

Title: Decontamination of Explosive Contaminated Structures and Equipment

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As a result of past operations, the U.S. Army has numerous buildings and large quantities of process equipment which is contaminated with explosives. Recent changes in laws also require all detonation scrap to be free of explosive residue prior to recycle. Before these materials can be recycled or disposed of, the residual explosives must be removed. Removal of residual explosives is necessary to avoid creating safety and environmental hazards. If the process equipment is to be landfilled, residual explosives may migrate into the soil and ultimately contaminate groundwater. Building structures which have been used for explosives manufacture are usually slated for demolition and disposal of the rubble. Demolition of a building which has residual explosive can be dangerous. Disposal of contaminated rubble may contribute to soil and groundwater contamination.

Probably the two most common methods in present use for decontamination are steam cleaning and decontamination by fire (burn it to the ground). Steam cleaning is in most cases effective but provides only surface decontamination and is not effective on hard to access areas. It is difficult to completely decontaminate concrete with steam. Steam cleaning of complex items such as motors can not assure that interior areas are cleaned. Burning of structures contaminated with explosives is no longer an environmentally acceptable method of decontamination. Buildings with asbestos should not be burned. Since open burning of a contaminated structure can be viewed as an uncontrolled release of toxic substances, local or state regulators view intentional building fires in the same light as open detonation..

In 1982, USATHAMA began a project aimed at developing new, improved procedures for decontaminating structures and equipment contaminated with explosives. The goal of this on-going project is to develop a method which will be safe, produce little or no waste and will assure a high degree of decontamination. Target compounds for removal are all the major military explosives such as trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-s-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), nitrobenzene (NB), 1,3-dinitrobenzene (DNB), 1,3,5-trinitrobenzene (TNB), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4,6-trinitrophenylmethylnitramine (TETRYL), smokeless powder (nitrocellulose/nitroglycerin), ammonium picrate (Yellow D). The process to be developed would have to be effective at removing contaminants from metal, wood, painted concrete and bare concrete. An additional goal of the project was to develop a decontamination method which is universally applicable and, thus, could be used on large structures as well as process equipment. The first phase of this project was a review of existing techniques and the consideration of novel techniques.

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Phase I of Development Program, Technology Screening

Under contract to USATHAMA, Battelle Columbus Laboratories performed an analysis of existing explosives decontamination techniques and also developed descriptions of novel concepts. Information was gathered from government and private industry manufacturers of explosives. Government facilities were visited to inspect contaminated structures and equipment. In a July 1983 report, Battelle documented the detailed analysis of the following technologies:

Thermal Decomposition Concepts

Flashblast
Microwave Heating
Solvent Soak/Burn
Burn to Ground

Contact Heating
Flaming
Infrared Heating

Hot Plasma
Hot Gases
CO₂ Laser

Abrasive Concepts

Electropolishing
Sandblasting
Ultrasound
Vacu-blast

Acid Etch
Demolition
Cryogenics

Scarifier
Drill and Spall
Hydroblasting

Extractive Removal Concepts

Solvent Circulation
Surfactants
External Steam Generator

Supercritical Fluids
Strippable Coatings
Vapor Phase Solvent Extract

Rad Kleen
Manual Steaming

Chemical Concepts

Radical Initiated Decomp.
Molten Decomp.
Microbial
Ultraviolet and Cat.
Nucleophilic Displacement
Solid State Hydrogenation

Base Initiated Decomp.
Sulfur Based Reduct
Reduction Cleavage
Gamma Rad.
Ozone
Gels

Decomp. with DS2
Sodium Borohydride
Reactive Amines
Chromic Acid
Ascorbate
Foams

Various combinations of methods were also considered. Each technology was evaluated and rated based on destruction efficiency, mass transfer, safety, damage to buildings, penetration depth, applicability to complex surfaces, operating costs, capital costs and waste treatment costs.

Among the thermal decomposition concepts, hot gases received the highest ranking overall and received high scores in all categories. The hot gas process involves exposing contaminated materials to hot gasses in order to vaporize or decompose the contaminants. The hot gasses together with the vaporized explosives and break down products are discharged to an afterburner for complete destruction.

The burn to ground method received high scores in most categories but received the lowest possible scores for safety and building damage. The only thermal concept recommend for further development was hot gases.

All of the abrasive concepts received poor scores for waste treatment costs. The abrasive concepts also received low scores for penetration depth. None of the abrasive concepts were considered for further development.

External steam generator (pumping steam into the structure) scored the highest of the extractive removal concepts. However, the low solubility of some explosives in hot water prevents the steam method from being universally applicable. Vapor circulation was the only extraction technology selected for further development.

Three chemical decomposition techniques where selected for further development. The concepts selected were radical initiated decomposition, base initiated decomposition and sulfur based reduction.

In all, 55 technologies or combinations of technologies were considered. Six concepts were selected for further investigation. The selected technologies were hot gasses, combination chemical/hot gas, vapor circulation, radical initiated decomposition, base initiated decomposition and sulfur based reduction.

From the combination methods evaluated, only a combined chemical/hot gas concept was considered to be worthy of further development.

Phase II, Laboratory Tests

In Phase II, the technologies selected from Phase I were developed in more detail. Probably the most important aspect of the development work was the laboratory tests. Test coupons of steel, painted concrete and unpainted concrete were spiked with known quantities of 2,4 DNT, 2,6 DNT, TNT, TETRYL, RDX and HMX. The test coupons were then subjected to the processes under investigation. After appropriate treatment times, the coupons were inspected for residual explosives. Hot gases and the combination of chemical/hot gases yielded the highest degrees of explosives removal. In many cases, the residual explosive levels were below detection limits. Although each of the six processes evaluated in the laboratory phase of testing offered some advantages and disadvantages for particular operations, it was the hot gas process which had a greater range of applications and provided the most complete decontamination.

The laboratory tests did identify some potential problems with the hot gas process. During testing the fomation of explosive crystals on the outside surface (originally uncontaminated) of concrete test coupons indicated that the hot gases may cause explosives to migrate through concrete. This raises the concern that during decontamination of a concrete structure the explosives may be driven out of the structure rather than destroyed. It was also noticed that the hot gas process dried out and, thus, weakened concrete.

Pretreatment of concrete with a caustic chemical led to quicker destruction of explosives and allowed hot gas decontamination to proceed at lower temperatures. Quicker destruction of explosives reduces the possibility of migration. Operating at a reduced temperature lessens the drying effects on concrete. Thus, it was concluded that combination of chemical treatment and hot gasses would be the best route to complete decontamination without migration of explosives and with minimal damage to concrete.

The hot gas process, complemented by chemical pretreatment, emerged from the laboratory tests as clearly the most promising technology for wide spread application. The next step was to see how well the process would perform outside the laboratory on a contaminated building.

Phase III Pilot Tests

The Cornhusker Army Ammunition Plant (CAAP) Tests:

Pilot tests of the chemical/hot gas decontamination method were conducted at CAAP in 1987. The tests were conducted for USATHAMA by Arthur D. Little, Inc. The objectives of these first pilot tests were:

1. Determine the effectiveness of hot gas with and without chemical pretreatment.
2. Evaluate the effects of test conditions on the integrity of an actual structure.
3. Provide design criteria for full scale systems.
4. Provide test data for regulatory permitting of the process.

After numerous potential sites were considered, a projectile washout building at Cornhusker AAP was selected as the test site. The building had concrete walls, a concrete floor and a wooden ceiling. Dimensions of the building were 25' long, 25' wide and 11' high. So that two separate tests could be conducted, a dividing wall was constructed in the center of the building. Other modifications to the building included construction of a false ceiling to protect the wooden roof, replacement of the windows and doors with sheet metal and insulation of the outside of the building. Although inspection of the building revealed some TNT contamination, the level of contamination was too low to sufficiently challenge the decontamination method. This problem was resolved by placing TNT contaminated concrete blocks, which were removed from a sump cesspool, inside the test building.

Hot gas was supplied to the building through ductwork by a 3.0 million BTU/hr propane fired burner. Gasses exited the building into a propane fired afterburner. Gasses entering the building, exiting the building and exiting the afterburner were analyzed. In tests where chemical pretreatment was used, a solution of sodium hydroxide and dimethylformamide was employed. Thermocouples were used to monitor temperatures inside the building during treatment. Concrete samples were subjected to mechanical properties tests before and after hot gas treatment.

Conclusions drawn from the Cornhusker pilot tests were:

1. Hot gas decontamination of a building is safe and feasible.
2. Although treatment of surfaces with caustic chemicals did increase explosive removal on the surface of concrete, it had no effect on interior contamination. Further, longer treatment with hot gas alone should be capable of providing complete decontamination.
3. The hot gas decontamination process caused concrete block to loose 5% of its compressive strength and 20 to 30% of its bend (tensile) strength. The effects of this loss in strength would have to be judged on a case by case basis for each building treated. Of course, if the building is not going to be reused, the condition of the concrete after treatment is of no concern.
4. Initial design criteria and cost estimates for decontamination of small and large buildings were developed.
5. Process data, such as composition of effluent gasses from the afterburner, were collected and can be used for applying for regulatory permits for future operations.

The Hawthorne Army Ammunition Plant (HWAAP) Pilot Tests:

Further pilot tests of the hot gas process (without chemical pretreatment) began in July 1989 at HWAAP. These tests are being conducted for USATHAMA by Weston, Inc. This test series is directed towards the decontamination of process equipment used in explosives operations. The objectives were:

1. Test the process on a variety of materials (vitrified clay, steel, copper, aluminum) with a variety of contaminants (TNT, NC, NG, Ammonium Picrate, RDX, HMX).
2. Test the process on a variety of items including intricate equipment which has areas inaccessible to other treatment processes (pumps, pipes, ship mines, risers, transfer containers, motors).
3. Determine the temperatures and treatment times required to reduce contaminant levels to below detectable limits. Define a process that will render equipment items fit for unrestricted use or disposal.
4. Render large quantities of contaminated equipment fit for unrestricted use or disposal.

A flashing chamber at HWAAP was modified to accommodate the hot gas process. The same burner and afterburner that was used at Cornhusker AAP are in use at HWAAP. HWAAP has a large store of equipment and munition items which require treatment. Test items have been selected from HWAAP's stores, placed in the modified flashing chamber and treated with hot gas. Test samples also include highly contaminated clay pipe removed from what was once the West Virginia Ordnance Works.

Test items were sampled for explosives prior to testing. Because of low levels of contamination, some items were spiked with explosives. After testing, items were sampled for residual explosives.

Ten test runs were conducted: nine tests evaluated the feasibility of the process on TNT and smokeless powder; one test run evaluated ammonium picrate. The operating conditions of the test runs were selected to form a temperature-residence time matrix. Three temperatures were evaluated: 400°F, 500°F, and 600°F. The duration of tests evaluating TNT decontamination was 6 hours, 12 hours, 24 hours, or 36 hours (after reaching steady state). A residence time of 48 hours was used for evaluation of ammonium picrate; this extended residence time (and a temperature of 600°F) was selected to ensure the decontamination process would be completed and to avoid potential safety problems associated with partially decomposed ammonium picrate (picric acid). To demonstrate the destruction and removal efficiency (DRE) of the process, stack testing was conducted at the afterburner inlet and outlet. Stack tests were conducted during the first three test runs for explosives and smokeless powder.

The hot gas process is effective for treating items contaminated with TNT and ammonium picrate. Analytical results indicate that temperature is a key factor in explosives removal. It was determined that a minimum temperature of 500°F is required to remove TNT below measurable levels on the treated test items. Since relatively large temperature gradations were evaluated (+100°F), the minimum effective operating temperature may lie somewhere between 400°F and 500°F. Test items that are treated for 6 hours at a minimum temperature of 500°F are not characteristically hazardous and are appropriate for disposal or potentially for resale as scrap. Items with contamination on external surfaces were generally the least difficult to treat; three failures were observed (one failure was associated with soil/debris in clay pipe). Test items with contamination on internal surfaces or within porous media proved to be more difficult to treat. Although three test items were observed to fail, residual concentrations were generally higher.

Generally, items constructed of steel or aluminum showed no signs of damage due to treatment. For clay, however, exposure to the hot gas resulted in cracks throughout the entire pipe sections. The clay became very brittle and was easily broken. The treated test items that are constructed of steel or aluminum and have not intricate of mechanical components should be appropriate for reuse in manufacturing or handling operations.

Due to the limited testing on smokeless powder and the variability in pre-test item contaminating, it is not possible to analyze trends in the data for smokeless powder. The sampling and analytical methods employed for determination of smokeless powder emissions in the stack gases (and presence of smokeless powder on test items) were determined to be inappropriate. The method did not allow NC and NG to be distinguished from one another or from other nitrated testers. The stack sampling protocol was also questionable; the sampling media may not have captured NC and NG.

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TNT emissions from the afterburner, as measured during the stack testing program were never above detectable levels. In cases where TNT inlet concentration was sufficiently high, the DRE exceeded 99.99 percent.

Combustion efficiency of the afterburner ranged from 99.9895 to 99.9933 percent during the stack testing program; efficiencies reflect the excellent performance of the afterburner.

The emissions of particulate from the afterburner, as measured during the stack testing program, ranged from 0.000017 gr/dscf to 0.00093 gr/dscf (corrected to 7 percent oxygen). Emissions are two orders of magnitude lower than applicable regulations.

Emissions of carbon monoxide and total hydrocarbons at the flash chamber inlet indicate that the existing air preheater at HWAAP is operating poorly. Emissions were one order of magnitude higher than emissions associated with typical gas-fired heaters. Combustion efficiencies for the air preheater ranged from 98.95 percent to 99.72 percent during the stack testing program.

Due to extended heatup and cooldown periods, it is difficult to evaluate the effects of the 600° F test runs. During the 600° F test runs, before the steady state temperature was achieved, the system had operated at conditions that were very similar to the 500° F/6 hour test run. The results of the 500° F/6 hour test run indicate decontamination of TNT. Therefore, during the 600° F test run, the test items may have been adequately treated before the steady state temperature was even achieved.