Generalized Data Correlations for Extinguishment Times and Acid Concentrations in Fire Tests with Fluorinated Suppression Agents

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Abstract

Correlations have been developed to predict the extinguishment time and peak hydrofluoric acid concentration for fires suppressed with heptafluoropropane (FM-200), trifluoromethane (FE-13), and perfluorobutane (CEA-410), as well as bromotrifluoromethane (Halon 1301). The extinguishment time correlations are of the form $t_{ex} / t_d = f_i (Q^*, C / C_{cb})$ where t_{ex} is the extinguishment time, t_d is the discharge time, Q^* is a non-dimensional heat release rate defined in Equation **3,** C is the agent concentration, C_{cb} is the heptane cup burner concentration, and the index i designates the particular agent. The HF concentration correlations are of the form $[HF] = g_i (Q^*, C / C_{cb})$. All correlations have a calculated F-statistic which meets the 0.01 significance level.

Introduction

Fluorinated halon replacement agents have been undergoing extensive fire testing evaluation in the past few years. ***Primary*** observations/measurements in these tests have been the time-to-extinguishment and the concentration of HF developed. The objective of this paper is to develop generalized data correlations for these two parameters, using results from several test programs. Previous data correlations [1, 2, 3] show HF production to be a hnction of discharge time and the ratio of heat release rate to enclosure volume. This work further examines these relationships by incorporating new data and several other variables, such as oxygen and suppression agent concentrations, as well as investigating correlations for extinguishing times.

Fire Tests Included in Data Correlations

Five test programs, as summarized in Table 1, are utilized in the data correlations for the extinguishment time and hydrofluoric acid production. These include *2* large-scale, 2 intermediate-scale, and one laboratory-scale test enclosures. Most of the fires were pool fires, but assorted other fires were also run as indicated. Multiple fires occurred in some tests. HF was measured with Fourier Transform Infrared Spectroscopy instruments in some tests [1, 3, 4], grab samples analyzed by ion chromatography in others [4, 6], and ion specific electrode methods in still others [3].

Table 1 Description of Test Programs

Test Facility & Sponsor	Enclosure Size (m^3)	Fire Size (kW)	Fuels (Fire)	Agents	Ref
Ex-USS Shadwell (U.S. Navy)	136	250 - 7000	Heptane (pool and spray), F-76 Diesel (pool), Cable, Wood	FM-200, FE-13, Halon 1301	4, 5
Mayo Lykes (U.S. Coast Guard)	526	500 - 5000	Heptane (pool and spray), Diesel (pool),	FM-200, FE-13, CEA-410, NAF-SIII, Halon 1301	1, 2
CBD (U.S. Navy)	56	500 - 3500	Heptane (pool)	FM-200, FE-13, CEA-410, Halon 1301	6
HAI enclosure (NASA)	29	25 - 250	Heptane (pool)	FM-200, FE-13, CEA-410	3
HAI enclosure (NASA)	1.2	0.79 - 4.0	Heptane (pool)	FM-200, FE-13, CEA-410, Halon 1301	3

Sorting of Data Points

The extinguishment data have been grouped in two ways for each test: individually, and as a unit. The individual fire test correlations include a separate extinguishment time for each fire in a particular test. Unit data correlations contain only one extinguishment time for each test. In any test where more than one fire was burning, the unit data extinguishment time represents the time that the last fire was extinguished. Acid analysis was done on a unit basis only. The peak HF measurement was taken for each test.

Since spray fires were extinguished much sooner than pool fires in most tests, the extinguishment time graphs are based on the pool fire data. In the HF graphs, one data point was discarded from the two-dimensional graphs due to an unusually low agent concentration below the cup burner concentration.

In order to make the analysis more complete, several oxygen concentrations have been estimated. The CBD test series reported oxygen data for two tests, one for the 500 kW fire scenario and one for the 3500 kW fire scenario. Therefore, all 500 kW fire scenarios were assumed to have an oxygen concentration of 18 percent, at the time of agent discharge, and all 3500 kW fire scenarios were assumed to have an oxygen concentration of 15 percent at that time. The NASA tests failed to report the oxygen concentration at the time of discharge. The estimations were based on the data available for similar fire scenarios, with the Same ratio of heat release rate to enclosure volume, and free bum time

Statistical Analysis of Data

The data are presented in both two-dimensional and three-dimensional graphs. Linear, second-order polynomial, logarithmic, exponential, and power function curve fits were tried for the two-dimensional graphs.

The two-dimensional graphs were also used to find a possible correlation between three variables. This was done in two steps. First, the best fits were found for each of the two independent variables. Then the two independent variables were multiplied together in the form of their best fit. The non-dimensional extinguishment time was plotted and curve fit against this new independent variable.

TableCurve 3D® Automated Surface Fitting Software **[7]** has been used to study the effects of two independent variables with three-dimensional graphs. Different fits were tried in the Tablecurve graphs including polynomial up to fourth order (because higher order polynomials produced unrealistically large numbers of maxima and minima), logarithmic, exponential, power, robust plane, and Gaussian functions. The points in the three-dimensional plots are connected to the surface fit by drop lines, as shown in Figure 1. The drop lines represent the difference between the height of the data point, and the height of the surface fit. Therefore, the length of the line represents the magnitude of the residual.

The goodness of fit for the correlations were **ranked** by the coefficient of determination, r^2 (or R^2 in two-dimensional graphs), and the F-statistic. The coefficient of determination is defined as:

$$r^2 = 1 - \frac{\sum_{i=1}^{n} (\hat{z}_i - z_i)^2}{\sum_{i=1}^{n} (z_i - \bar{z})^2} \quad (1)$$

where z_i = the dependent variable data value for a given (set *of)* dependent variable,

$\hat{z}_i$ = the estimated dependent variable value, and

$\bar{z}$ = the mean of the dependent variable data values

The F-statistic is defined as [7, 8]:

$$F = \frac{n - t - 1}{t} \frac{r^2}{1 - r^2} \quad (2)$$

where n = the number of data points used in the fit, and

t = the number of parameters in the fitting function excluding constant terms.

The reasonable fit with the highest F-statistic was selected to represent the data, because the higher the F-statistic value, the better a given equation models the data. The F-statistic is preferable to r^2 because r^2 can increase with increasing parameter count, t, without necessarily increasing the statistical significance level, α, which can be determined directly from the F-statistic. Frequently used standards are $\alpha = 0.05$ and $\alpha = 0.01$. If the calculated F value is equal to or greater than the significant F value at the accepted significance level, then the null hypothesis; i.e. the possibility that the data are not correlated, is rejected. Thus, a significance level of 0.01 indicates we can be 99 % certain that variations of the dependent variable are associated with variations in the independent variable. To determine the best fit when comparing graphs with differing sample populations (i.e. two-dimensional versus three-dimensional fits), the F-statistic is normalized to the F-statistic value significant to the 0.01 significance level for the respective number of points.

Dimensional Analysis

Dimensional analysis has been used to reduce the number of experimental variables which affect the extinguishment time and hydrofluoric acid production. For instance, the extinguishment time has been found to be dependent on discharge time, agent concentration, and fire size [1, 2, 6, 9, 10, 11]. Therefore, the extinguishment time may be scaled to discharge time, t_{ex} / t_d, to eliminate the need of incorporating the discharge time variable elsewhere, Non-dimensionalizing the variables also allows a direct comparison between agents with different characteristics. The agent concentration required for extinguishment varies widely among agents. Scaling the agent concentration to the agent cup burner concentration, C / C_{cb} allows for a direct comparison.

In an effort to generalize the heat release rate to enclosure volume ratio parameter, used in previous correlations [1, 2, 3], the heat release rate was normalized. The normalization is the ratio of total combustion energy released at the completion of discharge, to the combustion energy available in the compartment at the beginning of discharge. The non-dimensional heat release rate, Q^*, takes on the form:

$$Q^* = \frac{Q(t_d + t_{fb})}{V\ \Delta H_{c,o}\ n'''[O_2]MW_{ox}} \tag{3}$$

where Q = heat release rate (kW),
t_d = discharge time (sec),
t_{fb} = freeburn or prebum time (sec),
V = enclosure volume (m^3),
$\Delta H_{c,o}$ = heat of combustion per gram oxygen (heptane = 12.68kJ / g O_2),
n''' = moles of *air* per unit volume,
$[O_2]$ = oxygen concentration at time of discharge, and
MW_{ox} = molecular weight of oxygen (32 g / mole O_2).

The moles of *air* per unit volume was found with the ideal gas law assuming a compartment temperature of 100°C and a pressure of 1 atm at the time of discharge, as suggested by representative test data.

Several other formulations for non-dimensional heat release rate were utilized as described in the Master's Thesis by Heyworth[12]. However, overall results were no better than those obtained with **Q'.**

Extinguishment Time Correlations

The best extinguishment time curve fits incorporated both the non-dimensional agent concentration and the non-dimensional heat release rate. Results can be expressed as $t_{ex} / t_d = f_i(Q^*, C / C_{cb})$, and are shown in Table 2. Three dimensional surface fits provided the highest normalized F-statistic in all cases. Figures **1-4** illustrate the fits for FM-200 data, FE-13 data, CEA-410 data, and Halon 1301 data, respectively.

One general correlation for the three replacement agents **is** shown in Figure **5**. The general correlation is:

$$\frac{t_{ex}}{t_d} = 0.78 + \exp\left[-0.5\left(\left(\frac{\ln\left(\frac{C/C_{cb}}{0.50}\right)}{0.39}\right)^2 + \left(\frac{Q^* - 0.06}{0.02}\right)^2\right)\right] \tag{4}$$

with an r^2 value of 0.78 and an $F/F_{0.01}$ ratio of **14.2.** Comparing the $F/F_{0.01}$ ratios, Equation 4 **is** at least as significant as the individual correlations in Table 2 for all three agents. Furthermore, it emphasizes the peak at $0.05 < Q^* < 0.15$. The peak, **is** particularly pronounced at low agent concentrations because of the large t_{ex}/t_d values at agent concentrations close to the cup burner concentration.

Table 2 Results of Extinguishment Correlations

Agent	$f_i(Q^*, C/C_{cb})$	r^2 (n)	$F/F_{0.01}$
FM-200	$0.74+2.54\exp^{[-0.5(sq(\ln(C/Ccb)/0.24) + (sq(Q^*-0.06)/0.032))]}$ for $1.06 < C/C_{cb} < 1.64$ and $0.005 < Q^* < 0.61$	0.69 (39)	4.05
FE-13	$3.26 - 18.6(\ln(C/C_{cb})/(C/C_{cb})^2) - 1.87(Q^*)^{0.5}\ln Q^*$ for $0.96 < C/C_{cb} < 1.74$ and $0.005 < Q^* < 0.63$	0.79 (26)	7.46
CEA-410	$-3.91 + (0.69/\ln(C/C_{cb})) - 1242(Q^*)^2 - 358(Q^*/\ln Q^*)$ for $1.10 < C/C_{cb} < 1.46$ and $0.02 < Q^* < 0.16$	0.98 (9)	7.84
Halon 1301	$0.37 + \exp[0.14((C/C_{cb})/\ln(C/C_{cb})) - 2.21(Q^*)^{0.5}\ln Q^*]$ for $1.19 < C/C_{cb} < 1.84$ and $0.005 < Q^* < 0.55$	0.90 (12)	5.34

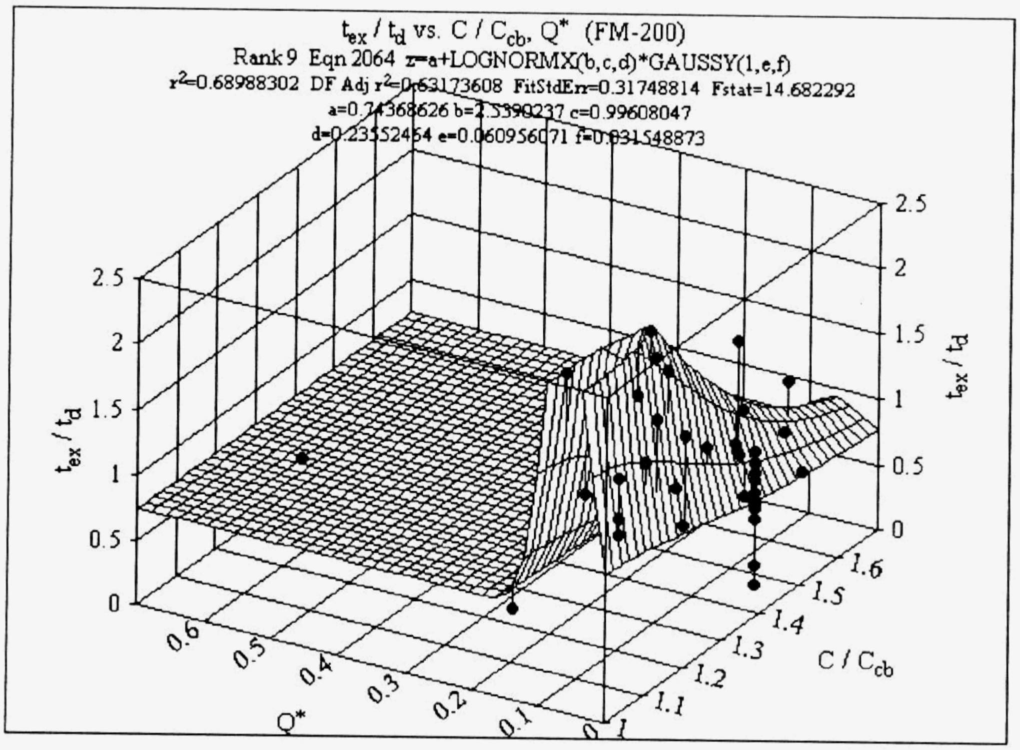

Figure 1 Effect of Non-Dimensional Agent Concentration and Non-Dimensional Heat Release Rate on Non-Dimensional Extinguishment Time for Fires Suppressed by FM-200

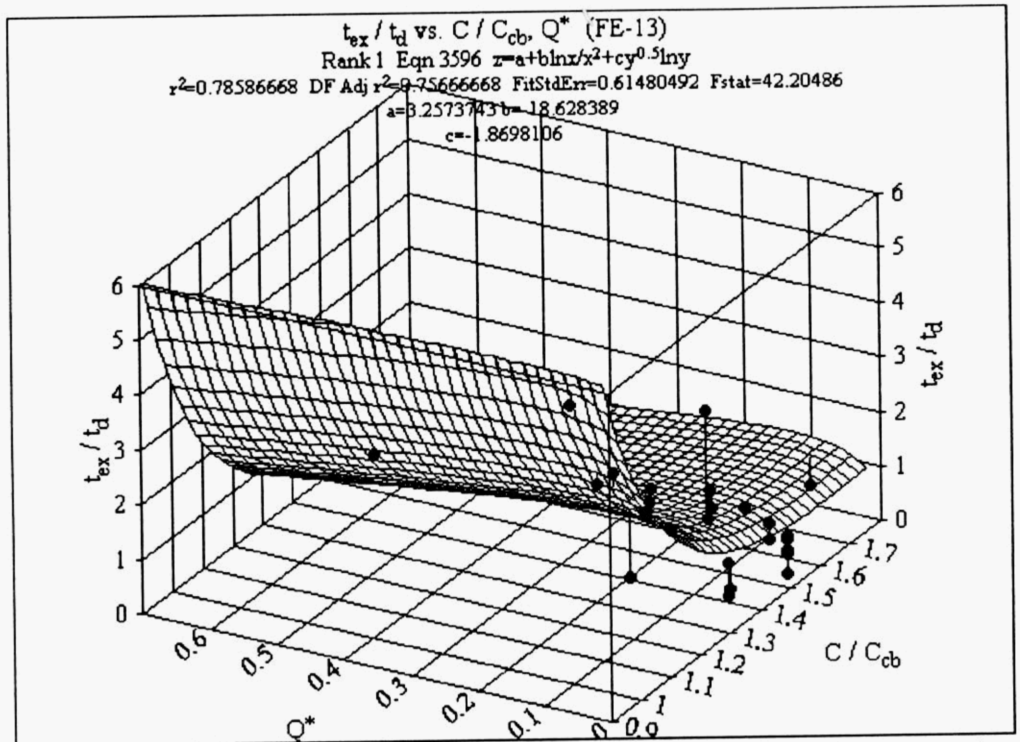

Figure 2 Effect of Non-Dimensional Agent Concentration and Non-Dimensional Heat Release Rate on Non-Dimensional Extinguishment Time for Fires Suppressed by FE-13

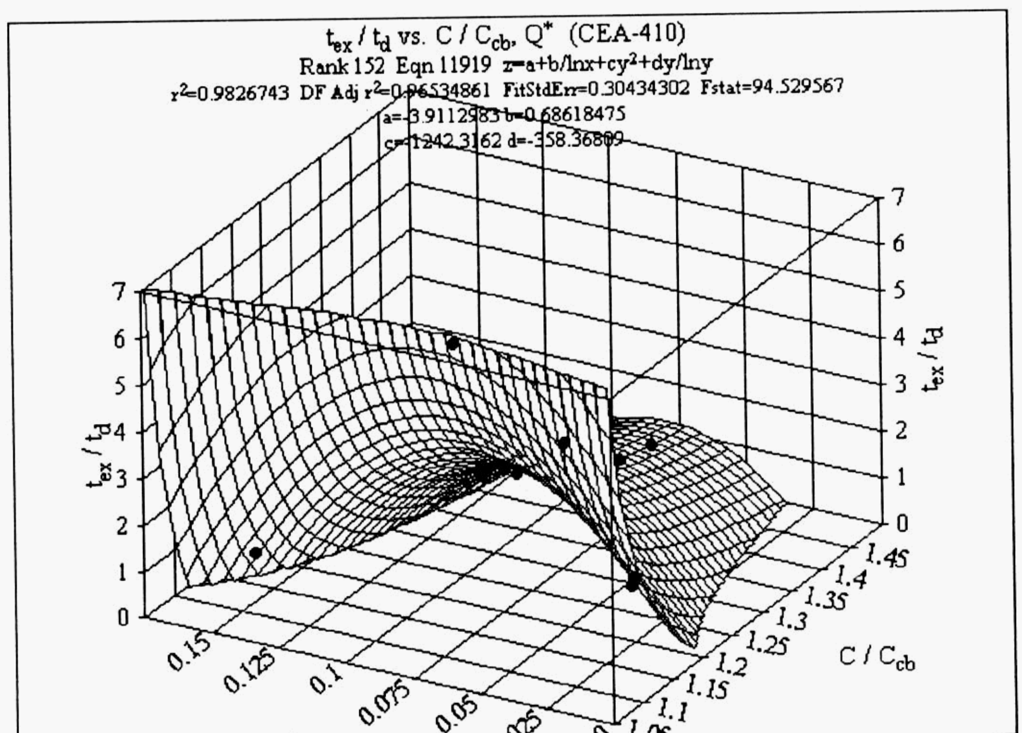

Figure 3 Effect of Non-Dimensional Agent Concentration and Non-Dimensional Heat Release Rate on Non-Dimensional Extinguishment Time for Fires Suppressed by CEA-410

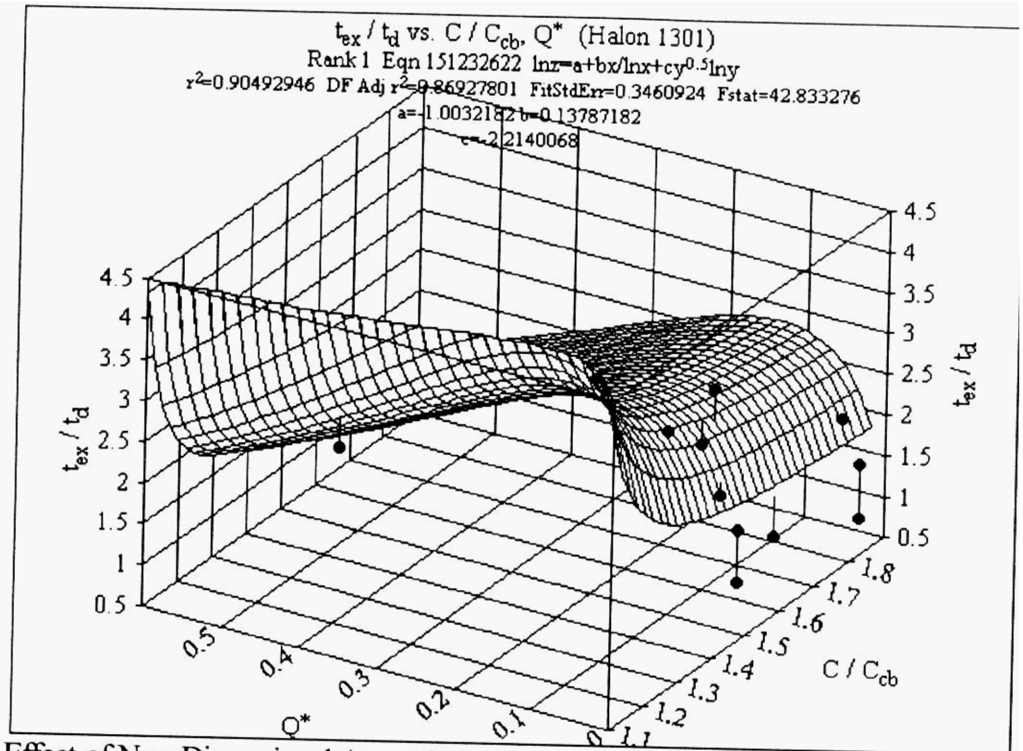

Figure 4 Effect of Non-Dimensional Agent Concentration and Non-Dimensional Heat Release Rate on Non-Dimensional Extinguishment Time for Fires Suppressed by Halon 1301

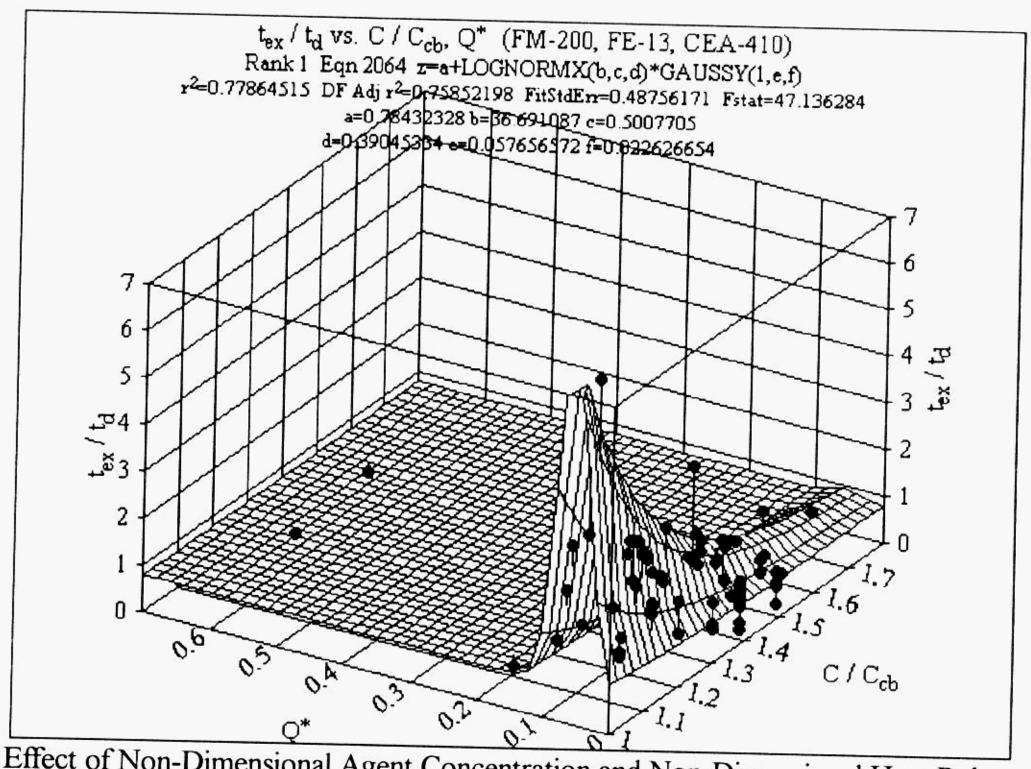

Figure 5 Effect of Non-Dimensional Agent Concentration and Non-Dimensional Heat Release Rate on Non-Dimensional Extinguishment Time for Fires Suppressed by FM-200, FE-13, and CEA-410

Acid Concentration Correlations

The best hydrofluoric acid concentration curve fits incorporated the non-dimensional heat release rate. FM-200 data and CEA-410 data produced an excellent correlation with the non-dimensional heat release rate by itself, but **FE-13** data and Halon 1301 data produced better results when incorporating the non-dimensional agent concentration as well. Results can be expressed as $[HF] = g_i\,(Q^*, C / C_{cb})$, and are shown in Table 3. The correlations for FM-200 data are shown in Figures *6* and **7.** The three-dimensional surface fit for FE-13 data, shown in Figure **8,** shows the high [HF] values generated with exceedingly low agent concentrations ($C / C_{cb} = 0.96$). Only one test in the entire data set had such a low agent concentration. CEA-410 data are plotted and curve fit in Figures 9 and 10 respectively. Halon 1301 data are shown in Figure 11.

Table **3** Results of Peak Hydrofluoric Acid Concentration Correlations

Agent	$g_i\,(Q^*, C / C_{cb})$	r^2 (n)	$F/F_{0.01}$
FM-200	$4.00 \times 10^4(Q^*) + 1249$ for $0.009 < Q^* < 0.61$	0.85 (25)	16.5
	$3.10 \times 10^4(Q^*)^{0.86}(C / C_{cb})^{0.86}$ for $0.009 < Q^* < 0.61$ and $1.06 < C / C_{cb} < 1.64$	0.81 (25)	12.4
FE-13	$5.42\mathrm{x}10^4 - e^{[(8.22\ln(C/C_{cb}) / (C/C_{cb})2)+0.135(\ln Q^*)2]}$ for $0.007 < Q^* < 0.63$ and $0.96 < C / C_{cb} < 1.74$	0.94 (21)	24.0
CEA-410	$2.23 \times 10^4(Q^*)^{0.73}$ for $0.007 < Q^* < 0.17$	0.84 (11)	4.47
	$1.46 \times 10^4(Q^*)^{0.60}(C / C_{cb})^{0.60}$ for $0.007 < Q^* < 0.17$ and $1.15 < C / C_{cb} < 1.46$	0.72 (11)	2.20
Halon 1301	$8.24 \times 10^3(Q^*)^{0.63}(C / C_{cb})^{0.63}$ for $0.007 < Q^* < 0.55$ and $1.19 < C / C_{cb} < 1.84$	0.96 (8)	9.68

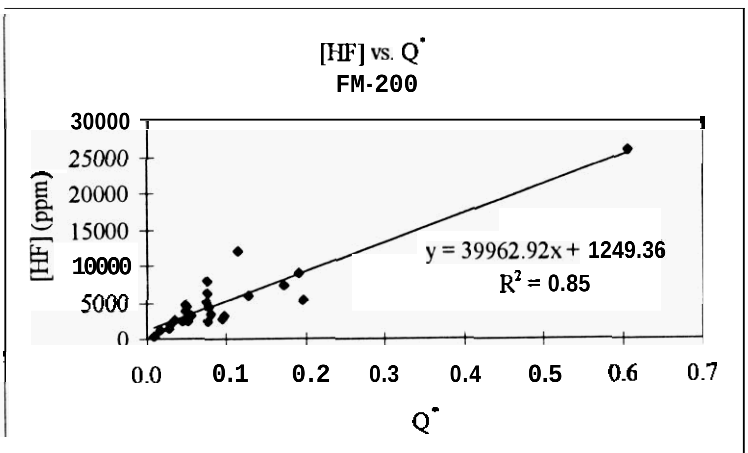

Figure *6* Effect of Non-Dimensional Heat Release Rate on **Peak** Hydrofluoric Acid Concentration for Fires Suppressed by FM-200

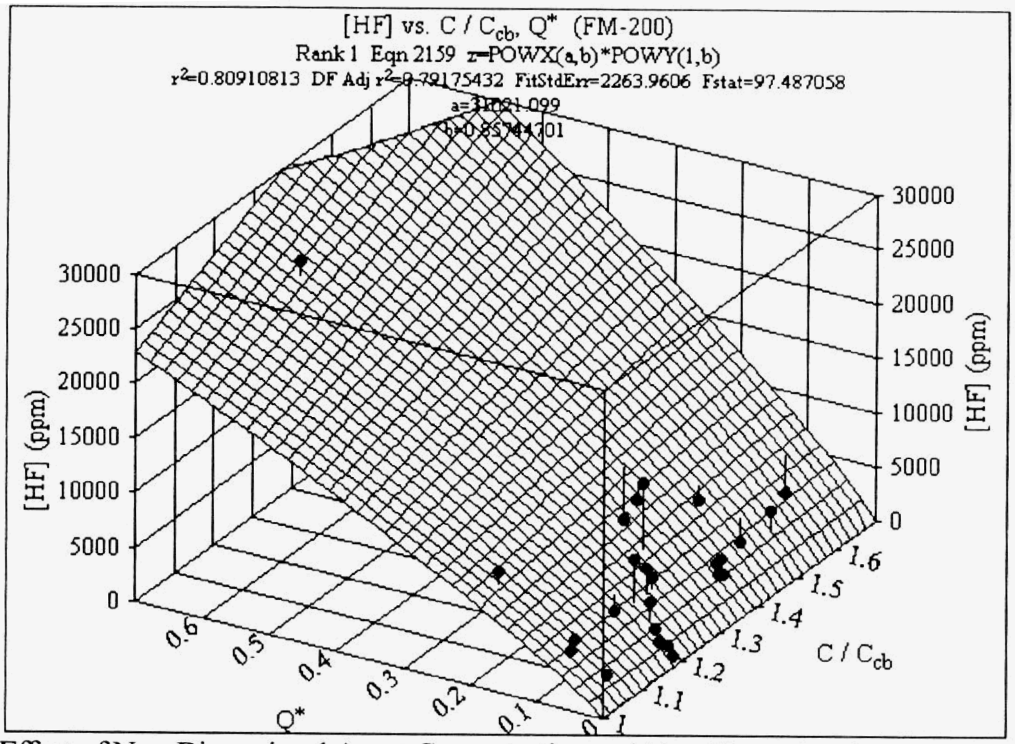

Figure 7 Effect of Non-Dimensional Agent Concentration and Non-Dimensional Heat Release Rate on Peak Hydrofluoric Acid Concentration for Fires Suppressed by FM-200

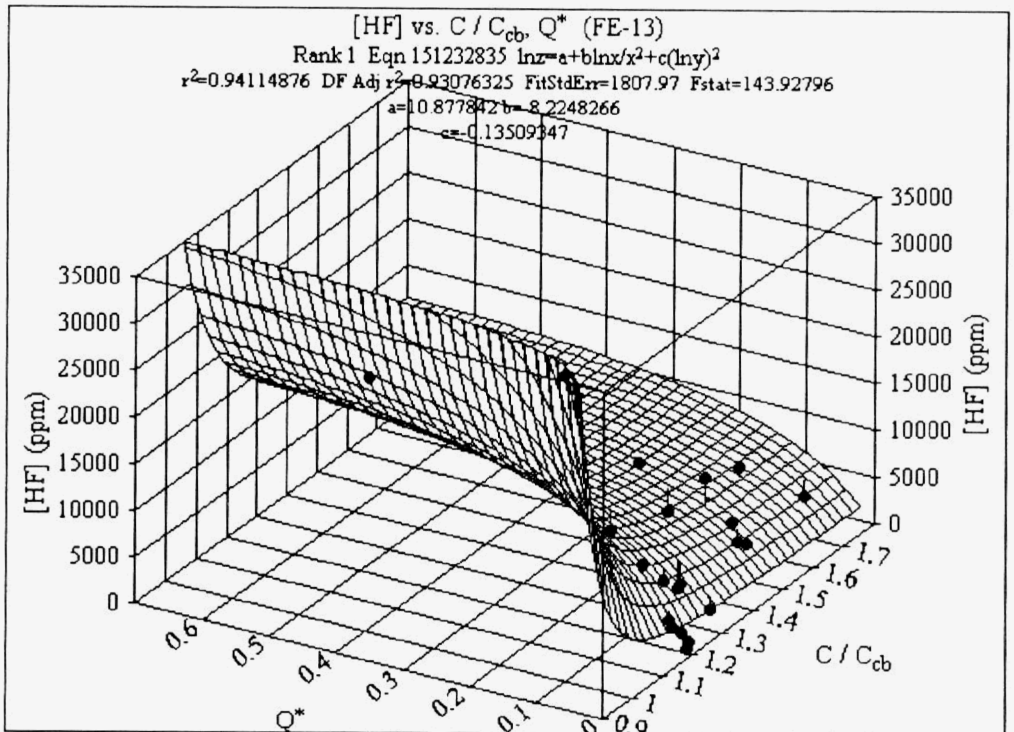

Figure 8 Effect of Non-Dimensional Agent Concentration and Non-Dimensional Heat Release Rate on Peak Hydrofluoric Acid Concentration for Fires Suppressed by FE-13

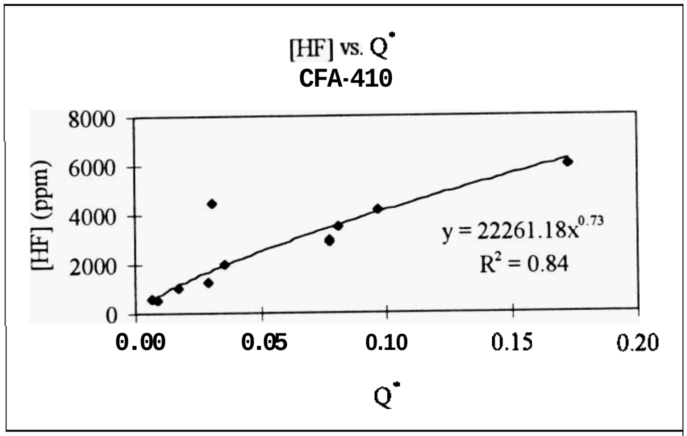

Figure 9 Effect of Non-Dimensional Heat Release Rate on Peak Hydrofluoric Acid Concentration for Fires Suppressed by CEA-410

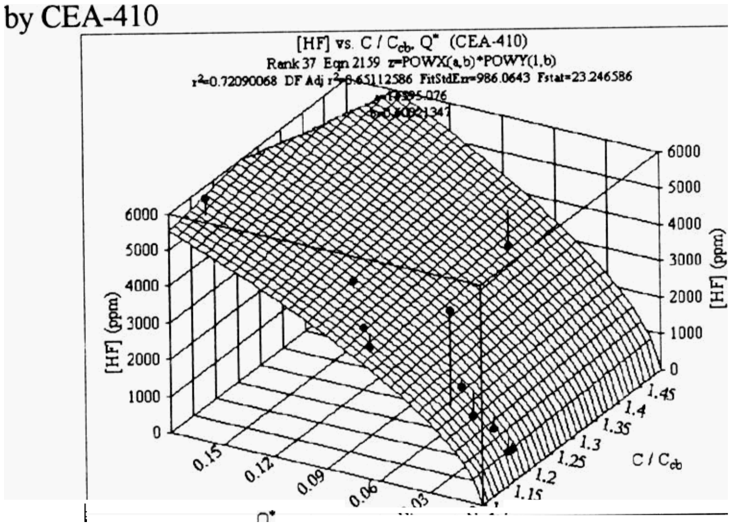

Figure 10 Effect of Non-Dimensional Agent Concentration and Non-Dimensional Heat Release Rate on Peak Hydrofluoric Acid Concentration for Fires Suppressed by CEA-410

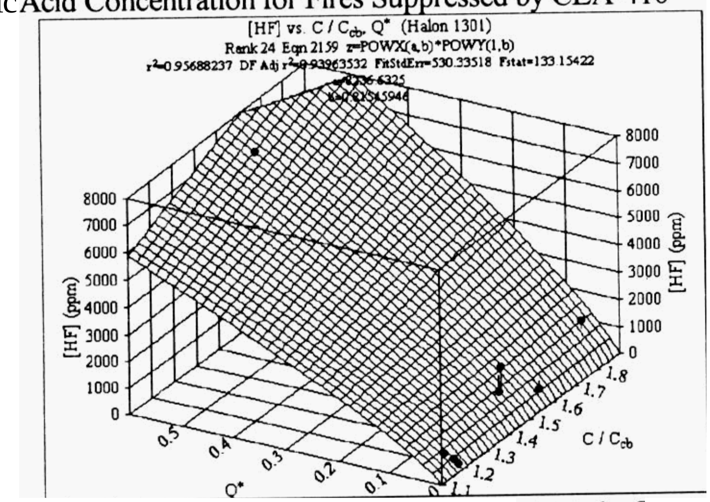

Figure 11 Effect of Non-Dimensional Heat Release Rate on Peak Hydrofluoric Acid Concentration for Fires Suppressed by Halon **1301**

For convenience, curve fits were tried for all replacement agent data combined. The curve fit, for all agents, which is a generalization of the previous correlations [1, 2, 3] in terms of Q / **V,** is simple and convenient. However, it does not account for the fact that, for a given value of Q', [HF] will increase in the order Halon 1301, CEA-410, FE-13, **FM-200,** as **shown** in Figure 12. The non-dimensional heat release rate curve fit is illustrated in Figure 12 along with those for the individual agent fits. The overall fit has a coefficient of determination of 0.79 and a normalized F-statistic of 28.5. The fitting function is shown as Equation **5**

$$[HF] = 2.72\times10^{4}\left(Q^{*}\right)^{0.74} \qquad (5)$$

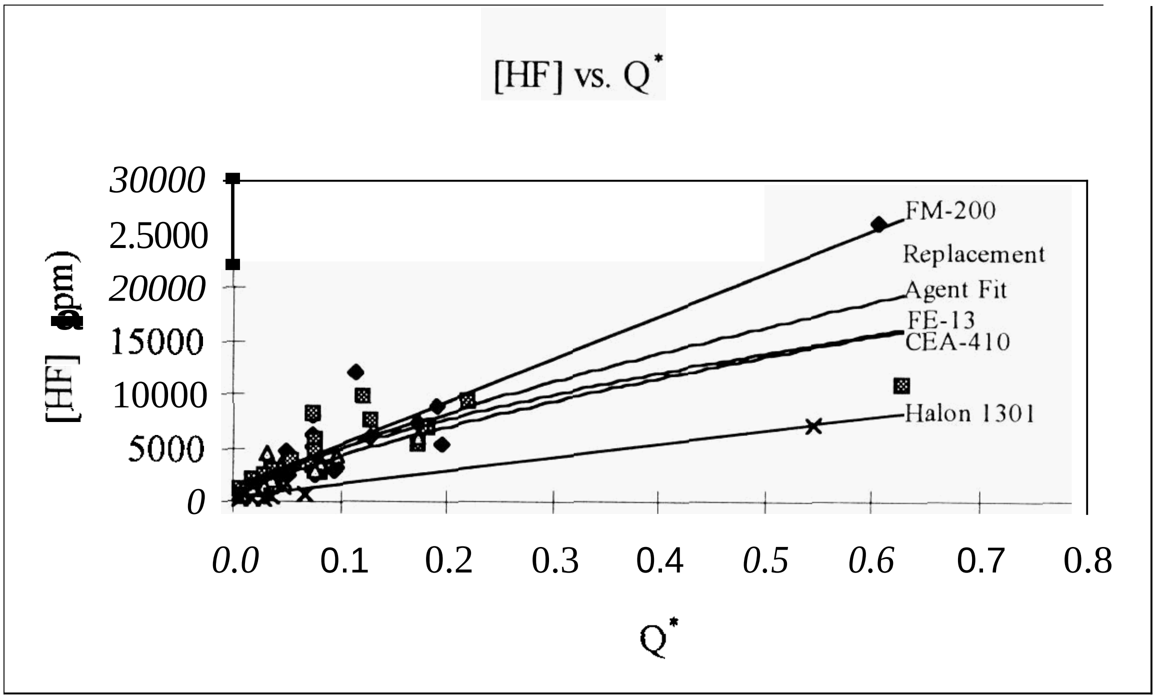

Figure 12 Effect of Non-Dimensional Heat Release Rate on Peak Hydrofluoric Acid Concentration for Fires Suppressed by FM-200, FE-13, and CEA-410

Conclusion

Correlations have been developed to predict the extinguishment time and hydrofluoric acid production for fires suppressed with clean agents. All correlations have a calculated F-statistic which meets or exceeds the 0.01 statistical significance level. Correlations are of the form $t_{ex} / t_d = f_i(Q^*, C / C_{cb})$ and $[HF] = g_i(Q^*, C / C_{cb})$. The correlations for t_{ex} / t_d show decreasing t_{ex} / t_d with increasing C / C_{cb}, and also show a maximum at **0.05** $< Q^* <$ 0.15. The hydrofluoric acid concentration curve fits, show [HF] being proportional to Q^{*n}, where $0.60 \le n \le 1.0$, depending on the agent. They show **FM-200** generating more **HF** than FE-13 and CEA-410, and much larger quantities than Halon 1301. The relatively high **[HF]** concentrations for **FM-200** are primarily due to **NRL** CBD fire tests with relatively **high** heat release rates per unit enclosure volume.

Hydrofluoric acid levels have been shown to decrease with an increase in agent concentration ***[6]*** for fires with the same heat release rate in similar environments. Figures **7,** 10, and 11 indicate a slight increase in the hydrofluoric acid concentration as the agent concentration is increased. However, the increase is very small compared to the effect of Q' on [HF] concentration.

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