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for the Destruction of Energetic Materials**

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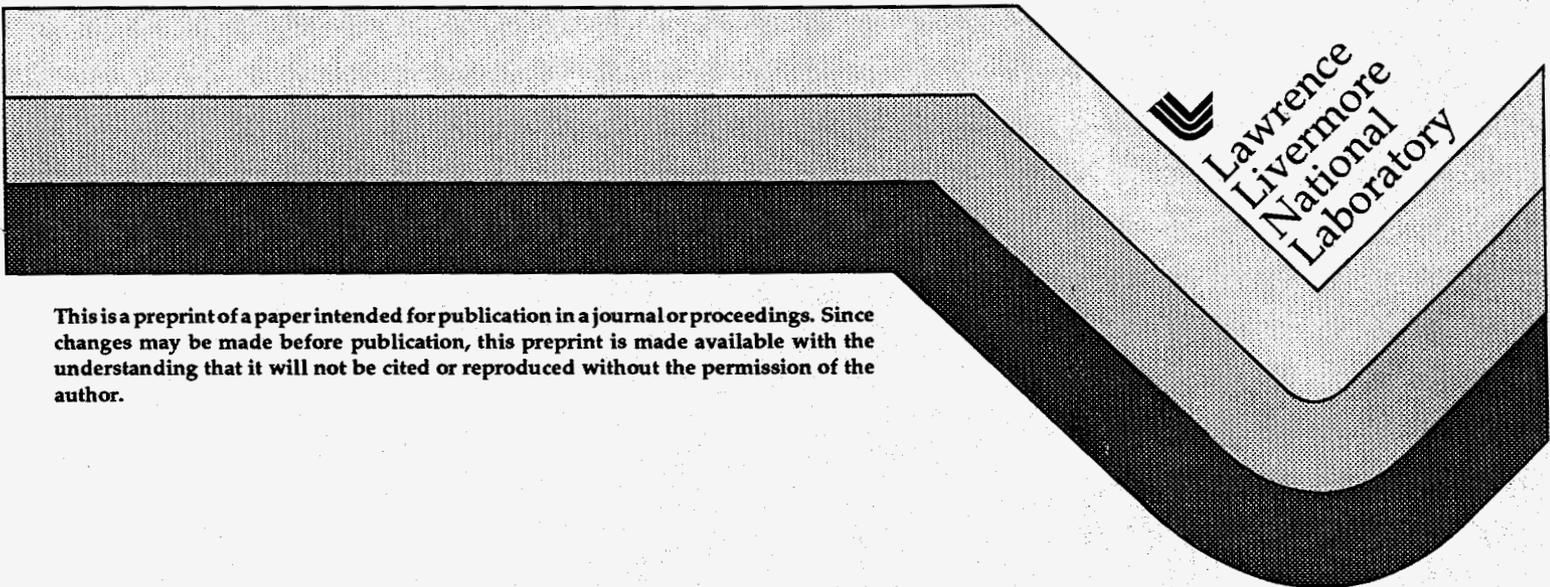
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RECENT ADVANCES IN THE MOLTEN SALT TECHNOLOGY
FOR THE DESTRUCTION OF ENERGETIC MATERIALS*

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ABSTRACT

We have demonstrated the Molten Salt Destruction (MSD) Process for the treatment of explosives and explosive-containing wastes on a 1.5 kilogram of explosive per hour scale(1,2,3,4,5) and are currently building a 5 kilogram per hour unit. MSD converts the organic constituents of the waste into non-hazardous substances such as carbon dioxide, nitrogen and water. Any inorganic constituents of the waste, such as binders and metallic particles, are retained in the molten salt. The destruction of energetic material waste is accomplished by introducing it, together with air, into a crucible containing a molten salt, in our case a eutectic mixture of sodium, potassium, and lithium carbonates. The following pure component DOE and DoD explosives have been destroyed in LLNL's experimental unit at their High Explosives Applications Facility (HEAF): ammonium picrate, HMX, K-6, NQ, NTO, PETN, RDX, TATB, and TNT. In addition, the following formulations were also destroyed: Comp B, LX-10, LX-16, LX-17, PBX-9404, and XM46, a US Army liquid gun propellant. In this 1.5 kg/hr unit, the fractions of carbon converted to CO and of chemically bound nitrogen converted to NO_x were found to be well below 1%. In addition, to destroying explosive powders and molding powders we have also destroyed materials that are typical of real world wastes. These include shavings from machined pressed parts of plastic bonded explosives and sump waste containing both explosives and non-explosive debris. Based on the information obtained on our smaller unit we have constructed a 5 kg/hr MSD unit, incorporating LLNL's advanced chimney design. This unit is currently under shakedown tests and evaluation.

INTRODUCTION

We are developing methods for the safe and environmentally friendly destruction of explosives and propellants as a part of the Laboratory's ancillary demilitarization mission. As a result of the end of the Cold War and the shift in emphasis to a smaller stockpile, many munitions, both conventional and nuclear, are scheduled for retirement and rapid dismantlement and demilitarization. Major components of these munitions are the explosives and propellants, or energetic materials. The DOE has thousands of pounds of

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energetic materials which result from dismantlement operations at the Pantex Plant. The DoD has several hundred million pounds of energetic materials in its demilitarization inventory, with millions more added each year. In addition, there are vast energetic materials demilitarization inventories world-wide, including those in the former Soviet Union and Eastern Bloc countries. Although recycling and reusing is the preferred method of dealing with these surplus materials, there will always be the necessity of destroying intractable or unusable energetic materials. Traditionally, open burn/open detonation (OB/OD) has been the method of choice for the destruction of energetic materials. Public concerns and increasingly stringent environmental regulations have made open burning and open detonation of energetic materials increasingly costly and nearly unacceptable. Thus, the impetus to develop environmentally sound alternatives to dispose of energetic materials is great.

We have previously demonstrated the Molten Salt Destruction (MSD) Process for the destruction of HE and HE-containing wastes(1,2,3). MSD converts the organic constituents of the waste into non-hazardous substances such as carbon dioxide, nitrogen and water. Any inorganic constituents of the waste, such as binders and metallic particles, are retained in the molten salt. The destruction of energetic material waste is accomplished by introducing it, together with air, into a crucible containing a molten salt, a suitable mixture of sodium, potassium, lithium carbonates. (See Figure 1 for the process flow diagram)

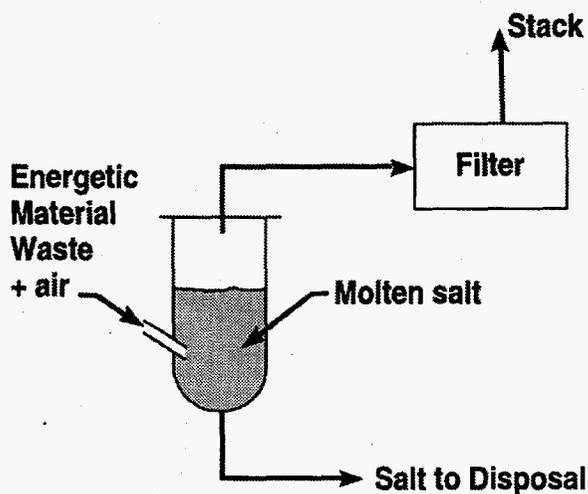


Figure 1: Process Flow Diagram

The temperature of the molten salt can be between 400° to 900° C, but in practice 750°C has been shown to be optimal for energetic material destruction. The organic components of the waste react with oxygen in air to produce carbon dioxide, nitrogen and steam. The inorganic components, in the form of ash, are captured in the molten salt bed as a result of wetting and dissolution. Halogenated hydrocarbons in the waste (which may be present as a result of halogenated solvents in the waste, or as a result of halogenated binders for the HE) generate acid gases such as hydrogen chloride during the pyrolysis

and combustion processes occurring in the melt. These are scrubbed by the alkaline carbonates, producing carbon dioxide and the corresponding salt, such as sodium chloride. Off-gases from the process are sent through standard clean-up processing (such as bag filters or HEPA filters) before being released to the atmosphere. At the end of the process runs, the salt is separated into carbonates, non-carbonate salts, and ash. The carbonates are recycled to the process, and the stable salts are disposed of appropriately.

EXPERIMENT

Figure 2 shows a schematic of the current experimental setup. The crucible (Figure 3) is made of stainless steel, which is resistant to corrosion by alkali carbonates at our working temperatures. It has the dimensions 14.4 cm inside diameter, 16.8 cm outside diameter, and 91 cm length, and is fitted with a flange on the top and a removable injection nozzle, on the side, or from the top. The crucible contains about 7 kg of salt, a equal weight mixture of lithium, sodium and potassium carbonates melting at approximately 400°C. Thermocouples are placed at various locations, including the crucible, the feed nozzle, and the exhaust gas outlet. The coolant gas flow is controlled to maintain the feed nozzle temperature under 100° C. Grab gas sample bottles with solenoid valves are attached to the exhaust line. Infrared meters and a mass spectrometer provide real time analysis for NO_x, CO, N₂, O₂, CO₂, Ar, and hydrocarbons. The whole assembly is placed inside an explosion-proof cell, designed to contain a detonation of up to 500 g HE (TNT equivalent). A remotely operated TV monitor allows us to monitor the experiment without entering the cell during the experiment. All the solenoid valves controlling the sample and the feed sequences are operated remotely. Data are continuously logged by computer.

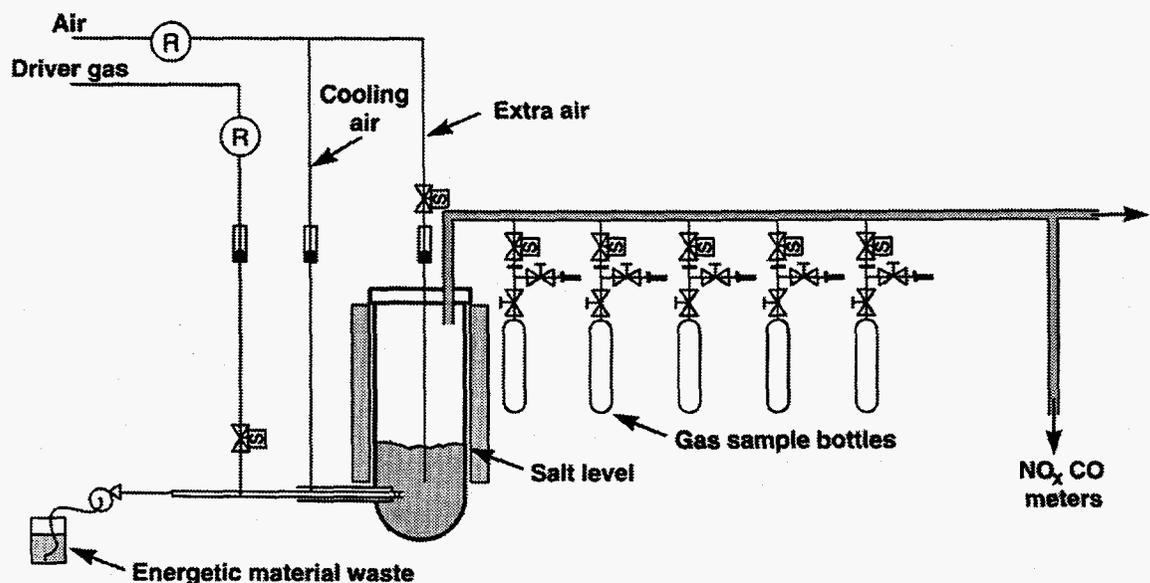


Figure 2: Experimental Schematic

A slurry of energetic material waste and water of desired proportions (typically 30 wt % solids in water) is made and kept in suspension using air driven stirrers (see Figure 2). The waste to be treated is injected in to the crucible using a peristaltic pump through the side nozzle. The gaseous product of the crucible is sent to the vent as shown in Figure 3. A slurry of up to 500 g TNT equivalent HE in water is fed at rates varying between 300 g/hr to 1800 g/hr in each run. Gas samples were collected at various intervals after steady state is obtained. A salt sample is withdrawn from the crucible at the end of the final run, and analyzed for traces of HE and residual inorganics.

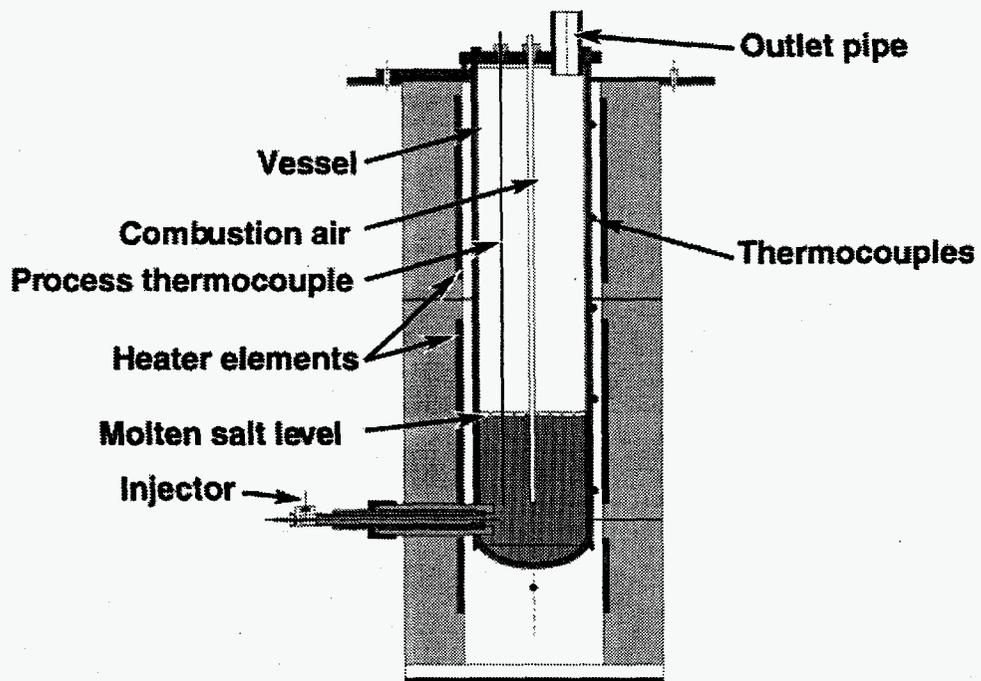


Figure 3: Details of the Crucible

An air-cooled side injector was used for the initial experiments (see Figure 4). This nozzle has an internal diameter of 6.4 mm and can handle HE particles up to 2 mm. HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), we have destroyed RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), PETN (2,2-bis[(nitroxy)methyl]-1,3-propanediol dinitrate), ammonium picrate, TNT (2,4,6-trinitrotoluene), nitroguanadine, and TATB (2,4,6-trinitro-1,3,5-benzenetriamine) have been destroyed by this unit. In addition to these pure components, we have destroyed a number of commonly used formulations, such as LX-10 (HMX/Viton), LX-16 (PETN/FPC 461), LX-17 (TATB/Kel F), and PBX-9404 (HMX/CEF/nitrocellulose). We have also destroyed a liquid gun propellant comprising hydroxyammonium nitrate, triethanolammonium nitrate and water (LP XM46).

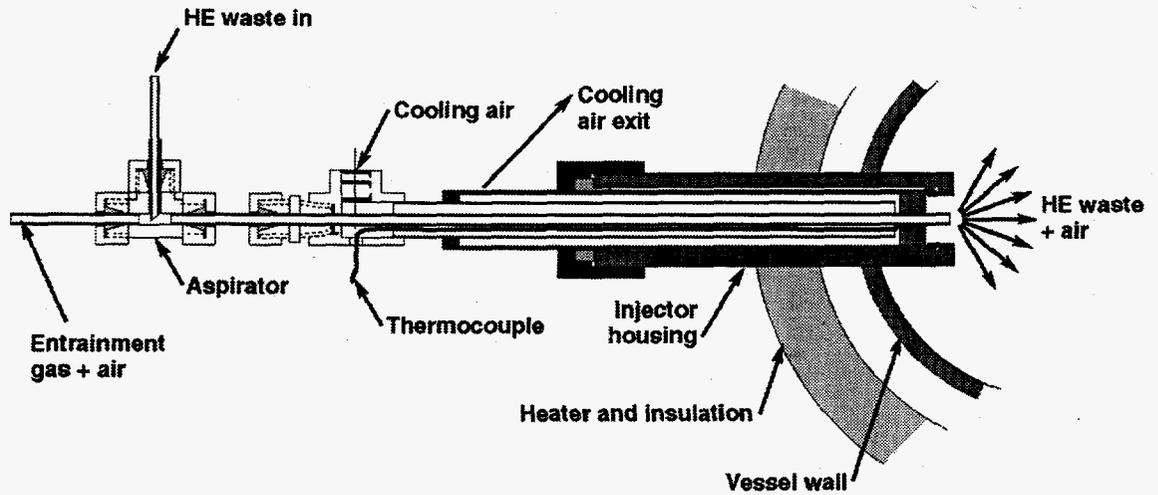


Figure 4: Details of the Nozzle

We have also implemented an insulated top feed downcomer (see Figure 5). This injector has an internal diameter of 19 mm and can handle larger particle sizes. Key materials run through this injector and destroyed by the molten salt unit are : shavings from machined, pressed parts of PBX 9404, and PETN sump sludge surrogate waste containing rust, wood, string and metal parts. This material was provided by Ensign-Bickford.

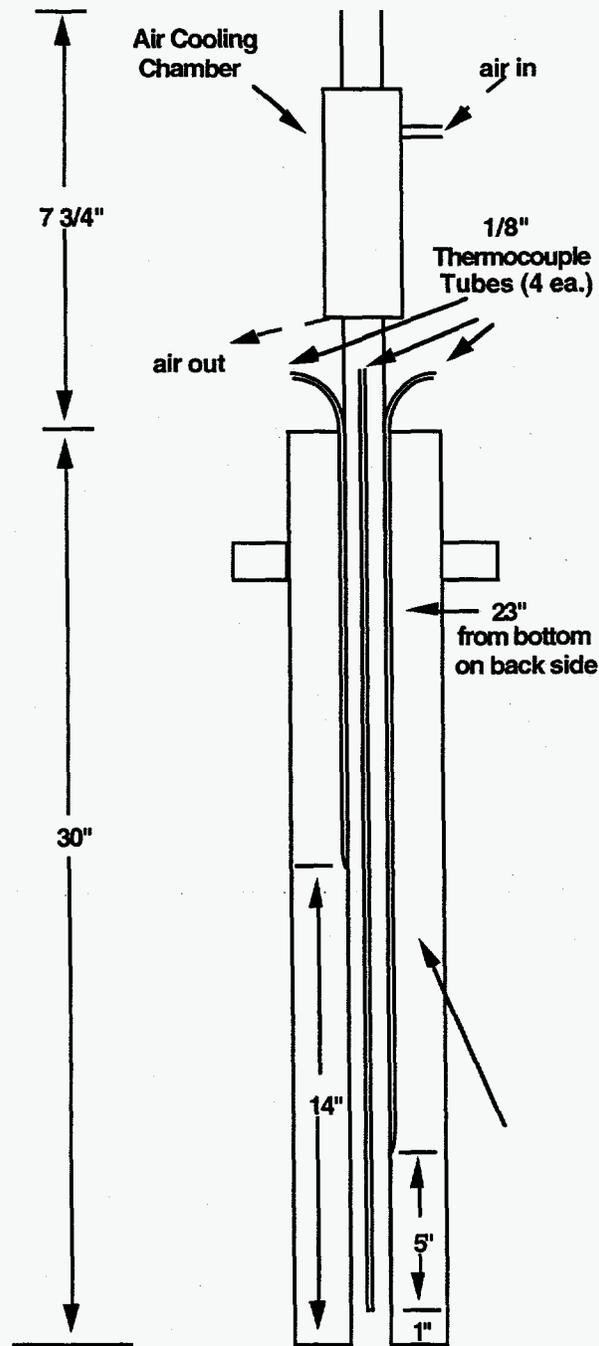


Figure 5. Top feed downcomer.

RESULTS

Gas samples were taken during the experiments, and analyzed using a gas chromatograph, infrared meters, and a mass spectrometer (GC/MS). Typical gas analyses

of untreated stack gases for a number of pure component explosives and formulations are shown in Table 1.

Table 1. Untreated Emissions from MSD treatment of Explosives

Explosive	%C→CO	%N→NO	Rate (kg/h)
RDX	0.035	0.05	1.8
HMX	0.035	0.11	1.4
TNT	0.006	0.45	0.50
Explosive D	0.028	0.18	0.49
Comp B 3	0.051	0.09	1.0
LX-10	0.029	0.019	0.99
LX-16	0.064	0.14	1.3
LX-17	0.029	0.20	0.69
PBX 9404	0.09	0.25	0.3
NTO	ND	0.75	2.0
NQ	0.4	0.5	2.0
LP XM46	0.11	0.58	2.6

Figure 6 graphically displays the CO emission data from the destruction of LP XM46. These data show that CO emissions are lower at higher temperatures, but an unexpected reduction in emissions with increased feed rate. It is not known why the production of CO should decrease with increased feed rate, but this is a general trend observed with all energetic materials tested to date in the 7.5 kg MSD unit. More predictably, higher feed rates produce larger amounts of unburnt hydrocarbons and hydrogen.

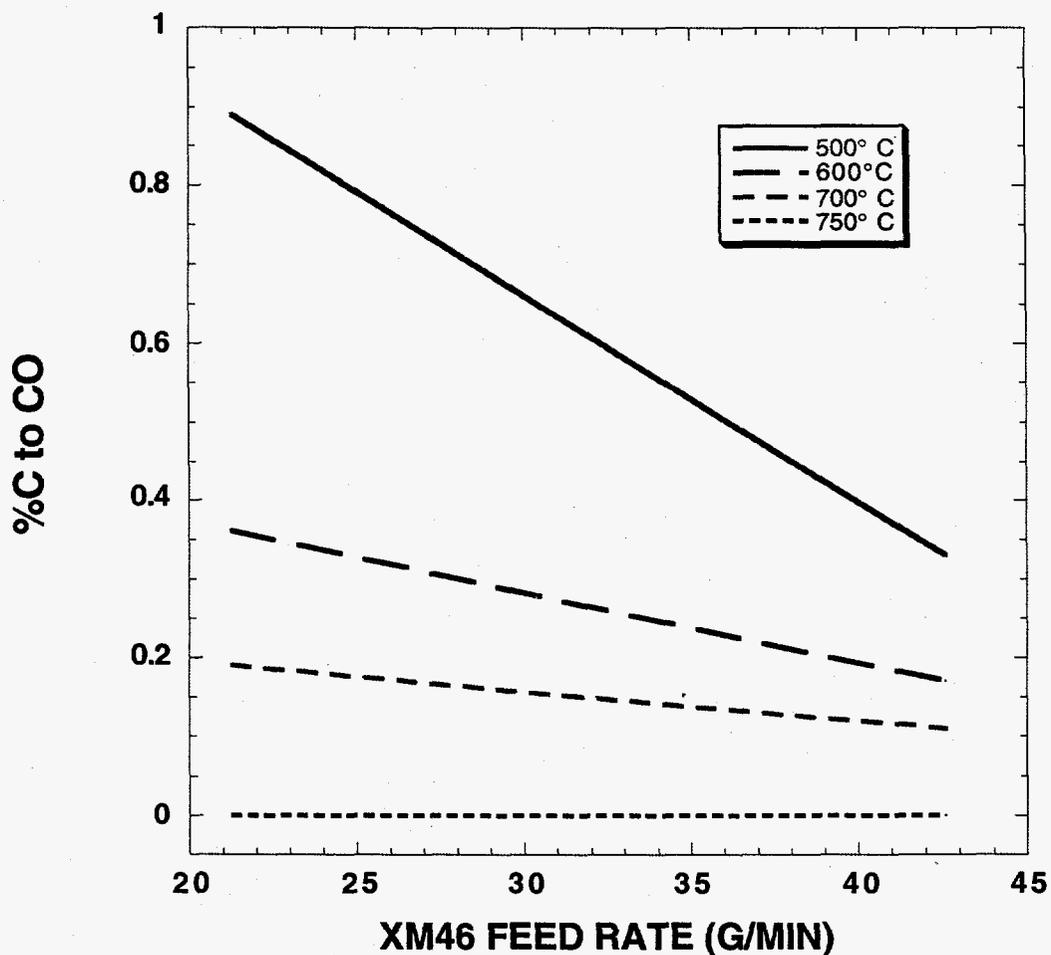


Figure 6. Carbon monoxide produced by MSD of LP XM46 as a function of temperature and feed rate.

We have also implemented a top feed injector for the explicit purpose of feeding real world waste streams rather than pure explosive powders. Since the length of the top injector must be longer than for side injection the time temperature profile of the HE in the top injector must be addressed. In practice if a 2/1 ratio of water to HE is maintained along with a nominal feed rate of 150 grams per hour of HE then the maximum temperature of the HE in the downcomer is 91°C. The top feed downcomer on the 1.5 kg/he unit has an internal diameter of 19 mm and was used to evaluate two real world surrogate waste streams. The first was machine shavings from a pressed part of PBX 9404. The latter was a sump sludge waste surrogate containing PETN and

rust, metal parts, string wood, sand, floor sweepings that are typically found in such sumps. In each of these cases feeding the waste through a peristaltic pump proceeded smoothly with no clogging of the feed line and without the internal temperature of the downcomer exceeding 80°C.

DISCUSSION

Our experiments have demonstrated that energetic materials can be safely and effectively treated by MSD. The emissions from the molten salt destruction of energetic materials are exceeding low. No HCN was found in the exhaust. This is significant since HCN is a common byproduct of the combustion of energetic materials. We may infer that the HCN, being an acid gas, was neutralized by the alkaline carbonate, producing NaCN, which undergoes further decomposition in the salt bath.

The amount of NO_x and CO was relatively small. This indicates that the major combustion products are N₂, CO₂ and H₂O. It may be possible to reduce further the NO_x emissions by changing the operating conditions of the MSD unit (6). At higher temperatures the amount of CO, unburnt hydrocarbons, and hydrogen are all reduced. This trend is expected due the increased rate of combustion at higher temperatures. These data show that gaseous emissions are lower at higher salt temperatures. We were limited to a 750° C operating temperature due to the materials of construction of the crucible. Extrapolation of these results suggests that emissions may drop further at temperatures of 800 or 850° C.

The salt samples are analyzed for traces of HE . All of the HE is expected to be fully decomposed in the molten salt. Fourier Transform-Infra Red (FT-IR) spectra of pure HEs and of molten salt into which the HE had been combusted in, respectively, show a complete absence of HE peaks in the cooled molten salt. Thus, within the detection limits of the method (5 ppm), no HE or propellant are detected in the salt, indicating complete oxidation. This is consistent with our expectations, given the ease of decomposition of the energetic materials at these temperatures.

We performed a comparison of MSD with a packed bed reactor. In the packed bed reactor combustion takes place under incinerator-like conditions. Incineration of XM46 produces large amounts of NO, with upwards of 48% of the nitrogen in the propellant emerging from the reactor as NO. However, operation of the MSD unit with air produces lower amounts of NO (0.46% of the nitrogen being converted to NO). Untreated emissions from the molten salt destruction of XM46 are two orders of magnitude lower than those from incineration.

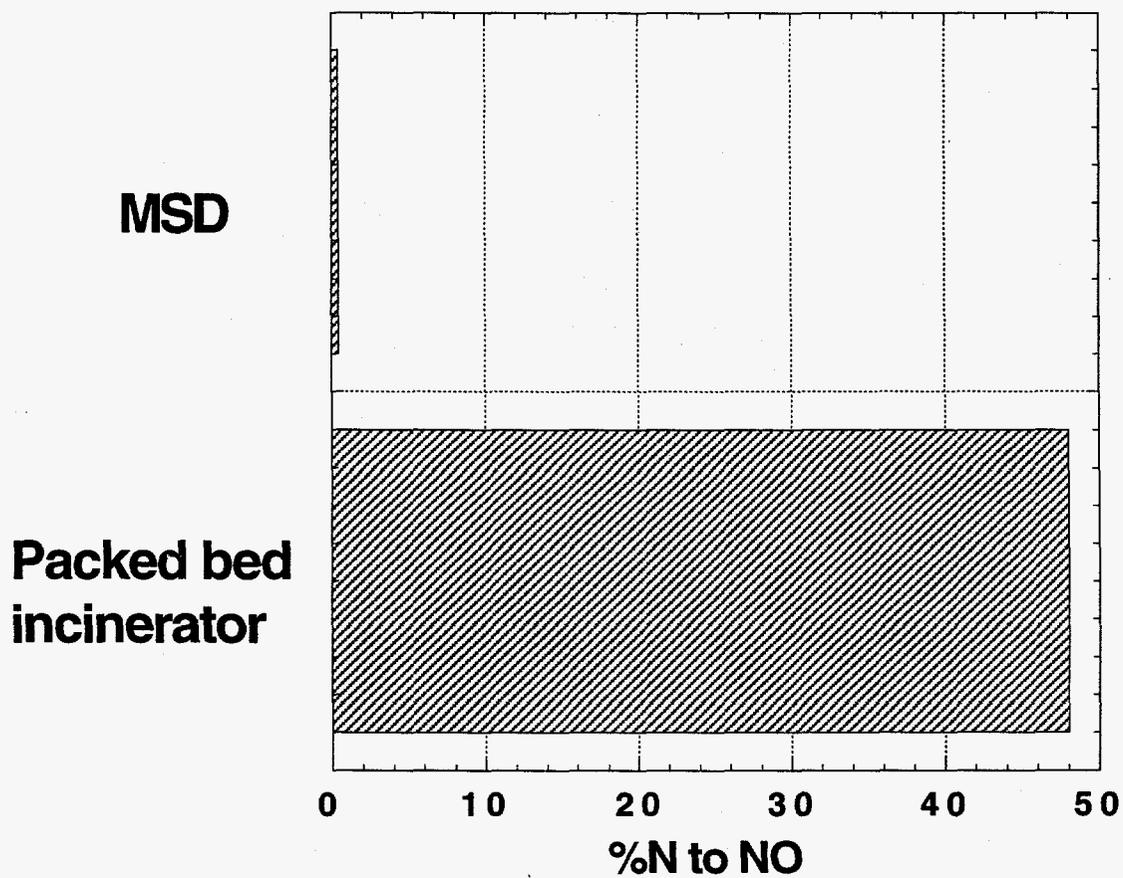


Figure 7. Comparison of NO produced by incineration and MSD of LP XM46

Based on the results of our experiments over the last four years, we have designed and constructed a third generation MSD unit. The schematic of the new crucible is shown in Figure 8.

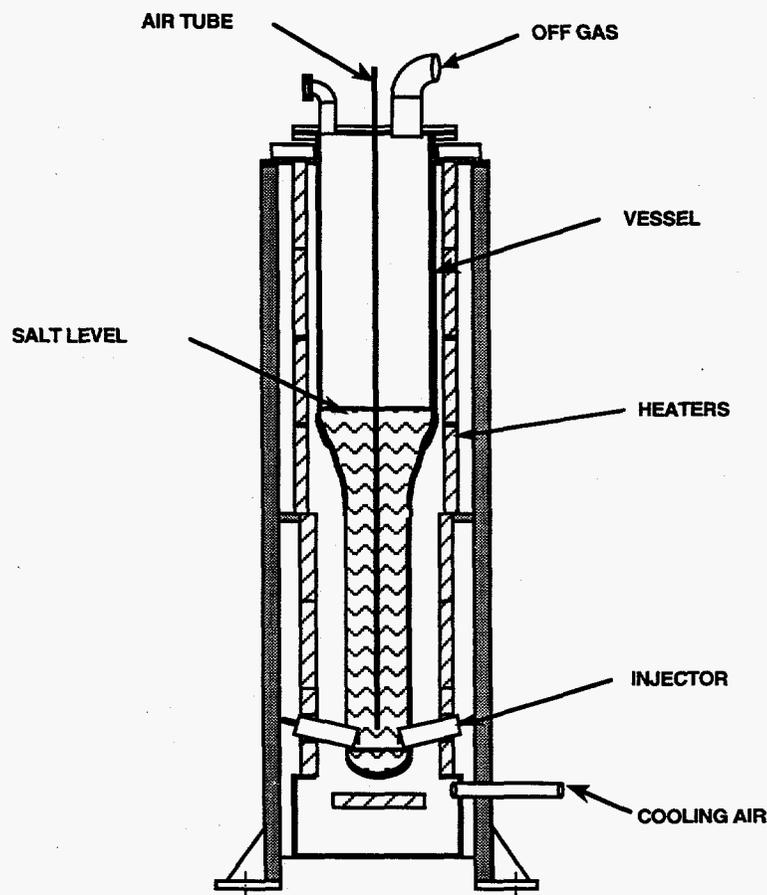


Figure 8: The Advanced Design Unit under Installation

A number of advanced features distinguish the new pilot unit from the previous one. The pilot unit has a "chimney" shape, with 40 cm nominal diameter for the top half, and 20 cm for the bottom half. The purpose of this design is to eliminate or minimize entrainment of liquid salt droplets. The increased area at the top results in about four-fold decrease in the product gas velocity, leading to substantially lower salt entrainment. The pilot unit is much taller than the previous unit: 221 cm vs. 91 cm. This allows higher residence time for oxidation and product gas scrubbing. The pilot unit has been fitted with two side injectors as well as a top feed system. This will allow the introduction of several different feeds simultaneously. The side injector nozzles are inclined, pointing downward, as shown. They are also offset from the center, thereby creating a vortex-like motion and promoting better mixing.

The unit was started up in early October, 1995, and is undergoing shakedown tests. After shakedown and some preliminary experimental work, it will be dismantled and re-installed at the Eglin Air Force Base as a field demonstration of the Molten Salt Destruction Technology.

We have also designed, fabricated and installed a vacuum assisted salt removal system, which allows us to remove salt from the unit without shutting it down. The main application of this system is for feeds that require periodic salt removal due to either chemical or physical degradation of the salt. For example, halogenated solvents in the feed tend to build up halides in the salt, which affect its ability to scrub acid gases, and also result in higher CO releases. An example of physical degradation is the introduction of "ash-forming" feeds, such as tritonal (TNT/aluminum), which results in the build up of alumina in the salt, leading to gradual loss of salt fluidity. The system consists of a catch pot, connected to a vacuum source via a series of vacuum ballast tanks. To initiate salt removal, the catch pot and the vacuum ballast tanks are isolated from the MSD crucible and evacuated. They are isolated from the vacuum source (either house vacuum or a vacuum pump), and the connection to the MSD crucible is opened. Depending on the level of the inserted tube connecting the salt and the catch pot, some or all of the salt can be removed safely and quickly.

CONCLUSIONS

We have demonstrated that HEs and liquid propellants can be safely and fully destroyed using the molten salt destruction process. The safety of this process has been demonstrated through our operating experience as well as a number of theoretical studies we have performed. In all cases studied, the NO_x and CO formations are well below 1%. We believe that the process is ready for a field demonstration, which is planned for FY 96 at Eglin AFB.

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