

US Army Corps of Engineers Construction Engineering Research Laboratories

USACERL Technical Report 97/32 April 1997

## **Reduced Smoke Propellant Binder Residue as a Fuel Source**

### Feedstock Processing Technology

#### by

Kathryn F. Miks and Richard J. Scholze

With an estimated 8.8 million lb of reduced smoke propellant targeted for demilitarization, recovery and beneficial reuse of propellant ingredients would reduce or minimize the quantity of waste requiring disposal. Recycling of ammonium perchlorate (AP), the primary propellant ingredient, has been established. Reuse of the AP-depleted binder residue has been studied on a limited basis; however, only aluminized Class 1.3 propellants have been evaluated.

This study identifies and evaluates alternate uses of Class 1.3 reduced smoke (nonaluminized) propellant binder residue, with a focus on use as a fuel or fuel supplement. Researchers characterized HARM, Maverick, and Sidewinder propellants by analytical, physical, and safety evaluations. A survey of combustion processes was also performed to determine reuse markets for binder residue.

Preliminary data indicate that both the HARM and Maverick propellant binder residues are suitable for use as a low-grade fuel, and market research identified three combustion reuse options. All the applications require a very high volume of fuel at a low price. Combustion emissions may be an environmental concern depending on how the residue is integrated into the system. This report refines and evaluates the alternate uses identified in a related technical report (Miks and Scholze, USACERL TR-97/30).



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## Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers, under Project 4A162720D048, "Industrial Operations Pollution Control Technology"; Work Unit UP6, "Reduced Smoke Propellants." The technical monitor was Lou Kanaras, U.S. Army Environmental Center, SFIM-AEC-ETD.

The work was performed by the Troop Installation Operation Division (UL-T) of the Utilities and Industrial Operations Laboratory (UL), U.S. Army Construction Engineering Research Laboratories (USACERL). Thanks are expressed to the many individuals who contributed to the success of this project: Ben Wilson of MICOM; Geoff Silcox, Jim Campbell, Dale Inkley, and Dana Overacker of the University of Utah; Jack Brouwer of Reaction Engineering International; David Dayton of the National Renewable Energy Laboratory; and to the many individuals—too numerous to list—from Thiokol Corporation. The USACERL principal investigator was Richard J. Scholze. Bernard A. Donahue is Chief, CECER-UL-T and John T. Bandy is Operations Chief, CECER-UL. The USACERL technical editor was Linda L. Wheatley, Technical Information Team.

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## 1 Introduction

### Background

An estimated 8.8 million lb of reduced smoke propellant is targeted for demilitarization and disposal. Open burning/open detonation (OB/OD) areas have been used for disposal in the past but are being phased out as they become more stringently regulated. For example, the U.S. Army is in the process of closing over 50 percent of the available OB/OD sites at their installations. States are taking increasingly strong steps to minimize the impact on environmental air quality, even in isolated geographic regions. Recovery and beneficial reuse of propellant ingredients would reduce or minimize the quantity of waste requiring disposal. Recycling of ammonium perchlorate (AP), the primary propellant ingredient, has been established. Of the amount of propellant to be demilitarized, 1.5 million lb of binder residue is estimated to be reuseable. Reuse of the AP-depleted binder has been studied on a limited basis; however, only aluminized Class 1.3 propellants have been evaluated.

### Objective

The objective of this program is to evaluate recovery of AP from reduced smoke (nonaluminized) propellants and identify and evaluate uses for the AP-depleted binder residue.

The objective of this particular phase of the project was to refine and evaluate alternate uses of Class 1.3 reduced smoke (nonaluminized) propellant binder residue previously identified. Reuse options focused on use as a fuel or fuel supplement. These efforts will demonstrate and evaluate a combustion process on a pilot scale and develop a process for integration into an industrial application.

### Approach

Initial investigation included demonstration of AP extraction from nonaluminized propellant, a market survey of potential combustion processes, and baseline combustion evaluations. This effort was reported in Miks and Scholze (September

1996). The second phase reported herein included identifying and evaluating specific industrial applications, developing processes to get the residue into configurations suitable for reuse, demonstrating a combustion process on a pilot scale, and devising an industrial integration plan. The final phase of the project will demonstrate a combustion process at the full-scale size.

The approach for this report included additional safety evaluations of both wet and dried HARM, Maverick, and Sidewinder residues to ensure that the materials could be safely integrated into industrial applications. For each residue, the fuel value was determined at various moisture levels.

Specific users were identified that could incorporate binder residue feedstock into their processes. Potential users were contacted to determine residue quantity requirements, energy requirements, the physical form of the residue needed, material handling issues, moisture level acceptability, and any other pretreatment requirements. The value of the residue in each application was determined. Subscale processing studies were performed to determine the most efficient method of configuring the residue as required for reuse. The studies involved size reduction, dewatering, and coating to prevent reagglomeration. Based on user evaluations for the applications considered feasible, processes were designed to form the residue appropriately for reuse.

Once 151 lb of properly configured HARM residue and 137 lb of properly configured Maverick residue were produced, the material was used in pilot-scale combustion evaluations. The pilot-scale testing analyzed combustion emissions (including dioxins and furans), evaluated nitric oxide ( $NO_x$ ) control techniques, measured burnout times, and determined the effect of binder residue on cement kiln clinker.

A literature search and market survey were performed to explore other possible reuse applications (not necessarily combustion). Experimental testing further evaluated two of the options that were identified: using the material as a modifier in asphalt mixtures and using the material as a biofuel.

Information garnered from the program was used to devise an industrial implementation plan. To estimate the amount of residue that would be available, a list of known reduced smoke propellant motor programs currently in production was assembled along with a list of reduced smoke propellant motor systems presently targeted for demilitarization. Finally, the total cost to implement each feasible application was determined.

## Mode of Technology Transfer

It is recommended that the information from this report be used to assist Department of Defense efforts in reuse or beneficial use of propellant residues.

### **Metric Conversion Factors**

U.S. standard units of measure are used throughout this report. A table of metric conversion factors is presented below.

1 ft	= 0.035 m
1 in.	= 25.4 mm
1 lb	= 0.453 kg
1 gal	= 3.78 L
°F	= (°C × 1.8) + 32
1 psi	= 6.89 kPa
1 ton	= 907.18 kg

## 2 Additional Safety Evaluation Performance

Additional safety tests were performed on both wet and dry residues as recommended by Miks and Scholze (1996). Testing was performed at the two moisture level extremes to evaluate best- and worst-case safety properties. The residue used was from the Phase 1 effort. Thiokol's Russian detonation susceptibility (DST), Russian deflagration-to-detonation (DDT), unconfined burn, and simulated bulk autoignition (SBAT) tests were run. Table 1 shows the results of the safety tests.

The DST test determines if a material will sustain a detonation when exposed to an explosive booster. The DST objective is to impulse the test material with a large enough explosive booster that a detonation could occur. If the explosive booster initiates a sustained detonation, a positive test result is reported. One test was run per condition. A moderate report (noise) was observed with the dried HARM residue, and a loud report was observed with the dried Sidewinder residue. Neither of these tests, however, indicated a sustained detonation. Testing on the dried

	HARM Residue		Maverick Residue		Sidewinder Residue	
	47% H₂O	Dried	53% H₂O	Dried	44% H <sub>2</sub> O	Dried
Russian DST	No go	No go Moderate report	No go	Marginal go 10.3% expansion. Loud report. Pierced 1/16-inch Al witness plate.	No go	No go Loud report
Russian DDT at 500 psi	No go	No go	No go	No go Loud report. No hole enlargement.	No go	No go
Unconfined burn	Could not ignite	Difficult to ignite. Burns non-energetically (like rubber).	Could not ignite	Easy to ignite. Burned energetically and very fast.	Could not ignite	Easy to ignite. Burned energetically and very fast.
SBAT, onset exotherm, °F	278	252	274	250	287	300

Table 1. Propellant binder residue safety analyses.

Maverick material, however, indicated a marginally positive result by expanding the bore approximately 10.3 percent and slightly piercing the witness plate.

The DDT test determines whether a material can go from burning to detonation. The test is performed at a confinement pressure of 500 psig. One test was run per condition. All test results were negative, indicating that burning material is not expected to detonate.

Unconfined burn tests were performed by holding a flame to 3 to 5 g of residue and visually observing if the material would sustain a burn. None of the wet residues ignited. Once ignited, the dried HARM residue sustained a nonenergetic burn. Both the dried Maverick and Sidewinder residues behaved similarly to propellant; they were easy to ignite and burned energetically.

SBAT was performed at a heating rate of 24 °F/hr, and the traces are presented in Figures 1 through 6. Figures 1, 3, and 5 are of wet residues and show endotherms starting around 150 °F due to moisture evaporation. The onset exotherm for the wet materials is difficult to pinpoint because of the endotherm locations. For the HARM residue shown in Figure 1, an exotherm begins at approximately 278 °F and peaks at around 390 °F. Figure 2 shows dried material and a slightly larger exotherm that begins at approximately 252 °F and also peaks around 390 °F. Neither sample ignited.

For the Maverick residue, the wet material in Figure 3 displayed a large exotherm beginning at approximately 274 °F and peaking at approximately 355 °F. The dried material in Figure 4 shows a similar exotherm that begins at approximately 250 °F and also peaks at approximately 355 °F. The wet material appeared to have ignited; however, the bulk of the dried material remained unburned.

Wet Sidewinder residue (Figure 5) displayed a large exotherm beginning at approximately 287 °F and peaking at approximately 370 °F. The dried material had a broad exotherm beginning at approximately 300 °F, with peaks at 370, 440, and 475 °F. The wet material appeared to have ignited; however, the bulk of the dried material remained unburned.

The safety data do not indicate any potential safety problems associated with combusting either wet or dried HARM binder residue in a commercial application. For both the Maverick and Sidewinder residues, although the wet material does not pose a safety concern, the dried material does. Both of the residues are sensitive to ignition and burn energetically. Furthermore, dried Maverick residue has the potential to sustain a detonation.

















These materials are "energetic" because they contain energetic constituents. The Maverick residue tested contained approximately 35 percent AP, while the Sidewinder residue contained approximately 22 percent cyclotrimethylinetrinitramine (RDX). Both of these propellants, prepared in Phase 1 of the program, were extracted using a 5-gal pilot-scale apparatus rather than through the M-528 reclamation facility. It is probable that the AP level in the Maverick residue would be reduced significantly if processed through the full-scale facility. The HARM residue, which is very similar physically to the Maverick residue (same binder system), contained just 6 percent AP out of the M-528 facility. The nominal range for M-528 residues is 3 to 6 percent AP. Safety properties of the Maverick residue would undoubtedly improve with reduced AP content, possibly improving to the level where it would be possible to use the residue as a commercial fuel source.

RDX is insoluble in water, so it remains with and is concentrated in the residue. Therefore, it is not possible to reduce the RDX level in the residue using the existing propellant reclamation process. Because RDX has a high market value (currently about \$26/lb, which is expected to increase significantly), it might be cost effective to reclaim the RDX using, for example, solvent extraction. Without RDX, the residue would likely be suitable for use as a fuel. Although evaluating RDX reclamation is outside of the scope of this effort, it is an option that should be considered if a high inventory of RDX-containing systems requiring demilitarization exists.

# 3 Fuel Value Determination at Various Moisture Levels

As recommended in the previous report, the heat of combustion was determined for the HARM, Maverick, and Sidewinder propellant residues at various moisture levels. Measurements were made in triplicate at approximately 30 atmospheres oxygen pressure using a Parr Model 1241 oxygen bomb calorimeter with a Model 1720 calorimeter controller. Moisture level was determined via gravimetric analyses on split samples, and Table 2 shows the results. Standard deviations are indicated in parenthesis. Figure 7 is a graphical presentation of the results.

The results indicate that dried HARM residue has the same fuel value as coal. The Maverick and Sidewinder residues, however, due to their high AP/RDX levels, have much lower fuel values more comparable to wood. Based on the composition, if the AP level in the Maverick were reduced to  $\leq$  6 percent, it too would be expected to have a combustion heat similar to that of coal.

Residue Type	Moisture Level (%)	Observed Fuel Value (kJ/g)
HARM	0	30.9 (0.18)
	31	24.7 (1.75)
	27	25.3 (1.97)
	37	15.3 (2.23)
Maverick	0	21.8 (0.20)
	17	16.0 (5.01)
	17	16.9 (0.89)
	62	7.4 (0.66)
Sidewinder	0	15.8 (0.45)
	3	15.1 (0.89)
	28	10.6 (2.03)
	62	6.5 (0.10)

Table 2. Binder residue fuel value vs. moisture level.



Figure 7. Binder residue fuel value.

## **4** Materials and Process Determination

## **User Feasibility Study**

Specific processes were identified and users were contacted that could potentially integrate the binder residue as a fuel source. Table 3 summarizes the feasibility of each application. Detailed descriptions of each application are presented in the remainder of this section.

### Ash Grove Cement

Application:	Cement kiln
Primary contact:	Duane Crutchfield, Plant Manager
	Leamington, UT
	801-857-2380

Company	Application	Feasible	Comments	Residue Form
Ash Grove Cement	Cement kiln	Yes	< coal value (\$23-\$28/ton)	Dry, carbon-coated, 1/2-in. pieces
Utah State University	Stoker furnace	Yes	< coal value (\$31/ton)	Dry, carbon-coated, 1-1/2-in. pieces
PacifiCorp	Steam boiler	Yes	≤ coal value (\$13-\$20/ton)	Dry, carbon-coated, 1-1/2-in. pieces
Holnam Cement	Long wet cement kiln	Yes	Take for no cost	Dry, carbon-coated, 2-in. pieces
International Cogeneration Development of Utah	Varied	Maybe	We pay \$52/ton	Wet blob
Davis County (Solid Waste Management and Energy Recovery Special Service District)	Incinerator with steam boiler	No	We pay \$62/ton	Wet blob
Geneva Steel	Blast furnace	No	In-line system	
Great Salt Lake Minerals and Chemicals	Chemical drier	No	Gas-fired	
U.S. Steel, Gary Works	Blast furnace	No	In-line system	
U.S. Steel, Claireton	Coke oven	No	Poor results with waste tires	

#### Table 3. User feasibility summary.

The Ash Grove Learnington plant was constructed in 1980 and produces Portland cement. Plant capacity is 600,000 tons per year. Raw materials (limestone, silica, alumina, and iron), fuel, and hot gasses from the cement plant are blended in a preheater tower to bring their temperatures to 2,000 °F before entering the kiln. The rotary kiln, measuring 12 ft, 3 in. in diameter by 80-ft long, is where raw materials are exposed to temperatures up to 2,800 °F. Heat from the preheater tower and the kiln transforms the raw materials into clinker of up to about 1 in. in diameter. Clinker is ground and mixed with gypsum to become cement.

Figure 8 shows a schematic of the preheater and kiln. Both are fueled primarily with coal. The plant consumes approximately 90,000 tons of coal a year, which is trucked to the site. Current price of the coal is between \$23 and \$28/ton, delivered. A Loeshe mill grinds the coal into approximately 2-in. lumps. The solid fuel ash is incorporated into the product.

A secondary fuel source for the plant is whole waste tires. The State of Utah pays Ash Grove \$65/ton to dispose of the tires. The tires are delivered by truck and unloaded onto a conveyor belt that meters the tires into the preheater. During normal operations the tires can comprise 10 to 15 percent of the total fuel feedstock.

Based on the composition of the residue and the chemistry in the kiln at the elevated temperatures, it is unlikely that using the residue as a fuel supplement would have an effect on the cement product. Because the environment inside the kiln is basic (approximately a pH of 12), the low levels of AP present in the binder will not likely be a concern within the kiln. However, depending on where the residue is fed into the process, the chlorine may be a concern within the preheater. Furthermore, the preheater is scheduled to be upgraded in the near future, so the location at which the residue would be introduced is not certain.

The plant manager at Ash Grove expressed interest in using the residue as a fuel supplement if the price of the residue were lower than the price of coal to make a process change worthwhile. Therefore, the value of delivered residue would be under \$23 to \$28/ton. The residue could be 10 to 15 percent of the fuel feedstock at any given time.

The residue would need to be supplied in small enough pieces so that it could be pneumatically fed into the system. Although 3-in. pieces might work, ½-in. pieces are preferable. Stickiness would be a problem. Although the system could probably tolerate moderate levels of moisture (up to 8 percent), the loss in Btus would significantly lower the value of the residue.



Figure 8. Ash Grove kiln system.

#### Utah State University

Application: Stoker furnace Primary contact: Brian J. Anderson Facilities Operation Manager Physical Plant Logan, UT 801-797-3752

> Ben R. Berrett, Mechanical Engineer Physical Plant Logan, UT 801-797-1957

Utah State University is in Logan Canyon, UT. Heat for all the campus buildings is provided by a centralized system of five stoker furnaces. All the stokers are Detroit-brand Rotostokers. The two primary furnaces are capable of operating on either coal or natural gas, but (depending on the current economies) have traditionally used coal. They both have a consumption capacity of 65,000 lb of coal per hour. One older furnace operates solely on coal and has a 45,000-lb/hr capacity. The remaining two furnaces can operate on either gas or oil at a rate of 30,000 lb/hr.

The University consumes an average of 17,000 tons/yr of about 1-½-in.-diameter stoker-grade coal. The coal has a heating value of between 11,000 and 13,000 Btu/lb (25.6 and 30.2 kJ/g) and is purchased for \$31/ton delivered. It is a low-sulfur coal and contains approximately 4.5 percent moisture.

Delivered by truck, the coal is stored outside in a large pile about 1 mile from the facility. A 30-day supply is normally kept on hand; however, the storage capacity is basically unlimited. The coal is loaded (using a tractor bucket) into a truck and delivered to the furnace facility where it is unloaded at a ground-level dump station. From the dump station, the coal is conveyed into a hopper, which services both of the large furnaces. The smaller furnace, which is rarely used, is loaded by dumping the coal directly into an overhead hopper.

The stokers operate at approximately 1,400 °F. The material resides in the stoker for approximately 45 min. Final ash content averages 12 percent. The ash is landfilled as clean fill at no cost to the University. The residue would need to be reduced to approximately 1- $\frac{1}{2}$ -in.-diameter pieces and dried somewhat to acquire an acceptable Btu level. The material would also need to be coated to keep it from reagglomerating and to remain free-flowing. Existing residue could be integrated easily into the process without any process modifications. The University is interested in using the residue because of the environmental benefits to the community and possible favorable public relations.

### PacifiCorp

Application:Steam boilerPrimary contacts:Kevin T. ThompsonStrategic Account ManagerUtah Power801-220-2337

Rick Pizza, Jr., General Business Manger Utah Power, Bear River District 801-257-5321

Comprised of Utah Power and Pacific Power, PacifiCorp is the third largest electric utility in the West, serving seven states. The corporation operates 15 thermal electric plants and 53 hydroelectric plants. Of the total power supply, 79 percent is derived from coal. Of the thermal electric plants, all but two are coal-fired. Annually, PacifiCorp consumes 30 million tons of coal of which approximately 20 million tons are from mines that PacifiCorp operates for a cost of between \$13.4 and \$20.0/ton.

The most likely candidate to use the residue is the Naughton plant in Kemmerer, WY. The Naughton plant uses a steam boiler, has a rating of 707.2 MW, and consumes 480 tons of pulverized coal daily. Although the coal is fed into the boiler via an in-line system, process modifications may be considered.

The most likely integration would be to pulverize the residue along with the coal. Currently, coal is pulverized from 1.5-in. lumps at a rate of 40 to 50 tons/hr. The pulverized material is carried from the grinder pneumatically. Warm air (150 to  $170 \, ^{\circ}$ F) is used to dry the coal. The coal used at Naughton contains between 8 and 10 percent moisture; however, coal used at other plants can contain as much as 25 percent moisture. Because the residue is so light, there is concern that it would be carried from the grinder before the appropriate size is obtained. Large particles will not fully combust in a steam furnace because of the short residence time (3 to 5 seconds).

Thus, for the residue to be effectively integrated at PacifiCorp, it would need to be free flowing and in approximately 1.5-in. lumps. To keep the material from reagglomerating after it has been reduced, it would have to be coated with something such as coal dust (PacifiCorp is currently land-filling coal dust [bug dust], which is too fine to use in their boilers). A moisture level of not more than 10 to 15 percent would be preferable.

Table 4.	Residual chlorine concentrations in
coal/resi	due mixtures.

Wt % Residue		Wt % Cl in Mixture
0		0.14
5	1	0.183
10		0.226
25		0.355

A cursory evaluation of the effects of residual chlorine in boilers was considered. The mean concentration in 101 coals is 0.14 wt percent (log-normal distribution). Assuming that the residue is 1 weight percent chlorine (Cl), the concentration in various coal/residue mixtures is calculated as shown in Table 4.

At the lower weight fractions of residue (5 and 10 percent), the increase in Cl is so small that it is unlikely to cause a problem in boilers.

### Holnam Cement

Application:	Long wet cement kiln
Primary contact:	Kevin Ovard
	Plant Environmental Manager
	Devil's Slide Plant
	Morgan, UT
	801-829-6821

The Devil's Slide process differs from the Ash Grove Learnington process in that the raw materials are introduced in a slurry containing between 33 and 33.5 percent moisture. Two long, wet rotary kilns, each 10 ft in diameter by 400-ft long, are used to produce the clinker. No preheater is used.

The kilns are fueled primarily with coal, consuming approximately 60,000 tons/yr at a cost of roughly \$26.7/ton. The fuel supply is 25 percent waste automotive tire chips and diapers (25 tons per day each). The tires are provided in  $2 \times 2$ -in. strips by the State of Utah at no cost to Holnam. A recycling firm in Salt Lake City shreds and delivers the tires for between \$65 and \$70/ton. A \$1.00 recycling fee collected from consumers on the purchase of each new tire covers the cost of preparing the tires for reuse. The tire pieces retain the steel strips, which serve as a source of iron but can hamper feeding by hanging up in the lines. The total fuel value of the tires is approximately 32 kJ/g. The Devil's Slide plant has been using waste tires as a fuel source for approximately 3 yr. Roughly 20 cement plants in the United States follow suit.

The waste diaper material is provided in 2-in. cubes from Kimberly Clark, also at no cost to Holnam. The material, generated during manufacturing, is composed of paper products. Kimberly Clark slightly wets the waste papers and extrudes them into the blocks that are compatible with Holnam's process. The total fuel value is slightly higher than for the tire material. The diaper material has been used at their plant for approximately 18 months.

Both supplemental fuels are delivered by truck and stored in piles outside the plant. A tractor bucket is used to load the tires and diapers into a hopper. The tires and diapers are mixed together and blown into the kiln via 6-in. piping. Residue could be integrated easily into this process without any process modifications. Holnam would be very interested in using the residue if it were provided to them at no cost (as with the tires and diapers). In the future, Holnam may be more interested in paying for the residue when a local tire recycling plant opens and eliminates (at least partially) the scrap tire source.

The residue would need to be reduced to less than 2-in. cubes and dried somewhat to acquire an acceptable Btu level. As with the previous applications, the material also would need to be coated to keep from reagglomerating and to remain free flowing.

### International Cogeneration Development (ICD) of Utah

Application:	Varied cogeneration
Primary contact:	Bill Patterson, Owner
	801-731-8020

International Cogeneration Development of Utah is building a \$5 million tire recycling plant 15 miles west of Ogden, Utah. Mechanical grinders will reduce tires to fine rubber crumb that can be used to make varied rubber products such as tennis shoes, slip-proof mats, equestrian surfaces to save horses from shin splints, playground material, or fuel supplements. The new plant was scheduled to start up in December 1995.

Initially, ICD is expecting to be paid \$65 to \$70/ton by the State of Utah to recycle scrap tires. However, because there are only an estimated 1.25 million used tires discarded per year in Utah, a bidding war could erupt between ICD and Holnam Cement, which would lower the price. Currently, ICD would charge \$52/ton to take the residue. The material could be delivered as-is out of the reclamation facility, without any additional processing. ICD has been provided with a sample of residue and is evaluating it for reuse in some of the applications mentioned above. The

price charged for the residue could be reduced if its performance was deemed exceptional.

### Davis County Solid Waste Management and Energy Recovery Special Service District (SWMERSSD)

Application:	Steam boilers with incinerator
Primary contact:	James Taylor, Plant Engineer/Supervisor
	650 East Highway 193, Layton, UT
	801-771-5661, Extension 26

This Davis County facility has two water-walled boilers with incinerators. Each furnace is  $10 \times 10 \times 10$  ft, uses a grate system, and is fueled solely with garbage. Operating temperatures are between 1,800 and 2,000 °F. Power generated from the facility is sold to Utah Power and to Hill Air Force Base. Businesses pay \$62/ton to dispose of their garbage. The Army would have to pay the same rate for the residue. The residue could be delivered as-is out of the reclamation facility, without any additional processing.

#### Geneva Steel

Application:	Blast furnace
Primary contact:	Les Jones, Project Engineer
	801-227-9273

Geneva Steel, located south of Salt Lake City, uses a blast furnace to produce pig iron from coke- and iron-bearing materials. Furnace operating temperatures are between 3,500 and 4,000 °F. The pig iron is oxidized to steel in a later process. Approximately 900 lb of coke is used per ton of hot metal produced, for a total consumption rate of 1 million lb of coke annually.

Coke is supplied via a fully automated in-line system, and particles must pass through a 200-mesh screen. The coke must have a compressive strength of at least 400 psi. Moisture levels of 1.5 percent are nominal. Composition of the coke is critical, as it affects the properties of the steel product.

Because the system is not set up to accommodate fuel supplements, and because of the possible effect of a supplement on the product, Geneva Steel is not interested in using the binder residue.

### Great Salt Lake (GSL) Minerals and Chemicals

Application:	Chemical drier
Primary contact:	Dr. Corey Milne
	801-731-3100, Extension 312

GSL Minerals and Chemicals uses a natural gas-fired rotary kiln to dry salt and potash. They are not equipped to use solid fuels and so were not interested in using the binder residue.

### U.S. Steel, Gary Works Plant

Application:	Blast furnace
Primary contact:	Ted Whitesill
	Energy and Environmental Division
	219-888-4992

U.S. Steel uses a process similar to that used by Geneva Steel. The Gary Works plant consumes coke at approximately 75,000 ton/mo. Like Geneva, they also have a fully automated in-line system, with no capability for injecting alternate fuels. Because of the relatively low volume of residue available for reuse, they were not interested in pursuing its integration at their facility.

### U.S. Steel, Claireton Plant

Application:	Coke oven
Primary contact:	Bill Keck, Process Technical Research
	412-825-2099

The U.S. Steel Claireton plant produces coke in ovens operated at 2,200 °F. The feed is derived from coal. The coke product is used in their blast furnace.

To evaluate using scrap tires as a fuel supplement, subscale tests were conducted using 1 and 5 percent tire additive. Results showed a significant reduction in coke strength, so U.S. Steel did not pursue the tire reuse program, despite government incentives to pay for their reuse. Neither were they interested in using binder residue.

### Subscale Processing Studies

Several subscale processing studies were completed to determine the most efficient process for configuring the residue as required for reuse. The studies involved size reduction, dewatering, and coating to prevent reagglomeration. Table 5 is a summary of the results. Appendix A documents the testing. Figures 9 and 10 are photographs of dried, extruded, coated residue.

### **Cost Estimates for Processing Dried Residue**

Based on the user evaluation for the applications considered feasible, two processes have been designed to achieve the appropriate residue configurations required for reuse. Process schematics are shown in Figures 11 and 12. Cost estimates for producing residue via these processes have been completed. To make the cost estimates, a number of gross assumptions were made relating to the predicted production rate, facilities, estimation of labor, utilities, and overhead costs.

#### Assumptions

These cost estimates were produced by evaluating the subscale processing studies, projecting a production method, and determining the quantity and cost of needed raw materials, utilities, and overhead costs of the proposed manufacturing process. The engineering estimations originated in guidelines presented in Peters and Timmerhaus (1980). The following assumptions were made and are important considerations for the overall validity of the cost estimate:

- The process rate is 400,000/lb of residue per year for 4 yr.
- An existing, fully depreciated, operational facility is available for production.
- No additional expense incurred due to loss or failure of equipment, facilities, or product.
- Most estimations were made at the low end of the projected range due to the simplicity and nonhazardous nature of the process.

### Table 5. Process study summary.

Process	Results	Conclusions	Comments
Oven-dried 3-india pieces 60 hr at 135 °F.	20% wt loss	Too slow and cumbersome	Need more surface area for efficient dewatering.
Microwave dried pieces from previous step.	15% wt loss in 5 min	Good method	
Ground "coarse" through a meat grinder; 8 ea 0.50-in dia die holes, short auger barrel. Oven-dried ground material.	Easily done manually if feed is spare. Run by drill. Some limits: don't overload feed. Air-dried 2 hr = $7.8\%$ H <sub>2</sub> O Oven-dried 3 dy at 135 °F = $0.14\%$ H <sub>2</sub> O Oven-dried 3 dy at 200 °F = $0.10\%$ H <sub>2</sub> O	Dewatered well. Ground material was extruded and chopped to size.	Is sticky and will reagglomerate.
Ground "fine" through a meat grinder; 72 ea 0.14-india die holes, short auger barrel.	Very difficult manually.	Dewater well.	Agglomerated as above.
Ground "coarse" and microwaved.	Material heats and loses weight.	Good method.	Looking for source of commercial microwaves. Used by Kirkhill Rubber Co. to cure rubber on conveyor belts.
Extruded pieces thru a 0.5- india die head.	Developed 1500 psi pressure. Extruded an irregular tube that expands to ~ 2 in. OD on leaving die.	Dewater well; i.e., extrusion was very wet as material exited the die.	Slow. Extruded material would need to be chopped.
Coarse ground into sawdust; hand-tumbled, screened, oven-dried for 2 dy at either 135 or 200 °F.	Processing was easy and worked good. Oven-dried 2 dy at 135 $^{\circ}F = 0.39\% H_2O$ Oven-dried 2 dy at 135 $^{\circ}F = 0.39\% H_2O$ Oven-dried 2 dy at 200 $^{\circ}F = 0.33\% H_2O$ Oven-dried 2 dy at 200 $^{\circ}F = 0.33\% H_2O$	Good method. Does not reagglomerate.	
Coarse ground into carbon.	Processing was easy and worked well.	Good method. Does not reagglomerate.	Carbon has a higher Btu value than sawdust, but is messier to handle.
Milled 2 hr then oven-dried for 3 dy at either 135 or 200 °F.	Milling was slow. Material stuck to rolls and rusted them. Air-dried 10 dy = $0.2\%$ H <sub>2</sub> O Oven-dried 3 dy at 135 °F = $0.07\%$ H <sub>2</sub> O Oven-dried 3 dy at 200 °F = $0.19\%$ H <sub>2</sub> O	Not a good method.	
Ground using Wiley mill, ambient temperature.	Residue smears instead of grinds.	Does not work.	-
Ground using Wiley mill, residue chilled with LN <sub>2</sub> .	Residue smears instead of grinds.	Does not work.	
Ground using pin mill, ambient temperature.	Residue smears instead of grinds.	Does not work.	
Cryogenic grind (-198 °C) using pin mill.	Works great (< 100-µ particles produced), but reagglomerates.	Does not work by itself.	
Cryogenic grind with carbon. Test 10% carbon/90% residue, and 50% carbon/ 50% residue.	Works great (< 100-µ particles). 10% carbon slightly reagglomerates; 50% carbon free-flowing.	Good method.	Small particles should dry readily.



Figure 9. Propellant binder residue, extruded, carbon-coated, dried.



Figure 10. Propellant binder residue, extruded, sawdust-coated, dried.


Figure 11. Process to manufacture dried residue.



Figure 12. Process to manufacture free-flowing dried residue.

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## Capital Costs

Method 1:	Purchased Equipment	<u>Price (\$K)</u>
	Single screw extruder	60
	Die and cutterhead	30
	Hot air belt dryer	80
	Conveyor system	<u>30</u>
	Purchased Equipment	\$200
	Installation (25% of purchased equipment)	50
	Instrumentation and controls (8% of PE)	16
	Engineering (10% of PE)	20
	Contingency (7.5% of PE)	<u>15</u>
	Fixed Capital	\$301
	Working capital (10% of fixed capital)	<u>   30.1</u>
	Total Capital Investment	\$331.1
	Amortized Cost (4 yr total product 1.6M lb)	<b>\$0.207/</b> lb
Method 2:	Purchased Equipment	Price (\$K)
	Single screw extruder	60
	Die and cutterhead	30
	Hot air belt dryer	80
	Conveyor system	30
	V-shell blender	10
	Carbon feeder	<u>5</u>
	Purchased Equipment	\$215
	Installation (25% of purchased equipment)	53.8
	Instrumentation and controls (8% of PE)	17.2
	Engineering (10% of PE)	21.5
	Contingency (7.5% of PE)	<u>16.1</u>
	Fixed Capital	\$323.6
	Working capital (10% of fixed capital)	32.4
	Total Capital Investment	\$356.0
	Amortized Cost (4 yr total product 1.6M lb)	\$0.223/lb

The following assumptions were made for capital costs:

- Facilities with all required utilities are available.
- Service and maintenance to meet requirements are available.
- Equipment prices are based on current prices obtained from used chemical equipment dealers.

#### **Direct Labor Costs**

The cost estimate for direct labor was done by evaluating the projected manufacturing process and determining the number of steps in the process. After determining the total number of steps, an equation by H.E. Wessel (Perry 1984) for estimating the operating labor for chemical processes was used to project the labor requirements per-day-per-processing step:

$$\log_{10} Y = 0.783 \log_{10} X + 1.252 + B \tag{1}$$

where: Y = operating labor per day per process step X = plant capacity (ton/day) B = 0.132 for multiple small steps

Using a production rate of 1 ton product/day, 400,000 lb/yr, 52 wk/yr, 4 days/wk = 1,923 lb/day.

$$log_{10} Y = 0.783 log_{10}(1) + 1.252 + 0.132$$
  
Y = 24.2 hr/day-process step

The unburdened labor rate used for estimation of labor cost was \$19/hr.

Method 1: Process steps = 3 Extrude Dry Package

3 process steps  $\times \frac{24.2 \text{ hr}}{\text{step} \cdot \text{day}} \times \frac{\$19}{\text{hr}} \times \frac{\text{day}}{2000 \text{ lb}} = \$0.690/\text{lb}$ 

Method 2: Process steps = 4 Extrude Blend with carbon Dry Package

4 process steps  $\times \frac{24.2 \text{ hr}}{\text{step} \cdot \text{day}} \times \frac{\$19}{\text{hr}} \times \frac{\text{day}}{2000 \text{ lb}} = \$0.920/\text{lb}$ 

#### Indirect Labor

The indirect labor costs include: payroll overhead, control laboratory, supervision, plant security, office expenditures, etc. A general rule of thumb for estimating labor costs is 125 percent of the direct labor costs. However, because this operation was of a relatively small scale, 50 percent of the direct labor cost was used for this estimation.

Method 1: Indirect Labor = 50% of \$0.690/lb = \$0.345/lb

Method 2: Indirect Labor = 50% of \$0.920/lb = \$0.460/lb

#### **Raw Materials**

No raw materials will be required for Method 1. A small amount of coal dust, carbon, or sawdust will be required for Method 2. Coal dust could be provided by PacifiCorp at no cost (other than transportation). Sawdust is generated as a waste at Thiokol and so could also be provided at no cost. Any cost incurred in transporting the coating materials to the processing location would likely be minimal; therefore, no material costs are included in this estimate.

#### Maintenance

Maintenance and repair expenses are necessary to keep process plants in efficient operating condition. These expenses include the cost of labor, materials, and supervision. For simple chemical processes, maintenance costs can be estimated at between 2 to 6 percent of the fixed capital investment (on an annual basis). Because both processes being considered are very simple and are part of a larger reclamation process, 2 percent of the fixed capital cost was used for this estimate. Method 1 Maintenance Cost = 2% of \$301K/yr for 400K lb/yr = \$0.015/lb

Method 2 Maintenance Cost = 2% of \$323.6K/yr for 400K lb/yr = \$0.016/lb

#### **General Costs**

General costs include administrative costs, transportation, legal fees, etc. General costs were estimated at an approximate level of 10 percent of the product cost. The product cost includes direct labor, indirect labor, raw materials, maintenance, and utilities. The product cost for Method 1 is \$1.050/lb less utilities, and for Method 2 is \$1.396/lb less utilities. So, a general cost of \$0.105/lb was used for Method 1, and a cost of \$0.140/lb was used for Method 2.

#### Utilities

For a very rough estimate, utility costs can be calculated at 10 to 20 percent of the product cost. Because neither method is energy-intensive, utility costs were estimated as 10 percent of the product cost.

Method 1 Utility Cost = 10% of \$1.050/lb = \$0.105/lb

Method 2 Utility Cost = 10% of \$1.396/lb = \$0.140/lb

#### Fixed Charges

Fixed charges include: local and state property taxes, insurance, and additional plant overhead costs like medical services and food services. These costs are normally estimated in the range of 10 to 20 percent of the product cost. It was felt that minimal costs would be incurred due to the nonhazardous nature of the processes and small production rate. Therefore, an estimation of 10 percent of the product cost was used for both methods.

Method 1 Fixed Charges = 10% of \$1.050/lb = \$0.105/lb

Method 2 Fixed Charges = 10% of \$1.396/lb = \$0.140/lb

#### Gross Earnings

Gross earnings include both profit and income taxes. General estimation procedures use a range of 10 to 15 percent of the product cost. A 10 percent estimate was used for both methods.

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Method 1 Gross Earning Cost = 10% of \$1.050/lb = \$0.105/lb

Method 2 Gross Earning Cost = 10% of \$1.396/lob = \$0.140/lb

#### **Total Costs**

All the listed charges, expenditures, and associated (estimated) process costs are summarized in Table 6. It should be stressed that the listed costs are estimates only.

Although the estimates are relatively high, \$1.68/lb and \$2.18/lb, they appear to be reasonable, based on the assumptions and traditional engineering cost estimating techniques.

Because the cost to process the residue outweighs its market value (expenses outweigh revenues), a tax write-off of approximately 38 percent would be available. The write-off is included in the total cost for each process, and the resultant figures are shown in Table 7. Although alternative energy tax credits were researched, none were identified that could be applied here.

#### Comparison of Current and Proposed Manufacturing Cost Estimates

Another meaningful approach to evaluate the costs was accomplished by examining the difference in price between the current manufacturing process (dewatering/ packaging/landfilling) and manu-

facturing reusable material. The estimated costs and the rationale for each cost are described below. Figure 13 shows a process schematic for the baseline (current) method.

#### Capital Costs

Both proposed methods would require the capital expenditures listed in Table 6. The baseline process is currently in operation at Thiokol and would not require any expenditures.

	Price (\$/Lb)		
Cost	Method 1	Method 2	
Capital	\$0.207	\$0.223	
Direct labor	0.690	0.920	
Indirect labor	0.345	0.460	
Raw materials			
Maintenance	0.015	0.016	
General	0.105	0.140	
Utilities	0.105	0.140	
Fixed charges	0.105	0.140	
Gross earnings	0.105	0.140	
Total Cost per Pound Residue	\$1.68/lb	\$2.18/lb	

Tahle 6	Costs	ner	nound to	o process	residue.
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#### Table 7. Total costs to process residue.

	Method 1	Method 2
Total cost per pound residue	\$1.68/lb	\$2.18/lb
Total processing cost (400,000 lb/yr over 4 yr)	\$2,688,000	\$3,488,000
38% tax write-off	-\$1,021,440	-\$1,325,440
Net cost	\$1,666,560	\$2,162,560



Figure 13. Current process to manufacture damp residue.

Baseline Method:	Total capital investment Amortized cost (4-yr total product 1.6M lb)	\$0 \$0/lb
Method 1:	Total capital investment Amortized cost (4-yr total product 1.6M lb)	\$331.1K 0.207 lb
	$\Delta$ Cost to Baseline	0.207 lb
Method 2:	Total capital investment Amortized cost (4-yr total product 1.6M lb)	\$356.0K \$0.223/lb
	$\Delta$ Cost to Baseline	\$0.223/lb

#### **Direct Labor**

Baseline	Process steps
Method:	Centrifuge
	Package in drums

Method 1: Process steps Centrifuge Extrude Dry Package in bulk

 $\Delta$  Steps = 1.75 (bulk packaging requires less labor)

1.75  $\Delta$  process steps  $\times \frac{24.2 \text{ hr}}{\text{step} \cdot \text{day}} \times \frac{\$19}{\text{hr}} \times \frac{\text{day}}{2000 \text{ lb}} = \$0.402/\text{lb}$ 

Method 2: Process steps Centrifuge Extrude Blend with carbon Dry Package in bulk

 $\Delta$  Steps = 2.75 (bulk packaging requires less labor)

 $\frac{2.75 \ \Delta \text{ process}}{\text{steps}} \times \frac{24.2 \text{ hr}}{\text{step} \cdot \text{day}} \times \frac{\$19}{\text{hr}} \times \frac{\text{day}}{2000 \text{ lb}} = \$0.632/\text{lb}$ 

Indirect Labor

No  $\Delta$ .

#### **Raw Materials**

**No** Δ.

#### Maintenance

Baseline equipment: Centrifuge

Method 1 equipment:	Centrifuge Extruder Oven
	Method 1 uses more complex equipment than the existing process. Therefore, only a 30 percent reduction in maintenance cost is used to estimate the difference between the two processes.
	Δ Cost to Baseline = 70% of Method 1 estimate = \$0.011/lb
Method 2 equipment:	Centrifuge Extruder V-shell blender Oven
	Method 2 uses more complex equipment than the existing process. Therefore, only a 20 percent reduction in maintenance cost is used to estimate the difference between the two processes.
	Δ Cost to Baseline = 80% of Method 2 estimate = \$0.013/lb

#### **General Costs**

For general costs, the differences between the current method and those that would enable reuse are (1) the residue would require transporting off-plant for reuse and (2) the residue would not be landfilled if it were reused.

The cost for transporting bulk materials is estimated to be 0.05/ton/mile. The material is not expected to be transported more than 60 mi, thus the transportation cost for Methods 1 and 2 is:

Methods 1 and 2  $\Delta$  Cost to Baseline =  $\frac{\$0.05}{\text{ton/mi}} \times \frac{\text{ton}}{2000\text{lb}} \times 60 \text{ mi} = \$0.0015/\text{lb}$ 

The cost of landfilling the material was estimated to be \$0.086/lb (Appendix B) and includes purchasing drums, digging trenches, and loading and covering the trenches. The cost does not include long-term management of the landfill or lost real estate opportunity.

Methods 1 and 2  $\Delta$  Cost to Baseline = \$0.0015/lb - \$0.086/lb = -\$0.085/lb

#### Utilities

Because the proposed processes would be added to an existing process, no new expense for building light or heat would be realized. Both methods, however, would use more energy than the existing process. Thus, to determine the difference in utility cost between the proposed processes and the baseline, 70 percent of the cost calculated for each method is used.

Method 1  $\Delta$  Cost to Baseline = 70% of Method 1 estimate = \$0.074

Method 2  $\Delta$  Cost to baseline = 70% of Method 2 estimate = \$0.098

#### **Fixed Charges**

No  $\Delta$ .

#### Gross Earnings

No  $\Delta$ .

#### **Total Costs**

The cost difference between the current manufacturing process and manufacturing reusable material is shown in Table 8. It should be stressed that the listed costs are estimates only. Applying a 38 percent tax write-off, the total cost (above the current method) to process the residue into a useable form is shown in Table 9.

Table 8.	Difference in cost between current
process	and manufacturing reusable residue.

	∆ Price \$/Lb		
Cost	Method 1	Method 2	
Capital	\$0.207	\$0.223	
Direct labor	0.402	0.632	
Indirect labor			
Raw materials	: 		
Maintenance	0.011	0.013	
General	-0.085	-0.085	
Utilities	0.074	0.098	
Fixed charges		_	
Gross earnings			
Total ∆/lb residue	\$0.609	\$0.881	

Table 9.	Total costs to	process residue above current method.

	Method 1	Method 2
Total cost per pound residue	\$0.609	\$0.881
Total processing cost (400,000 lb/yr over 4 yr)	\$974,400	\$1,409,600
38% tax write-off	-\$370,270	-\$535,648
Net cost	\$604,130	\$873,950

# **5** Propellant Accumulation and AP Extraction

Approximately 300 lb of residue were required to perform the pilot-scale combustion evaluations. Thus, approximately 650 lb of scrap Maverick propellant and 2,000 lb of scrap HARM propellant were obtained. Initially, AP was extracted from approximately 80 lb of the HARM propellant using a comminutor (a Comitrol comminutor was being evaluated to replace the macerator in a close-looped reclamation process). However, the test extraction was not successful at removing AP; approximately 50 percent AP remained in the extracted residue. Additional test runs were completed using different extraction parameters (process time, water volume) in an attempt to improve AP removal. Table 10 shows the AP levels remaining in the binder residue for each run.

Approximately 650 lb of Maverick propellant and 2,000 lb of HARM propellant were processed through the comminutor using the parameters from Run 3. Table 11 lists the results of analyses from two samples of Maverick propellant residue and three samples of HARM propellant residue. Each sample was tested in triplicate, and the standard deviations are shown in parentheses.

The values obtained for both the AP and moisture were higher than expected and so were retested. Table 12 shows the retest values, which confirm that a substantial amount of AP remains in the residue. Each sample was tested in triplicate, and the standard deviations are shown in parentheses.

Although it is not understood why the comminutor was unsuccessful at removing AP from the reduced smoke propellants, the higher levels of AP remaining in the

Table 10.	Comminutor	test	runs.

Run	% AP (of dried wt)
1	49.1
2	10.9
3	3.14

residue are not representative of what has been produced in Thiokol's AP reclamation facility. To obtain material representative of reclamation facility residue for the pilot-scale combustion evaluations, the residue

Table 1	1.	Comminutor	extraction	results.

Propeilant Type	Sample	% AP (of dried wt)	% <b>H₂</b> O
Maverick	1	31.8 (0,1)	41.9 (3.3)
	2	33.9 (1.8)	72.6 (1.6)
HARM	1	21.2 (2.6)	34.3 (2.1)
	2	24.9 (1.5)	37.8 (1.9)
	3	13.0 (0.6)	50.4 (0.2)

was reprocessed in a pilot-scale reclamation apparatus. Full-scale AP extraction was not possible because the once-processed residue was not in a form that could be fed into the AP reclamation facility. The reprocessing successfully removed the AP. The AP-depleted material was size-reduced to approximately ¼-in.-diameter by ½-in.-long "spaghetti" pieces using a single-screw extruder with a chopper. The pieces were coated with carbon in a V-shell blender and oven dried, producing 151 lb of dried, carbon-coated HARM residue and 137 lb of dried, carbon-coated Maverick residue. Analyses from one sample of each type of propellant residue are shown in Table 13. Each sample was tested in triplicate, and the standard deviations are shown in parentheses.

Table 12. Comminutor extraction retest results.

Propellant Type Sample		% AP (of dried wt)
Maverick	1	31.0 (1.5)
HARM	1	27.6 (0.7) 26.9 (0.7)

Table 13. Processed	l residue ana	lyses summary.
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Propellant Type	% AP (of dried wt)	% H <sub>2</sub> O (wt)
HARM	0.26 (0.03)	0.50 (0.10)
Maverick	1.05 (0.15)	4.32 (0.33)

# 6 Pilot-Scale Demonstration

Pilot-scale rotary kiln tests were conducted on both HARM and Maverick residues by the University of Utah, Department of Chemical and Fuels Engineering. The primary objective was to characterize the emissions of  $NO_x$  and polychlorinated dibenzo- $\rho$ -dioxins (PCDD) and dibenzofurans (PCDF) from the combustion of the residues, and to compare those emissions to those for coal. Other objectives were to test two  $NO_x$  control techniques, to analyze bottom ash, and to measure burn-out times.<sup>\*</sup>

The residues were burned separately in a pilot-scale rotary kiln with a nominal firing rate of 130 kW. The kiln bed contained cement kiln clinker. The kiln fill fraction was approximately 7 percent. Kiln temperatures of roughly 1,600 and 2,000 °F were maintained. The gases exiting the kiln were passed through a 100-kW secondary combustion chamber. The combustion characteristics and emissions of both residues were compared to those of coal. The flue gases were continuously monitored for oxygen (O<sub>2</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), and NO. Two techniques for NO reduction were tested: reburning with natural gas and selective noncatalytic reduction (SNCR) using ammonia.

Because of the presence of low levels of AP in the residues, a Pyrex-lined reactor was manufactured and attached to the exhaust duct of the secondary combustor, and conditions were established to test the potential for the formation of PCDDs and PCDFs.

The results indicate that the high heating values of the residues and their low ash, chlorine, and moisture contents (relative to coal) make them attractive as alternative energy sources for stoker and cement kiln applications. However, the high nitrogen content of the HARM residue, and its tendency to form soot, both suggest that caution is in order when using this residue as a fuel. The sooting tendencies can be fully controlled by continuous and steady feeding of the materials at rates that do not exceed the local availability of oxygen.

A complete report of test results is available from USACERL by calling CECER-UL-T, (217) 398-5590 or 1-800-USA-CERL.

Both reburning and SNCR are effective at reducing emissions of  $NO_x$  while cofiring natural gas and the propellant binder residues in a pilot-scale rotary kiln. SNCR can provide about 50 percent reduction for all the fuel types, at both the high and low kiln temperatures (1,600 and 2,000 °F). Reburning showed reductions of about 60 to 70 percent for these same conditions. One may expect similar reductions in a full-scale system, provided that the full-scale conditions are similar to those tested here.

Sampling and analysis for dioxins and furans indicate that the HARM residue has the potential for exceeding the proposed EPA regulations for cement kilns. Because the reactor was maintained at temperatures that are optimal for the formation of PCDDs and PCDFs (worst-case test), these results can only indicate the potential for the formation of these compounds. The high levels obtained with the HARM residue are believed to be due to its tendency to soot. Given the potential for the formation of PCDD and PCDF with the HARM residue, it is critical that the combustion conditions be such that incomplete combustion is minimized with this fuel. The design of the air pollution control train also becomes critical so that the optimal temperatures for PCDD and PCDF are avoided. These concerns will be fully addressed under "real-world" stoker conditions during full-scale testing.

# 7 Nontraditional Combustion Alternatives

#### Literature Search

A literature search was completed, and numerous references were obtained. Three general topics were searched: propellant residue reuse technology, scrap tire recycling, and asphalt fillers/modifiers. The list was narrowed to the most promising resources, and a synopsis of the relevant information follows, organized in the categories of propellant recycling, tire recycling, processing, asphalt, and miscellaneous.

#### **Propellant Recycling**

Environmentally Enhanced Disposal of Solid Propellants, Sheldon, Li, and Cole, April 1995.

- Review the inventory of Air Force (AF) solid propellants requiring disposal.
- Evaluate physical and chemical properties of propellant and primary fuels.
- Model chemical kinetic and thermodynamic behavior under select cofiring scenarios.
- Predict boiler performance impacts.
- Synthesize results into cofiring recommendations

The AF has about 2 million lb of propellant earmarked for demilitarization over FY95-FY01 (7 yr); most in the short term. Sources are Minuteman, Nike, and Sergeant.

Cofiring gives a disposal means that satisfies  $R^{3^*}$  better than any other option listed for true cost comparison: cost of cofire vs. cost disposal + cost equivalent level of conventional operation total vs. demil rate from all sources:  $31.5 \times 10^6$  kg/yr residue (out of total inventory of  $325 \times 10^6$  kg/yr).

<sup>\*</sup> Resource recycling, reuse, and recovery.

Summary of Demilitarization Benchmark Prices		
Method Process Cost per Short Ton*		
Open burn <sup>1</sup>	\$ 587	
Open detonate <sup>1</sup>	827	
Washout/steamout <sup>1</sup>	1054	
Meltout <sup>1</sup>	701	
Incinerate <sup>1</sup> 1710		
Cofiring residue <sup>2</sup> 2146		
*Does not include offset from sale of recovered material. AP revenue estimated at \$304/ton amortized over 20 years.		
<sup>1</sup> AAIS Database; data as of 1 October 1993		
<sup>2</sup> Shah, D., "Analysis of Propellants, Explosives and Pyrotechnics: Co- combustion in Fossil Fuel and Biomass Boilers as a Means of Resource Recovery and Recycle," Sandia National Laboratories		

- Ash deformation impacts are estimated (fouling—solid, slagging—molten) baseto-acid ratio  $R_{B/A}$  is the critical parameter driving slag.
- NASA thermochemical program to predict ∆ in flame T and NO generated. For binder with 2.5 percent AP, 0 to 20 percent total heat input (coal = primary), 1.166 O<sub>2</sub> stoichiometric ratio, maximum change in flame T < 40 °K, which is not a serious change at furnace T's equilibrium. NO changes by about 7 percent over range of cofiring conditions.</li>

Reapplication of Energetic Materials as Fuels, Baxter et al., April 1995.

- Address combustion-related aspects of using aluminized residue as fuel in boiler.
- Two obstacles: NO<sub>x</sub> generation and the behavior of metals.
- Estimate 3 million kg (U.S. Department of Energy (DOE) material) requiring disposal + 50,000 kg/yr (about 7 million pound + 110,000 pound per year). 376 million kg (DOD) + 73 million kg/yr (827 million lb + 160 million lb per year).
- Revenues from chemical recovery and power generation approximately equal costs of boiler modification and maintenance of new fuel feedlines.
- Class 1.1 (double-base propellants or primary explosives) are emulsed with water (about 30 percent), kerosene (about 65 percent), and propellant (about 5 percent).
- For redesigned solid rocket motor (RSRM) residue, 3 percent AP 0.4 percent N less likely to form NO, because of its chemical form.
- Aluminum (Al) melts at 660 °C, burns at potentially high temperature (adiabatic flame temperature > 3,000 °C).

- For 1.1 emulsions, NO = 90 percent of total NO<sub>x</sub>.
- RSRM residue particle temperature > 1700 °C, 1 to 20 percent  $O_2$ .
- Al-containing fuels may best be used in entrained-flow facilities, rather than grates due to extreme high combustion temperature.
- Ash generated is benign.
- NO<sub>x</sub> generated will not be a problem if blended with traditional fuels.

Feasibility of Cofiring Waste Solid Rocket Propellants with Coal, Li, Sheldon, and Cole, (need date for final).

- Estimated 327,000 metric tons (654 million lb) of energetic materials currently stockpiled by the National Aeronautics and Space Administration, DOE, and U.S. military are awaiting destruction.
- Resource recycling, reuse, and recovery is considered the ultimate demilitarization strategy.
- Looked at two types of propellants, nitroguanidine/nitrocellulose (NG/NC) and composite AP, in rubber binder.
- Used different models to predict the thermal performance impacts caused by cofiring solid propellants with conventional fossil fuels in an existing boiler.
- High metal content impacting furnace wall deposits is a critical issue (slagging).
- Residue evaluated 10, 2.5 percent AP, 40 percent  $H_2O$ .
- Aluminum oxide  $(Al_2O_3)$  has greater thermal resistance than coal ash.
- Ash loading is about 125 percent of baseline at 20 percent heat input from residue.
- Slight decrease in boiler efficiency due to 40 percent moisture in residue.
- For this specific boiler, the furnace exit gas temperature indicates that the cofiring upper limit for residue with 10 percent and 25 percent AP is 5 to 10 percent to avoid tube overheating. This limit is the most stringent technical impact from the standpoint of equipment lifetime.
- Maximum cofiring rate for residue in coal-fired boilers demands on:
  - maximum ash loading capacity for the ash collecting device
  - allowable increase of furnace exit gas temperature to avoid tube damage
  - maximum operating capacity of attemperators
  - maximum tolerable impact on boiler efficiency.

## Energy Recovery from Waste Explosives and Propellants Through Cofiring, Myler and Mahanna, October 1990.

The concept of economically using the energy content of energetic materials is being developed with the expectation of safely burning energetics mixed with fuel oil. Solvents will be used to bring the explosives TNT and RDX into solution. This approach does not seem feasible for propellants at this time, but pure propellant slurries may be able to be economically burned. Comparisons of this technology with incineration and OB/OD were made. Supplemented fuels depend on costs of the raw materials being used and may compete economically with OB/OD. A testing program is underway to obtain the necessary data to implement this technology.

## Use of Waste Energetic Materials as a Fuel Supplement in Utility Boilers, Myler, Bradshaw, and Cosmos, (need date for final).

Waste energetic material produced during the manufacture of explosives has been considered a by-product waste that must be disposed of. Methods such as open burning or open detonation pose potential environmental risks, while disposal in specially designed hazardous waste incinerators is costly. No current method capitalizes on these materials' inherent energy capacity. Efforts to use these wastes as supplements to fuel oil are underway. Laboratory- and bench-scale operations verify the principle, while economic analysis shows a positive advantage using this approach. Pilot-scale testing is in progress to develop fuel mixing/feeding procedures and to determine fuel mixture energy parameters.

- Study focuses on TNT and RDX.
- RDX = 9 kJ/g.
- TNT = 15 kJ/g.
- High No<sub>x</sub> emission when combusted.
- Pilot testing using a prototype combuster (300 kW) at Los Alamos lab.

Feasibility of Using Propellant-Fuel Oil Slurries as Supplemental Fuels, Norwood et al., September 1993.

The U.S. Army Toxic and Hazardous Materials Agency conducted a program with the Tennessee Valley Authority (TVA) to determine the feasibility of using propellants as supplemental fuels for the U.S. Army's industrial combustors. Disposing of obsolete and waste propellants in this manner could be both cost effective and environmentally sound, and as an added benefit, would use the energy value of these materials. The propellant studied during the 6-month course of the initial project in this program was a nitrocellulose containing 13.15 percent nitrogen by weight. A series of laboratory tests was conducted to evaluate the physical and chemical characteristics, as well as the chemical compatibility of nitrocellulosesolvent-fuel oil solutions. These tests indicated that solvation and mixing with fuel oil were not technically feasible or cost effective due to the low solubility of the nitrocellulose. However, an economic analysis did indicate potential cost effectiveness using propellant-fuel oil slurries as supplemental fuels.

The objective of the second project in the supplemental fuels program was to assess the technical, economic, and safety aspects of using propellant-fuel oil slurries as supplemental fuels. The materials studied during the 5-month course of this project were nitrocellulose, nitroguanidine, and a double-base propellant. A series of laboratory tests were conducted to evaluate the physical and chemical characteristics, as well as the chemical compatibility, of propellant-fuel oil slurries. Wet-grinding of the double-base propellant with fuel oil was required to prepare slurries for testing because the as-received material was in the form of paper-thin shavings. The physical characteristics studied were density, viscosity, settling rates, and particle size distribution. Chemical characteristics were flash and fire points, heat of combustion, and emissions, while differential scanning calorimetry was used to assess the chemical compatibility of the propellant-fuel oil slurries. The results from these laboratory tests, as well as from an economic analysis of the process, are discussed. Based on the cost comparisons, it was concluded that fueling boilers with 10 percent by weight nitrocellulose, nitroguanidine, or AA2 propellant-fuel oil slurries as supplemental fuels is not cost effective.

#### **Tire Recycling**

Tires to Energy: Where the Rubber Meets the Grid, Maize, 1993.

Idea: Energy from old tires.

The idea is both technically and economically feasible. Discusses several plants that have used tires for fuel. The most recent plant is operated by the TVA in Memphis. Uses 4 percent shredded tires with coal.

Developments to Watch, Using Waste Tires as Fuel, Makansi, April 1987.

Idea: Recovering energy from old tires.

Heat content will be between 12,000 and 15,000 Btu/lb. Two approaches for plants are being explored:

- Using whole tires.
- Using shredded tires and converting them into liquid and gaseous fuels.

A new plant in California is modeled after a German plant that has been in operation for 14 years. The key to the technology is a reciprocating stoker grate that (1) accepts tires as large as 6 ft in diameter, (2) has an air-distribution system that does not become plugged by sticky substances resulting from tire combustion, and (3) has an alloy composition that prevents slag from adhering to grate surfaces.

Agony and Ecstasy of Tire Recycling, Logsdon, July 1990.

Idea: Chop and shred tires to reclaim the rubber.

Main markets:

- Tire manufacturers, for use in new tires.
- A company that makes doormats, pick-up truck bed mats, muffler hangers, etc.

The biggest problem seems to be getting equipment that can process more at lower cost and be reliable. Breakdowns of equipment are costly.

Potential uses:

- Landscaping mulch. Preserves moisture better and smothers weeds.
- Bulking agents to speed up composting process.
- Aggregate in septic tank leach beds.
- Highway pavement.

Shredded Rubber Tires as Bulking Agents, Higgins et al., 1980.

Idea: Use chopped up rubber tires instead of wood chips for composting raw sewage sludge in New Jersey.

#### Pros:

- Ninety-nine percent of the bulking agent (shredded rubber tires) can be recovered versus 70 percent when wood chips are used.
- Lower cost.
- Use of old tires.

#### Cons:

- Higher heavy metal content (not a big concern, except for cadmium, which is toxic).
- Significantly lower levels of organic matter and carbon (as expected).

In general, shredded rubber tires have been used successfully as an alternative bulking agent to wood chips. Significant cost savings were realized without adversely affecting the composting process or *significantly* degrading the quality of the finished compost.

"Beyond Burning Tires," Environmental Action, Fall 1994.

Deals with the legislative battle that would mandate use of some rubberized asphalt in Federal highway projects.

#### Scrap Rubber Tire Utilization in Road Dressings, Brand, March 1974.

The objective of this study was to demonstrate the feasibility of using rubber obtained from discarded passenger car tires in water-thinnable emulsions of asphalt or coal tar for blacktop dressings for driveways, parking lots, streets, highways, etc. The use of rubber in this large volume market could result in an increased demand for the used tires and decrease the solid waste disposal problems connected with 200 million discarded tires each year.

The study has resulted in the production of nine different compositions containing from 5 to 25 percent rubber that were promising enough to apply to a high-traffic area in the parking lot (estimated passage of 1800 cars per day) to determine the respective service lives of the compositions.

After exposure for 1 yr under the above conditions, performance appears to have been as good as that of the control samples, and protection of the underlying blacktop is still being rendered by all samples.

Recycled Rubber in Roads, Stephens, April 1981.

Forty-six pavement test sections varying in length from 250 to 1,000 ft and containing reclaimed rubber (pulverized and devulcanized tire rubber) were placed in 1977 and 1978. The performance over a 3-yr period has been compared to similar construction without rubber.

#### Overlays

- For thick overlays, cracks developed slowest in the test sections with 1 percent reclaimed rubber.
- The improvement in performance was greatest in the medium condition pavement under medium to heavy traffic.
- For rubber to be effective in thin overlays, the layer thickness must exceed 1/2 in.

• The optimum rubber content in the thin overlays of adequate thickness was significantly higher than for the thick overlays. Although the optimum level was not established, it is at least 3 percent.

#### Stress Relieving Interlayer

- Reflection cracking was less where an interlayer was present.
- The crack reduction brought about by a stress relieving layer was not additive to that from a rubberized overlay. That is, the performance of a rubber-modified overlay combined with a stress relieving layer was about the same as either alone.

#### Seal Coat

- The rubber-asphalt binder provides a long-lived flexible binder which resists the formation of cracks better than the emulsion-sand seal.
- The placement of a light emulsion-sand seal over the stone chip increased the retention of the stone chips. The sand filled the void space between the stones, locking the stones in place.
- The cost of the stone chip seal is double that of a emulsion-sand seal, but the life is several times greater.

#### Joint Sealing

- The rubber-asphalt mixed in the field adhered to the concrete joint faces better than the control material.
- The field-mixed material remained adhesive longer.
- Narrow cracks need to be routed wider for either the field-mixed material or the control material to penetrate adequately.

#### A Scrap Tire-Fired Boiler, Lewis and Chartrand, May 1976.

Idea: Recover energy from old tires using a cyclonic, rotary hearth, boiler.

- A scrap tire-fired boiler has been in operation for about 1 yr.
- Nominal furnace rating is 3,100 lb of scrap automobile tires per hour, generating 25,000 lb of process steam per hour.
- One tire = 2.5 gal of oil heating value.
- Two hundred million tires disposed of per year, representing a heating equivalent of 500 million gal of oil per year.

Properties of Scrap Tires			
Proximate Analysis	Kaiser (%)	Bureau of Mines (%)	
Moisture	1.02	0.5	
Volatile matter	64.92	62.3	
Fixed carbon	27.51	31.5	
Ash	6.55	5.7	
Heating value, Btu/lb	13,906		
Ultimate Analysis - Moisture, Ash-Free			
Carbon	84.58	88.23	
Hydrogen	7.33	7.53	
Oxygen	6.34	2.65	
Nitrogen	0.13	0.32	
Sulfur 1.62 1.27			
Source: Lewis and Chartrand, 1976. Used with permission of the American Society of Mechanical Engineers.			

M	aterial Balan	ce for the Comb	ustion of 2000	) Lb Scrap Tire	s at 100% Ex	cess Air	
	Carbon (lb)	Hydrogen (lb)	Oxygen (lb)	Nitrogen (Ib)	Sulfur (Ib)	Inerts (Ib)	Total (ib)
INPUT							
Tires							
Moisture		2.3	18.1				20.4
Volatiles	1,563.6	135.4	117.2	2.4	30.0	131.0	1,848.6
Ash							131.0
Subtotal	1,563.6	137.7	135.3	2.4	30.0	131.0	2,000.0
Combustion air			9,874.6	32,780.2			42,654.8
TOTAL	1,563.6	137.7	10,009.9	32,782.6	30.0	131.0	44,654.8
OUTPUT							
Flue gas							
Carbon dioxide	1,479.0		3,944.0				5,423.0
Oxygen			4,937.3				4,937.3
Nitrogen				32,782.6			32,782.6
Sulfur dioxide			27.3		27.3		54.6
Water vapor		137.7	1,101.3				1,239.0
Subtotal	1,479.0	137.7	10,009.9	32,782.6	27.3		44,436.5
Char							
Carbon	84.6						84.6
Sulfur					2.7		2.7
Ash						131.0	131.0
Subtotal	84.6				2.7	131.0	218.3
TOTAL	1,563.6	137.7	10,009.9	32,782.6	30.0	131.0	44,654.8
Source: Lewis and Chartrand, 1976. Used with permission of the American Society of Mechanical Engineers.							

Heat and material balance, air pollution control analyses concluded that the rotary hearth furnace was an excellent design for the combustion of tires.

#### Processing

An Economic Evaluation of Cryogenic-Grinding of Scrap Automotive Tyres, Harrison, Tong, and Hilyard, 1986.

The most significant obstacle to the exploitation of scrap car tyres is the cost of producing recycled rubber in relation to the sales value of the end product. This cost has led to several firms leaving or significantly reducing their investment in the rubber recycling industry because of poor or negative returns on investment. The cryogenic-grinding (C-G) processes for the recycling of scrap rubber tyres hold out the promise of better prospects for the industry because (1) the ability to produce large quantities of rubber crumb of less than 40 mesh, while at the same time (2) not creating undue heat degradation of the rubber particles.

Although two C-G plants have been built and operated in the United Kingdom, no independent commercial plant is currently operating. The reasons for the cessation of production are both technical and economic. On the technical side, it is proving significantly difficult to reduce the liquid nitrogen requirement, but the work of Vil'nits et al. indicates that optimization of mill-seed and scrap temperature might be possible in the production of cryo-grind. On the economic side, overcapacity in the synthetic rubber manufacturing sector has led to low prices so that the incorporation of recycled rubber is of little economic significance in new product manufacture.

Development of Equipment for Pulverizing Used Polymer Materials, Gordienko, Morozenko, and Provolotskii, 1984.

Methods and equipment for abrasive pulverization of corded-rubber articles (automobile tires) based on pulsed interaction between prestressed volumes of materials and the abrasive grains of a high-speed grinding wheel have been developed:

Productivity, kg/h	300
Electric power consumption, kWh <sup>-1</sup> /kg of crumb	1
Area occupied , m <sup>2</sup>	80
Residual moisture of crumb, %	1-2
Dispersity of crumb, µm	10-150

#### Asphalt

Filler in Asphalt Mixtures, Puzinauskas, April 1983.

"The mineral filler shall consist of limestone dust, portland cement, or other suitable (inert) mineral matter. It shall be thoroughly dry and free of lumps consisting of aggregates of finer particles."

Usual required: all < 600 μ (No. 30 sieve) 65% < 75μ (No. 200)

Fillers change the properties of paving mixtures.

Asphalt pavement =	mineral aggregate particles +	asphalt film +	air voids
Dense grade, volume %	79%	17%	4%
Sand asphalt =	72%	24%	4%

- viscosity († better)
- ductility
- penetration.

#### Design of Hot Asphalt Mixtures, The Asphalt Institute, July 1979.

A hot asphalt mixture is defined as a combination of mineral aggregates uniformly mixed and coated with asphalt cement of a selected penetration or viscosity grade. The aggregate and asphalt cement are heated before mixing to dry the aggregate and obtain sufficient fluidity of the asphalt cement. The heating, proportioning, and mixing to produce the desired paving mixture are accomplished in a mixing plant.

Two primary properties are desirable in a hot asphalt mix—stability and durability. Nearly all the effort in the mix-design process will be toward getting as stable and durable a pavement as is possible with the materials used. Two important factors in the mix-design process are economy and workability. The most economical aggregate available that will meet all property requirements should be used.

# The Chemical and Physical Properties of Asphalt Rubber Mixtures, Part 1. Basic Material Behavior, U.S. Dept. of Commerce, March 1977.

The properties of asphalt-rubber mixtures composed of paving-grade asphalt and ground automobile tire rubber are examined. The mechanism of swelling of the rubber in asphalt and asphalt-like materials is proposed, and the effect of variables that affect the swelling is discussed. Experiments determining the swelling of tire rubber in selected oils are related to the swelling of tire rubber in asphalt. Several test methods are presented that measure the properties of the asphalt-rubber mixture. Data concerning the properties of a commercially available asphalt-rubber mixture and the effects of processing variables on these properties are presented. Techniques useful for the quality control of this material as well as suggestions for research into the theoretical aspects of the unique characteristics of this material are discussed.

#### Miscellaneous

Alkali, Chlorine, SO<sub>x</sub>, and NO<sub>x</sub> Release During Combustion of Pyrolysis Oils and Chars, Dayton and Milne, September 1994.

Hot gases liberated during the combustion of small pyrolysis oil and char samples in a variable temperature quartz tube reactor were directly sampled with a molecular beam mass spectrometer (MBMS) system, constructed and operated at the National Renewable Energy Laboratory (NREL). Four of the pyrolysis oils screened in this study (two switchgrass oils, an oak oil, and a poplar oil) were produced in the NREL vortex reactor. The other three oils screened (a switchgrass oil, a poplar oil, and a corn stover oil) were produced in a laboratory-scale (2-in.-diameter) fluidized bed combustor. The biomass chars were recovered from the hot filters on the NREL vortex reactor during pyrolysis oil production. Alkali metal is sequestered in the char fines during the production of biomass-derived pyrolysis oils, which suggests that efficient filtering should yield a lower alkali metal-containing pyrolysis oil. This result is desirable if pyrolysis oils are to become a competitive fuel for use in turbine combustors to generate feedstock material. High nitrogen-, sulfur-, and chlorine-containing biomass feedstocks yield pyrolysis oils with correspondingly high levels of nitrogen, sulfur, and chlorine. Release of NO<sub>x</sub> and SO<sub>x</sub> has important environmental implications, and releasing chlorines can lead to increased corrosion in combustion facilities.

## The Reuse of Petroleum and Petrochemical Waste in Cement Kilns, Gossman, February 1992.

The high temperatures and long residence times in the combustion zones of cement kilns have been used for over 10 years to burn flammable liquid hazardous wastes (e.g., solvents) as fuels. Increasing government regulation and control of this technology has actually resulted in expanded use as both waste generators and cement manufacturers have grown more comfortable and confident with this technology. Liquid petroleum and petrochemical wastes have been a part of this liquid fuel stream from its inception. Solid and sludgy petroleum and petrochemical wastes present greater handling difficulties. Nevertheless, the land ban of many of these hazardous wastes has resulted in the motivation to develop solid and sludge handling and processing technologies to allow their use as fuel. These processing options extend back to the point of generation. Changes in filter press media and drying technologies are allowing certain petroleum and petrochemical wastes to be pneumatically introduced into cement kilns. Quality control technologies, including laboratories at both cement kilns and the generating/processing location, have also been a critical part of these developments. As this technology matures, as much as 454 million kg of nation-wide capacity for hazardous waste fuel solids is likely to become available.

#### **Industrial Applications**

In addition to the literature survey, contacts were made with Koch Industries and the NREL. A description of each application follows.

#### Koch Industries

Application: Primary contact:	Modifier in asphalt Timothy O'Connell, Technical Manager
	Western Region
	801-292-1434

Koch Industries is one of the largest privately held corporations in the United States. The company is involved in virtually all phases of the oil and gas industry, as well as in chemical, chemical technology products, agriculture, hard minerals, real estate, and financial investment.

Koch owns nearly 100 U.S. asphalt plants, including one in Salt Lake City, UT. Among other products, Koch produces modified asphalts at this plant. Asphalts are modified by adding polymers, etc., to improve their properties (i.e., to increase elasticity over a wide temperature range, which reduces high temperature failure and low temperature fatigue). A typical asphalt binder will contain from 2 to 6 percent modifier. The binder itself is approximately 5 percent of the finished roadway mix. At the state level, Utah uses roughly 40,000 tons of modified asphalt annually, consuming between 80,000 and 240,000 lb of modifiers. Modifiers currently used include virgin polymers (usually supplied in crumb form) and scrap tire material. Cost for the polymers ranges between \$0.60 and \$1.20/lb. Cost for the tire material is less than or equal to \$0.20/lb (more processing is required). Currently, quality modifiers are in high demand because the largest supplier (Shell Oil Company) lost their manufacturing plant last year in an explosion. Koch is interested in evaluating the binder residue for use as a modifier. The material could be supplied in relatively large pieces,  $1 \times 2 \times 8$  ft, which would be reduced to less than 10 microns during the asphalt processing with a Montgomery hog grinder. Because asphalt is processed at 400 °F, moisture is probably not a high concern. Furthermore, Koch is experienced in handling tacky materials, as tackiness is considered an attribute in modifiers.

Preliminary evaluation of the binder residue as an asphalt modifier conducted at Koch Materials Company indicated that the residue showed considerable promise as a viscosity enhancer. Koch requested and received additional dried material for low temperature characterization testing at their St. Paul, MN, laboratories. After further consideration, Koch determined that they were not interested in the material because of its uncertain availability and potential chemical variability.

#### National Renewable Energy Laboratory

Application:	Biofuel
Primary contacts:	Dr. Robert Evans, Manager
	<b>Process Research Branch</b>
	303-384-6284
	Dr. David Dayton
	Senior Thermochemical Scientist
	303-384-6216

The NREL is a Federally funded government laboratory that researches and develops renewable energy systems (solar, wind, biogenerators, etc.). One program researched at NREL is biofuels and biofuel generators. A topic that has recently developed great interest within their area is the use of biofuel combustion gases to directly power turbines. Another area of particular interest is in mixing municipal wastes with biofuels such as grasses and woods as a method of recovering energy from waste products. A potential reuse application of the binder residue would be to blend it into a biomass matrix. Combustion evaluations of HARM binder residue with biomass were completed by NREL. A comprehensive report of the completed work is available from USACERL. A summary of the test results follows.

Because of the tight schedule, initial experiments were performed using HARM residue manufactured during the early effort (6 percent AP, 37 percent  $H_2O$ ). Follow-up testing was performed using the "improved" HARM residue (0.26 percent AP, 0.50 percent water [ $H_2O$ ]) manufactured during the next phase. Although the

results from the initial testing identified several concerns (low fuel value, high chlorine level, potential feed problems), these concerns were alleviated with the follow-up testing using the low AP, low moisture, carbon-coated residue.

The combustion behavior of HARM residue was studied using a unique MBMS system in conjunction with a variable, high-temperature quartz-tube reactor. The major products released during HARM binder combustion were identified at three different combustion conditions: 1,100 °C in helium/oxygen (He/O<sub>2</sub>) (20 percent), 800 °C in He/O<sub>2</sub> (20 percent), and 1,100 °C in He/O<sub>2</sub> (5 percent). These conditions were established to study the effect of varying temperature and oxygen concentrations on HARM binder combustion. Compared to the combustion of more traditional solid fuels like biomass and coal, a char phase was not observed during residue combustion. During the combustion phase, however, the major products observed during residue combustion at 1,100 °C in He/O<sub>2</sub> (20 percent) were H<sub>2</sub>O, CO<sub>2</sub>, CO (N), NO, and HCl. These products were anticipated based on the composition of the residue. Similar products were observed during residue combustion in a reduced oxygen atmosphere. The only difference in the combustion products observed was that less CO and CO<sub>2</sub> were produced at the lower oxygen concentration. Aside from the major products observed during residue combustion at the baseline condition, molecular chlorine was also observed as a combustion product when the furnace temperature was reduced to 800 °C.

Following results with "improved" residue, it was determined that reducing the amount of energetic material (AP) in the binder residue results in a reduction of gas phase chlorine released during combustion. A reduction of energetic material in the binder was not found to significantly affect NO formation.

Reduced energetic material in extracted binder residue means a substantial reduction in gas phase chlorine during combustion, which is a positive result in terms of burning binder material in a boiler. Less HCl vapor will reduce the threat of high and low temperature corrosion in the combustor.

# 8 Industrial Implementation Study

Only five known reduced smoke propellant motor programs are currently in production:

- AMRAAM
- Sidewinder
- RAM
- HARM
- RS Hellfire.

It has been estimated that from approximately 8.8 million lb of reduced smoke propellant targeted for demilitarization, 1.5 million lb of residue could be available for reuse.

For example, the amount of waste generated during the production of HARM motors at Thiokol (Table 14) was determined from OB/OD disposal records.

It is clear that the contribution of the current production programs to the total amount of reduced smoke propellant targeted for demilitarization is minor. Assuming that demilitarization is accomplished over a 4-yr time frame, a rough estimate of the amount of reduced smoke propellant residue that will be available for reuse is 400,000 lb annually over 4 yr.

Of the reuse applications identified and considered, it is apparent that the cost of processing the residue into a useable state exceeds the fair market value for competing fuels. Based on the processing cost analyses, researchers determined the total costs to implement each feasible application. Estimates are presented in Tables 15 through 19 and are based on a process rate of 400,000 lb of residue per year over 4 yr.

Year	HARM Propellant OB/OD (lb)		
1993	6,358		
1994	16,402		
1995 (January through July)	64,965		

Table 14. Harm propellant disposal at Thiokol.

Ash Grove Cement

#### Application: Cement kiln

Residue form: Dry, carbon-coated, 1/2-in. pieces

#### Table 15. Implementation costs for cement kiln residue processing.

	Total Cost	Total Cost Above Current Method	
Material preparation cost	\$2,162,560	\$873,950	
Additional transportation (100 mi)	4,000	4,000	
Estimated revenue (at \$11/ton)	-8,800	-8,800	
Total Cost for 1.6M lb of residue	\$2,157,760	\$869,150	

Holnam Cement

## Application: Long wet cement kiln Residue form: Dry, carbon-coated, ½-in. pieces

#### Table 16. Implementation costs for long wet cement kiln residue processing.

	Total Cost	Total Cost Above Current Method	
Material preparation cost	\$2,162,560	\$873,950	
Additional transportation (60 mi)	2,400	2,400	
Total cost for 1.6M lb of residue	\$2,164,960	\$876,350	

• Utah State University

## Application: Stoker furnace

Residue form: Dry, carbon-coated, <sup>1</sup>/<sub>2</sub>-in. pieces

#### Table 17. Implementation costs for stoker furnace residue processing.

	Total Cost	Total Cost Above Current Method		
Material preparation cost	\$2,162,560	\$873,950		
Total cost for 1.6M lb of residue	\$2,162,560	\$873,950		

• International Cogeneration Development of Utah

Application: Varied Residue form: Wet blob

Table 18.	Implementation	costs for IDC	of Utah to	process residues.
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	Total Cost	Total Cost Above Current Method	
Tipping fee (\$52/ton includes freight to St. Helens, WA)	\$41,600	\$41,600	
Landfill avoidance savings (\$0.086/lb)		-137,600	
Total cost for 1.6M lb of residue	\$41,600	-\$96,000	

• Davis County Solid Waste Management and Energy Recovery Special Service District (SWMERSSD)

Application: Incinerator with steam boiler Residue form: Wet blob

Table 19. Implementation costs for processing residues with a steam boiler incinerator.

	Total Cost	Total Cost Above Current Method	
Fee (\$62/ton)	\$49,600	\$49,600	
Transportation (50 mi)	2,000	2,000	
Landfill avoidance savings (0.086/lb)		-137,600	
Total cost for 1.6M lb of residue	\$51,600	-\$86,000	

The data indicate that the Ash Grove Cement, Holnam Cement, and Utah State University applications would cost approximately \$870,000 over 4 yr, above what it would cost to landfill the residue, to implement. This cost is relatively small compared with the long-term liability associated with landfilling. Therefore, based on the cost, environmental implications, likelihood of success, ease of integration, proximity, and also local community ties, Utah State University is the reuse application recommended for full-scale evaluation.

The data further indicate that both ICD and Davis County SWMERSSD are less expensive than the combustion applications identified, and also would be slightly cheaper disposal methods than the current system. Neither method requires capital investment, processing labor, or long-term landfill management. Although Davis County is less costly, it is a disposal method rather than a reuse application, and so does not satisfy the "green" goals of this program. ICD, on the other hand, appears to be a feasible reuse application. However, they are a new company, which may indicate that the costs are soft (susceptible to increase), and no experimental research has been done for this application. Therefore, it is recommended that bench- or pilot-scale testing of this application be performed before drawing conclusions regarding production feasibility.

• Cement Kiln Clinker Evaluations

Cement kiln clinker was processed in a subscale rotary kiln fueled with propellant binder residues and coal and natural gas. The solids removed from the bed of the kiln consisted almost entirely of cement kiln clinker. A small amount of ash from the coal and residues coated the clinker. The solids were analyzed for all elements with atomic weights greater than that of fluorine using energy dispersive x-ray spectroscopy (EDAX). The pH of slurried samples was also measured. Chlorine was not detected in any of the samples. The detection limit for chlorine was 0.1 weight percent. The results of the other analyses are summarized in Table 20. The weight percentages for Mg, Al, Si, Ca, and Fe in each row total 100. The first row of data in Table 20 is for the raw clinker, as received from the cement kiln. It was never placed in the rotary kiln. The second row of data is for clinker that was fired in the rotary kiln with natural gas only. The third row of data is for clinker that was fired with natural gas for at least 12 hr and then exposed to cofiring with gas and coal for 15 minutes. The last row of data in Table 20 is for clinker that was used the NOx testing and that was exposed to all of the fuels for extended periods. The data have no apparent trends, and nothing suggests that the residues had a detrimental effect on the clinker because of their compositions, their low ash contents, and their low firing rates.

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Table 10. Calification of the second s							
Fuels	Time (min)	pH of Slurry	Mg (wt %)	AI (wt %)	Si (wt %)	Ca (wt %)	Fe (wt %)
none natural gas gas/coal gas/coal gas/coal gas/coal gas/Maverick gas/Maverick gas/Maverick gas/Maverick gas/Maverick	(min) 0.0 720 15 30 45 60 15 30 45 60 15 30 45 60 15	Slurry 11.6 11.7 12.1 12.0 12.1 12.1 12.0 12.2 12.0 11.7 12.0	(wt %) 2.17 2.62 2.57 2.22 2.70 2.01 2.27 3.02 2.36 2.24 2.32	(wt %) 3.24 4.72 10.72 10.57 6.36 5.20 4.84 5.08 5.12 4.86 3.72	(wt %) 12.62 12.18 12.68 12.58 13.20 12.58 12.79 13.23 13.03 12.80 12.61	(wt %) 78.13 75.50 68.39 69.68 74.13 75.25 75.02 74.47 75.25 74.95 76.23	(wt %) 3.84 4.99 5.64 4.95 3.62 4.97 5.08 4.21 4.25 5.05 5.12
gas/HARM	30	11.9	2.53	4.00	12.57	77.17	3.73
gas/HARM gas/HARM from NOx work	45 60 >720	12.0 12.0 11.8	2.43 2.20 2.01	4.88 4.60 5.73	13.15 12.79 12.89	76.02 75.50 73.25	3.52 4.90 6.12

Table 20. Summary of results from analysis of clinker and ash samples.

# 9 Summary and Conclusions

#### Summary

Additional safety evaluations were performed on both wet and dried HARM, Maverick, and Sidewinder residues to ensure that the materials could be safely integrated into industrial applications. For each residue, the fuel value was determined at various moisture levels.

Specific users were identified that could incorporate binder residue feedstock into their processes. Potential users were contacted to determine residue quantity requirements, energy requirements, physical form of the residue needed, material handling issues, moisture level acceptability, and any other pretreatment requirements. The value of the residue in each application was determined. Subscale processing studies were performed to determine the most efficient method of getting the residue into the configurations required for reuse. The studies involved size reduction, dewatering, and coating to prevent reagglomeration. Based on the user evaluations for the applications considered feasible, processes were designed to get the residue into the appropriate form for reuse.

Once 151 lb of properly configured HARM residue and 137 lb of properly configured Maverick residue were produced, the material was used in pilot-scale combustion evaluations at the University of Utah. The pilot-scale testing analyzed combustion emissions (including dioxins and furans), evaluated  $NO_x$  control techniques, measured burnout times, and determined the effect of binder residue on cement kiln clinker.

A literature and market survey was performed to explore other possible reuse applications (not necessarily combustion).

Information garnered from the program was used to devise an industrial implementation plan. To estimate the amount of residue that would be available, a list of known reduced smoke propellant motor programs currently in production was assembled along with a list of reduced smoke propellant motor systems presently targeted for demilitarization. The total cost to implement each feasible application was determined.

#### Conclusions

- Safety properties of AP-depleted binder residue (≤ 6 percent AP) do not indicate any potential concern regarding using the material as a commercial fuel source.
- When dried, AP-depleted binder residue has the same fuel value as coal.
- High heating values of residues, low ash, chlorine, and moisture contents, relative to coal make an attractive alternative energy source for stoker and cement kiln applications.
- High nitrogen content of HARM residue and a tendency to form soot, suggest caution when using it as fuel. Control can be achieved by using continuous and steady feeding of material at a rate that does not exceed the local availability of oxygen. Reburning and selective noncatalytic reduction are effective at reducing NO<sub>x</sub> emissions.
- It is estimated that approximately 400,000 lb of reduced smoke binder residue will be available per year, for 4 years. This estimate is based on the amount of wastes currently generated by production programs and on the assumption that all motors presently targeted for demilitarization will be decommissioned at a rate commensurate with the AP reclamation facility process capacity.
- Several feasible (low-cost) combustion reuse applications have been identified. The cost to implement is estimated to be approximately \$870,000 total over 4 yr above what it would cost to defer treatment and landfill the residue. This cost is relatively small compared with the long-term liability associated with landfilling.

#### Recommendation

A full-scale evaluation aimed towards using the residue as a fuel supplement in the stoker furnaces at Utah State University is recommended. This recommendation is based on cost, environmental implications, the likelihood of success, ease of integration, and proximity to the reclamation facility.
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# Appendix A: Processing Recycled HARM Binder (Moisture)

SCIENCE AND ENGINEERING

P.O. BOX 707. M/S 242 BRIGHAM CITY, UT 84302-0707



## 13 September 1995 2466-FY95-M025

TO: K. F. Miks

CC: A. G. Christiansen, N. A. Mumford

FROM: C. L. Denton

## SUBJECT: Processing Recycled HARM Binder: Moisture

## BACKGROUND:

We're trying to turn "LUMP" recycled water wet HARM binder into a fuel supplement. The objective to reduce particle size and reduce the trapped water content to about 1%. Both milling and grinding reduce the water content of the "lump" binder. Oven drying at 135 and 200°F also drives off water.

We ran some quick and dirty testing to see what works best. Our starting material was about 49% water. We don't know how representative that is or how uniform it may be.

#### OBJECTIVE:

Develop means of reducing "lump" recycled binder into something like free flowing pellets. One potential customer wants it fine:  $\leq 500$  microns. Determine methods of de-watering and drying this material. Find ways of coating particles so they won't re-agglomerate.

## **RESULTS**:

- 1. The best means of de-watering and reducing particle size that we have found, is to coarse grind it via auger and die.
- 2. Milling was troublesome but successful also.
- 3. Tumbling ground binder in sawdust or carbon works. Sawdust worked best. Excess sawdust was easily screened off.
- 4. Oven drying at 200°F is fairly rapid: 5 hours or less. All oven drying was surprisingly successful.
- 5. Microwaving ground, dust coated particles has real potential. It's fast, more energy efficient and convenient.
- 6. We couldn't find any method of producing a 500 micron particle.

## CONCLUSIONS:

Recycled HARM propellant binder can be converted into a dry non-agglomerating, non-uniform pellet.

## **RECOMMENDATIONS:**

Continue Study

- Determine if multiple grinds reduce water content.
- Determine real dry time at 200°F and possible higher temperature (>212°F).
- Explore microwave drying further.
  - A microwave dedicated to non-food, non-solvent, non-energetic material use will be available in about two weeks.

## 2466-FY96-M025

13 September 1995

- Get some idea of what weight gain is due to surface dusting:
  - Sawdust
  - Carbon

## DISCUSSION:

## Milled Recycle Binder

This was a tedious operation. Large lumps de-watered well at first, but as more and more water left the lump, it warmed and became sticky. Salts rusted the rollers. We didn't bottle a sample right then. It rested open to M-53 Rm 13 ambient atmosphere for about 10 days before a sample was bottled for moisture testing (LWR 727045). Then it tested -0.2%: essentially dry. But, samples of milled material were oven dried at 135°F and 200°F and weight loss was monitored over three days. Material at 135°F had a weight loss of 5.6%. Material at 200°F lost 6.5%. After oven drying 3 days both tested about 01. - 0.2% H<sub>2</sub>O. Remember, these are rough tests and controls for material storage wasn't exact and monitored. Consequently, the feed material (milled) analysis didn't agree with oven dried weight loss.

## Ground Recycle Binder

We coarse-ground some "lump" material through a meat grinder one time. There are eight 0.5" holes in the die the auger feeds. Both ground chopped binder and water exited the grinder. A sample of ground material - air dried a couple of hours tested 7.8% H<sub>2</sub>O. But, once again, ground samples oven dried at 135°F and 200°F, experienced a 32 and a 31% weight loss, respectively, over 3 days. The finally dried materials were 0.1 - 0.2% water. At 200°F 29% weight loss was achieved in 5 hours. Five hours at 135°F produced an 18% weight loss, 24 hours produced a 29% weight loss. Note that this ground material is sticky and re-agglomerates easily.

We also coarse ground material and had mixed it with sawdust to keep the ground particles separated. That worked. At 135°F weight loss was 18% in 5 hours. 24.5% in 24 hours. and 25.5% in 2-1/2 days. At 200°F weight loss was 26% in 5 hours. The sawdust lost 18% of its weight in 5 hours at 200°F. It tested about 3-4%  $H_0O$  afterward.

## Microwaving

As stated previously, we only ran one microwave test for five minutes. It produced a 15% weight loss on a lump of material that was previously oven dried at 135°Ffor 60 hours. The oven dry produced a 20% weight loss. Kirkhill Rubber Company is using microwave units. I'm trying to get more information on the equipment.

## Extrusion

We extruded both lump and coarse ground feed stock through a 0.5" dia. die. As it exited the die it expanded to about 2.0" dia. O.D. and formed a non-uniform tube. Lots of water was released. We didn't have water content analyzed. The resultant material would have to be reprocessed to get small particles for drying as a fuel feed stock. Grinding seemed to be an easier method to accomplish both water reduction and particle size reduction.

C. L. Denton /sm Attachment

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13 September 1995

## LWR 727045 Moisture Analysis Identification and Results

		<u>% H-O</u>
Sample A	Milled - oven dried 3 days at 135°F	0.07
В	Coarse ground - oven dried 3 days at 200°F	0.10
С	Coarse ground - oven dried 3 days at 135°F	0.14
D	Milled - oven dried 3 days at 200°F	0.19
E	Coarse ground into sawdust - oven dried 2 days at 200°F	0.33
F	Coarse ground into sawdust - oven dried 2 days at 135°F	0.39 ·
G	Coarse ground into sawdust - oven dried 2 days at 135°F	0.39
Н	Coarse ground into sawdust - oven dried 2 days at 200°F	0.33
I	Sawdust - oven dried 2 days at 200°F	3.6
J	Milled - exposed to M-53 ambient atmosphere . 10 days afterward	0.2
К	Coarse ground - exposed to M-53 ambient atmosphere 2 hrs afterward	7.8

## Appendix B: Estimated Cost of Burying Residue

## INTEROFFICE MEMO

21 November 1995 3558-FY96-004

TO: K. F. Miks

CC: A. K. Lemon

FROM: G. O. Tooley

SUBJECT: Estimated cost of burying residue, in drums, at the M-336 Landfill.

Assumptions:

- 400,000 lbs./yr of residue is to be disposed of.
- Dewatered residue will weigh 300 lbs./drum.
- 1,350 drums/yr will be required.
- 1,000 drums/yr will have to be purchased others will be reused drums from on plant operations.
- Reconditioned drums cost approx. \$25.00 each.
- Drums would be disposed of in a trench dug specifically for these drums.
- Each drum would require 0.6 cu. yd. of airspace in landfill trench.
- A trench 150 ft. Long by 8 ft. Deep by 20 ft. Wide, would have to be dug each year for the drums.
- A dump truck holding 30 drums/load would be used to dump the drums at the landfill.
- Each load would take approximately 2 hours.
- Dump truck operations would be approximately \$60.00/hr.
- Landfill operations would be approximately \$65.00/hr.

Calculations:

Drums	\$25,000.00
Trench	1,215.00
Hauling	5,400.00
Landfill Ops.	2,925.00
TOTAL	\$34,500.00

Costs would increase if the barrels were stacked in the trench instead of being dumped.

G. O. Tooley

## **Abbreviations and Acronyms**

AP	ammonium perchlorate
DDT	deflagration-to-detonation test
DST	detonation susceptibility test
EDAX	energy dispersive x-ray spectroscopy
OB/OD	open burning/open detonation
MBMS	molecular beam mass spectrometer
NREL	National Renewable Energy Laboratory
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	polychlorinated dibenzofurans
RDX	cyclotrimethylenetrinitramine
RSRM	redesigned solid rocket motor
SBAT	simulated bulk autoignition test
SNCR	selective noncatalytic reduction
TVA	Tennessee Valley Authority
USACERL	U.S. Army Construction Engineering Research Laboratories

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