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Molten Salt Destruction as an Alternative to Open Burning of Energetic Material Wastes

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Introduction

The Lawrence Livermore National Laboratory (LLNL) is developing methods for the safe and environmentally sound destruction of explosives and propellants as a part of its program on dismantlement and demilitarization of nuclear and conventional munitions. 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 Department of Energy has thousands of pounds of energetic materials which result from dismantlement operations at the Pantex Plant. 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 surplus energetic material 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 OB/OD of energetic materials increasingly costly and nearly unacceptable. Thus, the impetus to develop environmentally sound alternatives to dispose of energetic materials is great.

The destruction of energetic materials and wastes containing energetic materials using the Molten Salt Destruction (MSD) Process has been fully described in earlier publications (1,2). 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 oxidant gases, into a crucible containing a molten salt, such as sodium carbonate, or a suitable mixture of the carbonates, chlorides or sulfates of sodium, potassium, lithium and calcium (1,2). The temperature of the molten salt can be between 400° to 900° C. The organic components of the waste react with oxygen 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 of the 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 polymeric binders for the explosive) 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 steam and the corresponding salt, such as sodium chloride. The off-gases from the process are sent through standard off-gas 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.

LLNL has built a small-scale (about 1 kg/hr throughput) unit to test the destruction of energetic materials using the MSD process(2). We have modified the unit described in the earlier references to inject energetic waste material continuously into the unit. In addition to the HMX (octahydro- 1,3,5,7- tetranitro- 1,3,5,7-tetrazocine), other explosives we have destroyed include RDX (hexahydro- 1,3,5-trinitro- 1,3,5-triazine), PETN (2,2- bis[{nitoxy}methyl]- 1,3-propanediol dinitrate), ammonium picrate, TNT (trinitrotoluene), nitroguanadine, and TATB (2,4,6- trinitro- 1,3,5-benzenetriamine). We have also destroyed a liquid gun propellant comprising hydroxyl ammonium nitrate, triethanolammonium nitrate and water. 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 /Nitro cellulose). Our experiments have demonstrated that energetic materials can be safely and effectively treated by MSD. We have also investigated the issue of steam explosions in molten salt units, both experimentally and theoretically, and concluded that steam explosions can be avoided under proper design and operating conditions. We are currently building a larger unit (nominal capacity 5 kg/hr, Figures 1 and 2) to investigate the relationship between residence time, temperature, feed concentration and throughputs, avoidance of back-burn, and determination of the products of combustion under different operating conditions.

Explosion Safety

Safety is a major consideration in any process where high explosives (HE) or wastes containing HE are destroyed. We have successfully and safely destroyed slurries (or solution, in case of the liquid gun propellant) of 35 weight percent energetic material (HE and HE formulations) in water. The liquid, in addition to keeping the HE concentration to a safe dilution level, provides a vehicle for handling the HE. The specially designed nozzle, described in earlier publications (1,2) keeps the HE well below its decomposition temperature. Further, the nozzle is designed to create froth comprising water, HE and air before introducing it into the molten salt to minimize the possibility of a burn back. Finally, the entire experiment is conducted remotely.

Other explosion scenarios, not related to high explosives, are possible in the MSD process:

- If the outlet from the MSD reactor gets plugged or restricted, and if the liquid feed to the molten salt bath continues, the resultant pressure increase in the vessel may lead it its explosive rupture.

- The rapid heat transfer from the hot liquid to the cold liquid may give rise, temporarily, to a region of superheated liquid, which may spontaneously nucleate, resulting in an explosion(3).

The first scenario can be avoided by installing pressure sensors in the reactor, the lines and the auxiliary equipment, and carefully monitoring the pressure rise continuously. Interlocks on the feed delivery system can be designed so that any excursion of pressure beyond the design limits stop the feed. Relief valves and rupture disks may also be used for additional safety. The new unit under construction is wider at the top so as to slow down the product gases, and thereby minimize salt carryover leading to the plugging up of the exhaust line.

The second scenario can be dealt with by choosing proper equipment (reactor, feed system, controls, etc.)design and operating conditions. The nozzle has been designed to disperse the feed into a stream of rapidly moving gas, thereby eliminating or reducing the probability of large slugs of cold water contacting the hot molten salt. Second, the contents of the reactor are constantly agitated by the driver gas and the air needed for oxidation. This ensures that quiescent layers of hot and cold liquids do not form in the reactor. Our analyses show that this eliminates the possibility of steam explosion in the molten salt system. We have demonstrated the safety of our specific experimental set-up by repeated injection of pure water under the molten salt bed for prolonged duration without any adverse consequences.

Results from the Experimental Program

The details of the experimental apparatus, the feed nozzle and the operating procedures have been described in detail elsewhere (1,2). In addition, another paper discussing the details of the experiments, along with the results of the off-gas analyses, is being presented at this conference (4).

Gas samples were taken during the experiments, and analyzed using a gas chromatograph and mass spectrometer (GC/MS). Typical gas analyses for a number of pure explosives and formulations indicate that(4):

1. No HCN was found in the exhaust gas. Since HE decomposition and oxidation may be accompanied by evolution of some HCN, we may infer that the HCN, being an acid gas, was neutralized by the alkaline carbonate, producing NaCN.

2. The amount of NO_x and CO was relatively small. This indicates that the major combustion products are N2, CO_2 and H_2O.

Analyses of the salt samples after the experiments indicate that, within the detection limit of 5 ppm, no HE or propellant is detected in the salt (1,2). This is consistent with our expectations, given the ease of decomposition of the energetic materials at these temperatures.

Conclusions and Future Work

We have demonstrated that HEs and liquid propellants can be safely and fully destroyed using the molten salt destruction process. We are currently working on a number of improvements to the process:

- We are building a larger unit (Figures 1 and 2) to investigate the effect of temperature, throughput and scale on the destruction efficiency of a number of explosives and explosive formulations on a larger scale.

- We are implementing an advanced feeder system for injection of larger particles.

- We are defining operating envelopes for a number of high explosives and formulations.

- We are developing models to study the temperature profile of a top-feed nozzle for feeding larger particles into the unit.

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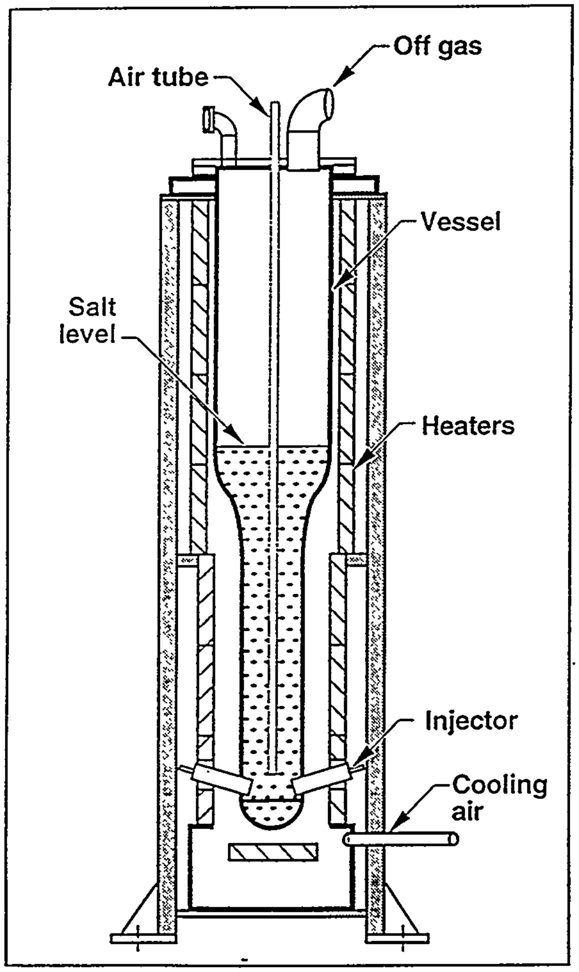

Figure 1. Schematic of the Advanced Unit.

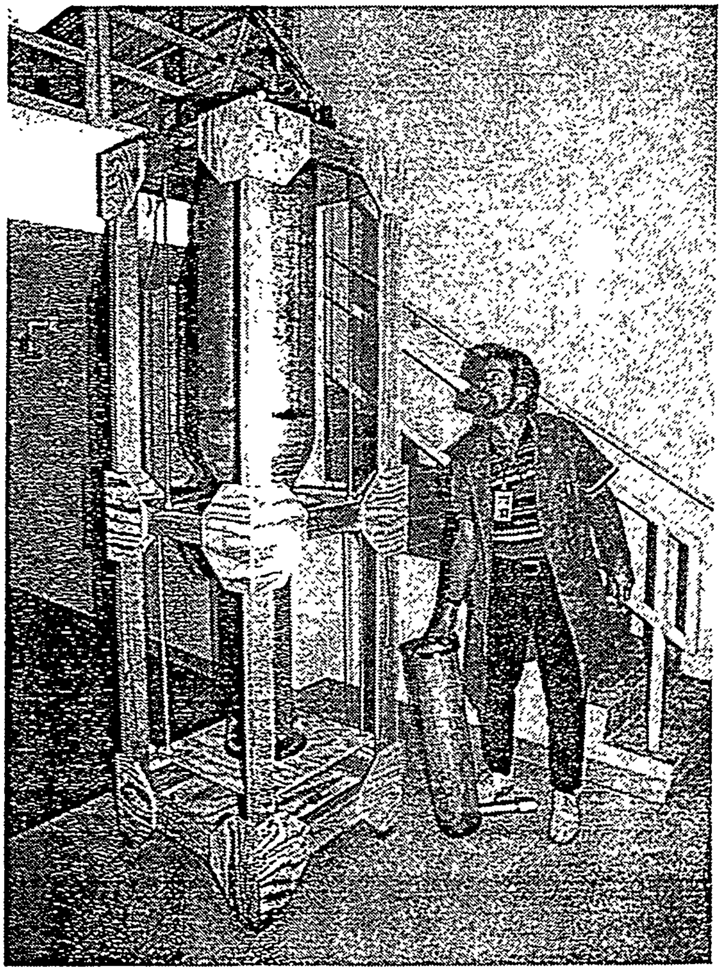

Figure 2. Advanced Unit vessel.

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