



# Transient puffs of trace organic emissions from a batch-fed waste propellant incinerator

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## Abstract

Emissions data have been obtained from a waste propellant incinerator. The incinerator is a dual fixed hearth, controlled air incinerator equipped with acid gas and particulate scrubbing. “Puffing” has been evident in this waste propellant incinerator by spikes in the CO concentration. Transient puffs of organics may travel down the combustion chambers and lead to stack emissions. The major conclusions from this study are that (1) transient puffs are formed due to the semi-batch feed nature of the combustion process (causing a local oxygen deficiency) and high water content of the desensitized propellant; (2) in batch-fed combustors, puffs can contribute to most of the organic emissions (which are relatively low) measured with US EPA sampling and analytical methods; (3) it is estimated that batch-fed combustion contributes up to 7–18 times more emissions than steady-state combustion will generate; (4) by applying dispersion analyses to determine the amount of oxygen deficiency in the flame zone, the combustion zone concentration of CO during batch-fed operation could be as high as 160,000 ppm, compared to a measured peak stack concentration of 1200 ppm CO; and (5) an organic sample is collected and averaged over at least a 2-h period that smooths out the transient peaks of organics emissions during batch-fed operation. For emissions that are associated with long-term potential health impacts, this is an appropriate sampling method. However, if a compound has a short-term potential health impact, it may be important to measure the time-resolved emissions of the compound. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Waste combustion; Stack sampling; Solid propellants; Health risk assessment

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## 1. Introduction

There has been tremendous controversy regarding the burning of hazardous waste. Special interest groups, the public and political leaders have all publicly opposed hazardous waste combustion, regardless of numerous test results that show that it can be done safely. In California, as in other parts of the world, millions of US dollars have gone into environmental studies of each proposed facility: more than a million US dollars for a trial burn, up to a million US dollars for a permit application, up to a million US dollars for a health risk

assessment and up to a million US dollars for an environmental impact report.

As the management of hazardous waste has become a real economic burden to manufacturing industries, it has become important to develop adequate and competitive processes to burn organic hazardous waste streams. The predominant method of disposing of waste propellant, munitions, explosives and other energetic material is to “open burn” or “open detonate” the material. This is done on pads, pans or on the earth. Uncontrolled emissions are generated when propellants are open burned, such as organics, metals, particulates and acid gases. An alternative to the open burning was developed at Aerojet, located in Sacramento, California to burn propellant waste streams in an enclosed combustion device. The research was overseen by the State of

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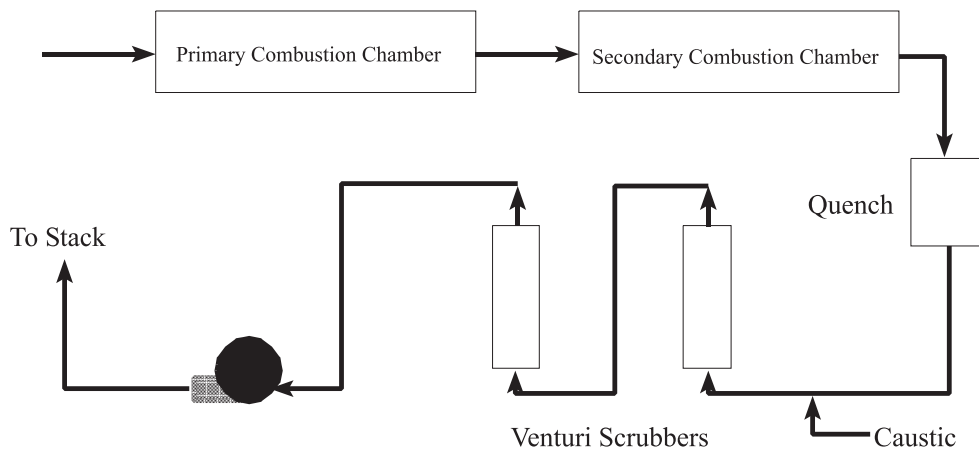


Fig. 1. Schematic diagram of Aerojet's waste propellant incinerator.

California Environmental Protection Agency, Department of Toxic Substances Control. The incinerator, equipped with acid gas and particulate scrubbing, is part of a two-unit system. The first unit desensitizes propellant to remove much of the oxidizer and to recover soluble materials such as ammonium perchlorate and alumina. This is done by first cutting propellant from rocket motors with a high-pressure water jet, followed by placing chunks of the propellant into a maceration unit that extracts the propellant from the binder mechanically (and also may include additional aqueous extraction in the maceration unit). The second unit is the incinerator which is the subject of this study. Fig. 1 presents a schematic of the Aerojet incinerator. Because most of the oxidizer is removed from the propellant, air is required to be fed to the incinerator.

## 2. Description of facility

The incinerator is a dual fixed hearth, controlled air incinerator originally manufactured by the MacBay. The combustion chambers are side by side, with a shared wall separating the chambers. A passage way is in the wall at the end of the first chamber for the combustion gas to enter the second chamber. The volume of the primary chamber is  $6.6 \text{ m}^3$  ( $230 \text{ ft}^3$ ) and the secondary chamber volume is  $4.4 \text{ m}^3$  ( $155 \text{ ft}^3$ ). The cross-sectional area of the primary chamber is about  $1.32 \text{ m}^2$  ( $14 \text{ ft}^2$ ) and the secondary chamber is  $\approx 0.88 \text{ m}^2$  ( $9.5 \text{ ft}^2$ ), and the overall lengths of the primary and secondary chambers are about 5 m each (16 ft). Waste propellant is fed in 19- or 23-l (5 or 6 gal) polypropylene buckets. Buckets are fed through the loading door, then pushed through to the floor of the PCC by a ram feeder. Temperature can be controlled in the primary chamber by a water quench,

which can include dissolved aqueous propellant waste up to 379 l/h (100 gal/h). Operating temperature in the primary chamber is  $\approx 1283 \text{ K}$  ( $1010^\circ\text{C}$ ). The temperature of the gas to the scrubbers from the secondary combustion chamber (SCC) is controlled by an additional water quench. The gas temperature of the secondary chamber is  $\approx 1422 \text{ K}$  ( $1149^\circ\text{C}$ ). The gas temperature is cooled to  $\approx 811 \text{ K}$  ( $538^\circ\text{C}$ ) by two venturi scrubbers in series.

The refractory-lined combustion chambers are heated by auxiliary fuel. During this study, the fuel used was natural gas. Each chamber is equipped with a Pyronics gas burner. The combined total heat duty of both chambers is 4.75 million kJ/h (4.5 million Btu/h). Depending on the waste heating value, the maximum waste propellant input rate to the incinerator is 170 kg/h (374 lb/h). The air flow and velocity in the primary chamber is designed to minimize the entrainment of particulates to the secondary chamber. In addition, during the feed cycle, the auxiliary burner to the primary chamber is reduced to low fire and the underfire air is reduced to minimize particulate entrainment. About 95% of the ash produced in the primary chamber remains in the primary chamber. A camera is installed to view the progress of the reaction of the waste propellant buckets.

Two venturi scrubbers, in series, comprise the air pollution control equipment. Caustic is added to the scrubber liquor. The first stage differential pressure drop is  $\approx 7.1 \text{ kPa}$  (29 in.  $\text{H}_2\text{O}$ ), and the second stage venturi pressure drop is about  $27.4 \text{ kPa}$  (110 in.  $\text{H}_2\text{O}$ ). The second stage venturi is of the collision-type design, where the gas is split equally and then brought back together in opposed flow. An induced draft fan follows the venturi scrubbers, and is capable of moving  $71 \text{ m}^3/\text{min}$  (2500 scfm). The stack contains ports for gas

sampling probes, and ports for continuous emissions analyzers. Emissions which are continuously monitored and recorded are oxygen, carbon monoxide, total hydrocarbons, sulfur dioxide and nitric oxide.

The facility has received a Research, Development and Demonstration permit from the US Environmental Protection Agency and the State of California Environmental Protection Agency, Department of Toxic Substances Control. Three sets of tests to measure detailed stack emissions have been performed on the incinerator under the permits. Currently, Aerojet does not plan to pursue further operation of the incinerator.

### 3. Results

The first series of tests (Radian Corporation, 1992a) were performed in October 1991 on Minuteman propellant containing ammonium perchlorate, aluminum and polybutadiene. The second series of tests (Radian Corporation, 1992b) were performed in October 1992 also on Minuteman propellant (data are averaged in the tables). The third set of tests (GenCorp Aerojet, 1993) were performed on waste propellant from Small Intercontinental Ballistic Missiles (SICBM), Hawk Booster and Sustainer missile propellants and Standard Missile (denoted SM or Missile Sustainer and Deload in tables) components.

#### 3.1. As-fired composition of propellants

Waste propellants are generated when the propellant is cut out of a rocket motor and desensitized by a high pressure water stream (called hydrolasing). The propellant is broken into chunks by this process, and a part of the propellant is dissolved into the water. Both parts of the waste propellant, the aqueous and solid streams, have been tested in the incinerator. Table 1 lists the average composition of the desensitized propellants, after they have been removed from the rocket motors. The table lists only the primary constituents. Others not listed are in trace quantities in the propellant. The heating values of the desensitized propellants are also listed, which range from 3000 to almost 19,000 kJ/kg (1300–8170 Btu/lb).

SICBM propellant is fed directly (stated as “Direct” in the table) and with lime (SICBM-Lime in the table). Standard missile sustainer and deload propellant were also tested. Note that water is the major constituent in the desensitized propellants, which, in part, causes the emission puffs to occur.

#### 3.2. Operating conditions of incinerator during tests

Table 2 contains the average operating conditions reported during the tests. Except for Minuteman propellant tests, an average and standard deviation is presented for most of the parameters. Waste feed rates

Table 1  
Composition of desensitized propellants – primary constituents only

Compound	Function	Hawk Booster (%)	Hawk Sustainer (%)	SM Sustainer (%)	SM Deload (%)	SICBM- Direct (%)	SICBM- Lime (%)	Minuteman (%)
Water	Maceration	30–50	30–50	30–50	30–50	65–85	55–70	30–50
Poly(1,2 butylene) glycol	Binder	10–20	10–20					
Carboxyl term. polybutadiene	Binder				5–10			15–25
C36 Aliphatic dеме- ryl di-isocyanate				2–6	1–3			
Hexamethylene di-isocyanate	Binder	2–5	2–4					
Propylene glycol	Binder			10–16				
Polyether polyol	Binder	2–5	5–10					
Aluminum	Fuel	20–30			12–18	5–15	3–7	20–30
Ammonium perchlorate	Oxidizer	9	13.7	4.1	7.9	1–6	0–2	8–16
Nitroguanidine	Oxidizer	0	14.6	21.9	5.4	1.84	<0.1	
Polyethylene glycol	Binder					1–6	1%_5%	
Cyclotetramethylene tetranitramine						3–8	3–8	
Calcium salts	Treatment						4–19	
Approx. heating value (kJ/kg)		15,100	10,500	15,300	19,300	3000	3700	18,800

Table 2  
Average operating conditions

	SICBM-Lime Average; S.D.	SICBM-Direct Average; S.D.	Hawk Booster Average; S.D.	Hawk Sustainer Average; S.D.	Missile sustainer Average; S.D.	Missile deload Average; S.D.	Minuteman Average
Waste feed	149; 6	155; 7	50; 2	60; 0.5	78; 3	91; 4	110.0
Natural gas	3.8; 0.2	3.9; 0.1	3.8; 0.3	3.6; 0.2	3.4; 0.3	3.5; 0.3	2.9
<i>Primary combustion</i>							
Chamber ave. temp.	1277; 3	1297; 9	1318; 4	1314; 4	1322; 1	1310; 13	1319
<i>Secondary combustion</i>							
Chamber ave.temp.	1437; 3	1435; 2	1436; 0.5	1436; 1	1436; 1	1436; 1	1420
Resid.time	1.13; 0.04	1.18; 0.03	1.21; 0.04	1.26; 0.02	1.29; 0.05	1.16; 0.01	1.31
PCC pressure	4.43E-3	4.18E-3	3.94E-3	3.94E-3	3.94E-3	3.94E-3	4.06E-3
PCC quench	18.9; 23	16.3; 23	35.2; 23	34.1; 11	27.6; 23	65.5; 11	131.0
Quench T out	812; 0	812; 0	812; 1	812; 0	812; 0	812; 0	813
Quench H <sub>2</sub> O	488; 42	424; 42	447; 49	435; 23	397; 38	477; 19	458
1 scrubber	8.0; 0	8.1; 0.1	8.6; 0.1	8.1; 0.1	8.5; 0.5	8.0; 0	8.4
2 scrubber	8.0; 0.3	8.0; 0.1	8.0; 0.2	8.0; 0.2	8.0; 0.1	8.3; 0.2	7.9
1 scrub -P	5.98E-2	6.08E-2	5.34E-2	5.41E-2	4.43E-2	5.66E-2	5.17E-2
2 scrub -P	1.47E-1	1.63E-1	1.75E-1	1.72E-1	1.69E-1	1.47E-1	1.73E-1

varied for the tests from 50 kg/h (23 lb/h) for Hawk Booster propellant to 155 kg/h (70 lb/h) for SICMB-Direct propellant. The primary combustion chamber (PCC) average temperature ranged from 1277 K (1004°C) for the SICBM-Lime propellant tests to 1322 K (1049°C) for the Standard Missile Sustainer tests. The SCC gas residence time ranged from 1.13 s for the SICBM-Lime tests to 1.31 s for the Minuteman tests. The SCC average temperature was a constant 1435 K (1162°C).

### 3.3. Average continuous emissions monitoring results

The average continuous emissions monitoring results are presented in Table 3. Oxygen ranged from 11.1% (dry) in the standard missile deload tests to 14.1% in the Standard Missile Sustainer tests. Average carbon monoxide (CO) ranged from 1 ppm in the Hawk Sustainer tests to 31 ppm in the Hawk Booster tests. Average emissions of total hydrocarbons were in the order of 1 ppm.

### 3.4. Sampling and analytical methods

During all of the tests reported in this paper, the stack gas was extractively sampled and analyzed with standard methods published by the US Environmental Protection Agency. Particulates were sampled with a Method 5 train (a heated filter followed by condensers). Semivolatile organics (including dioxins) were sampled by Method 23 (a modified Method 5 train consisting of a heated filter followed by condensers) and analyzed with high resolution (capillary column) gas chromatography (GC), followed by high resolution mass spectroscopy (MS). Volatile organics were sampled by the Volatile Organic Sampling Train (using two small sorbent traps), and analyzed by GC/MS.

Tests included current quality assurance and quality control measures adopted by the US Environmental Protection Agency (US EPA, 1992, 1993, undated; American Society for Quality Control, 1994).

### 3.5. Volatile organic emissions

Volatile organic mass emission rate results are presented in Table 4. Many of the analytes were not detected for the majority of tests (presented as ND “not detected” and less than the limits of detectability). Some compounds were in fact detected during the tests (please refer to Table 4 for details): chloromethane, trichlorofluoromethane, carbon disulfide, methylene chloride, chloroform, carbon tetrachloride, benzene, toluene, tetrachloroethene, 1,1,1-trichloroethane, trichloroethene, bromodichloromethane, *m,p*-xylene and *o*-xylene. Non-detect values are averaged over the two test runs, and the distinct emission values are reported separately for

the two test runs, except for the Minuteman tests. The Minuteman emissions numbers represent an average of six test runs, all at approximately the same operating conditions.

Although laboratory blanks were not utilized during the Minuteman tests, methylene chloride is a common laboratory contaminant which could account for the relatively high emission rate reported during these tests. The relatively high benzene concentration during the Minuteman tests could be due to its formation as a product of incomplete combustion (PIC) from toluene.

### 3.6. Semi-volatile organic emissions

Average reported values of semi-volatile organic emissions are listed in Table 5. Many of the analytes were not detected, including some of the dioxin and furan congeners. However, analytes detected were naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(e)pyrene, 2-methylnaphthalene and dioxins and furans reported as international toxic equivalents of 2,3,7,8-TCDD.

### 3.7. Destruction and removal efficiencies

Destruction and removal efficiency (DRE) is the US combustion performance standard (which is 99.99% for compounds other than dioxins and PCBs) for organics emitted during hazardous waste combustion. It is a measure of the most difficult to burn compound (principal organic hazardous constituent, or POHC), both in and out of the combustor, on a mass rate basis. These compounds were fed (spiked) with the propellants during the tests. Data are presented in Table 6 for DREs that have been demonstrated on the incinerator, even though the compounds selected will not be found in the waste propellants in significant quantities.

## 4. Discussion of experimental observations

The following observations are relevant to the data.

### 4.1. Transient puffs analysis

The production of transient emissions has been studied by Linak et al. (1987), on a pilot scale kiln burning batch-fed packets of material. Cundy et al. (1991), have studied the same transient puff phenomenon in a full-scale rotary kiln. Under starved-air conditions as in the PCC in the incinerator studied, organic emissions can be high (on the order of 20,000 ppm of total unburned hydrocarbons in the pilot-scale kiln studied by Linak (1987)). A batch-fed drum of organics often produces a local oxygen deficiency in a combustion

Table 3  
Continuous emissions monitoring and stack data

	SICBM-Lime		SICBM-Direct		Hawk Booster		Hawk Sustainer		Missile Sustainer		Missile Deload		Minuteman	
	Average; S.D.	S.D.	Average; S.D.	S.D.	Average; S.D.	S.D.	Average; S.D.	S.D.	Average; S.D.	S.D.	Average; S.D.	S.D.	Average; S.D.	S.D.
Gas flow	102; 3		106; 2		120; 9		105; 3		115; 3		107; 2		93	
Std. gas flow	43; 9		42; 2		50; 3		45; 3		52; 2		41; 2		41	
Velocity	23; 1		24; 0		27; 1		24; 1		26; 1		24; 0		21	
Secondary chamber														
Residence time	1.13; 0.04		1.18; 0.03		1.21; 0.04		1.26; 0.02		1.29; 0.05		1.16; 0.01		1.31	
H <sub>2</sub> O	48.2; 0.3		46.4; 0.6		40.4; 3.5		39.7; 3		38.5; 0.6		48.1; 2		42	
Oxygen	11.8; 0.9		11.8; 0.9		13.8; 1		13.4; 0.2		14.1; 0.4		11.1; 0.4		12.6	
Carbon dioxide	5.8; 0.1		5.4; 0.8		4.1; 0.4		4.4; 0.2		4; 0.5		6.4; 1.1		5	
NO <sub>x</sub>	138; 1		162; 21		45; 1		69; 2		66; 7		131; 35		85	
CO average	4.3; 4.9		15.3; 16.3		30.7; 37		1; 0		13; 21		23; 26		12.5	
THC average	0.9; 0.2		0.7; 0.5		1.9; 2.5		0.1; 0		1.3; 1		0.3; 0.1		1.25	
SO <sub>x</sub>	1.7; 0.6		53.8; 72		1.33; 3		3; 3		1.5; 5		5; 5			
Particulates	6.14; 0.47		5.92; 2.5		8.48; 5.8		8.62; 8.6		11.86; 3.8		5.92; 2.3		5.18	

Table 4  
Volatile organic emissions

Analyte	Emissions in units of mg/h						
	Hawk Booster	Hawk Sustainer	SICBM-Lime	SICBM-Direct	SM-Sustainer	SM-Delead	Minuteman
	Average	Average	Average	Average	Average	Average	Average
Chloromethane	<b>157 &amp; 189</b>	<b>188 &amp; 134</b>	<b>1 &amp; 10</b>	ND < 31	ND < 42.3	ND < 15	
Bromomethane	ND < 2.7	ND < 2.0					
Trichlorofluoromethane	ND < 2.9	ND < 11.5	ND < 1.5	<b>4.1 &amp; 1.7</b>	<b>3.7 &amp; 1</b>	ND < 1.5	<b>218.4</b>
Carbon disulfide	ND < 3.3	<b>2.6; 0.4</b>	ND < 1.9	ND < 9.4	ND < 1.8	ND < 2.3	
Acetone	ND < 8.6	ND < 9.0	ND < 8.1	ND < 8.3	ND < 8.9	ND < 7.7	
Methylene chloride	<b>33.8 &amp; 14.8</b>	<b>58.7 &amp; 34</b>	ND < 18.4	ND < 370	ND < 40	<b>9.6 &amp; 7.4</b>	<b>2183.8</b>
2-butanone		ND < 10.5					
Chloroform	ND < 6.6	<b>20.8 &amp; 6.3</b>	ND < 1.4	ND < 4.9		ND < 3.0	<b>13.0</b>
1,1,1-trichloroethane	ND < 1.5	ND < 1.7		ND < 1.5			<b>114.4</b>
Carbon tetrachloride	<b>2.4 &amp; 0.6</b>	ND < 1.6					<b>2.8</b>
Benzene	ND < 7.9	<b>14.9 &amp; 19</b>	<b>4 &amp; 2.1</b>	<b>24.8 &amp; 25</b>	ND < 113	<b>58.9 &amp; 28</b>	<b>453.6</b>
Trichloroethene		ND < 2.7					<b>1.8</b>
Bromodichloromethane		ND < 15.4		ND < 1.3			<b>3.7</b>
Toluene	ND < 6.0	<b>16.2 &amp; 15</b>	<b>11.6 &amp; 11</b>	<b>9.2 &amp; 6.5</b>	<b>30.9 &amp; 19</b>	<b>12.2 &amp; 9</b>	<b>55.4</b>
Tetrachloroethene	ND < 3.9	<b>4.4 &amp; 0.2</b>	ND < 1.3	<b>2 &amp; 0.3</b>	ND < 2.2		<b>13.5</b>
Dibromochloromethane		ND < 16.4					
<i>m,p</i> -xylene							<b>15.1</b>
<i>o</i> -xylene							<b>11.6</b>
Bromoform		ND < 4.1					

Table 5  
Semi-volatile emissions

Compound	Hawk Booster	Hawk Sustainer	SICBM-Lime	SICBM-Direct	SM-Sustainer	SM-Deload	Minuteman
	Emissions in mg/h						
	Average	Average	Average	Average	Average	Average	Average
1-TEQ ng/dscm	0.120	0.074	0.039	0.159	0.013	0.041	4.065
1-TEQ mg/h	0.000359	0.0002	0.0001	0.0004	0.00004	0.0001	0.01
Naphthalene	ND < 208	ND < 2	ND < 80	ND < 6.5	ND < 15	ND < 114	1.5
Acenaphthylene	3.56	ND < 0.007	0.1	0.3	0.7	7.5	0.1
Acenaphthene	1.37	0.01	ND < 0.02	0.06	0.08	2	0.000908
Fluorene	ND < 1	ND < 0.05	ND < 0.02	ND < 0.1	0.1	0.9	0.1
Phenanthrene	24.5	0.2	ND < 0.6	1	1	14	0.8
Anthracene	ND < 1	ND < 0.05	0.1	0.09	0.1	0.5	0.000227
Fluoranthene	7.9	0.06	0.2	0.4	0.4	12.5	2
Pyrene	22.3	0.07	0.3	0.8	1	59	6.3
Chrysene	ND < 0.1	ND < 0.008	ND < 0.01	0.015	ND < 0.01	ND < 0.09	0
Benz(a)anthracene	ND < 0.06	ND < 0.008	ND < 0.01	ND < 0.009	ND < 0.01	ND < 0.05	ND < 0.01
Benzo(b)fluoranthene	ND < 0.1	ND < 0.008	ND < 0.01	0.015	ND < 0.01	0.1	0.000454
Benzo(k)fluoranthene	ND < 0.03	ND < 0.008	ND < 0.01	ND < 0.009	ND < 0.01	ND < 0.03	ND < 0.01
Benzo(a)pyrene	ND < 0.04	ND < 0.008	ND < 0.01	ND < 0.009	ND < 0.01	ND < 0.02	ND < 0.01
Indeno(1,2,3-c,d)pyrene	ND < 0.05	ND < 0.008	ND < 0.01	ND < 0.009	ND < 0.01	ND < 0.04	ND < 0.01
Dibenz(a,h)anthracene	ND < 0.009	ND < 0.008	ND < 0.01	ND < 0.0009	ND < 0.01	ND < 0.009	ND < 0.01
Benzo(g,h,i)perylene	ND < 0.3	ND < 0.01	ND < 0.02	0.02	ND < 0.04	0.2	0.000908
Benzo(e)pyrene	ND < 0.2	ND < 0.01	ND < 0.02	0.02	ND < 0.02	0.3	0.3
Perylene	ND < 0.02	ND < 0.008	ND < 0.01	ND < 0.009	ND < 0.01	ND < 0.009	ND < 0.009
2-methylnaphthalene	ND < 2.8	ND < 0.4	ND < 0.7	0.2	ND < 0.6	4.5	4.5



Table 6  
POHC emissions and DRE for 1,2,4-trichlorobenzene

Input rate (kg/h)	Emission rate (kg/h)	DRE (%)
<i>1,2,4-trichlorobenzene with SICBM direct propellant</i>		
4.46	0.658E-6	99.999985
4.09	0.100E-6	99.999998
4.18	0.581E-6	99.999986

chamber. Puffing has been evident in this study's waste propellant incinerator by spikes in the CO and unburned hydrocarbons concentrations. The two phenomena that may result from this are:

1. Transient puffs of organics may travel down the kiln as a pulse of organic emissions, and be somewhat dispersed ("flattened") by the time the stack is reached.
2. Organic fragments from partial post-flame reactions in the hot gases might result in reformation reactions when the gases are quickly cooled at the "cold" end (where a large amount of cool secondary air is introduced) of the incinerator.

Equilibrium analyses have shown that no emissions should be detected for a combustion system at equilibrium (Hart and Franco, 1989), a condition that does not fully exist for full scale combustion systems. But, if a pulse, or puff, of emissions is generated from batch-fed operations, it could travel down the incinerator as a plug (Chang et al., 1987). The incinerator in this study approximates a plug-flow reactor because the Reynolds number is  $\approx 170,000$ , and the length-to-diameter ratio is  $\approx 5$  for the combination of the primary and secondary chambers (about 3 for the secondary chamber alone).

#### 4.2. Dispersion model

A dispersion analysis can be done to determine the amount of oxygen deficiency in the flame zone that caused the emission puffs. The dispersion of a pulsed input function has been studied previously for a plug-flow reactor by Levenspeil (1972). For dispersion without chemical reaction (this will generally not occur for most organics, but is useful in analyzing CO emission peaks), the governing equation is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2},$$

where  $D$  is an axial dispersion coefficient,  $C$  the CO concentration,  $t$  the time and  $x$  is the distance along the axis. For small dispersion (the pulse or puff traveling down the kiln intact, and  $d/(\mu L) = 0.002$ ), the solution takes the form

$$C_\phi = \frac{1}{(2(\pi d)^{1/2})/(\mu L)^{1/2}} \exp \left[ -\frac{(1-\phi)^2}{4d/\mu L} \right] = 6.31,$$

where  $\phi$  is dimensionless time. For large dispersion ( $D/\mu L = 0.2$ ),  $C_\phi$  is calculated as 0.7. Let us apply these results to the generation of a relatively stable molecule such as carbon monoxide. Time resolved data are available for CO emissions. The highest peak concentration found in the combustion exit (stack) gas stream during any test was  $\approx 1200$  ppm with a decay to its steady-state value in 7 or 8 min as seen on the CO stack monitor during the Hawk Booster tests. In order for this to occur under the model for small dispersion, a puff of 160,000 ppm would have been generated during 0.1 s (chosen as the puff duration) within the combustion chamber. For large dispersion, a puff of 110,000 ppm carbon monoxide would have been generated during the duration of 0.1 s. This is certainly possible in microscale, low oxygen regions of the flame zone found during batch-fed operations.

The first set of tests on Minuteman propellant also had CO spikes when buckets of propellant were fed to the incinerator. The second set of Minuteman propellant tests did not show the CO spikes because the underfire air was adjusted and the ammonium perchlorate feed rate was reduced by a factor of 3. A greater degree of air staging was used in these tests (a greater percentage of air was fed farther downstream in the primary chamber). The CO could have still been produced in the flame zone where sub-stoichiometric conditions exist, and then preserved (essentially "frozen") downstream when the relatively cold secondary air was injected (and more secondary air than primary air).

In addition to the spikes produced when buckets are fed to the incinerator, CO spikes are produced when the ash is raked by the "ash ram". The ash ram can be set to operate periodically at the end of the feed cycle in order to ensure that all of the propellant surface area is exposed. The ash ram operates concurrently to the gas flow in the PCC. The ash ram raked about once per four feed cycles, and can produce as high or higher a CO and hydrocarbon spike as feeding a bucket of propellant. This spike can actually be higher than a feed spike because there may be more unburned propellants in the unraked bottom ash pile than in a bucket of waste feed. The raked bottom ash is dropped out of the PCC once every 3 or 4 h. A CO and hydrocarbon spike occurs (always at the same time) 3 or 4 min after an ash is raked by the ram.

#### 4.3. Dispersion with chemical reaction

For dispersion with chemical reaction (all other factors remain the same), the governing equation (Levenspeil, 1972) is

$$(D/\mu L)(\partial^2 C/\partial x^2) - \partial C/\partial x - ktC^n = 0.$$

For first order reactions, and small deviations from plug flow, the solution reduces to

$$C/C_0 = \exp[-kt + (kt)^2(D/\mu L),$$

where  $k$  is a first order reaction rate constant,  $x$  the distance and  $n$  is the reaction order. For values of  $D/\mu L = 0.002$ ,  $k = 0.91 \text{ s}^{-1}$  (from Glassman, 1977) and  $t = 2 \text{ s}$ ,  $C/C_0 = 7.66 \times 10^{-4}$ . Therefore, a transient puff of 593 g/h (1.3 lb/h) of benzene could be generated and frozen to create a final emission of 454 mg/h (0.001 lb/h) of benzene at the exit during the Minuteman propellant test, with dispersion and chemical reaction. One can see that large transients are not required in order to produce observed levels in the exhaust.

It is important to note that sampling to quantify trace organics occurs over at least a 2-h period. Therefore, an average sample is collected and reported that smooths out the transient peaks of organics emissions. For emissions that are associated with long-term potential health impacts, this is an appropriate sampling method. However, if a compound has a short-term potential health impact, it may be important to measure the time-resolved emissions of the compound.

#### 4.4. Estimation of emissions generated by transient puffs compared to steady-state

As some transient data are available, it is possible to estimate the percentage of emissions generated by batch feeding buckets of the waste propellant compared to a continuous feed, steady-state operation. This can be done by observing the frequency of buckets fed and comparing the CO emission peaks against the steady-state peaks.

Depending on the propellant and the percentage of propellant in the desensitized propellant, the maximum frequency of feed to the incinerator is about 10 buckets each hour. This means that the number of CO peaks due to the feeding of buckets (or pulses of reactants) is about 10 each hour (not including the rake of the ash ram). During the Hawk Booster tests, five substantial CO and hydrocarbon spikes were observed (actually due to the ash rake, not due to the feed of buckets) and recorded. Strip chart traces indicate that the maximum peak height is  $\approx 1200 \text{ ppm CO}$  and 375 ppm total hydrocarbons (by FID), and that the peak subsides to a steady-state value after 7 or 8 min (see Fig. 2). Therefore, one can integrate under the curve to estimate the emissions generated by batch feed compared to steady-state operation. It is estimated that there were 18 times more emissions resulting from the batch feed compared to steady-state, continuous feed operation based on the CO spikes observed. Hydrocarbon spikes indicate that seven times more emissions were generated by the batch operation than the steady-state value. The increased

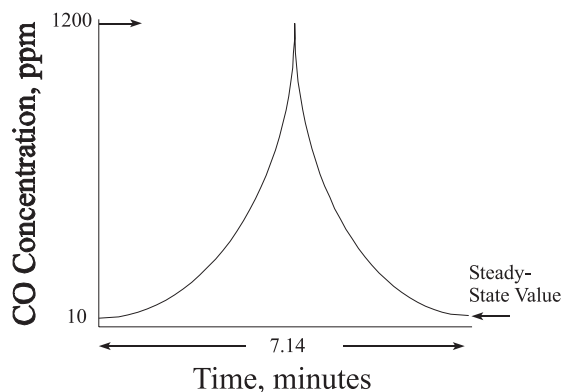


Fig. 2. Representation of a typical transient puff of CO emissions.

emissions generated from the batch-fed operation is a significant combustion system design issue.

#### 4.5. Amount of waste feed rate is governed by heat release and transient puffs

A practical consideration for the design of a waste propellant incinerator is that only a small amount of waste propellant can be fed in the buckets, depending on the heat of combustion of the propellant (and the maximum allowable temperature of the combustion chamber). The size of the incinerator combustion chamber governs the amount of waste feed possible because of the puffs generated during the batch-fed operation. An obvious solution is to modify the feed procedures to a steady-state operation, as long as safety hurdles could be overcome. If the propellant could be blown into the incinerator through a burner (either dry or as a slurry), and/or the amount of water in the feed could be reduced, the transient puff and heat release problems would be minimized.

## 5. Conclusions

The conclusions from this study are:

- Transient puffs are formed due to the semi-batch feed nature of the combustion process (causing a local oxygen deficiency) and high water content of the desensitized propellant.
- Batch-fed combustion in an enclosed device can be safely done on waste propellants, but at a fairly low feed rate (up to 155 kg/h in this study).
- Volatile organics detected during the tests were: chloromethane, trichlorofluoromethane, carbon disulfide, methylene chloride, chloroform, carbon tetrachloride, benzene, toluene, tetrachloroethene, 1,1,1-trichloroethane, trichloroethene, bromodichloromethane, *m,p*-xylene and *o*-xylene.

- Semi-volatile organic emissions detected were naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(e)pyrene, 2-methylnaphthalene and dioxins and furans reported as international toxic equivalents of 2,3,7,8-TCDD.
- In batch-fed combustors, puffs can contribute to most of the organic emissions (which are relatively low) measured with US EPA sampling and analytical methods.
- It is estimated that batch-fed combustion contributes up to 7–18 times more emissions than steady-state combustion will generate.
- By applying dispersion analyses to determine the amount of oxygen deficiency in the flame zone, the combustion zone concentration of CO during batch-fed operation could be as high as 160,000 ppm, compared to a measured peak stack concentration of 1200 ppm CO. When chemical reaction is considered in the dispersion analyses, the combustion zone production of benzene could be as much as 593 g/h (1.3 lb/h) to create a stack emission of 454 mg/h (0.001 lb/h) of benzene during the Minuteman propellant tests.
- An organic sample is collected and averaged over at least a 2-h period that smooths out the transient peaks of organics emissions during batch-fed operation. For emissions that are associated with long-term potential health impacts, this is an appropriate sampling method. However, if a compound has a short-term potential health impact, it may be important to measure the time-resolved emissions of the compound.

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