United States
Environmental Protection
Agency

Municipal Environmental
Research Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S2-84-051 Apr. 1984

EPA

Project Summary

Gaseous Emissions from Excess Air Combustion of Propellants and Explosives

J. Mahannah, D. Schubert, C. Culp, and T. Schomer

The purpose of this short-term project was to determine the levels of nitric oxide (NO), nitrogen dioxide (NO_2), and carbon monoxide (CO) in the off-gases from the open burning of explosives in excess air. The ultimate goal is to reduce the level of NO_x, CO, and particulates emitted during the destruction of surplus, waste, and off-spec explosives. Previous work (DOE) showed that a gravel/sand filter in the roof of a bunker reduced the level of particulates emitted during excess air combustion of propellants; few NO_x or CO measurements were reported. In this project, two HMX-($C_4H_8O_8N_8$)-based propellants (Chaparral* 6678, 200 to 538 g, and Arcadene 311B, 65 to 162 g) were burned in a 1.3-m^3 steel chamber fitted with a 30-cm-deep sand and gravel filter. Air (1 to 6 m^3/min) was blown into the chamber to ensure combustion and to force the gases through the filter, which included a 2-cm layer of damp activated carbon. Of the components measured, the NO-concentration was the predominant and most reproducible. Little NO_2 was observed. CO production fluctuated widely, probably because of inadequate mixing of the gases within the chamber. The NO and CO concentrations decreased across the filter. NO reductions were 25% to 67% for Arcadene and 10% to 57% for Chaparral; CO reductions were from 38% to 81% for Arcadene and 33% to 91% for Chaparral. The project demonstrated that the filter is effective in partially eliminating NO and CO emissions, but that additional work, including the incorporation of catalysts in the bed and the introduction of NO control gases (e.g., NH_3), should be undertaken.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction and Background

When surplus, waste, over-age or out-of-specification explosives and propellants must be disposed of, the conventional procedure is to destroy them by open buring or by detonation. Other processes, including incineration, are also used, but less frequently. Both open burning and detonation, although low in capital and operating cost and relatively safe, generate undesirable air pollutants, including NO, CO, NO_2, and, occasionally, N_2O, HCN, and free radicals (H, OH, N, O). The nature of these two destructive processes is also such that control of emissions has not been practiced or is impractical.

Thermal destruction with excess air in an incineration system makes it possible to control the emissions arising from decomposition of these high energy materials. The air pollution control equipment for such systems is, however, usually complex and costly. Further, the incinerator must be specially designed to handle fortuitous blast incidents. Inexpensive alternatives for the control of air pollution during the destruction of explosives make novel processes attractive.

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

The goals of this project were to evaluate an improved technique for open air burning of explosives and to recommend innovations. The improved destruction process for explosives (including propellants) was designed to lower the level of particulates and noxious gases released into the air space, when the level is compared with that attained during destruction by detonation or conventional open air burning. Data are generally available on the composition of gases and vapors released from explosives in actual-use situations (blasting, rocket propulsion) in which all (or most) of the oxygen is provided by the explosive; but few data are available on combustion products formed during burning (or incineration) in excess air. Thus, in this project, data had to be generated on the levels and proportions of nitric oxide (NO), nitrogen dioxide (NO_2), and carbon monoxide (CO) in the off-gases from the open burning of high explosives, including propellants, in excess air.

Previous work (DOE) showed that a gravel and sand filter installed in the roof of a bunker significantly reduced the level of particulates emitted during the excess air combustion of high explosives, but few NO_x or CO measurements were reported.

In the work now being reported, two HMX-$C_4H_8O_8N_8$)-based propellants (Chaparral 6678 and Arcadene 311B, i.e., C-4) were burned in a specially built steel chamber fitted with internal baffles and a top-side, layered, sand-on-gravel bed that also contained damp, granulated activated carbon. A blower furnished excess air to ensure smooth combustion and to force the off-gases, vapors, and particulates through the filter bed. Thermocouples and gas analysis probes were installed above and below the filter to monitor gas/vapor temperatures and compositions.

Explosives can be broadly classified as: (1) low explosives (black powder), (2) high explosives (dynamite, a mixture of nitroglycerine ($C_3H_5O_9N_3$) and diatomaceous earth; RDX ($C_3H_6O_6N_6$), cyclotrimethylenetrinitramine; HMX ($C_4H_8O_8N_8$), cyclotetramethylenetetranitramine; AMFO, (94% ammonium nitrite + 6% fuel oil), and (3) detonators (lead azide or styphnate, mercuric fulminate).

Detonators are used to set off high (and low) explosives for: blasting, setting off explosive military devices (bombs, mines, grenades) or propelling munitions (shells, bullets, flares). High explosives (propellants) are also used as thrusters to power rockets, space ships, and missiles.

Most explosives (excepting detonators) are usually formulated so that considerable initiating energy—from blasting caps, electric or powder squibs, sparks—must be concentrated on the material to initiate an explosion.

The explosive is usually in the form of a solid or liquid; on explosion, the material converts to hot gases (and possibly some particulate material), which exert great force on the container originally filled with the explosive. A gram-mole of HMX (MW 296) has volume of about 1/5 L (.052 gal), but on explosion quickly produces 270 L @ STP (at standard temperature and pressure) of very hot gas (equimolar N_2, CO, and H_2O (steam)). Many explosives are designed to require no extra oxygen. Note that the HMX has sufficient chemically bound oxygen to produce the gaseous products (so-called zero-oxygen balance).

It is not surprising that materials other than CO, N_2, and H_2O may also form: N_2O, NO, NO_2, HCN, and even free radicals. The conditions existing during explosion or burning define the applicable kinetics and thermodynamic constraints, which determine the products and by-products formed.

In unconfined (open) burning, one would expect that O_2 from the air would combine with CO to form CO_2, for example. The production of NO_x may be enhanced or decreased, depending on the temperature and evenness of the combustion, the access to air, and other factors. (The interested reader may wish to predict the combustion products of black powder, where the oxygen-balanced reaction is $2\,KNO_3 + S + C = K_2SO_4 + CO_2 + N_2$. As the proportion of C is increased, CO, sulfites, and sulfides will be formed.)

Explosives are generally formulated to make them suitable for a particular use (controlled burn rate, decreased shock sensitivity). Consider a military shell: the round must not explode during propulsion but only on reaching the target area. Additives include metal powders and inorganic compounds, which produce particulates (some soot may also form).

It should be clearly understood that open burning or detonation of waste explosives serves a very useful purpose in protecting human life and limb and will continue to be used. The work reported here, as well as any future related effort, is expected to provide a better understanding of the options for destroying explosives. We need approaches applicable not only to explosives but also to other hazardous materials—approaches maintaining not only the safety and low cost features of open burning but also improving air pollution control.

System Design and Results

The thermal destruction chamber used for these tests is about 1.3 m^3 (45 ft^3) in volume and is constructed of 3.2-mm (1/8-in.) steel plate. The overall design is shown in Figure 1. The filter bed is supported on an expanded metal grating overlaid with wire cloth 30 cm from the top of the chamber. The bed is assembled from the following materials (bottom-to-top): 10 cm (4 in.) of road gravel (2.5-cm (1-in.) diameter); 5 cm (2 in.) of pea gravel; 2 cm (1 in.) of activated carbon; and 13 cm (5 in.) of sand. An air blower and restricted air inlet were incorporated in the design to provide the proper volume of air for the combustion and to force the gases through the filter bed. Gas analyzer (CO, NO, NO_2) probes were placed in the chamber above and below the filter bed to monitor components of the combustion gases. The probes were calibrated with EPA "Protocol" gases. The temperature in the chamber was measured with a Type K (Chromel/Alumel) thermocouple.

The two propellants in this study (Chaparral 6678 and C-4) both contain HMX as the primary explosive (60% and 84.8%, respectively). Both propellants are soft solids that can be easily cut to size. The propellant was ignited by electrically heating a nichrome wire embedded in a block of the propellant charge.

A series of experiments was first carried out in the chamber with black powder to observe gas flow and to adjust internal baffles. The next tests established the minimum weight of propellant needed to generate measurable volumes of gases. Chaparral samples of 200 to 500 g and C-4 samples of 100 to 200 g were required to give measurable volumes of NO and CO (Table 1). The first 27 trial burns were also used to optimize conditions for the tests in terms of the minimum volume of air needed to ensure combustion of the propellant. When the air blower with restricted intake was used, the minimum air flow was 2.4 m^3/min (85 ft^3/min). Lower flows resulted in increased CO levels, indicating incomplete combustion to CO_2.

Though several runs were carried out during the study with each propellant (runs 28 through 42), considerable variations occurred in the volumes of gases generated and in the concentration of NO, NO_2, and CO in the gas, both before and after passage through the filter. These fluctuations did not correlate

Table 1. *Combustion of Chaparral and Arcadene 311B (C-4)*

Burn #	Propellant	Propellant Weight (g)	Air Flow Rate (m^3/min)	Chamber Temperature (°C)	Maximum Gas Concentrations (ppm) Bottom NO	Bottom CO	Bottom NO_2	Top NO	Top CO	Top NO_2
1	Chaparral	450	6.4	-	-	3000	-	-	3000	-
2	Chaparral	340	6.4	-	250	-	-	205	0	0
3	Chaparral	450	6.4	-	250	175	5	250	0	10
4	Chaparral	450	6.4	-	250	3000	5	250	3000	10
5	Chaparral	225	6.4	-	250	0	10	200	0	5
6	C-4	225	6.4	-	250	0	30	250	0	10
7	C-4	225	6.4	-	250	0	125	250	0	0
8	C-4	225	6.4	-	-	-	-	-	-	-
9	C-4	225	6.4	180	360	0	50	200	0	25
10	Chaparral	630	6.4	299	370	3000	15	190	0	0
11	Chaparral	180	6.4	136	125	0	-	80	0	0
12	C-4	180	6.4	147	375	0	50	210	1200	0
13	C-4	180	6.4	166	320	0	40	170	0	0
14	C-4	180	6.4	173	360	0	10	130	0	0
15	C-4	180	6.4	155	200	0	10	130	0	0
16	C-4	180	6.4	130	200	0	15	120	0	0
17	Chaparral	545	6.4	311	260	0	15	120	0	0
18	Chaparral	545	6.4	342	140	0	10	150	0	0
19	Chaparral	480	3.9	370	500	0	5	180	0	0
20	Chaparral	446	2.9	366	500	0	0	200	0	0
21	Chaparral	474	1.0	326	500	0	0	130	0	0
22	Chaparral	211	1.0	282	500	0	0	110	0	0
23	Chaparral	498	1.0	355	210	3000	0	230	3000	0
24	Chaparral	493	1.0	420	500	600	0	175	900	2
25	Chaparral	248	1.0	278	500	450	0	175	300	0
26	Chaparral	435	1.0	370	1250	2100	0	175	750	0
27	Chaparral	476	1.5	318	950	975	0	225	300	0
28	Chaparral	522	2.4	370	525	1050	5	275	225	0
29	C-4	162	2.4	194	525	150	5	250	75	0
30	C-4	65	2.4	92	150	-	-	125	-	-
31	C-4	70	2.4	172	1300	0	0	600	600	55
32	Chaparral	503	2.4	376	600	0	0	400	0	10
33	Chaparral	493	2.4	394	350	0	10	300	0	0
34	Chaparral	528	2.4	416	300	0	0	300	0	0
35	C-4	129	2.4	-	700	600	0	250	150	20
36	C-4	114	2.4	131	450	0	0	100	0	0
37	C-4	114	2.4	139	400	0	0	100	0	0
38	C-4	103	2.4	153	1100	30	2	250	0	5
39	C-4	84	2.4	-	1150	450	20	825	270	15
40	Chaparral	200	2.4	190	200	9	0	100	0	0
41	Chaparral	500	2.4	380	200	30	0	150	15	0
42	Chaparral	500	2.4	-	200	45	0	150	15	0

with the sample size, but may have arisen from incomplete mixing of the gases or uneven burning of the propellant. Of the gases measured, NO was usually the predominant product of combustion. Nitrogen dioxide (NO_2) was not detected during the burning of Chaparral and was found only in very small concentrations during the combustion of C-4. Results of the gas analyses and estimates of the removal efficiency of the filter are summarized in Tables 2 and 3 for the two propellants.

Conclusions and Recommendations

The results of tests on the excess air combustion of high explosives in a steel chamber fitted with a charcoal-containing sand and gravel filter (1) indicate that the levels of the evolved nitric oxide (NO) and carbon monoxide (CO) are effectively lowered, and (2) verify a prior observation that particulates are effectively removed.

By the reaction of CO with O_2 in the air, the level (quantity) of CO is much reduced over what is common during confined combustion (propellants) or during explosions. The filter is effective in further reducing the level of noxious gas (CO, NO, etc.) concentration during passage through the composite bed.

Definitive values for the achievable reduction in level of each gas cannot be presented because of the wide variation in data. Specifically, NO reductions by the filter ranged from 25% to 67% for C-4 and 10% to 57% for Chaparral; CO reductions ranged from 38% to 81% for C-4 and from 33% to 91% for Chaparral.

Little or no NO_2 results from the combustion of either C-4 or Chaparral 6678 under the conditions existing in the chamber used in this study. Low NO_2 generation has also been reported by other investigators.

The variations in removal of NO and CO may be due, at least in part, to the design of the excess air inlet system and the resulting uneven burning of the propellant and inadequate mixing of the gases in the chamber. These problems could be avoided by modifying the design of the chamber and by developing more effective means of providing air to the sample. For example, better mixing of the gases and a more even burn might be achieved by providing underflow and/or tangential air flow to the chamber. Investigation of

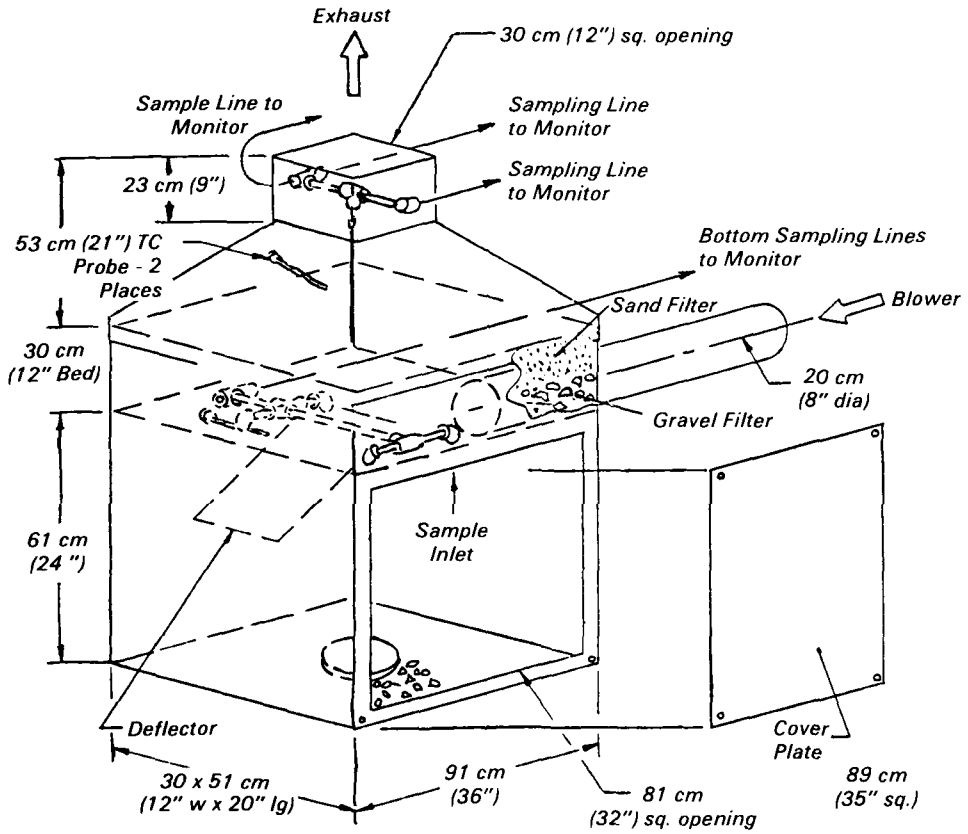

Figure 1. *Schematic of combustion chamber.*

Table 2. *Gaseous Products from Chaparral Incineration**

Pollutant	Before Filter (ppm)	After Filter (ppm)	%-Reduction by Filter†
NO	94-295	56-202	10-57
NO_2	0	0	--
CO	0-434	0-40	33-91

*Time-weighted averages.
Sample weight: 200 to 528 g.
Chamber temperatures: 376° to 416°C.

† The %-reduction was calculated for each burn and not from the "before filter" and "after filter" values cited.

Table 3. *Gaseous Products From C-4 Incineration**

Pollutant	Before Filter (ppm)	After Filter (ppm)	%-Reduction by Filter†
NO	182-676	69-304	25-67
NO_2	0-7	0-8	--
CO	0-475	0-132	38-81

*Time-weighted averages.
Sample weight: 70 to 162 g.
Chamber temperature: 131° to 172°C.

† The %-reduction was calculated for each burn and not from the "before filter" and "after filter" values cited.

these factors should be a major consideration in any future study.

Future work should be directed towai applying known or novel technology to changing the compostion of the gases emitted to the atmosphere, e.g., adding catalysts to the filter bed to reduce NO, NO_2, and CO emissions. A nickel oxide catalyst is reported to accelerate the reaction of NO with CO:

$$2NO + 2CO \xrightarrow{NiO} 2CO_2 + N_2.$$

When nickel catalysts were used in a fluidized bed incinerator to dispose of explosive wastes, NO, NO_2, and CO emissions were reduced substantially.

Similarly, although NO is a relatively difficult air pollutant to remove from a gas stream, NO_2 much more readily dissolves in water (ultimately forming nitric acid). Though adsorption is poor for NO_2 (but better than for CO and NO), it can be adsorbed on activated carbon. Therefore, it would be advantageous to explore methods to rapidly convert NO to NO_2, such as by adding copper or other oxidation catalysts to the filter bed, or to determine whether catalyzed reduction (using NH_3) can be effectively applied.

The full report was submitted in fulfillment of EPA Contract 68-03-3069 by IT Corporation under the sponsorsl of the U.S. Environmental Protectio.. Agency.