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EMISSIONS FROM THE OPEN BURNING OR DETONATION OF EXPLOSIVES

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INTRODUCTION

The Air Pollution Engineering Division of the US Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD, has been involved in the development of technology and monitoring progress of concurrent efforts toward the environmentally compatible demilitarization and disposal of excess or waste explosive materials. Our involvement stems primarily from a mission constraint which requires the monitoring and evaluation of environmental health aspects of such efforts within the Department of the Army. Additionally, this Agency has been requested to provide consultative support during the development and testing of disposal alternatives and to interface with regulatory concerns in those areas impacted upon. Recently, our involvement has been directly requested at the installation level to quantify emissions and to otherwise evaluate ongoing demilitarization of energetic materials.

"Demilitarization" refers to the disposal, destruction or alteration of a munition to the extent that it is inactive or unusable as a military weapon. Generally, the munition, or a component part thereof with energetic properties, is: (1) byproduct material generated during the production process or subsequent load and pack operation, (2) material declared "out of specification" due to age or mechanical alteration, or (3) bulk powder generated during the firing of separately loaded artillery projectiles. The material, and associated contaminated packaging, requires disposal in a safe manner. No acceptable alternate disposal technique exists for the burning or detonation of many items in open air or specially designed furnaces.

Available technical literature was reviewed and data compiled which would aid in responding to the above requirements in the most expeditious manner allowed by the present state-of-the-art. The basic thrust of this investigation was to provide a workable, scientifically-based procedure for the quantification and evaluation of air emissions which result from burning or detonation of energetic materials. [Note that Table I is a key to symbols and abbreviations found in this paper].

FINDINGS AND DISCUSSION

Character of Explosives

The thermochemistry of burning is distinctly different from that of detonation. In the conventional sense, the word "burning" implies the rapid oxidation of some fuel with a release of heat and products of combustion. Chemical explosives also may burn at a comparable rate provided that there is no confinement and the conditions are such to prohibit the transition to the detonation state (i.e., high moisture content).

Semantics are confusing since the literature refers to several terms which, in effect, describe various rates of chemical reaction of the explosive material: deflagration, violent deflagration and detonation. "Deflagration," as the term is used here, means a form of very rapid burning, a surface reaction where reaction products flow away from the

unreacted material below the solid surface. However, deflagration of a mass of finely divided explosive particles can occur nearly simultaneously. In this case, confinement of the mass, including the gaseous products, has the effect of increasing the pressure. This, in turn, increases the rate of reaction and temperature. The final effect of deflagration under confinement is explosion, which may be violent deflagration or even detonation.[1]

Strictly defined, "detonation" is a process by which an explosive undergoes chemical reaction with a certain type of shock wave called a detonation wave. The progress of this detonation wave through a column of explosive is illustrated in Figure 1. In some cases, the end results of violent deflagration (an extremely rapid surface phenomenon) and detonation (a depth or zone phenomenon) are much the same in terms of pressure produced.[1]

Detonation is therefore characterized, in general, by higher reaction rates, temperatures and pressures than deflagration. Table 2 shows distinguishing characteristics between detonating or "high" explosives and deflagrating or "low" explosives. Figure 2 shows the conceptual difference in terms of energy. High explosives may be subdivided into primary and secondary explosives. Primary explosives may be detonated by simple ignition from impact or heat, but secondary types usually require a "detonator" or booster charge to function in the desired manner. Such low explosives as loose black powder and pyrotechnics can, as a maximum, undergo burning or, under sufficient confinement, deflagration can become so rapid that detonation ensues. For most high explosives, deflagration produces so much heat that detonation follows quickly, but the rate of transition among types depends greatly on confinement. Note specifically that low explosives such as black powder and nitrocellulose make the best propellants because of their heaving effect, while high explosives such as TNT and HMX are best for warheads because of their shattering effect.[2] The strict classification of explosives is difficult in some cases because of differences in density, granulation, and the tendency toward combining two or more base types to obtain more desirable properties. Fortunately, a strict classification of explosive material in the manner described above is not necessary here, since there is not enough data to quantify the differences. As a result, the quantification of reaction products was made for only burning (deflagration) and detonation (regardless of type) of explosive materials.

Reaction Products from Burning

The production of gases from the burning of explosives is the result of the rapid conversion of solid material to gaseous end products. There are, of course, solid or particulate end products emitted which generally represent parts of the original material that is incompletely combusted. Factors which influence the character of emissions from explosives burning are the same as those for any fuel: (a) temperature, (b) time and (c) turbulence. Unfortunately, the factors are not controlled during open burning nor are they consistent from burn to burn. Also, emissions depend heavily on atmospheric conditions. As a result, there are little data available in the literature quantifying these end reaction products.

Table 3 summarizes the work reported for five different compounds. The numbers represent very creditable work, but it was, nonetheless, carried out under controlled laboratory conditions in an expandable chamber and probably does not accurately reflect the open air burn situation. However, these data are all that is currently available and may in the interim be used for gross estimates of the emissions.

Should data for other explosive compounds be needed or if supporting data are desired, calculations of end products may be made if certain thermodynamic parameters are known.[2] A computer program has been developed by the National Aeronautics and Space Administration (NASA) for this purpose.[3] The program computes the theoretical equilibrium composition, given the quantity and types of reactants, reactant enthalpies and other specific physical data. A free energy minimization technique is used. The results of such calculations are only as accurate as the input data supplied describing the burn conditions.

Reaction Products from Detonation

The products of reactions that take place during detonation depend on many complex variables such as composition (i.e., oxygen balance), loading density, degree of confinement, mode of initiation, type of imposing burden and the chemistry of the surrounding media.[2] Since at this point no practical benefit would be derived from a discussion of the interrelationships between those influencing factors, the reader must be referred to the literature for such information.

The sacrifice of realism to allow the conduct of experiments under laboratory conditions is great, usually requiring a tenuous extrapolation of results to actual field detonation conditions. Almost all experimental data on reaction products from detonation were obtained from bomb calorimetur tests, using small charges of explosive, and allowing the contents to cool to ambient conditions. Samples were then extracted for gas analysis. Some authors argue that the phenomenon is best approached theoretically using purely thermochemical principles, but there are drawbacks here as pointed out earlier, since several dynamic constants must be assumed or estimated in order to carry out the computations. In brief, the real and logically scientific basis upon which actual measurements are made offer a sound, practical set of data, while the utilization of thermodynamic theory offers a rigorous theoretical approach.

Based on the investigation leading to this report, it is believed that both approaches have merit and, at the present time, must be utilized in conjunction with one another to best evaluate environmental impact from explosive detonations. Where experimental data are available, they should, at this time be considered of higher reliability than theoretical computations. However, theoretically computed data should be used to support measured results and to fill in information gaps.

Table 4 contains an alphabetical listing of the measured emissions data available from the literature. The practical total volume of gaseous end products resulting from a particular detonation may be calculated using the following equation [an ambient temperature of 70°F (21°C) and pressure of 29.92 in Hg (760 mm Hg) have been assumed].

Cubic Feet Per Ton

$$V_{LT} = 359 \left[\frac{W_1}{M_1} + \frac{W_2}{M_2} + \ldots \frac{W_n}{M_n} \right] \quad (1)$$

Where: V_{LT} = total volume (cubic feet per ton)

W_1, W_2, W_n = weight of gas emitted (pounds per ton)

M_1, M_2, M_n = molecular weights of corresponding gases W_1, W_2, and W_n (grams per mole)

If experimental data for a particular explosive type is not available, then, theoretical data must be used. There are, obviously, an endless number of theoretical data that may be computed. For example, a slight change in temperature would certainly affect the reaction end products to some degree. When one considers the range of conditions that could be present during detonation, the quantitative combinations of reaction products are infinite. However, data have been reported in the literature which represent attempts at computing end products based on measured (or reasonably approximated) parameters which control the process of detonation. Table 5 summarizes these data. In most cases, the calculated data are compared with measured data in the listed references.

Computing Emissions From Emission Factors

Before using the data presented here, information is needed as to type of weapon, quantity of charge, type of detonator, cartridge designation, type of propellant and other physical data. The following sequence is recommended for the calculation of emissions:

(1) Determine components of munition - Bulk explosives may need no further investigation in this regard, but end items, such as artillery projectiles, need identification and quantification in terms of type and quantity of projectile filler, type of detonator and other physical data. Excellent sources of information in this regard are the Department of the Army Technical Manuals and Logistics' Complete Round Charts available for the various munitions. [4-14]

(2) Determine composition of propellant/explosive filler - In conjunction with the references mentioned above, one must further define the energetic material as to base components. Department of the Army Technical Manuals are also good sources of information here. [4-9] Table 6 shows typical composition for one grade of three different types of propellants.[1]

(3) Calculate emissions - Once the components are quantified, one may then try to find emission factors for that particular, or a nearly similar, compound, and perform the simple multiplication. Note that the emission factors are in terms of pounds per ton of explosive material.

CONCLUSIONS

When using the values presented in this report, or any calculated data, for gross air contaminant emissions, they should certainly be well qualified and the base assumptions and conditions discussed. How well the base conditions compare, based on an engineering judgment of the available data, should be presented.

Burning and detonation are two distinctly different processes which usually result in the emission of various amounts of gaseous end products. There exists a severe shortage of data defining the emissions of gaseous contaminants from demilitarizing energetic materials through burning or detonation. There are several theoretical procedures available for the calculation of end reaction products; however, the accuracy of these routines is predicated on the accuracy of assumptions made describing the base process conditions. It is recommended that measured data be used when available and supplemented with theoretically calculated emissions data as necessary.

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Table 1. KEY TO SYMBOLS AND ABBREVIATIONS

AL	Aluminum
ALO	Aluminum Oxide
AL_2O	Aluminum Oxide
AL_2O_3	ALumina
AN	Ammonium Nitrate
BTF	Benzotrifuroxan
$C_{(s)}$	Carbon, Solid
CaO	Calcium Oxide
CF_4	Carbon Tetrafluoride
CH_4	Methane
C_2H_2	Acetylene
C_2H_6	Ethane
CH_2O	Formaldehyde
CH_2O_2	Formic Acid
CH_3OH	Methyl Alcohol
C_2H_5OH	Ethyl Alcohol
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COMP B (A or C)	Composition B (A or C)
DNT	Dinitrotoluene
1,2 DP	1,2 bis (difluoroamino) propane
FEFO	Bis [2,2-dinitro-2-fluorethyf] formal
HCx	Hydrocarbons
HCL	Hydrogen Chloride
HCN	Hydrogen Cyanide
HF	Hydrofluoric Acid
HMX	Cyclotetramethylenetetranitramine
Hg(g)	Mercury, gas
H_2S	Hydrogen sulfide
lb	Pound
LX-11-0 (07, 09)	HMX/Viton A mixtures
Na_2O	Sodium Oxide
NG	Nitroglycerin
NH_3	Ammonia
NM	Nitromethane
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NO_x	Oxides of Nitrogen
N_2O	Dinitrogen Oxide
PB(g)	Lead, gas
PBX	RDX/polystyrene/dioctyl phthalate (now called PB-RDX)
PETN	Pentaerythritoltetranitrate
P_2O_5	Phosphorus Pentoxide
RDX	Cyclotrimethylenetrinitramine
RX-23 (AA) (AB or AC)	Hydrazine nitrate/hydrazine mixtures
SiO_2	Silicon Dioxide
TNT	2,4,6 trinitrotoluene
Ton	Short ton (2000 pounds)
XTX-8003	PETN/Sylgard 182

Table 2. CHARACTERISTICS OF HIGH AND LOW EXPLOSIVES[2]

	High	Low
Method of Initiation	Primary by ignition and secondary by detonator	By ignition
Time of Complete conversion of explosive to gaseous products	Microseconds	Milliseconds
Velocity of Consumption of explosive grains	1 to 6 miles/sec	A few in to ft per sec
Velocity of flame front	1 to 6 Miles/sec	1/3 to 1 mile/sec
Pressure of explosive	50,000 to 4,000,000 psi	Up to about 50,000 psi
Rock breakage in borehole blasting	1 to 30 tons/lb	1 to 30 tons/lb
Exploded in gun	Shatters gun	Good propellant
Demolition	Excellent to poor	Nil
Uses	Demolition, blasting	Propellent, blasting
Common Explosives	Primary Mercury fulminate Lead azide Secondary TNT Tetryl RDX	Nitrocellulose Black powder

Table 3. AIR EMISSIONS FROM BURNING OF EXPLOSIVES (lb/ton)[15-19*]

Compound	CO	HCL	HF	NO_x	N_2O	HC_x	P_2O_5	Soot	Ash
TNT	56			150		1.0		180	240
Comp B-3	5.0	0	0	37.1		0		0	
PBX 9404	5.5	22.9	0	37.9			13	0	59
LX-07-2	1.4	0	54	27.9	0.86	3.9		0	162
LX-09	1		6	29				0	64

* Data for H_2, CO_2, H_2O, H_2, and O_2 are available in the original reports.

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Table 4. MEASURED AIR EMISSIONS FROM DETONATION OF EXPLOSIVES (lb/ton)*

Compound	CO	$C_{(s)}$	NH_3	HCN	CH_4	H_2S	Other	Total Volume (ft^3/ton)
Amatol 80/20[21]	82.5		12.1	4.8	2.86			29,144
Amonal 72/23.5/4.5[20]	48				1.5		ALO-712	19,045
Ammonia Dynamite[22]	63.2				1.3	30.9		11,959
	(45.6-128)				(0.57-2.1)	(18.8-36.9)		
Ammonia Gelatin[22]	24.1				0.4	5.76		10,292
	(14.1-43.1)				(0.28-0.57)	(1.2-12.1)		
Black Blasting Powder[20,22]	170				4.2	24.4		11,350
	(75-240)				(0.57-9.7)	(0-73.4)		
BTF[23]	603	75	0.48	1.29	ND			
	(568-638)	(0-150)	(0.27-0.68)	(1.07-1.5)				
Blasting Gelatin[21,22]	159				0.68	0	NO-42	20,504
	(55-262)				(0-0.96)			
1,2 O_2P[23]	-	475	6.3		30.7		HF-901, C_2H_2-3.8, C_2H_6-0.82, CF_x-ND	
FEFO[24]	330	0	2.45		0.1		HF-234, CF_4-0	
Gelatin Dynamite[20,22]	72.0				0.69	3.9		10,869
	(14.6-292)				(0.28-1.7)	(0-5.5)		
Nitrocellulose[21]	640	36			3.2			26,419
	(576-704)	(12-60)			(1.6-4.8)			
Gunpowder[25,26]	76.0				1.31	20.6		8,560
	(68.8-84.7)				(0.71-1.5)	(19.8-21.4)		
HMX[23,24]	456	13.2	9.8	0.59	0.9		C_2H_6-0.20	
	(411-501)	(0-26.3)	(0-19.6)	(0.11-1.07)	(0-1.8)			
LX-11-0[23]	402	81	15.8	0.87	2.9		HF-268, CF_4-8.8	
	(190-773)	(0-161)	(0.10-31.6)	(0.1)-1.62)			(260-276)	
							(8-17.6)	
Nitromethane[24]	513	38	60	7.2	1.3		C_2H_6-1.0	
Pete[21,27]	297		2.5		0.35			25,714
	(276-319)		(0.02-5.0)		(0.02-0.35)			
Picric Acid[21]	749	92.3	9.25	22.3	4.33		C_2H_2-83.8	23,566
RX-23[23]			318				NO-0.16	
Straight Dynamite[20,22]	281				2.5	5.6		14,396
	(87.3-524)				(0.57-5.6)	(0-14.6)		
Tetryl[21]	609	159		32.4	8.64		C_2H_2-62.4	24,047
TNT[2,21,24]	796	214	26.7	26.9	14.3		C_2H_2-121, C_2H_6-1.06	24,495
	(642-944)	(107-320)	(27-30.4)	(21.9-32)	(13.2-15.4)			
XTX-8003[23]	720	31.2	13.6	0.52	13.1		SiO_2-324, C_2H_2-0.84, C_2H_6-1.2, NO-46.8	
	(600-840)	(0-62.4)	(1.36-25.8)	(0.49-0.54)	(6.08-20.2)			

* Straight line average of available data, equally weighted by source.

Table 5. CALCULATED EMISSIONS FROM DETONATION OF EXPLOSIVE MATERIALS (lb/ton)

Compound	CO	$C_{(s)}$	NH_3	HCN	CH_4	CH_3OH	C_2H_5OH	NO	Other
Amatol 50/50[2]	192 (22.4-392)		61.2	56 (41-51)	3.2	192 (128-256)			CH_2O-114(27.6-256), CaO-11.2
Amatol 80/20[2]	5.6							12	
Ammonia Gelatin[2]	11.6 (5.8-17.4)							6.0	CaO-5.6, Na_2O-256, SO_2-256
AN/AL Mix[2]			22.5 (0-68)					25.8 (4.2-62.4)	
AN/AL/H_2O[2]			180 (170-190)						AL_2O-304(196-476), AL_2O_3-1018(749-1612)
AN Dynamite[2]	8.7 (5.8-11.6)								CaO-5.1(4.5-5.6)
Blasting Gelatin[2,21]								96	
GTF[23]	506 (431-571)	106 (9.5-207)	0.17 (0-0.4)	1.02 (0-3.2)	1.9 (0.12-4.7)				HCL-6.7
Comp B[2]	448		6.8		19.2	320			CH_2O_2-83
DNT[2]	302	538	34	54	70.4	160			CH_2O_2-9.6
1,2D[23]		417	6.1 (3.0-9.1)		101				HF-1092(1088-1096), C_2H_2-0.04, CF_4-5.6 (0.47-10.7)
FEFO[24]	148 (146-149)	6.4 (0-12.8)	2.35 (1.92-2.77)		20.1 (16.1-24.1)				HF-233(232-234), CF_4 -1.2(0-2.4)
HMX[23, 24]	285 (13-490)	35.3 (0-156)	3.9 (0.02-8.73)	0.002 (0-0.004)	13.6 (0-41.1)				
Lead Azide[2]									Pd-1408
LX-11-0[23]	383 (5.6-767)	115 (0-230)	5.7 (0.03-11.6)	0.019 0.016-0.022					HF-153(3.6-276), CF_4 -139(0-299)
Mercury Fulminate[2]	2214	79.2							Hg-1480
Nitroglycerin[2]								57 (30-84)	
Nitromannite[2]								96	
Nitromethane[24]	167 (92-246)	0	12.5 (9.6-15.3)		4.2 (3-5.3)				

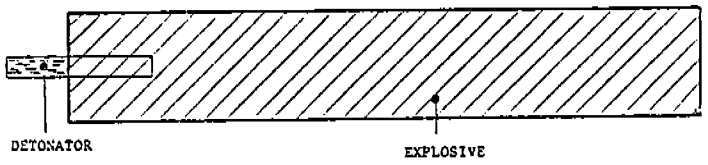
Table 5. CALCULATED EMISSIONS FROM DETONATION OF EXPLOSIVE MATERIALS (lb/ton) (continued)

Compound	CO	$C_{(s)}$	NH_3	HCN	CH_4	CH_3OH	C_2H_5OH	NO	Other
Nitrostarch Powder[2]	6.3 (5.8-6.8)								
Petn[2]	106 (0.56-263)		13 (7-27.2)		0.32	35.8 (19-45)		15 (6-24)	CH_2O_2-347(193-524)
RDX[2]	196 (5.6-554)		43.5 (24-122.4)			137 (6.4-373)	6.0		
RDX/TNT/AL[2]	209 (22-414)	60.1 (2.4-142)	7.93 (3.4-15.6)	46.7 (16-92)	12.8	33 (16-51)	114 (27.6-212)		CH_2O_2-336(166-497) C_2H_6-25.6(4.8-42), C_2H_4 -24.1(5.0-33.6), CH_2O_2 -30.5(9.2-64), AL_2O-437 (217-624), AL_2O_3-307 (34.7-628)
RX-23 (AA, AB, AC)[23]			385 (0-925)						
Straight Dynamite[2]	244 (112-375)		6.8 (3.4-10.2)						
Straight Gelatin[2]	103 (11.6-174)		15.9 (6.8-23.8)			25.6		10 (6-18)	CaO-28(22.4-33.6), Na_2O -224(138-310) CaO-13.1(5.6-22.4), Na_2O-285(198-372)
Tetryl[2]	524 (454-594)	73.7 (64.8-81.6)	35.7 (30.6-40.8)	181 (157-205)	38.4 (25.6-51.2)				
Tritonal (80/20)[2]	343 (67-582)	237 (122-360)	6.8	77.3 (38-108)	19.2 (12.8-25.6)	29.9 (6.4-45)	82.8 (9.2-184)		C_2H_6-43.6(4.8-78), CH_2O_2-27.5(9.2-64), C_2H_2-29.7(5.0-50.4) AL_2O-250(39.2-391), AL_2O_3-391(186-698) C_2H_6-33.6(1.06-66), CH_2O-18, C_2H_4-5.6, CH_2O_2-18.4
TNT[2,24]	305 (28-726)	335 (86-476)	23.9 (0.045-116)	39 (0.0004-108)	68 (3.2-307)	214 (76.1-301)	101		

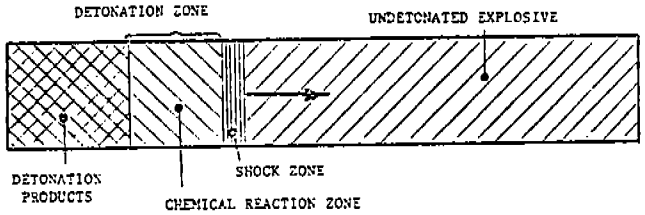
Table 6. COMPOSITION OF TYPICAL PROPELLANTS (PERCENTAGE)[1]

Composition	Standard Propellant (M-5)	Rocket Propellant (T-5)	Small Arms Single Base (11)
Nitrocellulose:			
12.60 percent N 13.15 percent N 13.25 percent N	81.5	57.5	98.3*
Nitroglycerin	15.0	39.2	
Barium Nitrate	15		
Potassium Nitrate	1.0		
Potassium Perchlorate			
Nitroguanidine			
Dinitrotoluene			Coat
Trinitrotoluene			
Dibutylphthalate			
Diethylphthalate			
Triacetin			
Potassium Sulfate		1.5	1.0
Tin			
Diphenylamine	0.75		0.7
Ethyl Centralite		1.75	
Graphite	0.25		Glaze
Carbon Black		0.05	
Cryolite			
Lead Stearate		0.1	
	100.0	100.0	100.0

* Can be either 13.15 percent or 13.25 percent Nitrogen.



A - EXPLOSIVE BEFORE DETONATION



B - EXPLOSIVE PARTIALLY DETONATED

Figure 1. Progress of detonation through a column of explosive.

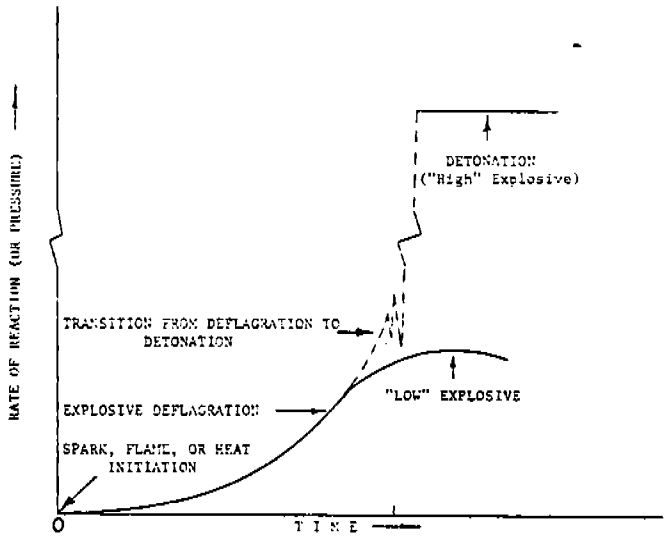


Figure 2. Explosive deflagration versus detonation and transition from deflagration to detonation.

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The presentation contains no material that warrants its disapproval for security or policy reasons.

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NOTE TO EDITORS