SANDIA REPORT

SAND99-8221

Unlimited Release

Printed February 1999

Combustion Tests of Rocket Motor Washout Material: Focus on Air Toxics Formation Potential and Asbestos Remediation

S. G. Buckley, G. C. Sclipa, L. L. Baxter

RECEIVED

APR 29 1999

OSTI

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of
Energy under Contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Prices available from (615) 576-8401, FTS 626-8401

Available to the public from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd
Springfield, VA 22161

NTIS price codes
Printed copy: A03
Microfiche copy: A01

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

**Combustion Tests of Rocket Motor Washout Material:
Focus on Air Toxics Formation Potential and Asbestos Remediation**

Steven G. Buckley
Exploratory Systems Technology Department

Gian C. Sclipa, and Larry L. Baxter
Industrial Combustion & Processes Department
Sandia National Laboratories
Livermore, CA

ABSTRACT

The objective of this investigation is to determine the suitability of cofiring as a recycle / reuse option to landfill disposal for solid rocket motor washout residue. Solid rocket motor washout residue (roughly 55% aluminum powder, 40% polybutadiene rubber binder, 5% residual ammonium perchlorate, and 0.2-1% asbestos) has been fired in Sandia's MultiFuel Combustor (MFC). The MFC is a down-fired combustor with electrically heated walls, capable of simulating a wide range of fuel residence times and stoichiometries. This study reports on the fate of AP-based chlorine and asbestos from the residue following combustion.

Using an FTIR spectrometer to sample gas-phase combustion products, no chlorinated hydrocarbons (detection limit 5-10 ppm) were found under any combustion conditions. HCl was the only detected chlorinated species under all combustion conditions; this acid gas is the thermodynamically preferred product for combustion of fuels containing chlorine, as it can be readily scrubbed from the products and eliminated. Under fuel-rich conditions at the lowest temperature (700 °C walls), evidence of fuel breakdown could be observed in the spectra obtained.

Asbestos fibers were found in the products only when the wall temperatures were 900 °C or lower. Significantly, even in these cases, asbestos was never found free-floating in the collected deposit, but was always found embedded in a larger rubber particle. Hence even when present, the asbestos from the residue would not be an inhalation hazard. At wall temperatures of 1000 °C and above, the asbestos transforms into harmless, amorphous particles that appear relatively spherical; no asbestos fibers were found in the collected deposit.

Table of Contents

Introduction and Background.....	5
Experimental Methods.....	8
Results	10
Fuel Analysis.....	10
Potential for Formation of Air Toxics	11
Asbestos Remediation.....	16
Summary and Implications	20
Ongoing Work.....	20
Acknowledgements	20

Combustion Tests of Rocket Motor Washout Material: Focus on Air Toxics Formation Potential and Asbestos Remediation

Introduction and Background

Millions of pounds of waste energetic materials (EM) such as rocket motor propellant and explosives are generated every year. While some of the material can be recycled, much of it is difficult to separate or has little intrinsic value, and some of the material contains additional hazards such as asbestos and chlorine. Typically this material is desensitized and then disposed of through incineration, open burning/open detonation (OB/OD) or, if nonreactive, in landfills. None of these disposal methods takes advantage of the energy content of the fuels and they may generate significant pollution. Combustion in an industrial furnace, boiler, or kiln (hereafter referred to jointly as "industrial furnaces") is a compelling alternative disposal option for desensitized EM that would capture the energy value in the fuel and also would mitigate many environmental hazards associated with other options through the use of furnace pollution controls.

At present the majority of EM disposal is by landfill interment or OB/OD. Landfilling of desensitized EM leaves an unwanted legacy for future generations, with the concurrent risk that chlorine and other constituents may leach into the surrounding soil and contaminate groundwater. OB/OD is typically accomplished at military installations removed from the public. Despite the relative isolation of these sites, detonation shock waves have been known to reflect off of the upper atmosphere and break windows in towns 10-20 miles distant¹, and plumes from the detonation and burning are typically visible for many miles. Recent measurements of emissions from OB/OD of antipersonnel mines indicate that significant quantities of pollutants can be emitted; measured emission factors (mass of pollutant/mass of EM) were 5.84×10^{-3} , 8.15×10^{-4} , and 3.06×10^{-3} for methane, benzene, and total aromatics, respectively.² In measurements from contained burns of solid rocket motors, the exhaust contained roughly 3% HCl, 100 ppm HCN, 2,500 ppm CH₄, and 100 ppm of volatile organics (such as chloromethane, benzene, and 1,2 dichloroethane) on a mass basis.³ In addition, NO_x emissions from uncontrolled combustion of EM can be quite high due to the high nitrogen content of the EM. Because of public and regulatory concerns, both landfilling and OB/OD of these materials are becoming increasingly unacceptable.

Given the combination of environmental concerns and disposal costs of approximately \$850 per metric ton,⁴ reapplication of EM is highly desirable. A preliminary assessment of the combustion properties of desensitized energetic materials has shown that the concept holds promise,⁵ but no pilot-scale investigation has been completed. Cofiring the energetic materials with standard fuels affords the advantage of pre-existing pollution control equipment to mitigate any environmental hazards, as well

¹ *Personal Communications with Sierra Army Depot Staff* (1996).

² Wilcox, J.L., *4th Global Demilitarization Symposium*, 1996 pp 388-399.

³ Steele, D., *4th Global Demilitarization Symposium*, 1996 pp 135-149.

⁴ Arbuckle, J., *4th Global Demilitarization Symposium*, 1996 pp 13-22.

⁵ Myler, C.A., W.M. Bradshaw, and M.G. Cosmos, *Journal of Hazardous Materials* 26:333-342 (1991).

as the benefit of energy recovery from the energetic material-derived fuels (EMDF). In the cofiring scenario(s) that we envision, EM are desensitized and transformed into EMDF, that would be fired in a 1-5% blend ratio with fossil fuels in an furnace.

We are cooperating with industrial partners to develop realistic EMDF cofiring opportunities. This investigation addresses a specific problem faced by Thiokol Propulsion Systems (Brigham City, UT) in their demilitarization efforts. By the year 2001, Thiokol is under contract to remove and treat propellant from 14 first-stage Minuteman boosters, 47 Titan IV booster solid rocket motor segments, and 16 Space Shuttle reusable solid rocket motor segments. Over the next ten years, this and similar efforts are expected to yield approximately 8.5 million pounds of solid rocket motor washout residue, all of which will require disposal or reuse. Thiokol is looking to avoid landfill disposal of the material, preferring to find a reuse/recycle option that will maximize the value of the output while minimizing any effects on the environment.

The subject of the investigation is residue from high-pressure water washout of solid rocket motors, in which high-pressure water jets are used to remove propellant material from the casing of a rocket. The high-pressure water also removes some of the insulation of the liner, which often contains asbestos. Treatment following washout recovers most of the ammonium perchlorate from the residue for reuse. The nominal composition of the material before and after the washout process is shown in Table 1. Because of the asbestos and residual ammonium perchlorate content, this material must be buried in a permitted landfill or burned under controlled conditions. These two components also introduce issues for a combustion disposal option, specifically the fate of the asbestos and the potential production of unwanted chlorinated byproducts. In addition, the presence of aluminum powder in the residue results in a measured combustion temperature of over 2000 °C for particles of approximately 1 mm in size. Concern over potential damage to furnace equipment from the high temperature material is therefore an issue. Finally, the effect of the residue on the ash stream from the furnace must be determined, if the ash has value in a particular application (e.g. cement additive, asphalt, fertilizer, etc.).

Table 1. Nominal composition of solid fuel and rocket motor washout residue.

Component	Approximate composition (percent)	
	Solid fuel	Washout residue (dry basis)
Ammonium perchlorate	65%	5%
Aluminum powder	20%	55%
Polybutadiene rubber binder	15%	40%
Asbestos (entrained from liner)	n/a	up to 1%

When Sandia and Thiokol began the collaboration searching for reapplication options for washout residue, the primary concern was the presence of 0.2 – 1% asbestos in the residue. Asbestos is defined as any one of six naturally-occurring silicate compounds (chrysotile, riebeckite, and grunerite are common). Asbestos is considered a

human health hazard when it has a fibrous shape that is more than 5 microns in length, less than 3 microns in diameter and has a 3:1 or greater aspect ratio.⁶ The inhalation danger from asbestos fibers results from the fact that the fibers are insoluble, hard, and nearly impossible for the body to remove from the lung. The fibrous shape causes irritation to the lung that may produce lung cancer, asbestosis, or mesothelioma, a rare type of cancer associated with asbestos exposure.⁷

All of the forms of asbestos melt at or below 1400 °C: grunerite melts at 1399 °C, riebeckite melts at 1193 °C, and chrysotile begins to soften at 600 °C, and is fully changed in chemical form below 1000 °C. Chrysotile is the most common form of asbestos because it is easily spun; it accounts for roughly 95% of the combined U.S. and Canadian asbestos production, and is the type of insulation used in strategic rocket motors. The melting temperature of all of these asbestos forms, particularly chrysotile, is low compared with the combustion temperature of the aluminum-containing fuel. Our initial hypothesis was that combustion of the residue would melt the asbestos fibers. Melting the fibers changes their shape, rendering them non-hazardous.

Figure 1 shows the results of our initial experiment. This series of photographs was extracted from a videotape of a roughly 150 µm (length) piece of washout residue suddenly subjected to a stream of air at 1000 °C. In the first frame (1A), small fibers can be seen protruding from the top of the piece of residue (not to be confused with the fibers from the alumina mat on which the residue piece is sitting). After the sudden heating, the particle ignites (1B), and the fibers melt onto the particle surface (1C).

Figure 1. A piece of solid rocket motor washout material of approximately 150 µm in length, suddenly heated with 1000 °C air. Asbestos fibers attached to the top of the particle melt, rendering them non-hazardous.

⁶ Lewis, R.J. Sr., *Rapid Guide to Hazardous Chemicals in the Workplace*, 3rd Ed. (Van Nostrand Reinhold: New York), 1994, p. 17.

⁷ Amdur, M.O., Doull, J., and Klassen, C.D., *Casarett and Doull's Toxicology: The Basic Science of Poisons*, 4th Ed. (McGraw-Hill: New York), 1991.

Also: <http://www.pp.okstate.edu/ehs/modules/asbwhat.htm>

This report discusses our findings concerning asbestos mitigation and the formation of chlorinated air toxics during combustion experiments with the rocket motor washout material in Sandia's MultiFuel Combustor (MFC). Later reports will discuss ongoing work, including the results of thermochemical equilibrium calculations and bed combustion experiments designed to determine the potential for material damage in a furnace.

Experimental Methods

The MFC is illustrated in Fig. 2. The MFC is a pilot-scale (30-100 kW, depending on fuel type) facility that simulates the local environment to which independently injected solid, liquid, or gaseous fuels are exposed as they pass through an entrained-flow combustion system. Fuels are introduced directly into the silicon-carbide-lined combustion section, where they may form a self-supporting flame. The MFC has an integral preheat burner (natural gas/air) which was used in some of these experiments. Combustion products are extracted from the combustor with a heated line to prevent water condensation, filtered by a heated filter, and quantified using NDIR NO_x, CO, CO₂, and SO₂ analyzers and a paramagnetic O₂ analyzer, all from Horiba Instruments (Irvine, CA). Analyzers are calibrated through the entire sampling system prior to each experiment.

A separate, identical heated sampling line transfers products to a heated 24-meter long-path gas cell, which is mated to a Mattson Instruments (Madison, WI) Infinity Fourier Transform Infrared (FTIR) spectrometer with 0.5 cm⁻¹ resolution. The majority of the spectra from these experiments were taken with the heaters set to 110 °C and a cell pressure of 300 torr. The reduced pressure was an extra precaution to prevent condensation of volatile hydrocarbons and water in the sample lines and in the cell, particularly in case areas of the cell and flow system were not uniformly heated. Sample continuously flowed through the cell during measurements to reduce the chance of adsorption and/or condensation of species in the cell and sample lines perturbing the concentrations of species in the sample. The flow in the transfer lines and cell was allowed to come to steady state for five minutes prior to recording a spectrum. Between samples, the cell was completely evacuated at least twice, and the cell and sample lines were flushed with dry nitrogen for at least 10 minutes. Under these conditions, detection limits of most hydrocarbons in the cell should be roughly 10 parts-per-million (ppm) on a molar basis, based on earlier work with butadiene and methane. As there was no need to quantify our findings, calibrations were not performed for these experiments. Additional description of the MultiFuel Combustor facility can be found in the literature.⁸

⁸ Baxter, L.L., *Combustion and Flame* 90:174-184 (1992).

Figure 2. Artist's rendition (left) and schematic diagram (right) of the MultiFuel Combustor.

Sandia's Environmental Safety and Health group performed personal and room monitoring in the vicinity of both the combustor exhaust and the feeder during the initial run of asbestos-containing fuel, to assess any potential exposure to asbestos. Workers were suited in portable powered air-purifying respirators and Tyvek suits during these initial experiments. Following a 60-minute experiment, they found no measurable asbestos from samples at any of the monitoring locations. Hence it was concluded that these experiments could be performed without the use of personal protective equipment.

The data reported here were obtained by injecting test EMDF in the top section of the MFC and sampling combustion products from the top of the 7th section. The gas residence time was 1.3 – 2 seconds, depending on the combustor wall temperatures, which were varied. The EMDF was fed using a custom screw-auger feeder developed by Thiokol, which was loaned to Sandia. The EMDF fuel itself (hereafter occasionally referred to simply as "fuel") is granular, with a characteristic size between 3 and 8 mm. It had been treated by Thiokol to remove the moisture and the tendency of the particles to re-agglomerate.

This report describes two sets of experiments. First, FTIR experiments were performed to determine the potential for formation of air toxics (particularly chlorinated species) for non-asbestos-containing fuel under a variety of combustion conditions. The original plan was to do an extensive matrix of temperatures and excess air conditions (700 °C – 1200 °C walls, 1% and 8% excess O₂), but results from the lower temperatures allowed us to perform a more limited matrix. Second, fly ash sample generated from the combustion of asbestos-containing fuel at a variety of conditions was collected and analyzed for asbestos.

Particle-capture experiments were initially performed using a sampling system consisting of a dilution sampling probe and two cyclones in series, followed by a 3 μm Millipore filter. This system was subject to rapid plugging of the collection funnel/dilution probe, which would occur after only 2 - 5 minutes in the combustor effluent, long before enough sample could be collected to perform an asbestos analysis. Several configurations were attempted. For the experiments reported here, sample was collected using a 333 micron mesh screen in a 4-inch diameter probe inserted into the flow downstream of the combustor where the temperature was approximately 300 °C. The collection device intercepted roughly 1/3 of the combustor flow, and would remain in the flow for 10 minutes, which was long enough to capture sufficient sample for analysis. During these experiments the gas flow in the combustor was 20 scfm, and the solid fuel feed was approximately 25 g/min. For a 900 °C gas temperature this yields an approximately 1.8-second gas residence time.

Results

Fuel Analysis

Triplicate analyses of the EMDF fuel and ash were performed by Huffman Laboratories (Golden, CO), and results are presented in Tables 2 and 3. Huffman encountered difficulty in ashing the fuel; following ashing at a particular temperature, they would raise the temperature and/or re-grind the ash and would get additional mass gain. We hypothesize that an aluminum oxide coating was covering the surface of the particles and halting reactions before the particles were completely ashed. Following regrinding the mass would continue to increase as Al was converted to Al_2O_3 . We took the Huffman ash data (presented as oxides) and calculated the ash elemental composition (Table 3). As expected, the major constituent of the ash is aluminum. From the ash elemental composition, we were able to calculate the true ash fraction on an oxidized ash plus organic fuel basis. Assuming that none of the aluminum in the fuel was oxidized, the ash percentage is 67.0% for the fuel sample without asbestos, and 55.8% for the fuel sample with asbestos, on a fuel basis. This is similar to the composition determined by Thiokol in previous work. Volatile matter and fixed carbon are reported on a dry, ash-free basis. The chlorine content is a good indicator of the residual ammonium perchlorate, while much of the increase in silica in the asbestos-containing fuel may be due to asbestos. An analysis of the fuel by Thiokol indicates that approximately 1% of the mass of the asbestos-containing fuel is due to liner material, and 20% of that mass is from asbestos. Significantly, Thiokol found that all of the asbestos in the tested washout material was chrysotile, which has the lowest softening temperature (600 °C) of any form of asbestos.

Table 2. Proximate and Ultimate analysis of EMDF.[‡]

	Washout Residue Type	
	Without asbestos	With asbestos
Loss on Drying (50°C,vac)	0.5	0.6
C, %	35.45	35.43
H, %	4.73	4.53
O, by difference	N/A	N/A
N, %	1.57	1.45
S, %	0.37	0.38
Cl, %	2.63	3.50
Heating value, BTU/lb.	13200	12900
Fixed carbon, DAF, %	15.0	19.4
Volatile matter, DAF, %	85.0	80.6
Ash	79.3	70.5

Table 3. Results of ash analysis for washout residue with and without asbestos, on an ash basis. An ashing temperature of 1000 °C was used in this analysis.

Element	Washout Residue percent of ash	
	Without Asbestos	With asbestos
Al	98.02	97.43
Ba	0.14	0.14
Ca	0.39	0.28
Fe	0.71	0.77
Mg	0.01	0.02
Mn	<0.008	<0.008
P	0.45	0.49
K	0.13	0.06
Si	0.14	0.81
Na	<0.037	<0.037
Sr	<0.001	<0.001
Ti	<0.006	<0.006

Potential for Formation of Air Toxics

FTIR analysis was performed on gas samples of combustion products generated under a variety of temperature and flow conditions. These conditions, shown in Table 4, represent a spectrum of operating conditions that might be encountered in a commercial furnace that could be used to cofire the solid rocket motor washout material. Typically, industrial furnaces are fired with at least 5% excess oxygen and have a background (radiative) temperature in the range 700 – 1200 °C. Gas temperatures are usually much higher; for example, exit temperatures at a cement kiln under consideration are reported

[‡] Ultimate analysis is on an as-received fuel basis. Fixed carbon and volatile matter are on a dry, ash-free basis. Ash is expressed as on an oxidized ash plus organic fuel basis.

to be 1650 °C. The combination of high temperatures, sufficient oxygen, and sufficient residence time assures good combustion with a minimum of unwanted toxic byproducts.

Table 4. Experimental conditions for FTIR air toxics analysis.

Wall temperature (°C)	Residence Time (sec)	Excess O ₂ (%)	CO (ppm)
700	2.0	12	<10
700	2.0	10	<10
700	2.0	3	<10
800	1.9	2.7	<10
800	1.9	Fuel-rich	>1000
800	1.9	7.5	<10
1000	1.5	6	<10
1100	1.4	3.7	<10
1100	1.4	0.5	≈500
1200	1.3	<1	≈300
1200	1.3	4.4	<10

In the combustion systems considered for cofiring, bulk temperature and residence time are well characterized and controlled. Typically, emissions of hazardous byproducts from these devices are the result of poor mixing between the fuel and the air, which can result in a hot, fuel-rich pocket of gas escaping from the combustion section. To determine the possibility of air toxic emissions from such incomplete combustion events, these tests also included extreme cases of low-oxygen (less than 1%). These tests are notable for the measurable CO in the product gases, which is a common indicator of incomplete and inefficient combustion.

Figure 3 shows a typical absorption spectrum of a pure compound (1,1,1-Trichloroethane) from the Mattson EPA vapor-phase library. The x-axis is in wavenumbers (ω), which are equivalent to energy units; $\omega = 1/\lambda \propto hc/\lambda = hv = E$, where h is Planck's constant, λ is wavelength, and c is the speed of light. The y-axis is in absorbance units, where the absorbance $\alpha \equiv \log_{10}(I_0/I)$. Here I_0 is the reference intensity of the light, and I is the intensity of the light after it has passed through the sample. An absorbance of 1 indicates that only 1/10 of the light passed through the system. Each of the features of a spectrum can be assigned to vibrations of one or more molecular bonds, as shown in the figure. In a more complex spectrum, such as the spectrum of combustion products shown in Figure 4, the window from 1200 – 1900 cm^{-1} is obscured by water bands. We use the region from 700 – 1200 cm^{-1} (called the "fingerprint region" due to characteristic C-C and C-H vibrations which are used to identify many hydrocarbons in this window) and the region from 1900 – 3200 cm^{-1} to identify potential gas-phase air toxic species. For species identification we use the Mattson Hazardous Chemicals Vapor Phase Library (304 species) and the EPA Vapor Phase Library (3300 species).⁹

⁹ Available from Nicolet, Inc., Madison, WI.

Figure 3. Absorption spectrum of 1,1,1-Trichloroethane ($C_2Cl_3H_3$) from the Mattson EPA vapor-phase library. Common infrared molecular features are highlighted.

Figure 4 shows the FTIR spectrum from the combustion of rocket motor washout material with wall temperatures of 700 °C and 10% excess O_2 . This spectrum is typical of almost all of the spectra taken in the test series. The H_2O and CO_2 bands are saturated, and features due to HCl and CO are the only resolvable features in the spectrum. Figures 5 and 6 show the 700 – 1200 cm^{-1} and 1900 – 3200 cm^{-1} regions in more detail. No features were found in any of the spectra that suggest the presence of chlorinated air toxics. The detection limit of the system for these species is 5 – 10 ppm under these conditions. The spectra were not only checked with the on-line Mattson libraries mentioned above, but were also compared with printed versions of high-resolution spectra of over 50 hazardous chlorinated combustion byproducts from the chlorinated hydrocarbon combustion research laboratory at U.C. Berkeley.¹⁰ The results indicate that the only gas-phase chlorinated species detected under all the conditions tested is HCl , which may be easily scrubbed from the exhaust stream.

¹⁰ Courtesy Professors Robert F. Sawyer and Catherine P. Koshland, and Graduate Student Lee Anne Sgro.

Figure 4. Typical FTIR absorption spectrum from combustion of rocket motor washout residue. This spectrum is from file 4_23ab_2: wall temperatures of 700 °C and 10% excess O₂.

Only in the coolest (700 °C walls), fuel-rich condition did we observe any gas-phase combustion products besides H₂O, CO₂, HCl, and CO. Figure 7 shows the interesting features in the spectrum corresponding to this experiment. Besides HCl, we observe evidence of CH₄, an aromatic type =C-H stretch bond, and OH/NH stretch bonds. These features are derived from fuel components. In the fuel-rich condition, methane could either be formed from incomplete hydrocarbon breakdown products, such as CH₂ and CH₃ radicals, or could come directly from unreacted natural gas from the preheat burner. Below the methane spectra, which consists of a tall peak (Q branch) surrounded by narrow features on either side (P and R branches), there is a broad absorption feature from 3000 – 3100 cm⁻¹. This feature is due to a double-bonded carbon atom bonded to a hydrogen atom: =C-H, commonly seen associated with aromatic molecules such as benzene and toluene. In this case however, it is most likely due to the binder material. Polybutadiene is a linear chain molecule with a structure of -HC=HC-HC=HC-. This structure is identical to that of a broken aromatic ring, and hence the spectral feature is shared. Hence this broad feature is probably due to incomplete breakdown of the polybutadiene in the fuel-rich combustor. Finally, the remaining spectral feature between 3200 – 3400 cm⁻¹ is in a region associated with NH and OH stretching vibrations. As part of the fuel preparation step, Thiokol treated the fuel with ammonia to eliminate the tendency for re-agglomeration. The spectral feature between 3200 – 3400 cm⁻¹ is almost certainly from an amine (NH) bond formed in the postcombustion zone due to incomplete reaction of either the ammonium perchlorate (NH₄ClO₄) or the ammonia in the fuel.

Figure 5. Fingerprint region from Figure 4 enlarged.

Figure 6. 1900 – 3200 cm^{-1} region from Figure 4 enlarged.

Figure 7. Underoxidized fuel components observed at 700 °C, fuel-rich conditions.

Asbestos Remediation

Fly ash was collected from the MFC during EMDF combustion experiments, over a wide range of experimental conditions. As noted above, some of the samples were collected isokinetically using two cyclones in series, followed by a 3 μ m Millipore filter, but the majority of the samples were collected using a 4-inch diameter probe into which a 333-micron mesh screen was inserted. The funnel was placed in the combustion flow for 10 minutes, which was long enough for the fly ash to cover the screen completely. Typical material, comprised largely of molten aluminum, exiting the combustor is shown in Figure 8; often, the material would extinguish soon after it was collected on the screen, but in some cases it would continue burning for a significant amount of time. The presence of this molten aluminum would plug our 1/4-inch diameter isokinetic probe within minutes, which necessitated use of the modified probe with the screen. Following data collection, some samples were sent to Huffman Laboratories (Golden, CO) for proximate, ultimate, and ash analysis. All samples were sent to Thiokol's analytical lab (Brigham City, UT) for asbestos analysis in their OSHA-certified laboratory.

Figure 8. Burning particles of solid rocket motor washout materials exiting the MFC during combustion testing. The combustor diameter is 6 inches; the particles enter an exhaust just below the level of the table. The exhaust system draws approximately 1800 scfm, roughly 100 times more than the combustor flow.

Table 5 summarizes the test conditions and experimental results, with the corresponding sample numbers as sent to Thiokol and Huffman. Tests were completed over a range of combustor wall temperatures between 500 – 1200 °C, with the natural gas preheat burner on and off. The preheat burner increases the temperature of the gas entering the combustor, but also lowers the O₂ concentration. Table 5 shows that unconverted asbestos fibers were only found in samples for which the combustor walls were at or below 900 °C, whether or not the natural gas preheat burner was running. Samples A6-1, A8-1, A9-1, A10-1, and A10-2 were run with wall temperatures between 600 – 900 °C and the preheat burner on, and all showed the presence of asbestos in unburned rubber particles.

Analysis of sample A13-1, obtained in a 700 °C test with the natural gas preheat burner off, also showed the presence of asbestos in unburned particles. Based on experiments A6-1 – A10-2 (preheat burner on, 600 – 900 °C), we expected also to see asbestos in the fly ash collected from A11-1, A12-1, A14-1, and A15-1, experiments with the preheat burner off in the temperature range 500 – 900 °C, but did not. There are two possible reasons that asbestos was not detected in these low-temperature samples

obtained with the combustor off. First, more O_2 was available with the preheat burner off, which may have allowed the fuel particles to ignite more easily. Second, the collection screen in these experiments was somewhat closer to the exit of the combustor. As a result, burning particles may have persisted on the screen for a longer time than they would have in the set of experiments with the preheat burner on, which could have caused all of the asbestos fibers to melt. Residual carbon measured in these samples shows an increasing combustion efficiency (indicated by decreasing residual carbon) as the wall temperature increases. For many of the samples in which no asbestos fibers were found, amorphous ("heat-converted") asbestos was found in the fly ash sample.

Significantly, no free-floating asbestos fibers were found in any of the samples. This indicates that the asbestos, which is always found bound in the rubber liner material, is destroyed when the liner material burns.

Table 5. Experimental conditions and results for asbestos remediation investigation.

Sample Name	Description	Wall Temp. (°C)	NG Preheat Comb?	Resid. C.	Asbest. fib. embedded in rubber	Free-floating asbestos fib.
A1-1	Large cyclone	1200	Y	---	N	N**
A1-2	Filter	1200	Y	---	N	N
A2-1	Large cyclone	1100	Y	---	N	N**
A2-2	Filter	1100	Y	---	N	N
A3-1	Large cyclone	1000	Y	---	N	N
A3-2	Filter	1000	Y	---	N	N
A3-4	Funnel plug sample	1000	Y	---	N	N**
A4-1	Large cyclone	1000	Y	---	N	N
A4-2	Filter	1000	Y	---	N	N
A4-4	Funnel plug sample	1000	Y	---	N	N**
A5-1	Large cyclone	900	Y	---	N	N**
A6-1	333 µm screen	900	Y	---	Y	N
A8-1	333 µm screen	800	Y	---	Y	N
A9-1	333 µm screen	700	Y	---	Y	N
A10-1	333 µm screen	600	Y, lean	---	Y	N
A10-2	333 µm screen	600	Y	---	Y	N
A10-3	333 µm screen	600	N	---	N	N
A11-1	333 µm screen	500	N	9.12	N	N
A12-1	333 µm screen	600	N	8.60	N	N
A13-1	333 µm screen	700	N	1.55	Y	N
A14-1	333 µm screen	800	N	1.44	N	N
A15-1	333 µm screen	900	N	0.85	N	N
A16-1	333 µm screen	1000	N	1.42	N	N
A17-1	333 µm screen	1100	N	0.49	N	N
A18	Fuel w/o asbestos	---	---	---	N	N
A7	Fuel w/asbestos	---	---	---	Y	N
A19	Fuel w/asbestos	---	---	---	Y	N
A20	Fuel w/asbestos	---	---	---	Y	N

Y=yes, N=no. "NG Preheat Comb." column indicates whether the natural gas preheat combustor was on during the test. "Resid. C." column indicates residual carbon in some samples. Converted silicates, which were formerly asbestos fibers, were found in many of the post-combustion samples, particularly those indicated with **.

Summary and Implications

The findings of this investigation of the combustion properties of rocket motor washout material are positive in terms of the potential for cofiring as a recycle / reuse option to landfill disposal for solid rocket motor washout residue. First, fuel analysis shows that between 2 and 4 percent by mass of the residue is chlorine, which could pose a hazard due to the formation of chlorinated air toxics. However, no chlorinated air toxics were found at any combustion condition (fuel-rich to 10% excess O₂, 700 – 1200 °C combustor walls). All of the chlorine appears to be converted to HCl, which can be readily scrubbed from the exhaust gases.

Second, no respirable asbestos fibers were found in the fly ash under any condition tested (wall temperatures 500 – 1200 °C, natural gas preheat combustor on and off). Asbestos fibers were found bound in unburned rubber pieces when the combustor wall temperatures were 900 °C and below, particularly when the preheat combustor was on. We note that peak temperatures in all of the combustion devices under consideration exceed 900 °C by a comfortable margin.

These observations suggest that good combustion practice in a commercial furnace or kiln facility is likely to guarantee mitigation of both the air toxic and asbestos hazards that are potentially associated with cofiring solid rocket motor washout residue. For this reason, we believe cofiring is a viable alternative to other disposal options for this material.

Ongoing Work

Ongoing and future work includes thermochemical equilibrium analyses and bed combustion experiments. The thermochemical equilibrium analyses will predict the effect of 1-5% cofiring of the solid rocket motor washout residue in various commercial furnace settings on the ash chemistry. The bed combustion experiment is being constructed to allow us to investigate the potential for damage to furnace equipment during cofiring. Pending positive results in these efforts, a commercial test burn is planned for the near future.

Acknowledgements

This project is supported by a joint DOE/DoD Memorandum of Understanding, and accomplished in coordination with the Demil Technology Office of the Defense Ammunition Center. We would like to thank our colleagues at Thiokol, particularly Glenn Mower, Bill Munson, Gene Curtis, and Dean Howard, for helping to make this phase of the project a success. We would also like to thank Don Hardesty (8361), Joel Lipkin and Howard Hirano (both 8119) for programmatic guidance and support.

Distribution:

Ms. Alice Atwood
Physical Scientist
Engineering Sciences Division
Research Department
China Lake, CA 93555-6001

Dr. Michael Berman
AFOSR
AFOSR/NC
Bolling AFB, DC 20332

Dr. Thomas Boggs
Naval Weapons Center
Code 389
China Lake, CA 93555

Dr. Surya N. Bulusu
ARDEC
SMCAR-AEE-WW
Dover, NJ 07801-5001

Dr. Robert D. Chapman
Naval Air Warfare Center
Code 464220D
China Lake, CA 93555

Dr. Ronald L. Derr
Naval Weapons Center
Code 389
China Lake, CA 93555

Chester Clark
Naval Surface Warfare Center
Indian Head Division
101 Strauss Avenue
Indian Head, MD 20640-5035

Charles Painter
Naval Surface Warfare Center
Indian Head Division
101 Strauss Avenue
Indian Head, MD 20640-5035

John Dow
Naval Surface Warfare Center
Energetic Mat. Res. & Tech. Dpt.
Indian Head Division
101 Strauss Avenue
Indian Head, MD 20640-5035

Dr. David S. Downs
US Army ARDEC
SMCAR-AEE-B
Picatinny Arsenal, NJ 07806-5000

Timothy J. Dunn
Naval Surface Warfare Center
Code 9420T / Bldg 695
Indian Head Division
101 Strauss Avenue
Indian Head, MD 20640-5035

Doug Elstrodt
Naval Surface Warfare Center
Code 9130
Energetic Materials Chemistry Division
Indian Head, MD 20640-5035

Dr. Robert A. Fifer
US Army Ballistic Research Laboratory
SLCIBR-IB-I
Aberdeen Proving Ground, MD 21005-5066

Brad Forch
US Army Ballistic Research Laboratory
SLCIBR-IB-I
Aberdeen Proving Ground, MD 21005-5066

Dr. Arpad A. Juhsz
US Army Ballistic Research Laboratory
SLCIBR-IB-B
Aberdeen Proving Ground, MD 21005-5066

Louis Kanaras
US Army Environmental Center
Environmental Technology Division
Tech. Demonstration & Transfer Branch
Aberdeen Proving Ground, MD 21010-5401

Dr. Solim S. Kwak
Defense Ammunition Center
1 C Tree Road
SIOAC-TDS
McAlester OK. 74501-9053

Ed Ansell
Defense Ammunition Center
1 C Tree Road
SIOAC-TDM (Ed Ansell)
McAlester OK. 74501-9053

James Wheeler, Director
Defense Ammunition Center
1 C Tree Road
SIOAC-TD
McAlester OK. 74501-9053

Dr. J.A. Lannon
U.S. Army ARDEC
Picatinny Arsenal, NJ 07806-5000

Dr. Donald Liebenberg
U.S. Office of Naval Research
800 N. Quincy St.
Arlington, VA 22217

Dr. David M. Mann
U.S. Army Research Office
PO Box 12211
Research Triangle Park, NC 27709-2211

Walter Marx
Naval Surface Warfare Center
Indian Head Division
Energetic Mat. Res. & Tech. Dpt.
Indian Head, MD 20640-5035

Dr. Ingo W. May
US Army Ballistic Research Laboratory
SLCIBR-IB-B
Aberdeen Proving Ground, MD 21005-5066

Ray Goldstein
US Army ARDEC
Bldg. 321
Attn: AMSTA-AR-WEA
Picatinny Arsenal, NJ 07806-5000

Dr. Robert L. McKenney, Jr.
Air Force Research Laboratory
Energetic Materials Branch
WL/MNME
Eglin Air Force Base, FL 32542-5434

Dr. Richard S. Miller
Office of Naval Research
800 North Quincy St.
Arlington, VA 22217

Dr. Tim Parr
Naval Air Warfare Center
Code CO2392
China Lake, CA 93555-6001

Betsy Rice
US Army Ballistic Research Laboratory
SLCIBR-IB-I
Aberdeen Proving Ground, MD 21005-5066

Dr. Robert W. Shaw
U.S. Army Research Office
PO Box 12211
Research Triangle Park, NC 27709

Rose Tesce-Rodriguez
US Army Ballistic Research Laboratory
SLCIBR-IB-I
Aberdeen Proving Ground, MD 21005-5066

Merrill Beckstead, Professor
Brigham Young University
Chemical Engineering Department
350 Clyde Building
Provo, UT 84602

Professor Melvyn C. Branch
University of Colorado
Department of Mechanical Eng.
Boulder, CO 80309-0427

Professor M. Quinn Brewster
University of Illinois
Dept. of Mech. and Indus. Eng.
Urbana, IL 60801

Professor Thomas B. Brill
University of Delaware
Department of Chemistry
Newark, DE 19711

Professor Thomas Litzinger
The Pennsylvania State University
Department of Mechanical Engineering
University Park, PA 16802

Jerry Cole
Energy & Environmental Research
18 Mason
Irvine, CA 92718

Dr. Marc DeFourneaux
Project Manager
NIMIC
International Staff
NATO-1110
Brussels, Belgium

Kevin Davis
Reaction Engineering International
77 West 200 South
Suite 210
Salt Lake City, UT 84101

Stan Harding
Reaction Engineering International
77 West 200 South
Suite 210
Salt Lake City, UT 84101

Leon Hyde
Thiokol Propulsion Division
Cordant Technologies
PO Box 689
Brigham City, UT 84302-0689

Kathy Miks
Thiokol Propulsion Division
Cordant Technologies
PO Box 689
Brigham City, UT 84302-0689

Bill Munson (5 COPIES)
Thiokol Propulsion Division
Cordant Technologies
PO Box 689
Brigham City, UT 84302-0689

Gene Curtis (5 COPIES)
Thiokol Propulsion Division
Cordant Technologies
P.O. Box 689
Brigham City, UT 84302-0689

Louis Cannizzo
Thiokol Propulsion Division
Cordant Technologies
P.O. Box 689
Brigham City, UT 84302-0689

Glenn Mower (5 COPIES)
Thiokol Propulsion Division
Cordant Technologies
P.O. Box 689
Brigham City, UT 84302-0689

Eddie Diehl
Thiokol Propulsion Division
Cordant Technologies
PO Box 689
Brigham City, UT 84302-0689

John Slaughter
Thiokol Propulsion Division
Cordant Technologies
PO Box 689
Brigham City, UT 84302-0689

Hap Stoller
TPL, Inc.
3768 Hawkins St. NE
Albuquerque, NM 87109

Hanna Hörnström
Försvarets Materielverk
Vapenavdelningen
Kemi- och utbildningsmaterielbyrå
115 88 Stockholm
SWEEDEN

Paul Reinke
Booz-Allen & Hamilton, Inc.
8283 Greensboro Drive
McLean, VA 22102-3838

Stefan Lamnevik
FOA
Division of Weapons and Protection
Department of Energetic Materials
Grindsjön
S-147 25 Tumba
SWEEDEN

Donna M.-U. Hart
Director of Business Development
Fraunhofer USA
24 Frank Lloyd Wright Drive
Ann Arbor, MI 48106-0335

Dr. Larry Waterland
Acurex Corp.
Environmental Systems Division
485 Clyde Ave
PO Box 1044
Mountain View, CA 94039

Professor Robert F. Sawyer
Department of Mechanical Engineering
72 Hesse Courtyard
University of California, Berkeley
Berkeley, CA 94720

Professor K. Seshadri
Department of AMES
University of California at San Diego
9500 Gilman Drive
La Jolla, CA 92093-0411

1	MS 9001	T. O. Hunter, 8000; Attn: J. B. Wright, 2200 M. E. John, 8100 L. A. West, 8200 R. C. Wayne, 8400 P. N. Smith, 8500 T. M. Dyer, 8700 L. A. Hiles, 8800
1	MS 9054	W. J. McLean, 8300
1	MS 9052	G. C. Sclipa, 8361
10	MS 9052	L. L. Baxter, 8361
1	MS 9052	J. Ross, 8361
1	MS 9052	R. Berhens, 8361

1	MS 9052	S. Margolis, 8361
1	MS 9052	C. R. Shaddix, 8361
1	MS 9052	D. L. Hardesty, 8361
1	MS 9052	S. F. Rice, 8361
10	MS 9102	S. G. Buckley, 8120
1	MS 9102	W. Bolton, 8120
1	MS 9103	G. Thomas, 8120
1	MS 9105	H. Hirano, 8119
5	MS 9105	J. Lipkin, 8119
1	MS 9105	J. A. Lamph, 8118
1	MS 0834	L. M. Minier, 9112
3	MS 9018	Central Technical Files, 8940-2
1	MS 0899	Technical Library, 4916
1	MS 9021	Technical Communications Department, 8815/ Technical Library, MS 0899, 4916
1	MS 9021	Technical Communications Department, 8815 For DOE/OSTI

This page intentionally left blank