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Recent Advances in the Molten Salt Destruction of Energetic Materials*

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Abstract

We have demonstrated the use of the Molten Salt Destruction (MSD) Process for destroying explosives, liquid gun propellant, and explosives-contaminated materials on a 1.5 kg of explosive/hr bench-scale unit (1, 2, 3, 4, 5). In our recently constructed 5 kg/hr pilot-scale unit we have also demonstrated the destruction of a liquid gun propellant and simulated wastes containing HMX (octogen). 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 metallic particles, are retained in the molten salt. The destruction of energetic materials waste is accomplished by introducing it, together with air, into a vessel containing molten salt (a eutectic mixture of sodium, potassium, and lithium carbonates). The following pure explosives have been destroyed in our bench-scale experimental unit located at Lawrence Livermore National Laboratory's (LLNL) High Explosives Applications Facility (HEAF): ammonium picrate, HMX, K-6 (keto-RDX), NQ, NTO, PETN, RDX, TATB, and TNT. In addition, the following compositions were also destroyed: Comp B, LX-10, LX-16, LX-17, PBX-9404, and XM46 (liquid gun propellant). In this 1.5 kg/hr bench-scale 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 compositions we have also destroyed materials that are typical of residues which result from explosives operations. These include shavings from machined pressed parts of plastic-bonded explosives and sump waste containing both explosives and non-explosive debris. Based on the process data obtained on the bench-scale unit we designed and constructed a next-generation 5 kg/hr pilot-scale unit, incorporating LLNL's advanced chimney design. The pilot unit has completed process implementation operations and explosives safety reviews. To date, in this pilot unit we have successfully destroyed liquid gun propellant and dimethlysulfoxide containing HMX in continuous, long-duration runs.

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Introduction

We are developing alternative methods to open burning and open detonation (OB/OD) for the safe and environmentally acceptable destruction of energetic materials. As a result of the end of the Cold War and the shift in emphasis to smaller weapons stockpiles, 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 other energetic materials. The Department of Energy (DOE) has thousands of pounds of energetic materials which result from weapons dismantlement; explosives processing operations; and, research, development, and testing operations. The Department of Defense has many millions of 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, 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 reported on the use of the Molten Salt Destruction (MSD) Process for destroying explosives and explosives-containing wastes (1, 2, 3). MSD converts the organic constituents of the waste into non-hazardous substances such as carbon dioxide, nitrogen, and water (steam). Any inorganic constituents of the waste, such as metallic particles, are retained in the molten salt. The destruction of energetic materials waste is accomplished by introducing it, together with air, into a vessel containing molten salt, a eutectic mixture of sodium, potassium, and lithium carbonates. Figure 1 illustrates the process flow.

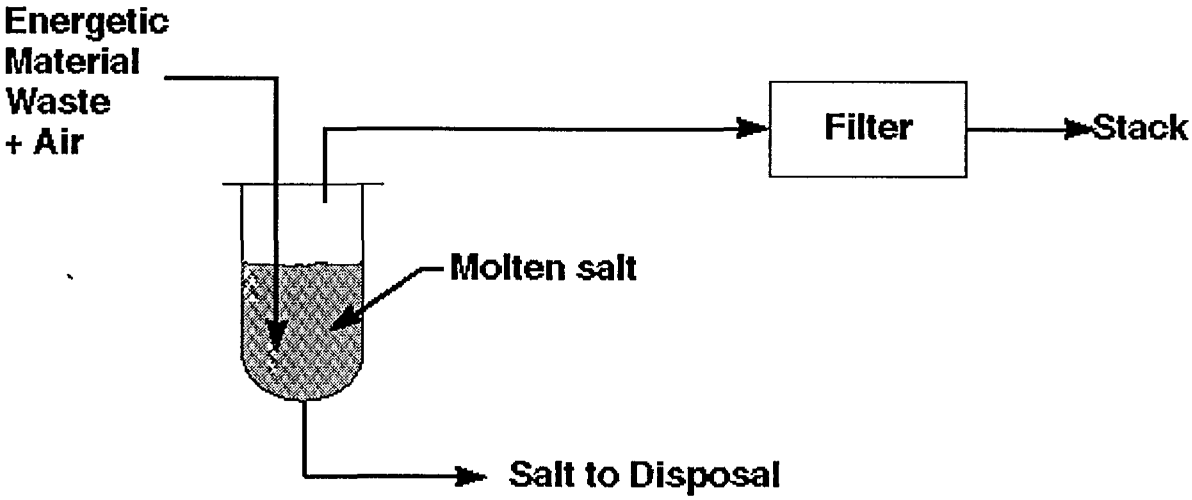

Figure 1. Process Flow Diagram

The temperature of the molten salt can be between 400° to 900° C, but in practice, 750°C has been experimentally determined to be optimal for energetic materials destruction. The organic components of the waste react with oxygen in the air stream to produce carbon dioxide, nitrogen, and steam. In the case where the waste also contains inorganic components, these are retained in the molten salt bed as a result of wetting and dissolution (and called ash). 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 or plasticizers for the explosives) generate acid gases such as hydrogen chloride during the pyrolysis and combustion processes occurring in the molten salt. These are scrubbed (or neutralized) 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 can be separated into carbonates, non-carbonate salts, and ash, depending on the nature of the waste destroyed. For example, in the case of wastes which contain only C, H, N, and O, the molten carbonate salt can be used indefinitely.

Experimental

Figure 2 shows a schematic of the experimental setup for the bench-scale unit. The vessel (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 vessel contains about 7 kg of salt, an equal weight mixture of lithium, sodium, and potassium carbonates which melts at approximately 400°C. Thermocouples are placed at various locations, including the vessel, 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 and mass spectrometers provide real-time analysis for NO_X, CO, N_2, O_2, CO_2, Ar, and hydrocarbons. The bench-scale assembly is placed inside an explosives work room, designed to contain a detonation of up to 500 g of explosives (TNT equivalent). A remotely operated TV monitor allows monitoring of the experiment without entering the cell during the experiments. All the solenoid valves controlling the sample and the feed sequences are also operated remotely. Data are continuously logged by computer.

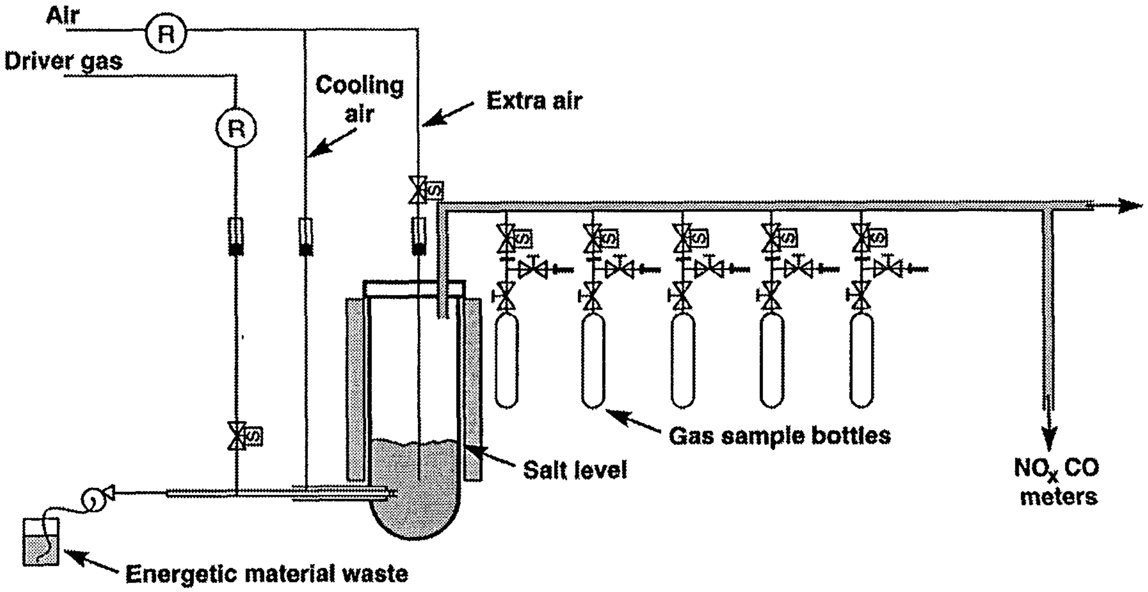

Figure 2. Experimental Schematic

A slurry of energetic materials waste and (typically 30 wt % solids in water) is made and kept in suspension using air-driven stirrers. The waste to be destroyed is injected into the vessel side nozzle using a peristaltic pump. The gaseous products of the vessel go to the outlet pipe as shown in Figure

2. Slurries of up to 500 g explosive (TNT equivalent) in water were 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. Salt samples are typically withdrawn from the vessel at the end of the final run and analyzed for traces of explosives and residual inorganics.

An air-cooled side injector was used for the initial experiments (see Figure 3). This nozzle has an internal diameter of 6.4 mm and can handle explosives particles up to 2 mm. The following pure explosives were destroyed in the bench-scale unit: HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), PETN (2,2-bis[(nitoxy}methyl)]-1,3-propanediol dinitrate), ammonium picrate, TNT (2,4,6-trinitrotoluene), nitroguanadine, and TATB (2,4,6- trinitro-1,3,5-benzenetriamine). In addition to these pure components, we destroyed a number of common explosives compositions: Comp-B (RDX/TNT), 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 comprised of hydroxylammonium nitrate, triethanolammonium nitrate, and water.

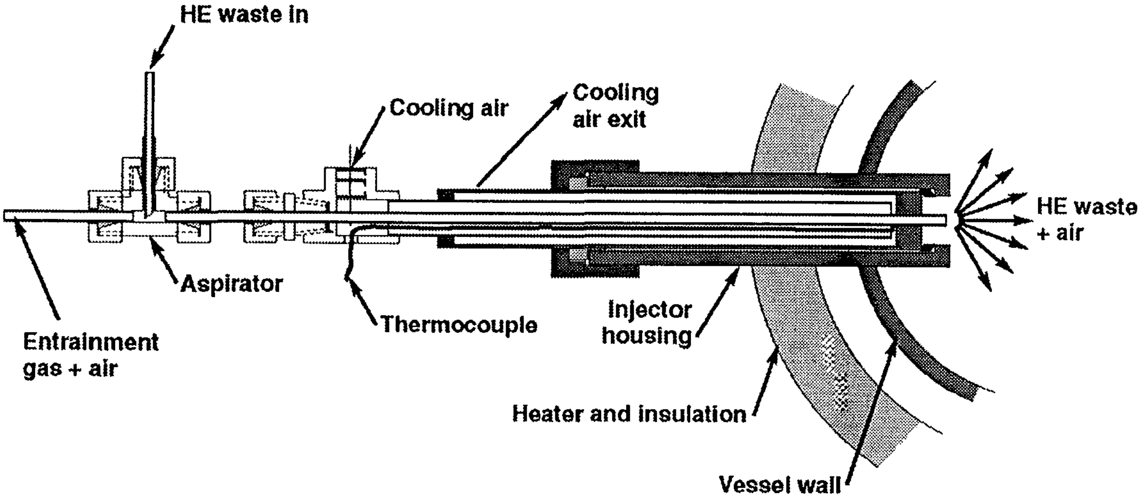

Figure 3: Details of the Nozzle

We also designed and implemented an insulated top feed downcomer (see Figure4). This injector was designed to handle larger particle sizes of solid feeds and has an internal diameter of 19 mm. Materials used to test this new injector design and destroyed by the molten salt unit include: shavings from machined, pressed parts of PBX 9404 and PETN sump sludge containing rust, wood, string and metal parts (this material was provided by Ensign-Bickford).

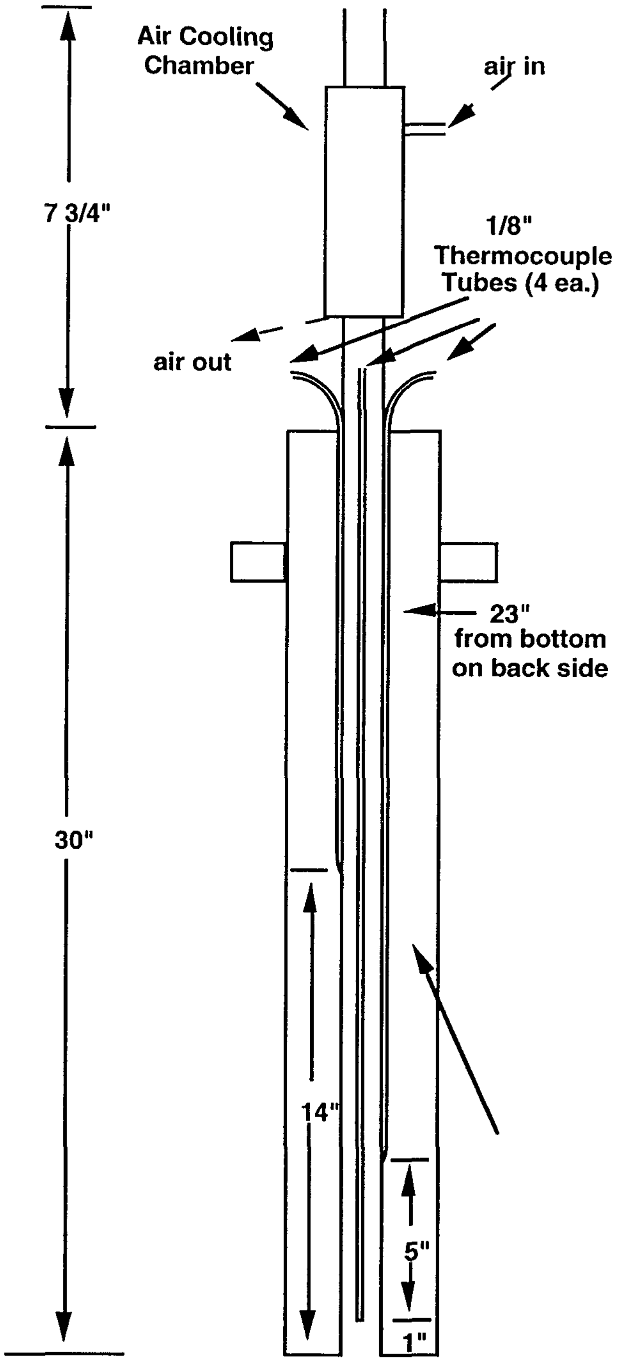

Figure 4. Top-Feed Downcomer.

Results

Gas samples were taken during the experiments and analyzed using gas chromatography and infrared and mass spectrometry (GC/MS). Typical gas analyses of untreated emission gases for a number of pure component explosives and compositions are shown in Table 1.

Table 1. Untreated Emissions from MSD Treatment of Explosives

Explosive	%C to CO	%N to 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	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

*ND refers to not detected.

Figure 5 graphically displays the CO emission data from the destruction of the liquid gun propellant XM46. These data show that CO emissions are lower at higher temperatures, but with 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 bench-scale unit. More predictably, higher feed rates produced larger amounts of unburned hydrocarbons and hydrogen.

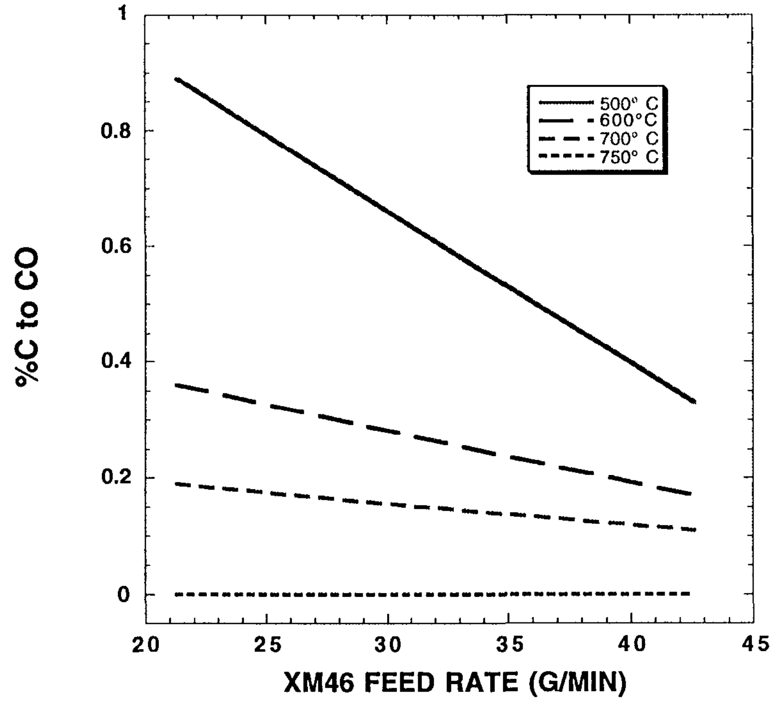

Figure 5. Carbon monoxide produced by MSD of XM46 as a function of temperature and feed rate.

We also implemented a top feed injector for the specific purpose of feeding larger, more realistically-sized solid waste feed streams rather than just pure explosive powders. Since the length of the top injector must be longer than for side injection the time-temperature profile of the explosive in the top injector must be addressed. In practice, if a 2/1 ratio of water to explosive is maintained along with a nominal feed rate of 150 g/hr of explosive, then the maximum temperature of the explosive in the downcomer is 91°C. The top feed downcomer on the 1.5 kg/hr bench-scale unit has an internal diameter of 19 mm and was used to evaluate two realistic feed streams. The first was machining shavings from a pressed part of PBX 9404. The latter was a sump sludge from a PETN production facility containing PETN, rust, metal parts, string, wood, sand, and 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 destroyed by MSD. The emissions from the molten salt destruction of energetic materials are exceedingly low. No HCN was found in the exhaust. This is significant since HCN is a common byproduct of the combustion of energetic materials. We 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 N_2, CO_2, and H_2O. 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, unburned hydrocarbons, and hydrogen are all reduced. This trend is expected due to the increased rate of combustion at higher temperatures. These data show that gaseous emissions are lower at higher salt temperatures. We however, optimized destruction of energetic materials at 750°C given competing requirements of materials-of-construction constraints and energetic materials decomposition temperatures. Extrapolation of these results suggests that emissions may drop further at temperatures of 800 or 850°C.

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

We destroyed liquid gun propellant in MSD and in a packed-bed incinerator to compare the NO emissions from each process. In the packed-bed incinerator, combustion takes place under conditions similar to those found in standard incinerators. Incineration of XM46 in the packed-bed incinerator produced large amounts of NO, with 48% of the nitrogen in the propellant emerging from the reactor as NO. Operation of the MSD unit with air produces significantly lower amounts of NO (where 0.46% of the nitrogen is converted to NO). Untreated NO emissions from the molten salt destruction of XM46 are two orders of magnitude lower than those from incineration.

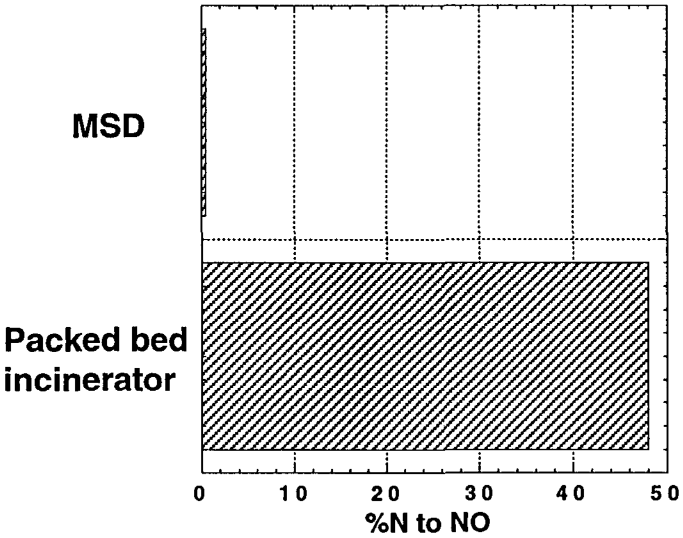

Figure 6. Comparison of NO produced by destroying XM46 in an incinerator and by MSD.

Based on the results of experiments performed over the last four years at LLNL, we designed and constructed a third generation pilot-scale MSD unit. The schematic of the new vessel is shown in Figure 7.

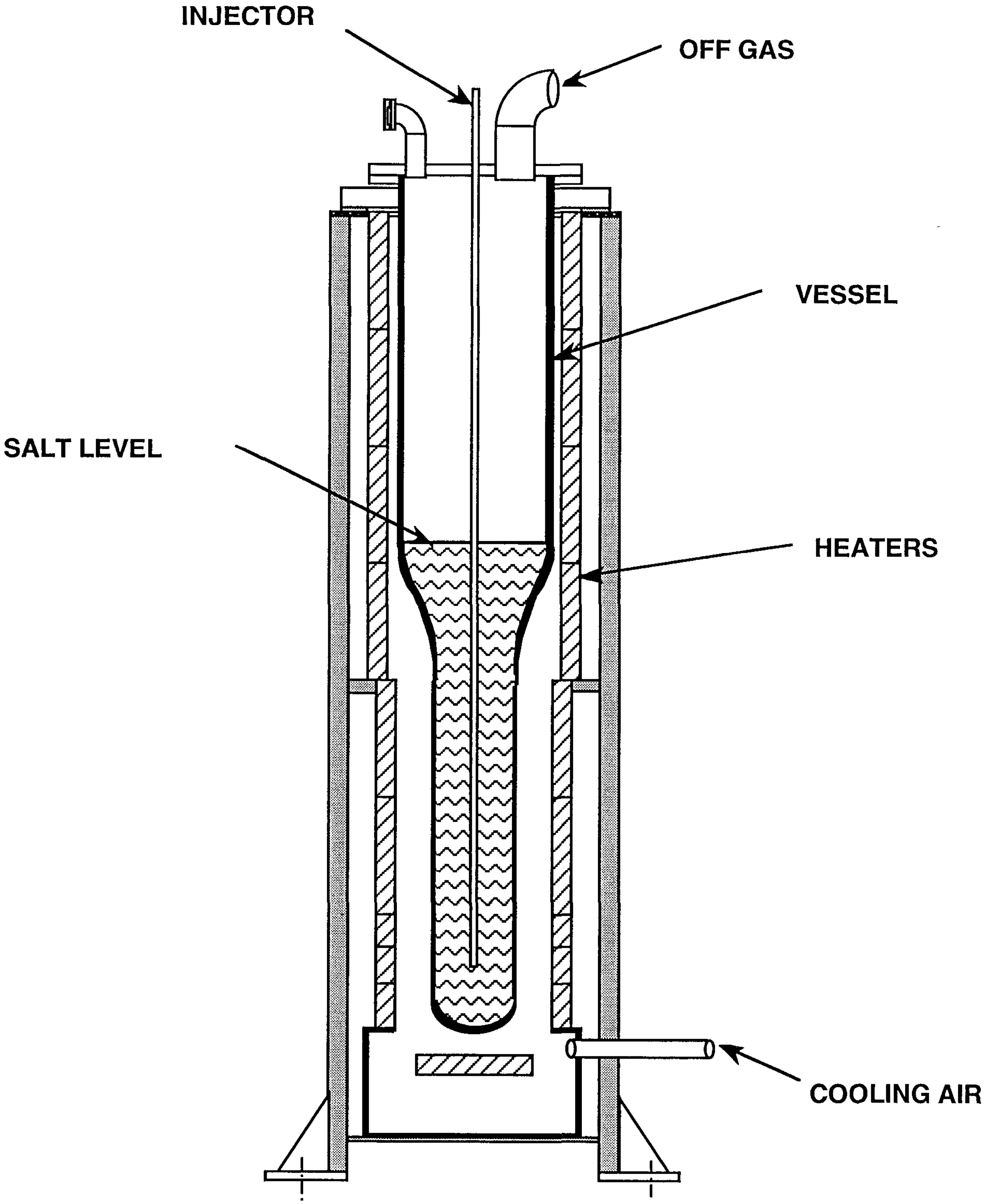

Figure 7: Advanced Design Pilot-Scale MSD Unit

A number of advanced features distinguish the new pilot-scale unit from the bench-scale unit. 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 chimney design is to eliminate or minimize entrainment of molten salt droplets into the outlet pipe. The increased area at the top results in a four-fold decrease in the initial product gas velocity, thus 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 pilot unit was started up in early October, 1995. Initial operational tests and explosives safety reviews have been completed. To date, we have destroyed XM46 (a liquid gun propellant) and simulated wastes containing HMX in this unit. After final operational tests and further experimental work, the pilot unit will be dismantled and re-installed at Eglin Air Force Base as a field demonstration unit.

We also designed, fabricated, and installed a vacuum-assisted salt removal system, which allows removal of salt, in the molten state, from the unit without turning off the operation. The main application of this system is for feeds that require periodic molten salt removal due to either chemical or physical degradation of the salt. For example, halogenated solvents in the feed will 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 would result in the build up of alumina in the salt and would further lead to gradual loss of molten salt fluidity (or viscosity). 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 vessel and evacuated. After these are isolated from the vacuum source (either house vacuum or a vacuum pump), the connection to the MSD vessel is opened. Depending on the level of the inserted tube connecting the molten salt and the catch pot, some or all of the salt can be removed safely and quickly (within seconds). The effectiveness of this process has been demonstrated by performing many salt removal cycles on the pilot-scale unit. In these series of experiments, several hundred gallons of dimethlysulfoxide (DMSO) containing HMX (at 8 - 10 % HMX) were destroyed, resulting in chemical depletion of the carbonate salts and formation of the sulfate salts. Fresh carbonate salts are then inserted into the vessel, melted and the destruction process continued again until carbonate depletion occurs and the removal cycle begins again. Carbonate depletion is determined by monitoring gas emissions and looking for SO_2 gas breakthrough on the online gas meters.

Conclusions

We have demonstrated that explosives and liquid gun propellants can be safely and fully destroyed using the molten salt destruction process. The safety of this process has been demonstrated through extensive operating experience as well as a number of theoretical studies we have performed. We have also demonstrated the effective removal of depleted salt in many-cycle process runs. In all cases studied, the NO_X and CO formations are well below 1%. We believe that the process is ready for field demonstration followed by transition to a production facility.

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