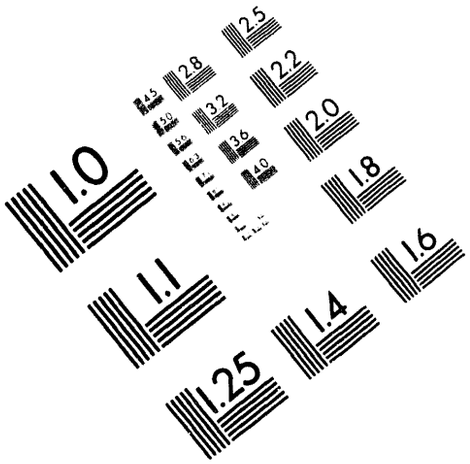

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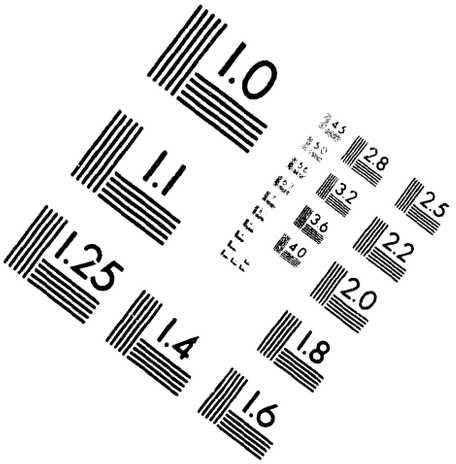

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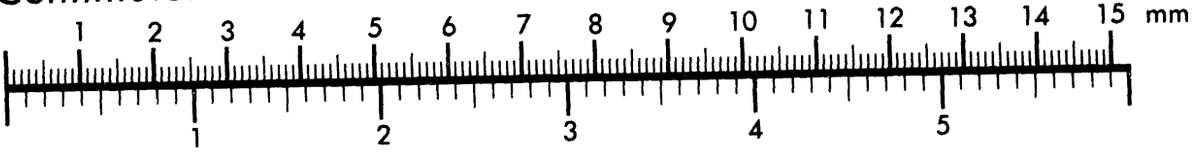

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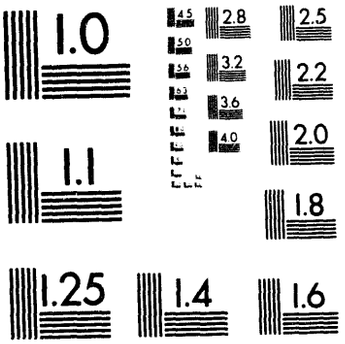

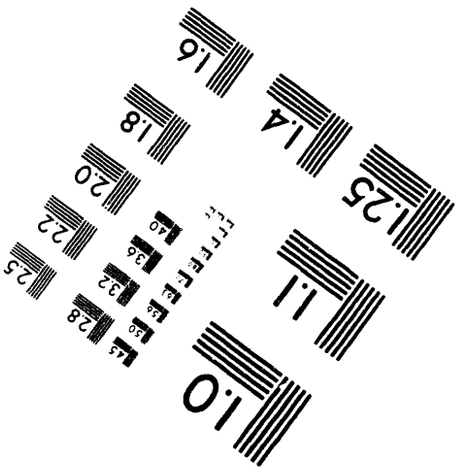

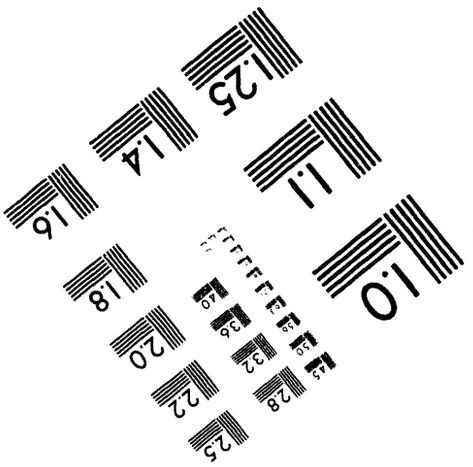

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PREPRINT

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Emissions from Energetic Material Waste during the Molten Salt Destruction Process*

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Introduction

The Lawrence Livermore National Laboratory (LLNL) is developing methods for the safe and environmentally sound destruction of energetic materials. Open burn/open detonation (OB/OD) is currently the most common method of destruction of energetic materials (EM), and the United States has many OB/OD-permitted facilities for the destruction of these materials. Public concerns and increasingly stringent environmental regulations have made OB/OD of energetic materials increasingly costly, and may ban OB/OD in the near future.

The Molten Salt Destruction (MSD) process is an alternative to OB/OD for the destruction of energetic materials and energetic material-containing wastes as described by Upadhye *et al.* during this conference (1). MSD is an attractive technology due to its inherently low gaseous emissions and the ability of the salt bath to scrub both acidic gasses and particulates. LLNL is currently operating nominal 1 kg/h molten salt bath (Fig. 1). This unit is being used to address key issues before this process can be commercialized. Concerns related to safety are being addressed by Upadhye (1); issues related to emissions are addressed in this preprint.

Methods and Materials

The stainless steel crucible (5.76" inside diameter, 6.63" outside diameter, and 24" length) is charged with 7.5 kg of an equal weight mixture of lithium, potassium and sodium carbonates having a melting point of approximately 400° C. It is fitted with a side injection nozzle. Thermocouples are placed at various locations, including the crucible, the feed nozzle, and the exhaust gas outlet. Coolant gas flow is controlled so as to maintain the feed nozzle temperature under 100° C. Gas sample bottles with solenoid valves are attached to the exhaust line. The unit typically operates at 700-750°C.

Energetic materials were obtained as pure powders, molding powders or pressed parts. Pressed parts were water machined to a powder and all materials were passed through a 1.5 mm screen. A slurry, consisting of energetic materials (25 to 33% by weight), 1% methyl cellulose and water, was entrained in a stream of air and injected into the salt bath.

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The following pure high explosives (HEs) were destroyed by continuous feeding into the MSD unit: HMX (octahydro- 1,3,5,7-tetranitro- 1,3,5,7-tetrazocine), RDX (hexahydro- 1,3,5-trinitro- 1,3,5-triazine), ammonium picrate (Explosive D), TNT (2,4,6-trinitrotoluene). In addition to these pure components, we have destroyed a number of commonly used formulations, such as LX-10 (HMX/Viton[DuPont]), LX-16 (PETN (2,2-bis[{nitoxy}methyl]-1,3-propanediol dinitrate)/FPC 461 [Firestone]), LX-17 (TATB (2,4,6-trinitro-1,3,5-benzenetriamine)/Kel F [3M]), and PBX-9404 (HMX/tris(2-chloroethyl) phosphate/nitrocellulose). We have also destroyed a liquid gun propellant, LP XM46, (hydroxyammonium nitrate, triethanolammonium nitrate and water) diluted to 1:3 with water.

The slurry or solution of energetic material was injected into the crucible using a peristaltic pump through the side nozzle. Up to 500 g TNT equivalent HE in water is fed at rates varying between 20 g/h to 2000 g/h of energetic material in each run. Carbon monoxide and nitric oxide were measured continuously by infrared spectroscopy. Gas samples were collected at steady state and analyzed by mass spectrometry (Fig. 2). Salt and water condensate samples were analyzed for contaminates and traces of energetic materials.

Results and Discussion

Analysis of NO and CO are shown for a number of pure explosives and formulations in Table 1. These data are presented as the percent of nitrogen or carbon in the feed that leaves the unit as NO or CO. Presenting data in this manner allows the separation of gas feed rate from emission quality of stack gas. At the 700 to 750°C operating temperatures thermal NOx is not expected to significantly contribute to the emissions. Grab-gas sampling has shown that NO is the principal NOx species formed under these operating conditions and the amount of NO_2 and N_2O were insignificant when compared to NO concentrations. The major combustion products are N_2, CO_2 and H_2O, and the amount of NO_x and CO produced by the MSD process was relatively small.

Table 1

Explosive	%C→CO	%N→NO	Throughput (kg/h)	EM Form
RDX	0.035	0.05	1.8	pure powder
HMX	0.035	0.11	1.4	pure powder
TNT	0.006	0.45	0.50	pure powder
Explosive D	0.028	0.18	0.49	pure powder
LX-10	0.029	0.019	0.99	machined part
LX-16	0.064	0.14	1.3	molding powder
LX-17	0.029	0.20	0.69	machined part
PBX 9404	0.09	0.25	0.3	machined part
LP XM-46	0.11	0.58	2.6	diluted solution

We wished to compare the MSD process to more conventional thermal processed. For this comparison we pumped LP XM46 (diluted 1:3 with water) at a propellant feed rate of 5.1 kg/h of into a moving packed bed of alumina spheres at 570° C. Under these conditions 54% of the nitrogen in the liquid propellant was emitted as nitrogen oxides. The principal nitrogen oxide species was NO_2 with NO levels 60% of the NO_2 levels. A trace of N_2O is also produced. The amount of nitrogen oxides produced by destruction of LP XM46 by MSD is significantly less than for destruction in a packed-bed combustor.

The salt samples were analyzed for traces of HE and other contaminates. Fourier Transform-Infra Red (FT-IR) spectroscopy shows a complete absence of HE in the cooled molten salt. In addition the presence of HE in the water condensate was analyzed by MS or HPLC for HE. These data indicate complete destruction of EMs in the MSD process and are consistent with

Figure 1. The 1 kg/h molten salt bath.

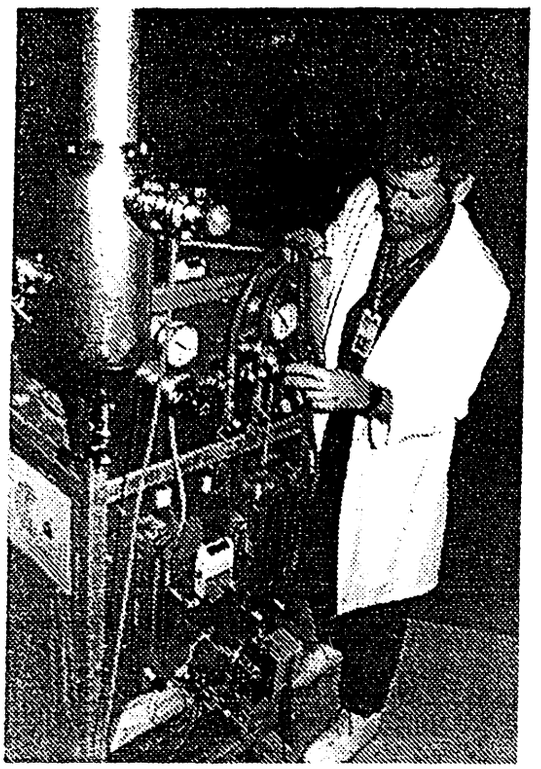
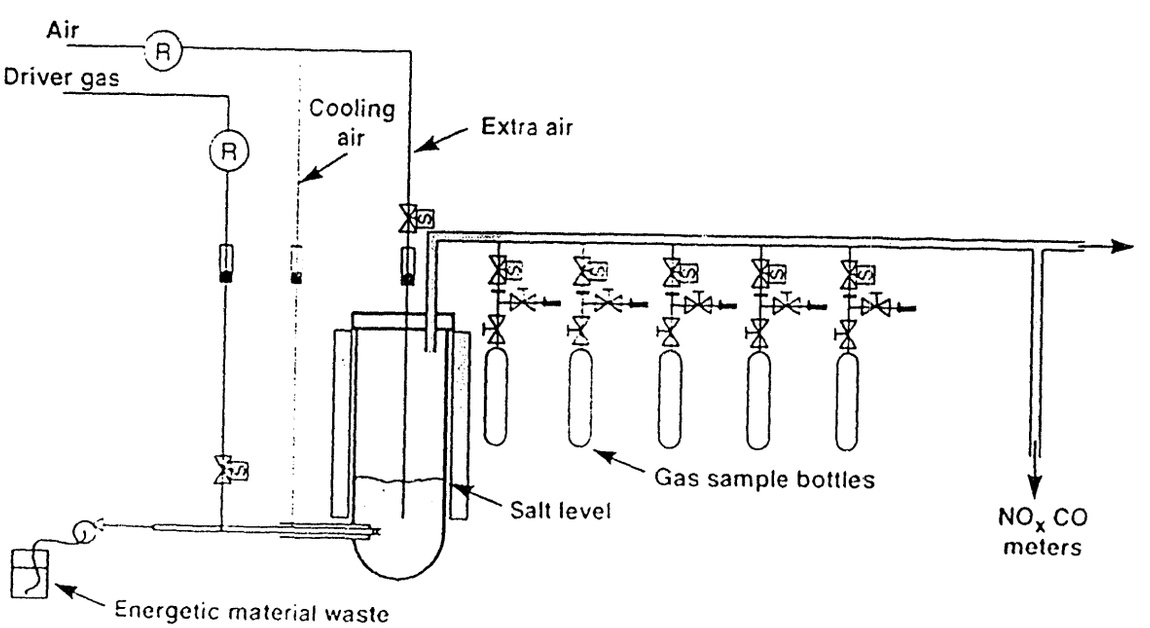


Figure 2. Molten salt unit with gas sampling devices.



our expectations, given the ease of decomposition of the energetic materials at these temperatures.

Analysis of the salt bath show halogens, chloride and/or fluoride from the "LX" formulations and PBX 9404. We examined the composition of the salt bath after 2.5 L of diluted LP XM46 had been processed. The concentration of nitrate in the bed was 4.50% and of nitrite 0.42%. Thus, roughly 50% of the nitrate in the LP XM46 remained in the salt bath after the termination of the run. If additional fuel, such as 2-propanol, is injected after the bed has built up an inventory of nitrate, the concentration of nitrate in the bed drops and NO is the principal nitrogen oxide species emitted. It appears as if the organic materials in the propellant are preferentially oxidized by oxygen leaving nitrate in the bed. Addition of additional fuel reduces the nitrate to NO.

Conclusions and Future Work

We have demonstrated that high explosives and a liquid propellant can be safely and completely destroyed using the molten salt destruction process. Gaseous emissions of NOx and CO are very low. Nitrate builds up in the salt bath when nitrate rich materials are destroyed, but addition of fuel reduces the nitrate to NO.

We have begun a program to add catalytic materials to the bed to further reduce emissions, and possibly eliminate the need for any down stream gas treatment. We have also constructed a small molten salt bath to obtain chemical kinetic information and to develop mechanistic models for the destruction process. These will be useful in suggesting process changes that will lead to even lower emissions and to aid in scale up of the MSD process.

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1. Upadhye, R.S., Watkins, B.E., Pruneda, C.O., and Brummond,, W.A "Molten Salt Destruction as an Alternative to Open Burning of Energetic Material Wastes", presented at the I&EC Special Symposium, American Chemical Society, Atlanta, Georgia, September 19-21, 1994.

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