

**ASSESSMENT OF THE FIRE SUPPRESSION MECHANICS FOR
HFC-227ea COMBINED WITH NaHCO₃**

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ABSTRACT

Numerical and experimental studies have illustrated the principal suppression mechanisms for HFC-227ea combined with NaHCO₃ being due to chemical kinetics along with physical properties of high heat capacities and heats of vaporization by solid NaHCO₃ particles. Removal of hydrogen fluoride gases produced from the thermal decomposition of HFC-227ea was investigated and determined to be primarily caused by reduction in HFC-227ea concentrations when HFC-227ea is blended with NaHCO₃.

1. INTRODUCTION

Environmental concerns related to the destruction of stratospheric ozone have initiated the phasing out of the ubiquitous fire-fighting agent Halon 1301 (CF₃Br) from the U.S. Army inventory. The loss of this superior fire-fighting chemical resulted in a U.S. Army test and evaluation program between the U.S. Army Tank-automotive and Armaments Command (TACOM) and the U.S. Army Aberdeen Test Center (ATC) [1]. The replacement program was designed to evaluate potential replacement agents and systems for Halon 1301 combat vehicle fire extinguishers. The results of this extensive program determined that for unoccupied spaces, such as an engine compartment, HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane) is an effective agent capable of replacing the Halon 1301. For occupied spaces, such as the crew compartment where fires must be suppressed in 250 ms or less to minimize crew exposure to extreme heat and toxic fumes, a mixture of HFC-227ea with NaHCO₃ or water with potassium acetate were determined to be viable Halon replacement candidates.

Automatic fire extinguishing systems (AFES) using Halon 1301 typically generate 5.0–7.0% volumetric concentrations to extinguish fire situations in occupied spaces. Substituting HFC-227ea combined with NaHCO₃ for Halon 1301 typically requires increasing the volumetric concentration of the HFC-227ea portion to 8.0–10%. The increased concentration requirement for HFC-227ea, while effective, becomes toxicologically concerning because the principal decomposition product of HFC-227ea, or any halocarbon suppressant for that matter, is hydrogen fluoride (HF). Toxicity studies on rats indicate that lethal HF concentrations after 1 hr exposure are 0.12% or 1200 ppm [2]. Thus a means for mitigating the developed HF levels from HFC-227ea decomposition in fire situations is needed, which is why HFC-227ea and NaHCO₃ are combined when employed as a Halon replacement agent in occupied spaces.

The HF mitigation pathway of combining (blending) NaHCO₃ with HFC-227ea, which has been thoroughly tested, is due to the ability of NaHCO₃ to act as a HF scavenger [3]. Initially it was believed that NaHCO₃ mitigated HF because it easily reacts with HF based on acid-base reactions in both gas-solid and gas-gas-phases creating the release of CO₂. However, it is well known that sodium-containing compounds are also highly effective flame inhibitors [4, 5, 6, 7, 8], and thus HF levels might be mitigated because the NaHCO₃ helps suppress the fire, which reduces HFC-227ea suppression concentrations and hence decreases HF production. Several studies have demonstrated NaHCO₃'s inhibition effectiveness with observations of decreased burning velocities relative to Halon 1301 by a factor of 10 to 20 in the range of small concentrations [8].

Even though HFC-227ea plus NaHCO₃ fire suppressions systems have demonstrated effectiveness under test and evaluation studies [1], the complete mechanism (i.e., governing chemistry and physics) behind this Halon alternative's effectiveness has never been mapped out. In this paper, the effectiveness of HFC-227ea with NaHCO₃ as a Halon replacement candidate will be described through numerical and experimental studies. Experimental characterizations of ground vehicle fire extinguishers releasing HFC-227ea or HFC-227ea with NaHCO₃ will also be discussed with respect to the physical characteristics and impact of HFC-227ea as it is released under operational

conditions. The numerical and experimental findings will then be used to evaluate test data from the Halon replacement program [1,3] to provide further insights to the observed results.

2. KINETIC MODEL CONSTRUCTION

The kinetic model for HFC-227ea was compiled using several kinetic submodels. For inhibition by HFC-227ea, the kinetics were adopted from the previous work of Williams et al. [9], which is based on two other kinetic models [10,11]. Flame inhibition by sodium species is believed to be due to chemical scavenging of major radical species (e.g., OH, H) in the flame [12]. The kinetic sub-model describing the effect of sodium species is based on the works of Williams and Fleming [13] and Zamansky et al. [14]. Thermochemical data for sodium-containing species were taken from Gurvich et al. [15]. Additional reactions with sodium-containing species along with the modification of rate constants were included based on recent kinetic data and analysis of possible reaction pathways. Only sodium reactions that effect the main species of the radical pool for methane combustion were considered in the mechanism construction. The considered reactions contained the sodium species: Na, NaO, NaOH, NaO₂, Na₂O, Na₂O₂, (NaOH)₂, and NaH. Additional block of reactions to describe reactions between sodium and fluorine, which primarily produce the species NaF and Na₂F₂, was included as well. Where needed, the kinetic parameters of reactions were estimated based on analogous reactions and thermochemistry. The overall HFC-227ea / NaHCO₃ gas-phase kinetic model contains 1075 reactions with 108 species.

2.1 NaHCO₃ FIRE CHEMISTRY

NaHCO₃ is a solid particle powder whose overall kinetics of decomposition are relatively well studied. The decomposition of NaHCO₃ was represented in the kinetic model by the overall chemical process [7, 16].



It should be noted that the use of an overall NaHCO₃ decomposition process in the kinetic model is valid for small sized particles (less than 10 to 20 microns), which will completely evaporate in the flame reaction zone. The decomposition process begins with sodium carbonate melting at 270 °C (543.15 K) and proceeding to form CO₂, H₂O, and Na₂CO₃(s). The second step, decomposition of Na₂CO₃(s), produces Na₂O and CO₂. The overall decomposition process is endothermic; enthalpy change is 135 kJ/mol and when above 400 K, the decomposition is very fast. The decomposition reaction rate demonstrates a first order dependence based on the amount of unreacted NaHCO₃ (A=1.43E11, 1/s; E=102kJ/mol; 373–473K [16]). The gas-phase suppression kinetics for NaHCO₃ can be represented by reactions forming NaOH, NaO and Na₂O species. In the presence of moisture NaHCO₃ hydrolysis also occurs, relatively fast, through the following two reactions



For the numerical simulations, the Chemkin software package (version 3.6) was used to simulate a premixed methane/air flame [17, 18]. The methane flame kinetics was taken from the kinetic model Grimech–3.0 [19]. Prior to suppression modeling of the premixed methane flame by HFC-227ea with NaHCO₃ using the constructed mechanism, comparison of modeling results for flame inhibition by only NaHCO₃ was conducted with known literature data. Figure 1 presents the results of comparing NaHCO₃ numerical simulations with experimental data obtained by Rosser et al. [4]. Rosser et al.'s experimental data represent measurements of premixed methane flame velocity reductions due to inhibition caused by the addition of NaHCO₃. The experimental data were obtained for 2.3-micron-sized NaHCO₃ particles.

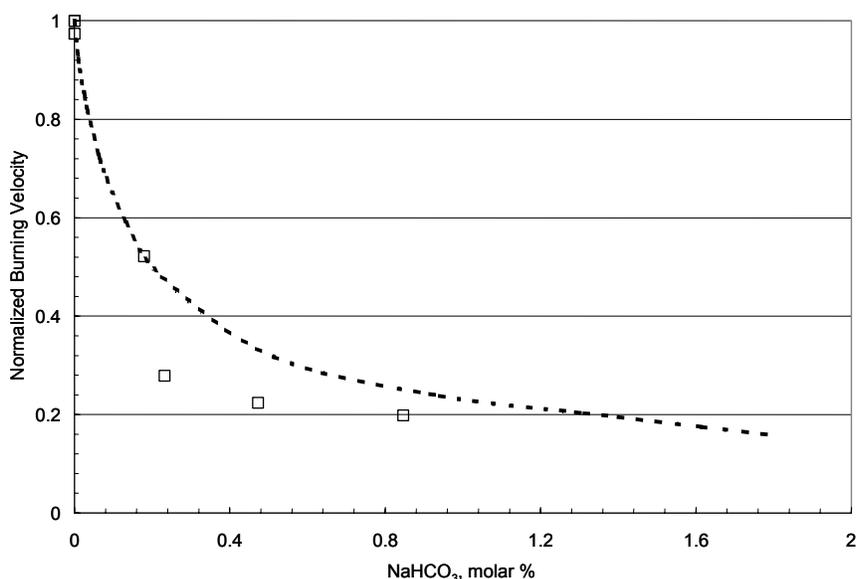
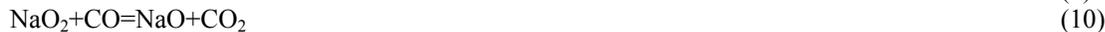


Figure 1. Premixed methane flame burning velocity reductions due to inhibition caused by the addition of NaHCO₃. The dashed line is computational data [9] and the (□) symbols are experimental data [4].

The comparisons between the numerical and experimental data were conducted on the basis of normalized flame velocity. For normalization purposes, flame speeds were obtained for the methane flame without suppression additives. It should be noted that the experimental flame velocity (in Figure 1) represents the linear speed of flame propagation along a 2-cm-diameter tube and the apparent velocity of flame propagation. The data in Figure 1 indicate reasonable agreement of modeling results with experimental measurements.

2.2 CHEMICAL CONSIDERATIONS FOR COMBINING HFC-227ea WITH NaHCO₃

The influence of the HFC-227ea / NaHCO₃ blends on flame suppression was determined by calculating the reductions in premixed methane flame burning velocities as a function of added suppressant concentrations. The suppression calculations were performed over a concentration range of 0–5% for HFC-227ea and NaHCO₃ respectively. Reaction pathway and sensitivity analysis demonstrate the primary sodium specie containing reactions are the following:



Decomposition of NaHCO₃ leads to the formation of catalytic recombination species: Na, NaOH and NaO. The foremost limiting reaction stage is the recombination reaction of sodium atom with hydroxyl leading to the formation of sodium hydroxide, which further reacts with hydrogen (i.e., scavenges) by way of



Williams and Fleming also note these two reactions as the primary radical scavenging reactions [13]. Note that the rate constants for the reaction 11 and 12 were assumed in accord with estimation of Jensen and Jones [12]. These reactions are also the main consumption pathways of sodium atoms along with the reactions



Calculations of the premixed methane flame inhibited by HFC-227ea demonstrate that the main reactions of pathways of HFC-227ea decomposition and H atom scavenging are



Calculations of different composition ratios of HFC-227ea with NaHCO₃ demonstrated that the main reaction between the two compounds is the formation of NaF, which is caused by the reaction of sodium atom with CF₂O in the flame reaction zone as



NaF is consumed in flame zone by its interaction with hydrogen atom



The rates of these reactions are comparable with the rates of



at concentration levels of 0.1% for NaHCO₃ and approximately 1.5% for HFC-227ea.

3. RESULTS

3.1 PREMIXED FLAME CALCULATIONS

The influence of HFC-227ea / NaHCO₃ blends on flame suppression was determined by calculating the reductions in premixed methane flame burning velocities as a function of added suppressant concentrations. Note that when burning velocities values are ≤ 5 cm/s typically indicates that premixed combustion has been suppressed. The suppression calculations were performed over a concentration range of 0 to 5% for HFC-227ea and NaHCO₃ combinations. Figure 2 presents profiles of the species Na, NaOH, NaF, NaHCO₃, as well as fluorine containing species HF, CF₂O, and HFC-227ea in the reaction zone of a premixed methane flame inhibited by 1.03% HFC-227ea and 0.081% NaHCO₃. The calculations indicate that free sodium reacts with CF₂O, which forces the sodium containing species to participate in reactions with fluorine containing species and form NaF. The formation of NaF decreases the overall concentration of sodium species available for catalytic radical recombination.

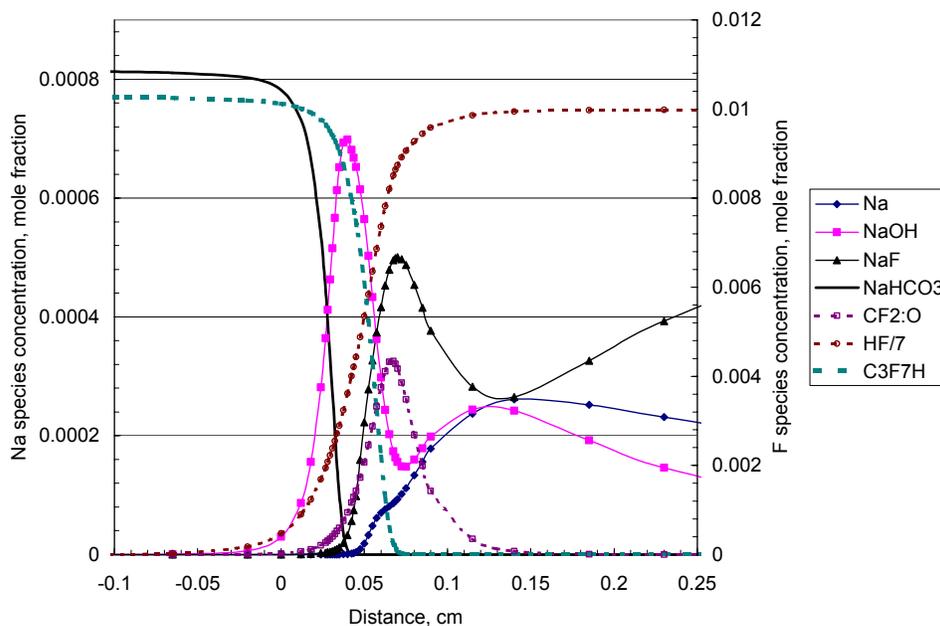


Figure 2. Profiles of HFC-227ea and NaHCO₃ and the primary Na and F products produced in the flame reaction zone. Note the HF concentration has been divided by 7 for graphical purposes.

Additional equilibrium calculations for a suppressant combination of 1% NaHCO₃ and 10% HFC-227ea demonstrate that once equilibrium NaF concentrations are achieved and no free sodium exists, the free fluorine become HF and CF₂O, which achieve toxic levels. Even though equilibrium conditions are not always achieved in actual fire extinguishing conditions, the calculations for the considered HFC-227ea / NaHCO₃ agent composition suggest that radical scavenging by Na atoms does not completely describe the suppression mechanism of NaHCO₃ when blended with HFC-227ea. Also, the likelihood of Na scavenging of HF species in the gas-phase is not supported.

Thus there are several suppression mechanisms responsible for the effectiveness of HFC-227ea plus NaHCO₃ when applied to a fire situation. The involved mechanisms include both HFC-227ea's and NaHCO₃'s chemical kinetics along with physical properties of high heat capacities and possibly heats of vaporization by solid NaHCO₃ particles and liquid HFC-227ea droplets. Figure 3 illustrates burning velocity reductions of a methane flame caused by the addition of HFC-227ea, NaHCO₃, or a blend of 10% HFC-227ea with 1.0% NaHCO₃ with either combined or independent chemistries. The reductions in burning velocities for NaHCO₃ and HFC-227ea added independently are much stronger for NaHCO₃ than HFC-227ea. When HFC-227ea is combined with NaHCO₃ but their chemistries are treated independently, the reduction in burning velocity is greater than HFC-227ea by itself but not as substantial as NaHCO₃ alone. Realistically, the two agents are not independent and their chemistries do mix, so when HFC-227ea is combined with NaHCO₃ and their chemical interactions are allowed to co-exist the reductions in burning velocities are again greater than HFC-227ea by itself but not as substantial as NaHCO₃ alone. However, the reductions in burning velocity (for combined chemistries of NaHCO₃ with HFC-227ea) are less effective than when the two agents were treated independently suggesting that a negative synergistic effect takes place when the two agents are chemically combined due primarily to the formation of NaF. Calculations for NaHCO₃ combined with HFC-227ea demonstrate that on average at suppression concentrations (Burning velocity ≤ 5 cm/s) 30% of the suppression is due to chemical kinetics while the other 70% can be attributed to physical effects.

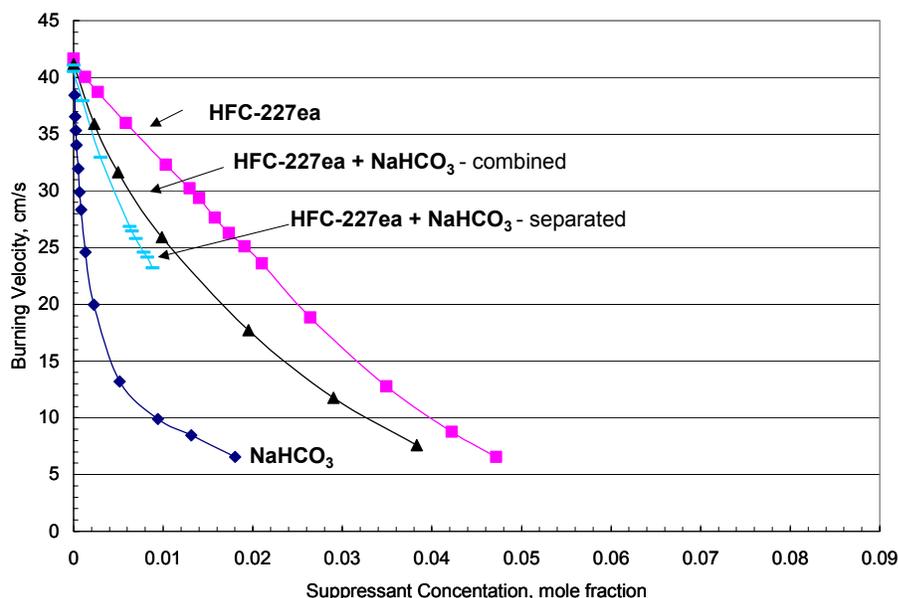


Figure 3. Burning velocity reductions in a premixed methane/air flame with HFC-227ea, NaHCO₃, or a blend of 10% HFC-227ea with 1.0% NaHCO₃ added.

Given these mechanistic results, the developed mechanism for HFC-227ea with NaHCO₃ has been applied to combustion computations and experiments to provide insight to previously obtained results.

4. RESULTS

4.1 PSR CALCULATIONS

The data in Figure 3 alone do not provide a complete understanding behind the effectiveness of blending HFC-227ea with NaHCO₃ in real fire situations. Thus, calculations have been performed for a perfectly stirred reactor (PSR) containing C₈H₁₈/air, HFC-227ea, or HFC-227ea combined with NaHCO₃. The PSR was operated for a residence time of 0.01 s with inlet reactant temperatures of 300 and 900 K (ambient and fire conditions). The PSR calculations are intended to illustrate the effect of adding NaHCO₃ to HFC-227ea with respect to the ultimate HFC-227ea concentration required to extinguish the combustion process in the reactor and the resultant total fluorine concentrations in the reactor (sum of the HF and CF₂O levels), see Figure 4. The results for the 300 K PSR in Figure 4 indicate that adding NaHCO₃ has no effect on the amount of HFC-227ea required to extinguish the reactor as well as the no significant reduction in total fluorine levels occur. The temperature decrease for the reactor at extinguishment was negligible as well (1427 vs. 1417 K). For the 900 K PSR case in Figure 4, the addition of NaHCO₃ decreases the required HFC-227ea by 19% (0.42 vs. 0.34 mole fraction), which in turn contributes to the total fluorine concentration reduction by 29% (0.11 vs. 0.075 mole fraction). It should be noted that a greater amount of HFC-227ea is required for extinguishment of the 900 K PSR because suppressant thermal decomposition losses are greater at elevated temperatures. The 900 K reactor temperature decrease was 31 K (1216 vs. 1185 K).

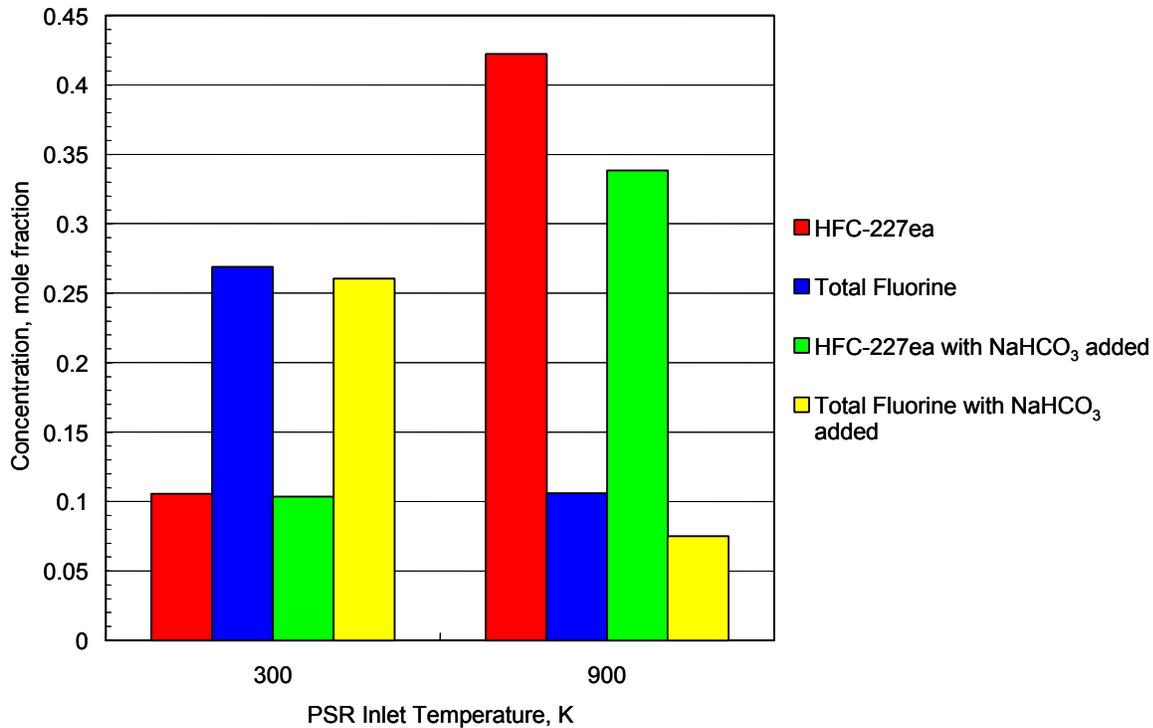


Figure 4. Computational calculations for two PSRs containing C₈H₁₈, air, HFC-227ea, or HFC-227ea combined with NaHCO₃. The PSR was operated for a residence time of 0.01 s at with inlet reactant temperatures of 300 and 900 K.

4.2 TEST AND EVALUATION DATA

The findings of the PSR calculations in Figure 4 support previous testing and evaluation data from the combat vehicle Halon 1301 replacement program [1]. Table 1 lists three testing scenarios that evaluated HFC-227ea and HFC-227ea plus NaHCO₃ agents in equivalent developmental fire extinguishing systems. The table data consists of three fire suppression performance metrics for assessing the capability of a given agent: average fire out times, average temperatures in the crew compartment area, the average total fluorine concentrations, and the calculated differences between the performance metrics for the two agents.

Table 1: Average data from three field scale testing scenarios that evaluated HFC-227ea and HFC-227ea plus NaHCO₃ systems for replacement of Halon 1301 in ground combat vehicles.

| | | HFC-227ea | HFC-227ea with NaHCO₃ | Delta |
|---------------|---|------------------|---|--------------|
| Test 1 | (12 lb HFC-227ea vs. 12 lb HFC-227ea +0.3 lb NaHCO ₃) | | | |
| | Fire Out Time, ms | 708.6 | 173.3 | 535.2 |
| | Temperature, K | 818.1 | 783.8 | 34.2 |
| | Fluorine Concentrations, ppm-30sec | 2482 | NA | NA |
| Test 2 | (12 lb HFC-227ea vs. 12 lb HFC-227ea +0.6 lb NaHCO ₃) | | | |
| | Fire Out Time, ms | 143 | 117.8 | 25.1 |
| | Temperature, K | 327.7 | 305.0 | 22.7 |
| | Fluorine Concentrations, ppm-30sec | 779.5 | 264.2 | 515.2 |
| Test 3 | (12 lb HFC-227ea vs. 12 lb HFC-227ea +1.2 lb NaHCO ₃) | | | |
| | Fire Out Time, ms | 179.1 | 165.2 | 13.8 |
| | Temperature, K | 391.6 | 334.4 | 57.2 |
| | Fluorine Concentrations, ppm-30sec | 895.3 | 407.8 | 487.4 |

The data presented in Table 1, while not evaluated statistically, demonstrate that the addition of NaHCO₃ to HFC-227ea acts to decrease the average fire out times and averaged temperatures. Interestingly, the average crew compartment temperature reduction for all three tests was 38 K, which is close to the temperature reduction observed previously for the 900 K PSR calculations (31 K). The most dramatic performance metric reduction occurs for the total fluorine levels, which appear to be at least 50% lower when NaHCO₃ is added. As demonstrated in the PSR calculations, the addition of NaHCO₃ to the extinguishing concentration of HFC-227ea reduces HF levels by only 29% due to reduced HFC-227ea loads, so the overall decrease in total fluorine levels observed in the three tests, Table 1, must be attributed to additional interactions of NaHCO₃ with the fire, i.e., gas-solid phase scavenging interactions. That is, in the actual suppression of fires, excess suppressant exists, and after/during suppression, HF is scavenged by NaHCO₃ mixing with cooled combustion products because large NaHCO₃ particles ($\geq 50 \mu\text{m}$) will not decompose before the cooling of combustion products occurs.

5. DISCUSSION

Evaluation of the previous PSR calculation and test and evaluation data still leave several questions with respect to HF mitigation and physical contributions from AFES systems containing HFC-227ea with NaHCO₃. Two recent experimental efforts concerning HF reduction by NaHCO₃ scavenging and fire extinguisher spray characteristics are discussed to provide further mechanistic information.

5.1 HF SCAVENGING

A recent study by the New Mexico Engineering Research Institute [20] evaluated the gaseous HF scavenging capability of ammonium polyphosphate (APP), calcium carbonate, NaHCO₃, and potassium bicarbonate powders, of which NaHCO₃ was observed to be the most effective. From this study, a rough estimation for the overall NaHCO₃ HF scavenging rate constant (reaction $\text{NaHCO}_3 + \text{HF} \rightarrow \text{NaF} + \text{CO}_2 + \text{H}_2\text{O}$; $\text{NaHCO}_3 - \text{solid}$) was made as $0.137 \text{ (cm}^3\text{)}/(\text{s cm}^2\text{)}$ or $674 \text{ ppm HF}/(1 \text{ g/L NaHCO}_3)$ (or $6.6 \times 10^{-4} \text{ g HF}/(1 \text{ g NaHCO}_3)$). Based on the estimated scavenging rate, HF reduction estimates can be made for the experimental data (total fluorine reduction observed when NaHCO₃ added to HFC-227ea) in Table 1. For example, in Table 1, Test 1, 0.3 lb of released sodium bicarbonate is estimated to scavenge 7.2 ppm of HF, while in Table 1, Test 2, 0.6 lb of sodium bicarbonate is estimated to scavenge 14.4 ppm of HF, and in Table 1, Test 3, 1.2 lb of sodium bicarbonate is estimated to scavenge 28.7 ppm of HF. The calculated HF reductions are far less than the observed reductions in Table 1, which is attributed to the molar inefficiency of HF scavenging by NaHCO₃ solid particles: 0.00279 (mol HF/mol NaHCO₃) based on the NMERI data. Note that during cooling of combustion products there will be additional destruction and decomposition of NaHCO₃ particles, which can lead to an additional HF scavenging by sodium containing species that might not be accounted for here. On the contrary, several groups have suggested that scavenging of HF by NaHCO₃ via the reaction, $\text{NaHCO}_3 + \text{HF} \rightarrow \text{NaF} + \text{CO}_2 + \text{H}_2\text{O}$, is a 1:1 mole process. That is, for every mole of

NaHCO_3 introduced into an HF environment, 1 mole of HF will be scavenged. Thus, in the 450-ft³ crew compartment for the previously discussed three field scale testing scenarios, introducing 0.6 lb of NaHCO_3 will scavenge 6491.78 ppm of HF— a very efficient process that does not reflect test results. However, calculating the amount of NaHCO_3 needed to scavenge 515 or 487 ppm of HF (Tests 2 and 3, respectively) only requires 0.046 lb of NaHCO_3 , which appears more reasonable given the test results except for the unaccounted NaHCO_3 .

5.2 EXTINGUISHER CHARACTERIZATIONS

Recently an experimental effort was undertaken to characterize the suppressant physical characteristics, as extinguishers filled with HFC-227ea and HFC-227ea with NaHCO_3 were released [21]. The extinguisher sprays were characterized by a particle image velocimetry (PIV) technique (Dantec Dynamics, Model FlowMap 1500). The essential principle of PIV is to illuminate a droplet or particle-laden flow field with two pulses of laser light and record multiple images for size and velocity analysis. Figure 5 (a and b) present images taken at the nozzle exit of two different extinguishers filled with 6 lb of HFC-227ea or 6 lb of HFC-227ea combined with 0.3 lb of NaHCO_3 .

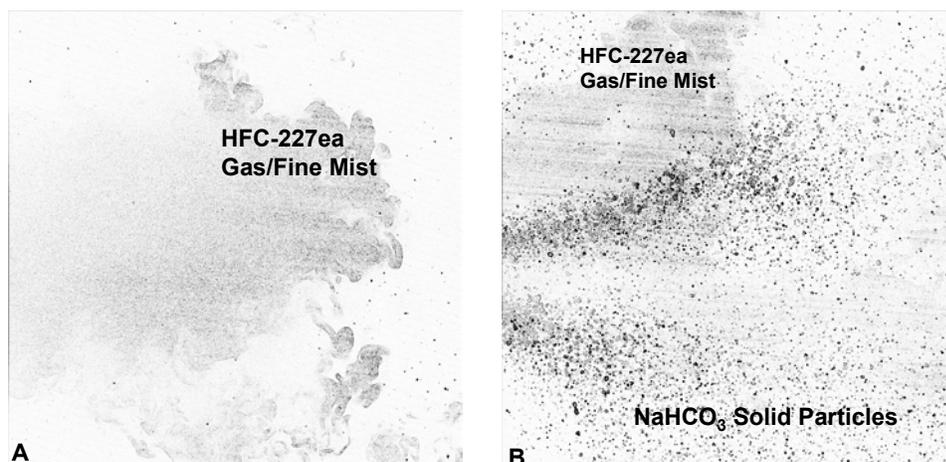


Figure 5. Particle image velocimetry images of 900-psi extinguishers filled with either (A) HFC-227ea or (B) HFC-227ea plus NaHCO_3 . The images were acquired at the nozzle exit of the extinguisher with a field of view 4.87 in. \times 4.91 in.

The existence of significant liquid HFC-227ea upon release from an extinguisher, Figure 5 A, is surprising since the boiling point of HFC-227ea is 3.9 °F [22]. It is believed that the detected liquid droplets are attributed to expansion of the HFC-227ea as it rapidly disperses the extinguisher nozzle. The gas expansion thus causes some liquid phase HFC-227ea to exist within mostly gas-phase HFC-227ea. The experiment demonstrated that liquid yields could range from 584 mg to 1.950 g depending on the output extinguisher nozzle. Thus the percentage of liquid measured in the imaged spaces was between 0.021 to 0.071% of the total amount of HFC-227ea in the extinguishers. These quantities of liquid HFC-227ea in the measurement space must vaporize and thus their contribution to cooling the fire is relatively small (15 K).

The images in Figure 5 were taken at roughly the same physical and temporal locations to illustrate that when the NaHCO_3 is added to the extinguisher, the NaHCO_3 particles precede the HFC-227ea gas/fine mist. This observation becomes important in actual AFES applications because the large NaHCO_3 particles ($\geq 50 \mu\text{m}$), might be responsible for initial cooling/suppression of the fire and thus lowering the amount of HFC-227ea needed for extinguishment. It is estimated from the mechanism information developed here that releasing 1.8 lb of NaHCO_3 (typical application weight in crew compartments of ground combat vehicles) would lower fire temperatures by 180 K.

6. SUMMARY

Numerical modeling of premixed methane/air flames suppressed by HFC-227ea and HFC-227ea blended with NaHCO₃ has been conducted to determine the effectiveness of HFC-227ea plus NaHCO₃ as a Halon replacement candidate in U.S. Army ground combat vehicles. A limited experimental effort to characterize actual fire extinguishers containing HFC-227ea and HFC-227ea blended with NaHCO₃ was also utilized to describe suppressant physical characteristics and behavior upon release. These efforts have illustrated that the principal suppression mechanisms for HFC-227ea combined with NaHCO₃ are due to chemical kinetics along with physical properties of high heat capacities and heats of vaporization by solid NaHCO₃ particles but not liquid HFC-227ea droplets. Removal of HF gases produced from the thermal decomposition of HFC-227ea was investigated and determined to be primarily caused by reduction in HFC-227ea concentrations when NaHCO₃ is blended with HFC-227ea not necessarily from solid particle-gas-phase acid gas (HF) scavenging.

Future efforts will investigate the numerical findings by measuring relative OH concentration profiles and maximum flame temperatures in an atmospheric pressure, opposed flow, methane (CH₄)/air flame suppressed by HFC-227ea plus NaHCO₃ as well as develop a global suppression model.

7. ACKNOWLEDGMENTS

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