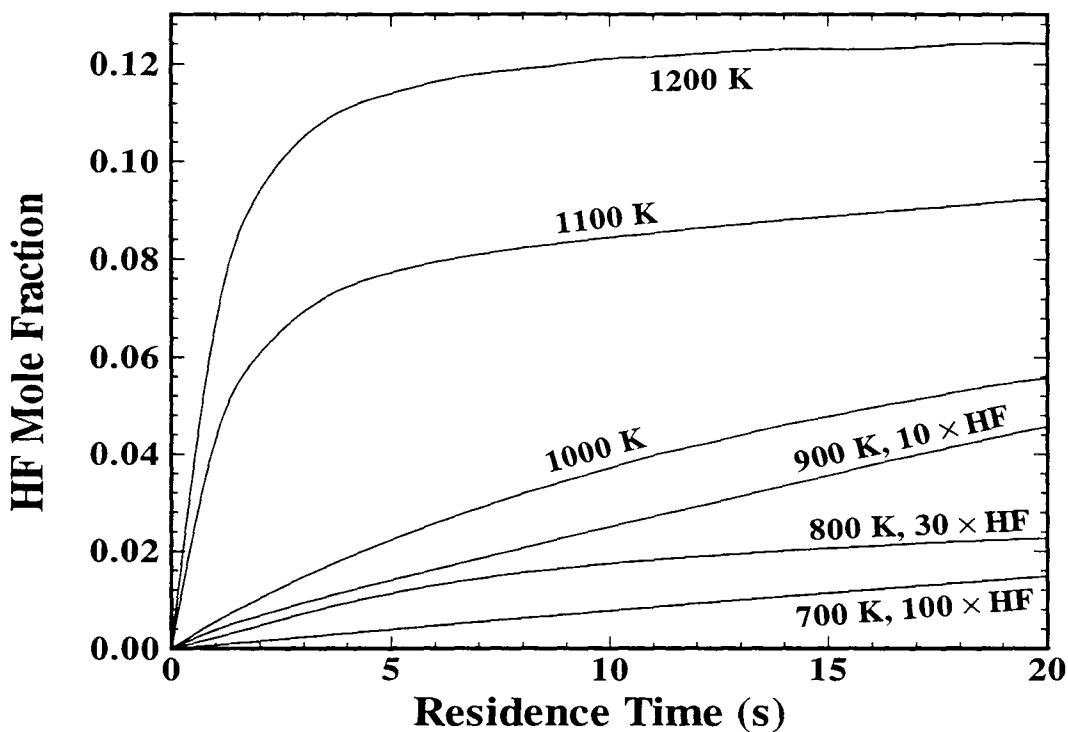
The concentrations of the major chemical species resulting from the decomposition of  $\text{CF}_3\text{Br}$  in a hot layer (1200 K) are plotted in Figure 3 as a function of the global equivalence ratio. It can be seen that for both lean ( $\phi_g < 1.0$ ) and rich ( $\phi_g \geq 1.0$ ) hot layer mixtures, the concentration of HF is much higher than those of other species and, hence, HF would be the major threat in an enclosure fire under suppression. On the contrary, the effect of  $\text{CF}_2\text{O}$  would be negligible because, as Figure 3 illustrates, in typical enclosure fires where  $1.2 \leq \phi_g \leq 2$   $\text{CF}_2\text{O}$  is almost non-existent. This may not be true for species like CO and HBr which their concentration become significant in the range of:  $1.2 \leq \phi_g \leq 2$  (see Figure 3).

Effect of the temperature on the formation of HF is shown in Figure 4 where HF mole fraction generated from the decomposition of  $\text{CF}_3\text{Br}$  in a rich ( $\phi_g = 2$ ) isothermal hot layer mixture, is plotted as a function residence time at different reactor temperatures ranging from 700 K to 1200K. As Figure 4 shows, at low temperatures the production of HF is insignificant. However, at temperatures above 1000 K, HF production is substantially higher. This can be explained in terms of the reaction rates which are functions of temperature. As a result, hot layer gases are unreactive for temperatures less than 700 K and become reactive for temperatures greater than 900 K. Typically for the lowest temperatures, very long residence times were required for complete reaction, while periods of less than 1 sec were quite sufficient for complete reaction at high temperatures like 1200 K. Although Figure 4 only considers  $\text{CF}_3\text{Br}$ , results of this study (not shown here due to space limitation) indicate that the

temperature has, more or less, a similar effect on other extinguishing agent. This is quite consistent with the recent findings of other researchers [5-7].



**Figure 3:** Concentration of major species, in a hot layer (1200 K) after the application of  $\text{CF}_3\text{Br}$ , as a function of global equivalence ratio.

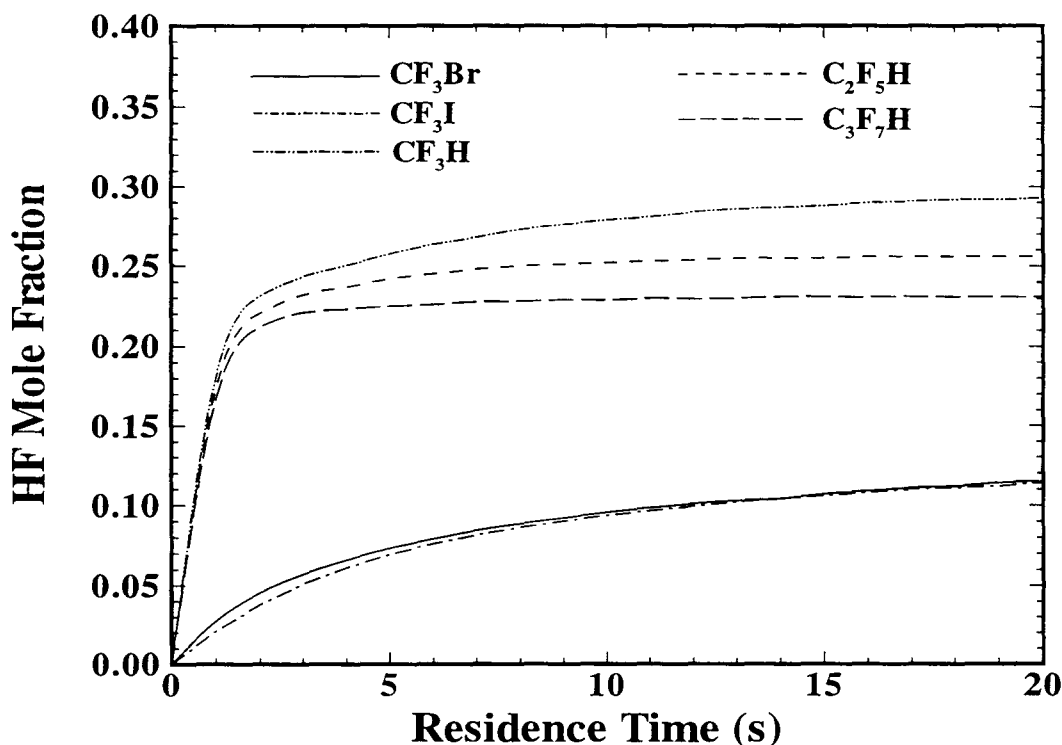


**Figure 4:** Mole fraction of HF as a function of residence time at different hot layer temperatures for  $\text{CF}_3\text{Br}$  in a rich ( $\phi_g = 2$ ) hot layer mixture.

Figures 5 and 6 show HF mole fractions as a function of residence time for high temperature ( $>1000$  K) decomposition of various extinguishing agents. All results presented in these two figures were calculated using the isothermal plug-flow reactor model with a reactor temperature of 1200 K. The equivalence ratio was set to the values of 0.5 and 2 for Figures 5 and 6, respectively. As both figures show, under high temperature conditions, the behaviour of  $\text{CF}_3\text{I}$  is almost identical to that of  $\text{CF}_3\text{Br}$ . However,  $\text{CF}_3\text{H}$ ,  $\text{C}_2\text{F}_5\text{H}$  and  $\text{C}_3\text{F}_7\text{H}$  produce much more HF in comparison with  $\text{CF}_3\text{Br}$ . Generally speaking, it seems that under high temperature conditions, HF production primarily depends on the initial concentration of the extinguishing agent.

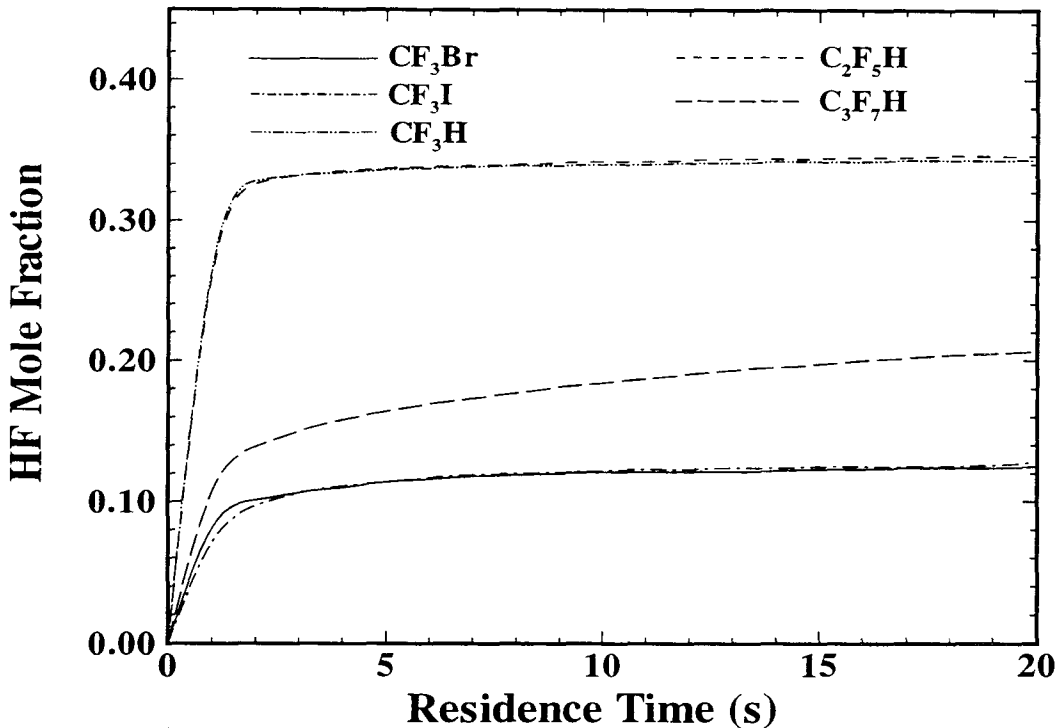
In the case of  $\text{CF}_3\text{H}$ , the ultimate HF mole fraction is roughly three times higher than the HF produced by  $\text{CF}_3\text{Br}$ . This is approximately equivalent to the minimum design concentration of  $\text{CF}_3\text{H}$  divided by that of  $\text{CF}_3\text{Br}$ . Therefore, both agents have similar HF production potential. If the minimum design concentration of  $\text{CF}_3\text{H}$  was equal to that of  $\text{CF}_3\text{Br}$ , one would expect similar HF yield from both  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{H}$ .

In the case of  $\text{C}_3\text{F}_7\text{H}$  there is no significant change between the high temperature production of HF under lean and rich mixture conditions (see Figures 5 and 6). For  $\text{C}_2\text{F}_5\text{H}$  however, HF production is very similar to that of  $\text{CF}_3\text{H}$  despite the fact that the minimum design concentration of  $\text{C}_2\text{F}_5\text{H}$  is about 33% less than that of  $\text{CF}_3\text{H}$ . This can be explained in terms of the reaction pathways available for production of HF from  $\text{C}_2\text{F}_5\text{H}$ . There are at least two direct (eqs 1 and 2) and one indirect (eqs 3 and 4) pathways from  $\text{C}_2\text{F}_5\text{H}$  to HF. The reaction rates of these pathways, particularly eqs 3 and 4, are very sensitive to the temperature. As a result, under high temperature conditions the contribution of the indirect pathway to

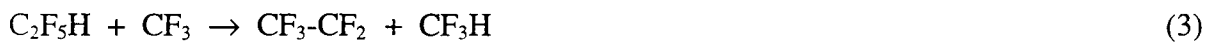


**Figure 5:** HF production resulting from the high temperature decomposition of various extinguishing agents as a function of residence time. All results shown in this figure were calculated at a temperature of 1200 K and  $\phi_g = 0.5$ .



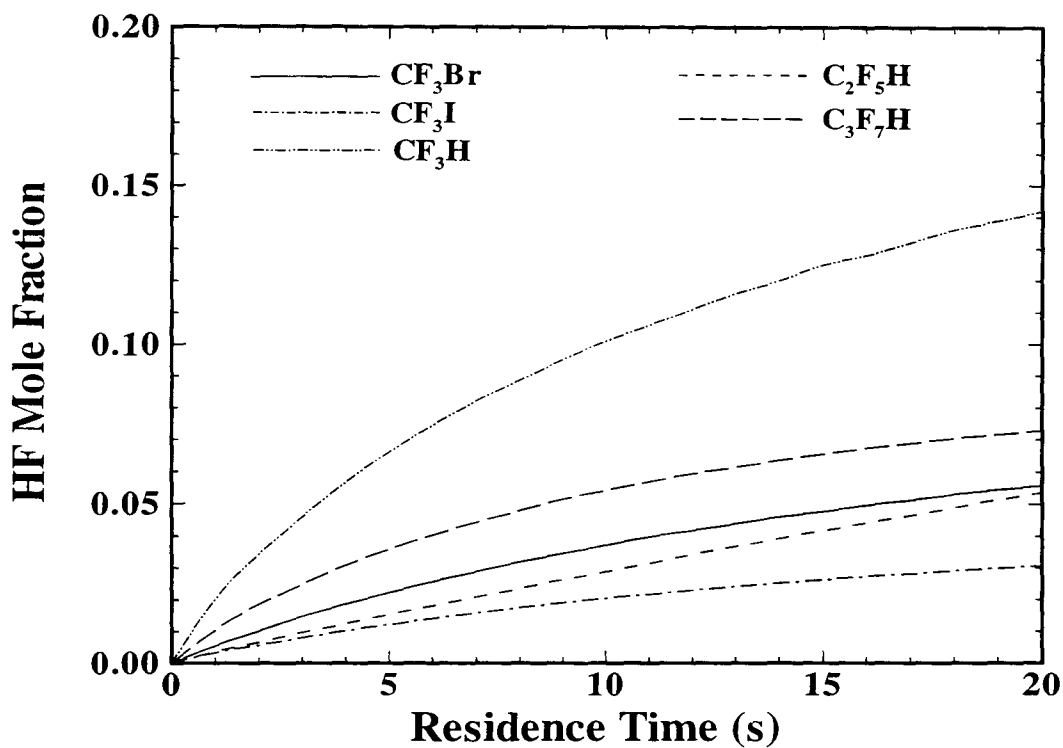


**Figure 6:** HF production resulting from the high temperature decomposition of various extinguishing agents as a function of residence time. All results shown in this figure were calculated at a temperature of 1200 K and  $\phi_g = 2$ .

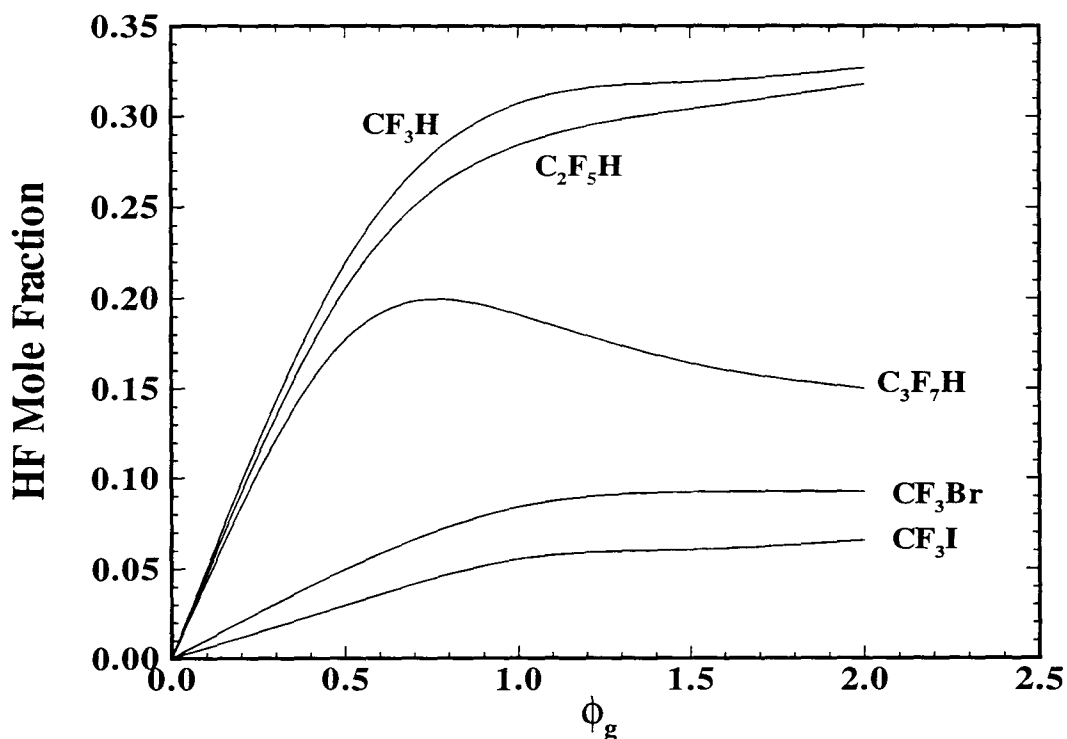


the overall HF production becomes quite significant. Since the indirect pathway primarily works through the decomposition of  $\text{C}_2\text{F}_5\text{H}$  to  $\text{CF}_3\text{H}$ , the total yield of HF from  $\text{C}_2\text{F}_5\text{H}$  becomes very similar to that produced by  $\text{CF}_3\text{H}$ . However, for low temperature conditions ( $\leq 1000$  K), the role of the indirect pathway becomes insignificant and consequently HF formation is dramatically decreased (see Figure 7).

Despite all differences, the set of results plotted in Figures 5 and 6 represents a similar trend leading to the following statement: regardless of the equivalence ratio, the halon alternative agents considered in this study can be ranked as  $\text{CF}_3\text{H} > \text{C}_2\text{F}_5\text{H} > \text{C}_3\text{F}_7\text{H} > \text{CF}_3\text{I}$  in terms of their potential for HF generation under high temperature conditions (1100-1300 K) associated with typical enclosure fires, (see Figure 8 as an example). It should be noted that, exactly the same ranking exists for agents minimum design concentration (see Table 2). Therefore, the above statement is of great practical importance since it highlights the relation between the minimum design concentration of the agent and its potential to form toxic by-products.



**Figure 7:** HF production resulting from the low temperature decomposition of various extinguishing agents as a function of residence time. All results shown in this figure were calculated at a temperature of 1000 K and  $\phi_g = 2$ .



**Figure 8:** HF production of various extinguishing agents as a function of  $\phi_g$ . All results shown in this figure were calculated at a temperature of 1100 K and 20 s residence time.

## CONCLUSIONS

Detailed chemical kinetic modelling techniques were employed to predict the formation of toxic by-products from the decomposition of halon alternative agents in enclosure fires under suppression. The calculated results for a variety of new extinguishing agents were used to study the conditions under which the toxic by-products are formed. The behaviour of new agents in suppressed fires, has also compared with those of  $\text{CF}_3\text{Br}$ . This study leads to the following conclusions:

1. the formation of major toxic by-products is kinetically controlled;
2. all agents, but  $\text{C}_3\text{F}_7\text{H}$ , tend to suppress the production of CO in hot layer;
3. hydrogen fluoride (HF) constitutes the bulk of toxic by-product in enclosure fires under suppression;
4. in a typical hot ceiling layer, the decomposition of extinguishing agents occurs at temperatures greater than 1100 K;
5. for new halon alternatives, the concentration of toxic by-products (particularly HF) generated from the interaction between hot ceiling layers and extinguishing agents, is primarily a function of minimum design concentration;
6. on the basis of HF production potential, the extinguishing agents studied in this work can be ranked in the following order:  $\text{CF}_3\text{H} > \text{C}_2\text{F}_5\text{H} > \text{C}_3\text{F}_7\text{H} > \text{CF}_3\text{I}$ .

## ACKNOWLEDGMENTS

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