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Final Report

Solid Propellant Reclamation Study

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November 1982

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TWR-31084

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Prepared for the:

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FOREWORD

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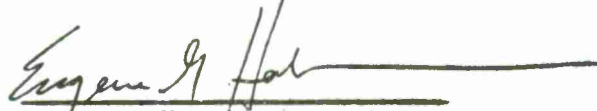


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SUMMARY

Three general methods for the disposal of waste Class 1.1 solid propellants were evaluated as economically and environmentally acceptable alternatives to open pit burning:

- a. Alternate use or application
- b. Ingredient reclamation
- c. Incineration

The alternate use evaluated was conversion of the waste propellant to an explosive booster for use in mining, construction, and other industrial applications. The ingredient reclamation process evaluated recovers the major propellant ingredients, including the nitrate ester, nitramine, and inorganic oxidizer by a selective solvent extraction process. Incineration techniques evaluated included the APE 1236 deactivation furnace, the rotary kiln, and the fluidized bed incinerator. Similar disposal methods for composite Class 1.3 solid propellants were evaluated in a separate contract.* These methods are identified but not evaluated in this report.

Bench scale tests were conducted to provide proof of principle and engineering design and scale up data for the explosive booster and the selective solvent extraction processes. A preliminary pilot plant design was provided. The state of the art incineration technology was assessed from published reports and personal contacts and visits. A preliminary economic analysis of each disposal method was conducted.

It was concluded that:

- a. Alternate use of waste Class 1.1 propellant as an explosive booster is technically feasible and economical on an intermediate production scale. Distribution and marketing is restricted, however, due to the security classification of many Class 1.1 propellant formulations.

*Manufacturing Technology for Solid Propellant Ingredients/Preparation Reclamation (F33615-81-C-5125), Air Force Wright Aeronautical Laboratories.

- b. Reclamation of major ingredients from Class 1.1 solid propellant by a selective solvent extraction process is technically feasible but economical only on a comparatively large production scale. This large scale is probably not compatible with the projected waste propellant quantities of most manufacturers. Economical operation would therefore be restricted to specialized applications such as obsolete motor demilitarization programs.
- c. Incineration of waste Class 1.1 solid propellants has been demonstrated in full scale incinerators. Economic incineration also requires a comparatively large production rate. Intermediate size incinerators which address the full spectrum of propellant and propellant contaminated wastes and their characteristic emissions are not readily available.

In summary, open pit burning remains the most simple and cost effective method for disposal of intermediate quantities of Class 1.1 solid propellants. The alternative would involve large capital investments for either an ingredient reclamation facility or an incinerator and operation of the facility on an inefficient and costly basis.

SOLID PROPELLANT RECLAMATION STUDY

L. W. Poulter
M. P. Coover

1.0 INTRODUCTION

1.1 BACKGROUND

The solid propellant industry in the United States produces millions of pounds of propellant annually. Propellant types vary from simple composite formulations containing a polymeric binder, aluminum powder, and ammonium perchlorate oxidizer to high performance crosslinked, double-base formulations containing nitrate esters and nitramines. Inherent to the production process is the generation of waste propellant from mixing, casting, and machining operations and the accumulation of overaged, obsolete and out-of-specification propellant for disposal.

The majority of this surplus propellant is disposed of by open pit burning. This technique has been widely accepted by the industry because of its inherent simplicity and low cost. In recent years, however, the passage of strict environmental protection laws has made open pit burning unacceptable in many localities.

Alternative controlled incineration processes have been developed and evaluated on a limited scale for disposal of waste propellant. Army plants at Radford, Virginia, and at Tooele, Utah, have developed rotary kiln incinerators. The unit at Radford is a firebrick/ceramic-lined rotary kiln while the unit at Tooele Ordnance Depot is a 3-in. thick steel walled rotary kiln, sometimes referred to as a popping furnace. The Army depot at Dover, New Jersey (ARRADCOM) has experimented with fluidized bed incinerators. A third experimental method of propellant disposal is a wet-air oxidation process evaluated at the Naval Ordnance Station in Indian Head, Maryland, where high pressure/high temperature steam was used to decompose the waste propellant. While the controlled incineration processes generally meet air quality standards, large capital investments for equipment are required and operating costs are high compared to open pit burning.

Interest in recent years has shifted to the recovery and reuse of ingredients from waste propellants. This approach has the potential for achieving acceptable air quality standards as well as offsetting operational costs through reuse and/or commercial markets for the reclaimed products. Several propellant reclamation studies have been conducted on a laboratory scale with promising results.

1.2 OBJECTIVE

The objective of this program was to identify economically and environmentally acceptable disposal or reclamation methods other than incineration for waste solid propellants.

1.3 SCOPE

The program was conducted in two phases over a ten month period. The two phases were: (1) identification of treatment methods, and (2) laboratory demonstrations and economic design analysis.

During Phase I, a survey was conducted to identify existing nonincineration methods for the disposal of waste solid propellants. The survey included a literature search and personal contacts. Original and unique disposal concepts were also considered. A descriptive summary of each disposal method was provided. Supporting laboratory tests were conducted to verify the feasibility of original and/or unique concepts and to supplement published results, as required. The disposal methods were evaluated and those methods which appeared to be economically and environmentally acceptable were selected for further evaluation in Phase II of the program.

During Phase II, bench scale demonstrations were performed for each disposal method selected in Phase I to provide proof of principle and to provide engineering design and scaleup data. An economic and design analysis of each method was conducted and the cost of operation compared to the cost of state-of-the-art incineration. The economic and environmental impact resulting from incineration of waste solid propellants was evaluated. A pilot plant design for the disposal method was provided and recommendations made for follow-on work.

2.0 TECHNICAL DISCUSSION

2.1 REVIEW OF NONINCINERATION DISPOSAL METHODS

2.1.1 Descriptive Summary of Existing Disposal Methods

A survey was conducted to identify existing nonincineration methods for the disposal of waste, solid propellant. This survey included a literature search and industrial and government contracts. The literature searches were made through the following agencies:

1. Chemical Propulsion Information Agency (CPIA)
2. Defense Technical Information Center (DTIC)
3. Lockheed Dialog
4. National Aeronautics and Space Administration (NASA)

The following industrial and government contacts were made:

1. Aerojet General Corporation (AGC)
2. Atlantic Research Corporation (ARC)
3. Hercules Incorporated (HI)
4. Naval Surface Weapons Center (NSWC)
5. Naval Weapons Center (NWC)
6. Naval Ammunition Depot (NAD)
7. United Technology Corporation (UTC)

A bibliography of disposal methods identified from this survey is presented in Table 1. It includes disposal methods for flares and plastic bonded explosives as well as solid propellants. A brief summary of each of the solid propellant disposal methods is presented in the following paragraphs and in Table 2.

The summary includes a process description, chemical reactions, effluents, intermediate and final products, and a list of major equipment.

TABLE 1
BIBLIOGRAPHY OF DISPOSAL METHODS

PROPELLANTS

- McBride, W. R. and Thun, W. E., Sensitivity and Characterization of Selected Ammonia Systems: Reclamation Methodology for Ammonium Perchlorate Propellants. Naval Weapons Center, China Lake, California, April 1979.
- McIntosh, M. et al., Solid Rocket Propellant Waste Disposal/Ingredient Recovery Study. Thiokol/Wasatch, July 1975.
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- Williams, Carvar and Hugkins, Recovery of NHC From Propellants. MICOM, T-78-92, October 1978.

TABLE 1 (Cont)

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- Musselman, K. A., Isolation and Disposal of Chemical Ingredients Utilized in Illuminating Flares. Naval Ammunition Depot, Crane, Indiana, 1973.

PLASTIC BONDED EXPLOSIVES

- Dahlberg, L. F., et al., Procedures for Recycling and Reclaiming Plastic Bonded Explosives (U). Naval Weapons Center, China Lake, California, 1973-1975.
- Leake, E. E., Recovery of HMX From Scrap PEX-9404 High Explosive. Silas Mason Company, Inc., Burlington, Iowa, October 1973.

TABLE 2

SUMMARY OF DISPOSAL METHODS

PROCESS	DESCRIPTION	CHEMICAL REACTIONS	EFFLUENTS	INTERMEDIATE PRODUCTS	FINAL PRODUCTS	MAJOR EQUIPMENT
Composite Propellants						
MC BRIDE - AP Recovery	Extraction of AP with ammonia	Ammonolysis	Binder Residue	AP/ NH_3 solution Benzene/Binder Solution	AP AI (CTPS Prop)	Shredder Leach Tank Crystallizer Dryer Wash Tank Still
MC INTOSH - Fire Starter	Alternate use as fire starter	Polymerization	None	Unpolymerized Propellant	Cured Propellant	Curing Oven
- Slurry Explosive	Use as ingredient in a slurry explosive	None	None	Propellant/ Water slurry Oxidizer/ Water solution	Slurry Explosive	Shredder Macerator Mixer
- AP Recovery	Aqueous Extraction of AP	None	AI/Binder Residue	AP/Water solution	AP	Shredder Leach Tank Crystallizer Filter/Centrifuge Dryer
- AI Recovery	(e) Pyrolysis of binder (b) Degradation of binder	(e) Pyrolysis (b) Transacetalification	(e) Pyrolytic products (b) Degraded binder/spent chemicals	(e) None (b) Ester alkoxyd	AI	(a) Furnace/Scrubber (b) Dryer Reactor Solids Separator Solvent Still
SINCLAIR - Confined Space Shot	Substancian Detonation with Recovery of Gaseous Products	Combustion/Detonation	NO_x CO_x HCl H_2O	None	Not Defined	Not Defined
TOMPA - Mg/AP Recovery	Aqueous Extraction of AP and Mg	None	Binder Residue Saturated Carbon	AP/Water solution Mg/Water solution	AP Mg	Shredder Leach Vessel Crystallizer (2) Solvent Still Filter (2) Carbon Absorption Column Storage Tank

TABLE 2 (CONT)

PROCESS	DESCRIPTION	CHEMICAL REACTIONS	EFFLUENTS	INTERMEDIATE PRODUCTS	FINAL PRODUCTS	MAJOR EQUIPMENT
- Tarter/Standard Missile	Degradation/Dissolution of binder and separation of solid ingredients.	Ammonolysis	Binder Residue	AP/Water Solution	AP Al	Shredder Reactor Crystallizer Solvent Still Dryer
- Sidewinder	" "	Solvolyse	Binder Residue	AP/Water Solution	AP Al	Shredder Reactor Crystallizer Solvent Still Dryer
WILLIAMS - NHC Recovery	Extraction of NHC with Pentane	None	Binder Residue Spent Chemicals	NHC/Pentane Solution	N-hexyl-carborane (NHC)	Shredder Basket Leach Tank Filter Solvent Still Condenser Storage Tank (2)
High Energy Propellant						
TOPPA - Sol ysis	Degradation/Dissolution of binder and separation of solid ingredients	Solvolyse	Degraded Binder	NE Depleted Residue Nitramine/ Oxidizer/ Solvent Sol'n Oxidizer/Solvent Solution	Nitrate Ester Nitramine Oxidizer Aluminum	Shredder Leach/Digestion Tank Crystallizer Dryer
Explosive Booster	Alternate use as an explosive booster	Polymerization	None	Uncured Propellant	Cured Propellant	Casting Equipment Cure Oven
Selective Solvent Extraction Process	Extraction of major ingredient with selective solvents	None	Al/Binder Residue	NE Depleted Residue nitramine/ oxidizer/ solvent sol'n Nitramine/ oxidizer mixed crystalline Oxidizer/Water Solution	Nitrate Ester Nitramine Oxidizer	Shredder Leach Tank Crystallizer (2) Filter Solvent Still

2.1.1.1 McBride, William R. and Thun, Wayne E., Sensitivity and Characterization of Selected Ammonia Systems: Reclamation Methodology for Ammonium Perchlorate Propellants. Naval Weapons Center, China Lake, California, April 1979

A method for the recovery of ammonium perchlorate (AP) from CTPB and HTPB composite propellants using liquid ammonia was studied by McBride and Thun. The liquid ammonia serves a dual function in this process. It is an excellent solvent for extraction of AP and a solvolytic reagent for the chemical breakdown of the CTPB Binder. The HTPB Binder was not affected. AP recoveries of up to 99% were reported. The chemical purity of the recovered AP was not determined. The rate of AP extraction was found to increase with larger AP particle sizes. Agitation during AP extraction produced mixed results due to adhesion and flotation problems. Process conditions ranged from -33°C (14.7 psia) to 100°C (1,000 psia). A major disadvantage of the process is the characteristic of AP-Ammonia solutions to propagate from deflagration to detonation.

Process Description - A process flow chart, constructed from the report narrative,* is presented in Figure 1. It includes unit operations for size reduction, leaching, crystallization, and drying.

The propellant is first shredded into small pieces or chips to produce a high surface-to-volume ratio. Since the rate of AP extraction appears to be diffusion limited, this ratio together with the AP particle size is a major controlling factor affecting cycle time and efficiency of subsequent leaching operations. Chip sizes evaluated in the study ranged from 6 to 25mm in thickness.

The propellant chips are then charged into a leaching vessel containing liquid ammonia for the extraction of AP. A contact period of 1 to 4 hours, depending on process temperature and propellant chip size, is required to obtain high recoveries of AP. Several conventional contact processes are available for leaching operations. A batch contact method appears to be best suited for the ammonia contact process because of the high vapor pressure of ammonia and the probable pressurization requirements.

*A process flow chart was not included in the report.

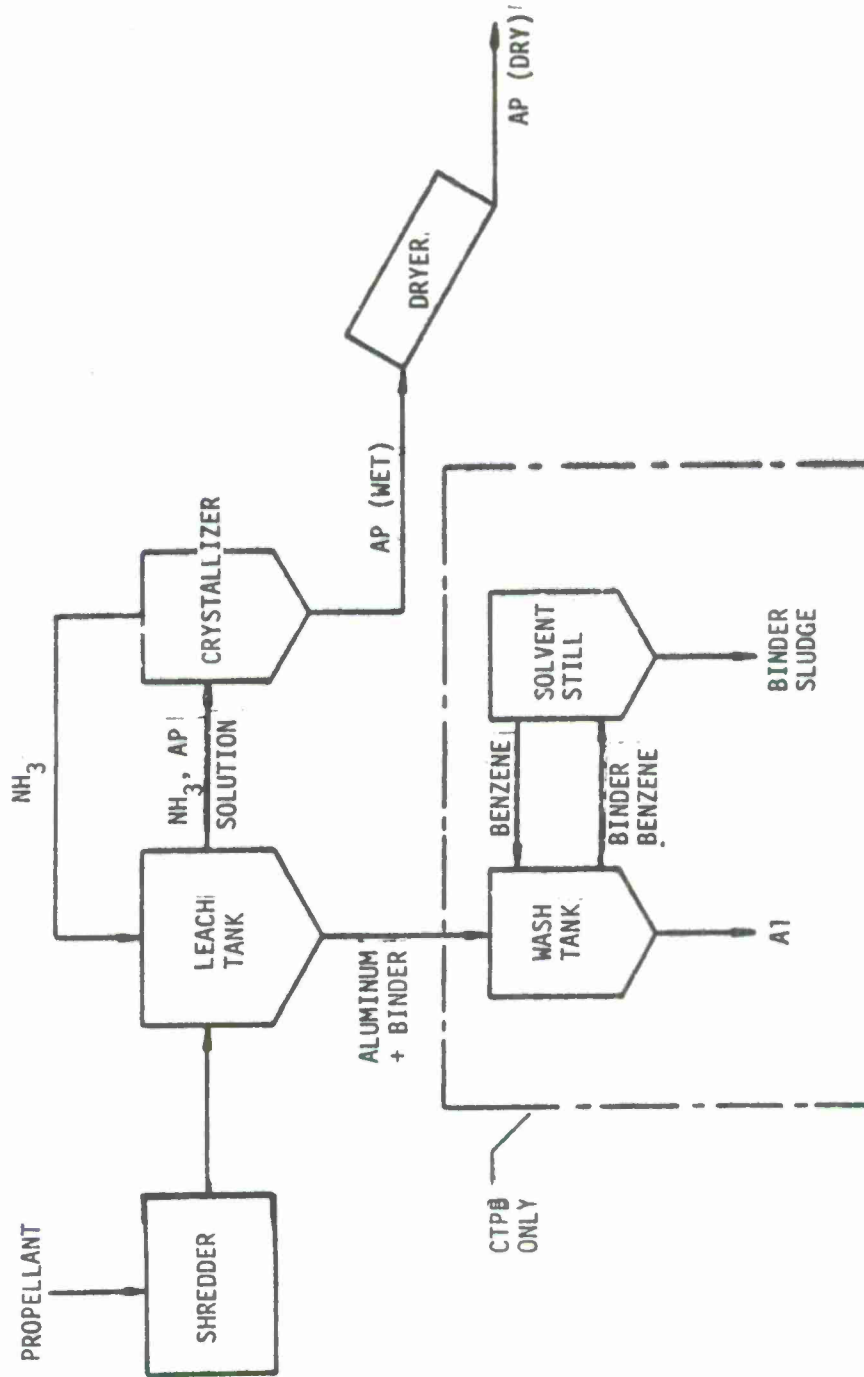


Figure 1. Process Flow Chart

The solid and liquid phases are then separated to form an ammonia extract solution and an aluminized binder sludge residue. The extract solution is metered to a crystallizer for precipitation of AP. Precipitation was initiated in the study by solvent removal although solution cooling is an optional method. In either method the ammonia solvent is recovered and re-used.

The aluminized binder residue from CTPB propellants may be washed with benzene to remove the degraded binder. Aluminum (Al) powder and other insolubles would be left. The benzene would be recovered for reuse. Since HTPB binders do not appear to be affected by ammonolysis, washing of the residue is ineffective.

Chemical Reactions - The CTPB Binder is degraded by ammonolysis. A postulated reaction mode is described below.



No other chemical reactions were noted.

Effluents - The following materials, by-products of the extraction process, are effluents from the process:

1. Aluminized binder residue (HTPB propellants)
2. Binder residue (CTPB propellants)

All solvents used are recovered for reuse.

Intermediate and Final Products - The following intermediate products are present in the process:

1. AP, ammonia solution
2. Binder, benzene solution (CTPB propellants only)

The following final products are formed:

1. AP
2. Al (CTPB propellants only)

Major Equipment - The following items of major equipment are required:

1. Shredder
2. Leaching tank, pressurized
3. Crystallizer
4. Dryer
5. Wash tank
6. Solvent still

2.1.1.2 McIntosh, M. J., et al., Solid Rocket Propellant Waste Disposal Ingredient Recovery Study. Thiokol/Wasatch, July 1975

In a study conducted under contract to the Jet Propulsion Laboratory (JPL), four nonincineration methods of waste composite propellant disposal were developed. These methods were (1) direct utilization of waste propellant as fire starters for the U.S. Forest Service, (2) direct use of waste propellant as an ingredient in a slurried explosive or blasting agent, (3) recovery of ammonium perchlorate (AP) from the waste propellant, and (4) recovery of aluminum (Al) powder from the waste propellant.

Fire starters are used by the U.S. Forest Service to ignite and burn wet, snow-covered piles of timber slash during the fall and winter seasons. Field tests conducted indicate that propellant fire starters would ignite snow-covered wood slash piles that conventional kerosene and gasoline fire starters would not.

Slurried explosives are used as blasting agents for mining, construction, and other industrial applications. Waste composite propellant and aluminized binder residue, a by-product of the AP leaching process, were successfully used as ingredients in slurried explosive formulations. Other ingredients included sensitizers such as PETN and HMX, water soluble oxidizers such as ammonium and sodium nitrates and surfactants to reduce agglomerations and gel agents. Formulations containing as much as 40 percent by weight of waste composite propellant were successfully tested. Relative energies as high as 1.32 TNT equivalents were obtained in demonstration tests.

AP was extracted and recovered from waste composite propellants by an aqueous leaching process. Test results indicate that extraction efficiencies as high as 95 percent were obtained. Fresh water residue washing increased this efficiency to as high as 98 percent. Analytical tests indicate that reclaimed AP meets acceptance criteria for reuse in composite propellant manufacture.

Aluminum powder was recovered from aluminized binder residue, a by-product of the AP leaching process, by two methods: pyrolysis and transesterification. In the first method, binder residue is heated to 450° to 500°C. When the AP content of the residue is low, the binder pyrolyzes and fumes off. When the AP content approaches 15 percent, the fumes may ignite and

burn part of the residue. The Al residue left from partial ignition often was slightly caked, but readily formed a free flowing powder when moved or stirred. Analysis of the active aluminum content present before and after the ignition shows that it was decreased by approximately 2%. In the second method, PBAN binder is depolymerized, filtered, and washed from the aluminum residue. This method uses a solvent with an alcoholic solution of sodium methoxide to transesterify the crosslinked sites of the binder system. When moisture is excluded from the system, the highly basic alkyl oxide radical has little effect upon the Al present, but reacts very rapidly with the binder. Mixed solvents of either methanol and tetrahydrofuran or toluene were effective in the transesterification reactions. Reaction products were readily soluble in toluene. Test results indicate aluminum recoveries of 98.7 to 99.7 percent.

Process Description - An integrated process flow chart for the four disposal methods is presented in Figure 2. A description of each process is summarized in the following paragraphs.

1. Fire starters - uncured, waste, composite propellant is cast into 1/2- to 1-gallon ice cream cartons. A fuse is then inserted, the flaps taped shut, and the cartons placed in an oven for propellant cure. The completed fire starters would be packaged and shipped as a Class B explosive.
2. Slurried explosive - waste composite propellant is shredded and then macerated in water to form a finely divided slurry. A surfactant is added to reduce adhesion and agglomeration of the propellant particles. A water soluble oxidizer, a sensitizer, and a gel agent are added and the slurry blended. The completed explosive is then packaged for shipment.
3. Ammonium Perchlorate Recovery - the initial step in this process is to shred the waste propellant into small chips to increase the surface area to mass ratio. This ratio is a major controlling factor effecting both the rate and efficiency of subsequent leaching operations. Surfactants may be added to reduce adhesion and agglomeration of propellant particles.

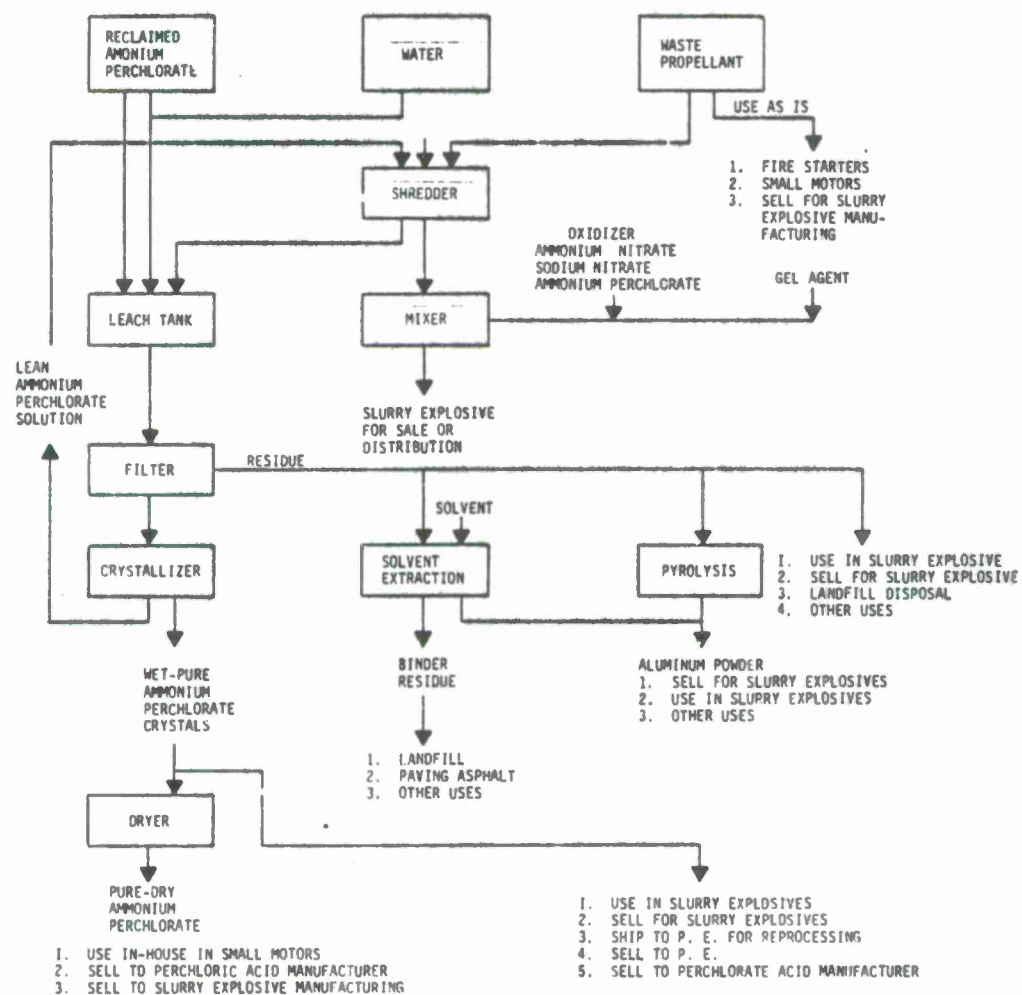


Figure 2. Waste Propellant Disposal Methods

The ammonium perchlorate is then leached from the propellant by intimate contact of the propellant with hot water. Leaching may be accomplished by any one of several conventional contact methods including multistage countercurrent, multistage cocurrent, batch continuous contact, and others. The propellant slurry is agitated during the contact phase of the leaching process to promote mass transfer.

The solid and liquid phases are then separated to form a concentrated AP-water solution and an aluminized binder sludge residue. Separation may be accomplished by any conventional liquid-solids separation process including screening, settling, and filtration. The degree of difficulty in making the separation is proportional to the degree of subdivision and adhesion of propellant particles.

The concentrated extract solution is metered to a crystallizer where it is cooled to precipitate AP crystals. The resulting dilute solution exiting the crystallizer is returned to the leaching vessel for reuse. Recycle of the solvent constitutes a closed loop process, thereby eliminating a potential effluent waste stream. The recovered AP may be dried or left in wet cake form depending on the planned utilization. The overall yield of the process may be increased by washing the aluminized binder sludge with fresh water.

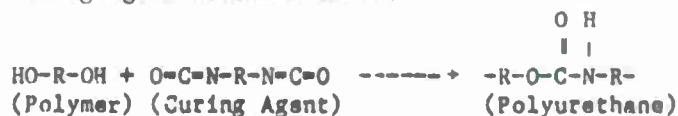
- 4.a Aluminum powder recovery (pyrolysis) - aluminized binder residue, a by-product of the AP leaching process, is charged into a furnace or retort by a slurry pump or other conventional sludge conveyor. The residue is heated in the retort to a temperature of 450° to 500°C at which the binder pyrolyzes and fumes off. The retort may be operated on a batch or continuous basis. The fumes would exit the retort

through a bag collector, water scrubber, or other pollution control devices.

- 4.b Aluminum powder recovery (transesterification) - the first step in this process is to dewater and dry the aluminized binder residue from the AP leaching process. Total water exclusion is necessary to preclude side reactions in subsequent chemical treatments. The dried residue is charged into a reactor. An alcoholic solution of sodium methoxide is added and the mixture heated to a temperature of 60°C for approximately 1 hour. The mixture is then filtered and washed with toluene. The degraded binder is dissolved and removed in the toluene leaving aluminum powder on the filter media. The aluminum powder wet cake is placed in a dryer and the residual toluene removed. The methanol, toluene, and residual sodium methoxide may be recovered for reuse.

Chemical Reactions - The following chemical reactions occur in the four disposal methods:

1. Fire starters - the propellant binder is polymerized in this process. A typical polymerization reaction for an hydroxy terminated polymer and an isocyanate curing agent is shown below.



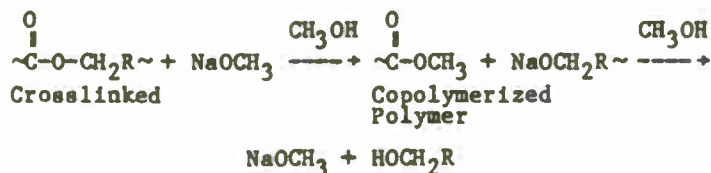
The polymer formed in this reaction is referred to as a polyurethane.

2. Slurried explosives - no chemical reactions occur in this process.
3. AP recovery - no chemical reactions occur in this process.
4. Aluminum powder recovery
- a. Pyrolysis - the residual binder is decomposed under heat according to the general equations:



Other miscellaneous additives would likewise be decomposed to their pyrolysis products.

- b. Transesterification - the ester groups in the binder are reacted with sodium methoxide.



Note that the sodium methoxide is reformed in the second phase of the reaction.

Intermediate and Final Products - The following intermediate products are formed in the disposal methods.

1. Fire Starters
 - Unpolymerized propellant
2. Slurried explosives
 - Propellant-water slurry
 - Oxidizer-water solution
3. AP Recovery
 - AP-water solution
4. Aluminum Recovery
 - a. Pyrolysis
 - None
 - b. Transesterification
 - RCO_2CH_3 (ester)
 - NaOCH_2R (alkoxide)

The following final products are produced in the four disposal methods.

1. Fire Starters
 - Cured propellant
2. Slurried Explosives
 - Propellant-water-oxidizers-sensitizer slurry
3. AP Recovery
 - Ammonium perchlorate
4. Al Powder Recovery
 - Aluminum powder

Waste Effluent Streams - The following waste effluent streams are formed by the four disposal methods.

1. Fire Explosives
 - None
2. Slurried Explosives
 - None
3. AP Recovery
 - Aluminum-binder residue
4. Al Powder Recovery
 - a. Pyrolysis
 - Pyrolysis products
 - b. Transesterification
 - Degraded binder sludge
 - Spent chemicals

Major Equipment - The following items of major equipment are required in the four disposal methods.

1. Fire Starters
 - Propellant curing oven
2. Slurried Explosives
 - Propellant shredder
 - Propellant macerator
 - Slurry mixer-blender
 - Solids feeder
 - Metering pumps
3. AP Recovery
 - Propellant shredder
 - Leaching tank
 - Crystallizer
 - Filter-centrifuge
 - Dryer
4. Aluminum Powder Recovery
 - a. Pyrolysis
 - Furnace or retort
 - Water scrubber

b. Transesterification

- Dryer
- Reactor
- Solids separator
- Solvent stripping unit

2.1.1.3 Sinclair, J. E., et al., Investigation of Propellant and High Explosive Disposal by Confined Space Shots - II. Naval Postgraduate School, Monterey, California, July 1974.

A method for the disposal of both high energy explosives and solid propellants via detonation or deflagration, respectively, in a subterranean spherical chamber has been proposed by Sinclair and coworkers. The concept was developed using supporting experimental evidence from laboratory scale disposal of representative materials (see Table 3). It was found that the combustion gas product distribution and the relative concentrations are reasonably independent of the starting material. This suggested the possibilities of processing the gases for material recovery, general pollution abatement, or the generation of electricity via expansion through a turbine. None of these ideas were pursued in any detail. The authors concluded that except for high explosives too sensitive to risk uncasing, this method of disposal is at a disadvantage compared to wet-air oxidation and controlled incineration. Furthermore, it was stated that reclamation of the gaseous combustion products did not, at the time of the report, seem practical.

TABLE 3

MATERIALS USED FOR LABORATORY TESTING

Secondary High Explosives

1. PETN
2. MRX
3. RDX
4. TNT
5. C-4 (91% RDX, 9% Plasticizer)

Specific propellant compositions were not detailed, but it was implied that those propellants tested were of the high energy type (that is, containing nitrocellulose and/or nitroglycerine).

Process Description - A detailed description of how to prepare and handle the waste materials for positioning in the chamber was not provided. It would be necessary to attach an ignition or detonation device on the waste material bundle and then lower it into the chamber. For detonable wastes it would be necessary to suspend the bundle at the center of the spherical cavity to minimize the shock wave energy reaching the cavity walls. It is essential that the walls react elastically to the shock. The chamber would then be sealed and the charge initiated. As indicated earlier, no ideas for dealing with the combustion product were explored in great detail. A look at gas recovery for the production of useful materials was found to be infeasible.

Chemical Reactions - Numerous reactions take place in this process since it is based on material combustion.

Effluents - Two effluent phases result from this process:

1. Ash which would be composed primarily of metal oxides in the case of propellants.
2. All of the gas phase combustion products consisting primarily of H_2O , CO , CO_2 , NO_x and HCl .

Intermediate and Final Products - There are no products generated in this process unless components of the effluent stream are recovered.

Equipment - The investigators explored the possibility of using salt domes as sites for disposal chambers. Mining costs were evaluated as were the logistical problems that would be encountered. Transportation and site storage equipment would need to be provided since the sites would more than likely be located far from the waste producing facilities. Other equipment items can be envisioned which were not detailed in the report, such as a winch device for lowering the waste bundles into the chambers and another for lowering and raising the chamber plug.

2.1.1.4 Tompa, A. S., A TG Study of Solvolytic Breakdown of a Crosslinked Double Base Propellant. Naval Surface Weapons Center, Silver Spring, Maryland, October 1980

A separation scheme whereby crosslinked double base propellant ingredients may be recovered for reuse has been suggested by A. S. Tompa. The scheme features the degradation of the propellant binder via chemical reaction followed by separation of oxidizer, fuel, and energetic filler by taking

advantage of their differing solubility characteristics. Tompa found that polyurethane binders could be efficiently degraded by reacting ethanolamine (EA) with the urethane linkages in the binder network. The propellant he studied was a polyurethane crosslinked double base nitroglycerin (NG) composition which, in addition, contained ammonium perchlorate (AP), aluminum (Al) and HMX.

Process Description - The separation scheme that Tompa suggested is presented in Figure 3. The first step in any process based on this scheme would be to reduce the size of the propellant waste to much smaller dimensions using a shredder or some similar size-reduction equipment. High surface to mass ratios are essential to the efficient processing of solid materials in a reaction system.

The next operation is an extraction of NG from the propellant using a suitable solvent. Tompa suggested using dichloromethane as the solvent. As indicated in the scheme, the extraction solution contains NG, but will in addition contain any stabilizers, plasticizers, and unreacted binders present in the propellant that are soluble in the selected solvent. It would be necessary to process this solution in some manner to recover most of the solvent or dispose of it in an environmentally sound fashion.

The solids remaining after the NG extraction step are then reacted with EA in toluene and isopropanol. This step, shown in Figure 3, indicates isopropanol alone as the solvent, but Tompa showed the two solvents combined to be a more effective reaction medium because the reaction rate was found to be higher. The slurry is agitated and may be heated to accelerate the reaction.

The reaction step is followed by a phase separation. The liquid phase would contain solvents, unreacted EA, degraded binder, and any soluble materials not removed in the NG extraction operation. It would be necessary to process this solution to recover solvent and unreacted EA as a cost reduction measure. Tompa suggested that the solids be washed prior to separation, presumably to remove any residual soluble organic materials.

The next operation involves dissolving both AP and the nitramine in dimethylsulfoxide (DMSO). The insoluble aluminum metal is then separated from the solution. Tompa suggested crystallizing the HMX by adding water to

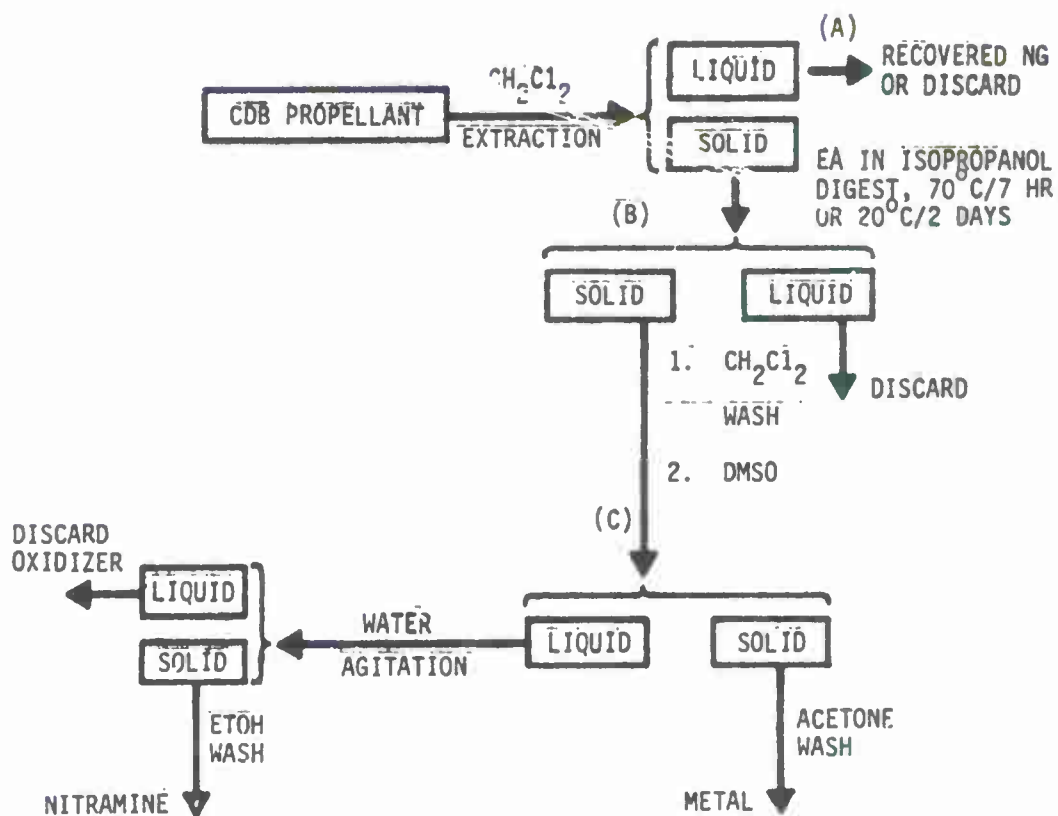


Figure 3. Separation Scheme for Crosslinked Double Base Propellant

the solution and then simply discarding the solvent oxidizer solution. From an economy standpoint this would be rather expensive since it would be desirable to recover the DMSO.

A number of modifications to this separation scheme could be made to improve its potential as a method for treating waste propellant. Solvent cross-contamination is perhaps the most important drawback to the scheme as presented. Thus, either including drying steps between certain operations or selection of solvents to reduce cross-contamination would be necessary. For example, toluene could be used in the NG extraction step and since toluene-isopropanol is the solvent medium in the subsequent reaction no contamination problems would result from carryover of solvent into the reaction vessel. Furthermore, toluene could be used in the post-reaction washing of the solids and then combined with the liquid phase separated from the reaction mixture for solvent recovery.

The AP and HMX recovery operations could be modified to avoid the expensive recovery of solvent by distillation. For example, after the solids wash step with, say, toluene, the material could be dried to remove all traces of the solvent and then treated with water to remove AP. The AP could be crystallized and the water recycled. The wet Al-HMX mixture could be dried and treated with acetone to remove HMX for subsequent recrystallization and recycling of the acetone.

Chemical Reactions - The postulated reaction of ethanolamine and the urethane linkage is as follows:



This is the only chemical reaction in the process.

Effluents - Several effluent streams would accompany a process based on Tompa's separation scheme.

1. The solvent-NG solution which will include other soluble components would need to be treated to recover the NG, or it could be discarded.
2. The liquid phase resulting from the reaction step would contain binder residue, unreacted EA, and perhaps plasticizer. A solvent recovery step would

be necessary to reduce solvent and reactant loss.
The eventual effluent could be a binder-residue-rich liquid which could then be either burned or disposed of by landfill.

Intermediate and Final Products - The following intermediates are present in the separation scheme (as described):

1. Propellant after NG extraction
2. Al, AP, HMX
3. AP, HMX, DMSO

The final products are as follows:

1. Al
2. AP
3. HMX
4. NG (possibly)

Equipment - Necessary equipment includes:

1. Shredder
2. Leaching tanks
3. Crystallizers (2)
4. Driers

2.1.1.5 Tompa, A. S., French, D. M., Utilization and Disposal of Solid Propellant and Explosive Wastes. Naval Surface Weapons Center, Silver Spring, Maryland, April 1977

Separation schemes for the recovery of ingredients from several composite propellants have been proposed by Tompa and French. Each of the suggested schemes involves either degrading the binder via chemical reaction with subsequent recovery of the desired materials or leaching the desired ingredients out of the binder network leaving the polymer intact. All of the propellants studied and for which separation schemes were suggested contained ammonium perchlorate (AP) as the oxidant. The binder degradation method was proposed for those formulations which in addition contained aluminum (Al), since that method is the only reasonable means of recovering this material. Propellants which did not contain Al were subjected to a leaching process to remove soluble ingredients. The five propellants which were extensively studied by the investigators and for which processing schemes were suggested are presented in Table 4. Three separation schemes were described as indicated in the table and flow diagrams for each are depicted. The following

TABLE 4
PROPELLANTS INVESTIGATED AND INGREDIENT RECOVERY TECHNIQUES PROPOSED

<u>Propellant</u>	<u>Binder</u>	<u>Curing Agent</u>	<u>Polymer Type</u>	<u>Recovery Technique</u>
Sidewinder 1C	Polybutadiene	Imine	Amide	Binder Degradation
Standard Missile Booster	Polybutadiene	Imine	Amide	Binder Degradation
Standard Missile Sustainer	Ether/Ester Copolymer	Isocyanate	Urethane	Leaching
Tartar Booster	Polyether	Isocyanate	Urethane	Binder Degradation
Tartar Sustainer	Polyether	Isocyanate	Urethane	Leaching

discussion of each of the processes details the operations involved, equipment requirements, intermediates, products, and effluent streams.

Ammonium Perchlorate - Nitroguanidine Leaching Process

Process Description - The propellants studied which led to the development of this process were the Tartar and Standard Missile Sustainer formulations. The investigators designed a batch mode pilot plant for which the equipment-flow diagram is shown in Figure 4. The process takes advantage of the differing solubilities of AP and nitroguanidine (NQ) in water (see Figure 5).

Since ingredient separation in this process is accomplished by leaching the materials from the propellant, it is important that the slurry introduced to the extraction vessel contain propellant chunks having a reasonably consistent size distribution. Thus a shredder or some other suitable size reduction equipment must necessarily precede the slurry storage vessel.

The next operation involves charging the extraction vessel with a batch of the propellant slurry. The investigators indicated that a long contact time between propellant and water in the slurry storage tank at ambient temperature would be sufficient to remove most of the AP from the propellant. It was thus implied that little if any time is required at this point for removal of AP from the solids. Since NQ is significantly less soluble in water than AP at the temperature of the mixture, cross-contamination is minimized.

The aqueous AP solution is separated from the solids and filtered to remove suspended fines. An activated carbon absorption column is then utilized to remove the small amount of NQ present in the solution.

The final operation in the AP recovery segment of the process is the evaporative crystallization of AP from the solution followed by an acetone wash. The wash is presumably necessary to remove residual organics. The spent acetone is then fed to a solvent recovery unit which also serves the NQ recovery segment of the process. The aqueous solution resulting from the crystallization could be recycled to the slurry tank.

After the aqueous AP solution has been separated from the solids in the extraction vessel, fresh water and filter cake from the filter described

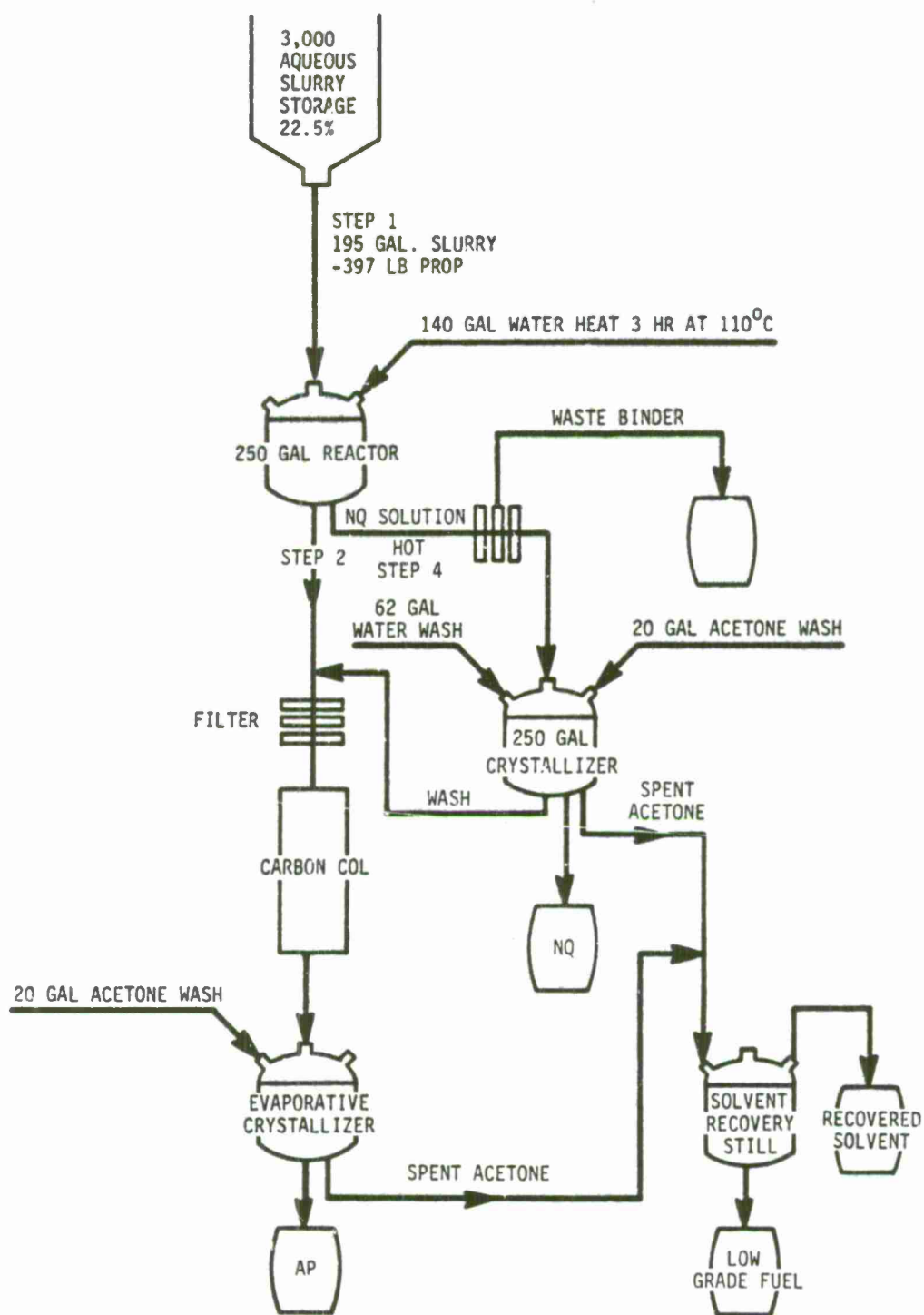


Figure 4. Propellant Reclamation Process, 100 Ton/Yr Plant for Extraction of Nitroguanidine and Ammonium Perchlorate

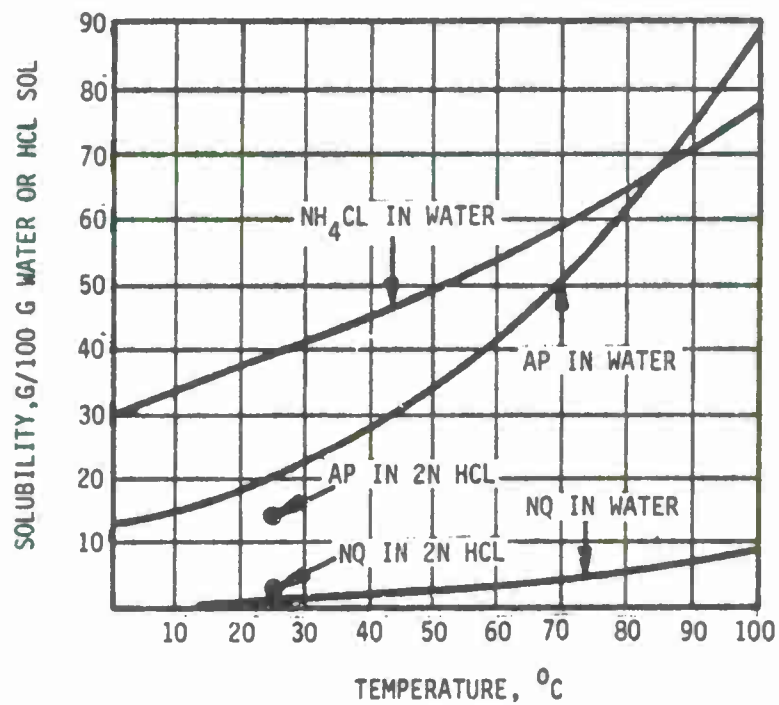


Figure 5. Solubility of AP and NQ in Water and in HCL

above are added to the vessel and the mixture is heated for several hours at 110°C. At this temperature the solubility of NQ is sufficiently high to permit effective removal from the solids provided a high enough water-to-solids ratio is used.

After this digestion operation is completed, the liquid is separated from the solid residue. It is then filtered and cooled to crystallize the NQ. The resulting filtrate will have a low concentration of AP and the investigators suggested coupling the filtrate stream to the AP separation stream just above the filter. In this way a potential pollution problem is avoided.

The crystallized NQ is then washed with cold water and acetone to remove residual contaminants. The acetone is recovered by distillation along with acetone used in the AP segment of the process.

It was pointed out that the spent binder and bottoms from the solvent still have some fuel value and thus can be sold or used to defray operating costs.

Data showing the dependency of percent recovery on the temperature and time of the extraction process were included in the report and are here reproduced in Table 5 in support of the discussion. Note that if the initial slurry of propellant were to require no further processing in the extraction vessel as was suggested earlier, it would have to be blended with water about 2 weeks prior to processing. The slurry would have to be kept at about 25°C to preclude appreciable dissolution of NQ.

Chemical Reactions - There are no chemical reactions involved in this process. Ingredient separation is based solely on the relative solubilities of AP and NQ in water.

Effluents - The following describes process effluents.

1. The binder residue resulting from the NQ leaching operation is one of the process effluents. If the NQ solution was simply drained from the residue for further processing, the waste would hold up a quantity of the NQ-rich liquid. Depending on the efficiency of the AP leaching operation, there would

TABLE 5

EFFICIENCY OF AQUEOUS EXTRACTION OF AP AND NQ
(1/2-In. Cubes)

Aqueous Extraction of Standard Missile Sustainer^a

Extraction Exper No.	1	2	3	4	5	6	7	8
Time, Days (25°C) Hours (110°C)	1	7	14	1	2	3	2 ^c	3 ^c
% AP Recovered ^b	62	83	99	73	90	96	99	99
% NQ Recovered ^b	0	0	0.5	29	55	72	76	85

Aqueous Extraction of Tartar Sustainer^a

Extraction Exper No.	1	2	3	4	5	6	7	8
Time, Days (25°C) Hours (110°C)	1	7	14	1	2	3	2 ^c	3 ^c
% AP Recovered ^b	63	76	99	64	73	83	84	90
% NQ Recovered ^b	0	0	0.2	32	43	60	63	74

^a33.3 ± 0.20 g in 100 ml of water.

^bPercent based on recovered divided by theoretical.

^cSolvent decanted after each hour and fresh solvent added.

also be some AP in both the liquid holdup of the binder residue and in the waste as the solid. Thus, a number of factors will influence the composition of this waste stream.

2. Another process effluent is the bottoms product of the acetone recovery still. If the AP and NQ precipitates are not dried prior to washing with acetone, the feed to the still will contain water. Since water has the lower vapor pressure, it will wind up in the bottoms product. Furthermore, AP has a significant solubility in acetone and thus will appear in this effluent stream. If NQ is at all soluble in acetone, it will also appear in the bottoms.
3. Carbon in the absorption columns would need to be replaced periodically and thus constitutes an effluent.

Intermediate and Final Products - The following intermediates are present in the separation scheme:

1. AP-water solution
2. NQ-water solution

The final products are as follows:

1. AP
2. NQ

Equipment - The following equipment is required.

1. Extraction vessel
2. Crystallizers (2)
3. Solvent recovery still
4. Activated carbon absorption column
5. Filters (2)
6. Shredder
7. Slurry storage tank

Process Raw Materials - These materials are:

1. Water
2. Acetone

Ammonium Perchlorate and Aluminum Recovery From the Tartar and Standard Missile Booster Propellants

Process Description - The process scheme that Tompa and French developed for the recovery of Al and AP from the Tartar and Standard Missile Booster propellants entailed chemically degrading the binder and then proceeding with ingredient separation and purification. A flow diagram of the separation scheme is presented in Figure 6.

As with any process for the recovery of propellant ingredients, a plant designed around the scheme in Figure 6 must include suitable size reduction equipment for the waste propellant. The propellant is then combined with an ammonia-water solution and is heated to 110°C. The binder is degraded during this operation by the reaction of ammonia on the urethane linkage of the Tartar formulation or the amide linkage of the Standard Missile propellant.

After the reaction is completed, the binder and aqueous phases are separated, with the former containing the bulk of the Al and the latter containing the AP. The binder phase is then washed twice with fresh water, presumably to remove any residual AP. The wash water is combined with the aqueous solution and AP is crystallized by evaporating the solvent. The precipitate is washed with acetone if additional purification is necessary. Although not discussed by the investigators, the acetone wash would probably be combined with the acetone wash in the Al purification segment of the process and recovered by distillation. Also, the aqueous AP and ammonia solution resulting from the crystallization step could possibly be recycled to the reaction step.

Aluminum is recovered by dissolving the degraded binder into a toluene-isopropanol solution. (According to the investigators, only toluene was needed when processing the Tartar propellant.) Since the Al is insoluble, it can be separated from the solution by simply allowing it to settle and decanting the liquid. The Standard Missile propellant contains ferric oxide in small quantities. To separate it from the Al, the investigators found that a small concentration of ethanolsamine in the solvent system aided dispersion of the oxide so that it could be decanted with the liquid. There was no difficulty in removing other insoluble ingredients, presumably because they were much lighter than Al and easily suspended in the solution. It was reported that several solvent washings are necessary for isolation of Al, at least with

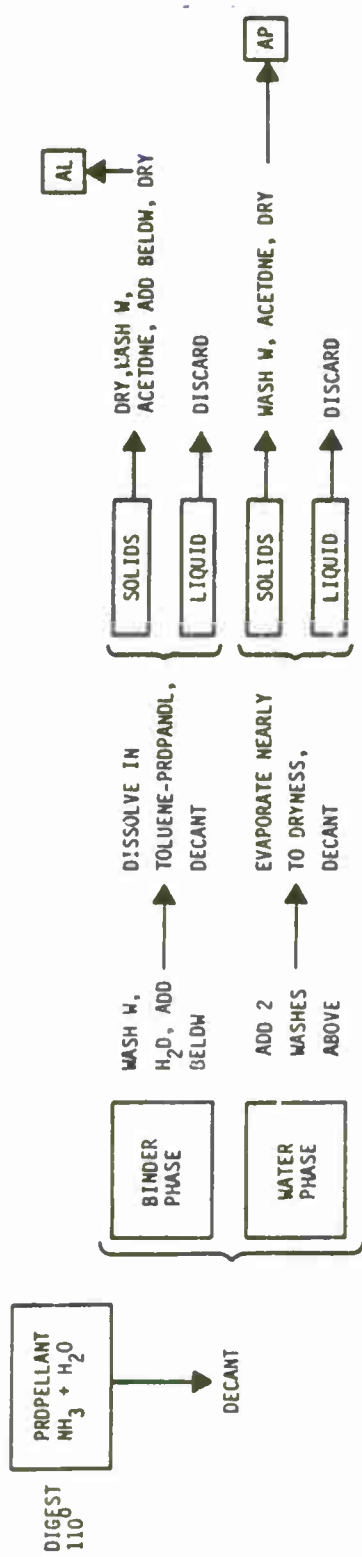


Figure 6. Separation Scheme for Tartar Booster and Standard Missile Booster

the Standard Missile propellant. The isolated Al is then dried, washed with acetone, and dried again. Most of the toluene-isopropanol solvent can be recovered by distillation and reused.

AP recoveries of 73 to 86 percent and Al recoveries of about 90 percent were reported for these two propellants. Purities were reported to be within federal specifications including particle size for the Al.

Effluents - The following describes process effluents.

1. The bottoms product from the toluene-isopropanol solvent recovery would be one of the major effluents. It would contain the binder residue and solids removed during the decanting procedure as well as some solvent.
2. The bottoms from the acetone recovery would be an effluent. It would contain a small amount of AP and any soluble organics picked up in the Al wash step.

Intermediate and Final Products - The intermediate products in this process are as follows:

1. Degraded propellant in ammonia-water system
2. AP-water solution
3. Degraded binder, Al, and other solid ingredients

The final products are:

1. AP
2. Al

Equipment - Equipment required is:

1. Shredder
2. Slurry tank
3. Reactor vessel
4. Crystallizer
5. Solvent recovery stills (2)
6. Tanks
7. Drier

Process Raw Material - These materials are:

1. Water
2. Toluene

3. Acetone
4. Isopropanol
5. Ammonia

Ammonium Perchlorate and Aluminum Recovery From Sidewinder IC Propellant

Process Description - The binder degradation approach was suggested for this propellant using EA rather than ammonia as the reactive ingredient in the solvent system. A toluene-propanol solution of 50% in each solvent was selected for use because toluene aided the swelling of the propellant chunks thus improving the transport of ingredients out of the material, and because the solvent system dissolved, the ethanalamine perchlorate analog of AP.

The separation scheme is presented in Figure 7. As before, size reduction equipment would need to be a part of the process. The propellant is reacted with EA in the toluene-propanol solution at 110°C. After the reaction is completed, the AP and Al are separated from the degraded binder-solvent solution. The solvent can, in part, be recovered by distillation leaving a binder-rich, solvent-poor solution as waste.

Tetrahydrofuran (THF) was the solvent selected to wash the AP and Al free of residual binder material. The investigators indicated that several washings were necessary to free the Al of residue. The solvent is recovered by distillation while the solids are dried and then blended with hot water to dissolve the AP. After decanting the liquid, perhaps one washing of the Al with water would be necessary if high purity of the Al was desired. The Al is then washed with THF to yield metal high in purity.

Evaporative crystallization is performed on the aqueous solution to precipitate the AP. The liquid filtrate would have a small concentration of AP and could be recycled to the AP dissolution step previously described if a high Al purity is not a requirement. If it is a requirement, then some of the solution would have to be treated as waste since, otherwise, an inventory of this contaminated water would be continually built up. The investigators suggested washing the AP with acetone to remove any soluble contaminants. This solvent would, of course, need to be recovered or treated as waste.

It is possible that if the initial washing of Al and AP with THF is thorough enough, the last washing of Al might be avoided. Otherwise the THF

from both steps can be combined and purified in the same recovery step. Introducing the additional solvent acetone in the AP wash step is something that would be better avoided in a scaled up process. Therefore, either recrystallizing the material or insuring that the initial crystallization is sufficiently clean are two alternatives that deserve attention.

Effluents - The following describes process effluents:

1. The bottom product from the THF recovery unit would be an effluent containing THF, binder residue, and perhaps a little AP.
2. The bottoms product from the toluene-propanol recovery unit would be an effluent rich in binder residue and other organics present in the original propellant. Of course it would also contain some solvent.
3. A water solution weak in AP would constitute an effluent if Al purity is a concern.

Intermediate and Final Products - The intermediate products encountered in this process are as follows:

1. Al and AP
2. AP-water solution

The final products of the process are Al and AP.

Equipment - Equipment required is:

1. Shredder
2. Tanks (2)
3. Drier
4. Crystallizer
5. Solvent recovery units (2)

2.1.1.6 Williams, Carver, and Huskins, Recovery of NHC From Propellants.
MICOM, T-78-92, October 1978

A process for the recovery of n-hexylcarborane (NHC) from Viper propellant was developed by Williams, Carver, and Huskins. The incentive for the process is the high cost of NHC, estimated at \$1,350/lb. The method, by its nature, is very specialized with limited application to other propellant ingredient reclamation processes.

Process Description - A process flow chart for NHC recovery is presented in Figure 8. The propellant is shredded to increase the specific surface area and contacted with pentane to extract the NHC. The extract is filtered, evaporated and distilled to yield the final product. The pentane is recycled in the process.

Chemical Reactions - There are no chemical reactions in the process.

Effluents - The major effluents from the system would be the extracted propellant residue and the residue filter cake. Some pentane and pentane vapor losses would also be expected.

Intermediate and Final Products - The following intermediate products are present in the process:

1. Shredded propellant-water slurry
2. Propellant-pentane slurry
3. NHC-pentane solution

The final product is n-hexylcarborane.

Major Equipment - The following items of major equipment are required to support the process:

1. Propellant shredder
2. Propellant screen basket
3. Extraction tank
4. Filter
5. Solvent recovery still
6. Condenser
7. Storage tanks (2)

2.1.2 Unique and/or Original Concepts

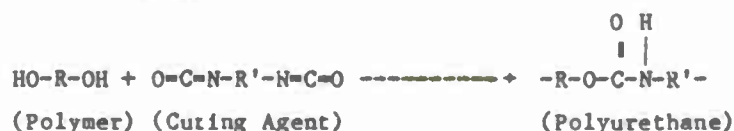
Two unique and/or original concepts were proposed for disposal of waste Class 1.1 solid propellant. The first method, manufacture of explosive boosters, provides an alternate use or application for the waste propellant. The second method, selective solvent extraction process, provides a method for the recovery of major propellant ingredients. These concepts are discussed in the following paragraphs.

2.1.2.1 Explosive Booster

The detonation characteristics of Class 1.1 propellants make them excellent candidates for use as explosive primers or boosters. These boosters are used as an initiation charge for blasting agents and are widely used in mining, construction, and other industrial applications. A typical explosive booster configuration would be approximately 3 in. in diameter and 2-1/2 in. long with a 5/16-in. diameter center perforation for placement of a blasting cap or primacord.

Description of Process - Uncured Class 1.1 propellant would be cast into mold sets to produce the desired size and shape for the primer or booster. The mold sets would be placed in an oven and the propellant cured. The cured propellant grains would be removed from the mold sets and packaged for shipment. A process flow sheet is presented in Figure 9.

Chemical Reactions - The propellant binder is polymerized in this process. A typical polymerization reaction for a hydroxy-terminated polymer and an isocyanate curing agent is shown below.



The polymer formed in this reaction is referred to as a polyurethane.

Intermediate and Final Products - The following intermediate product is formed in the disposal method.

- Unpolymerized propellant

The following final product is produced in the disposal method.

- Cured (polymerized) propellant

Major Equipment - The following items of major equipment are required in the disposal method.

- Propellant casting equipment
- Propellant curing oven

Waste Effluent Streams - There are no waste effluent streams formed by the disposal method.

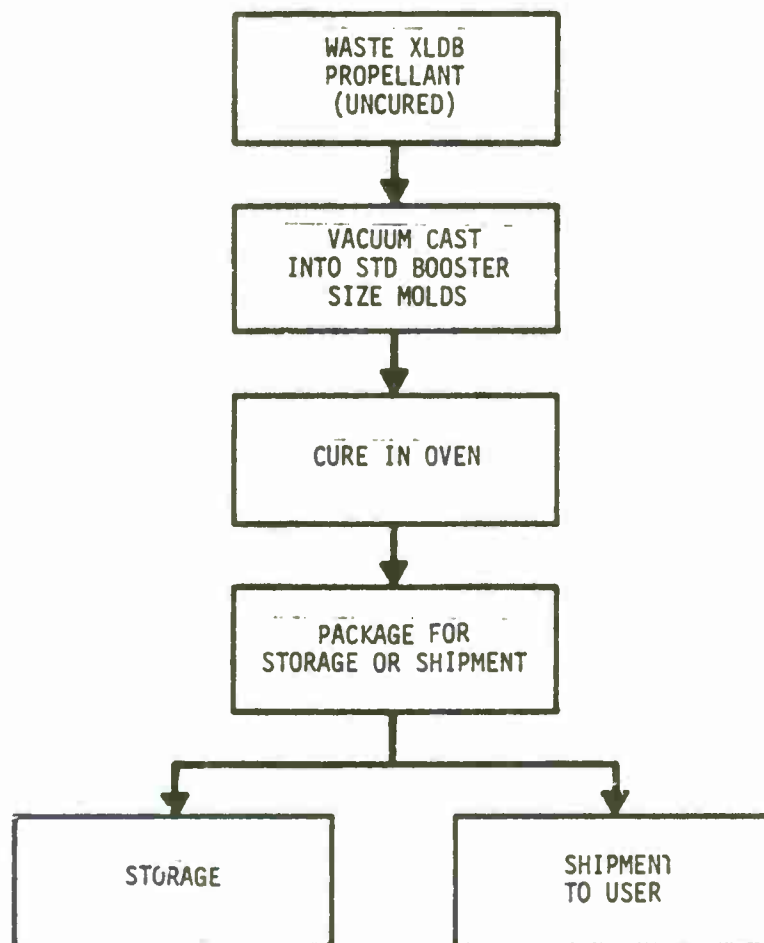


Figure 9. Explosive Booster Process Flow Chart

2.1.2.2 Selective Solvent Extraction Process

The selective solvent extraction process, for the recovery of ingredients from waste propellant, is derived from analytical techniques developed for the AFRL-sponsored Minimum Smoke Chemical Structural Aging Program. These analytical techniques, shown schematically in Figure 10, were designed to isolate and separate the unpolymerized (binder sol) and the polymerized (binder gel) fractions of the propellant binder. Other propellant ingredients are also separated in the process. This separation technique is based on the differential solubilities of major propellant ingredients.

This process is original in that it considers the unpolymerized fraction of the binder (binder sol) as a separate ingredient. Binder sol causes the shredded propellant to adhere and agglomerate. Removal of the binder sol, as planned in this process, greatly improves propellant handling and increases the efficiency of subsequent operations.

The selective solvent extraction process will, theoretically, accommodate composite, high energy and crosslinked, double-base propellants. However, preliminary hazards analysis indicates incompatibility between the nitrate ester and many additives present in composite propellants.

<u>Materials Incompatible With Nitrate Ester</u>	
<u>Ingredient</u>	<u>Function in Propellant</u>
Ferrocene	Burn rate catalyst
Catocene	Burn rate catalyst
Ferric Oxide	Burn rate catalyst
HEMAP	Bonding agent
Tepanol	Bonding agent
Liquid Imines	Bonding-curing agents
MAPO	Curing agent
Iron Linoleate	Cure catalyst

Incompatibility is determined by the Taliani test, in which the two ingredients are combined in a confined vessel for 24 hours at a temperature of 200°F. Incompatibility is defined as an explosion, burning, or a pressure increase greater than 335mm mercury during the test. Incompatible combinations of ingredients may be avoided with separate pretreatment facilities for

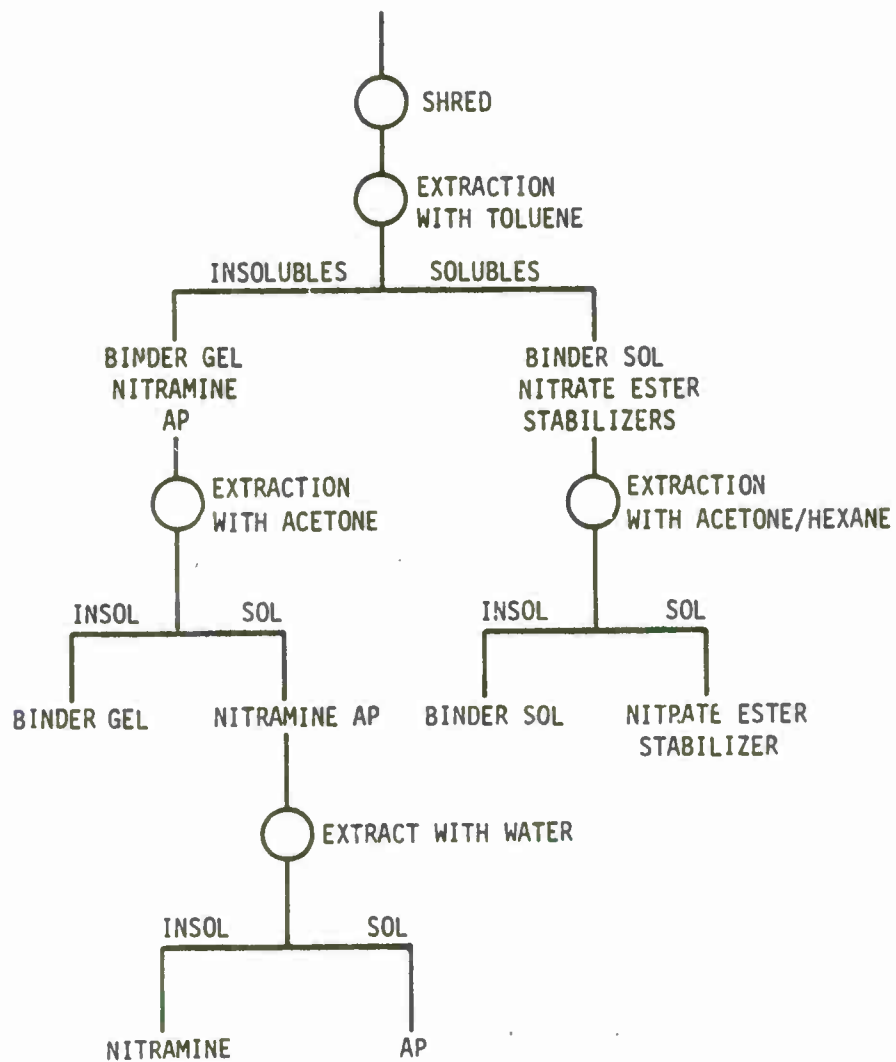


Figure 10. Sol-Gel Extraction from Solid Propellant Chemical Structural Aging Program

composite and nitrate ester propellants. The nitrate ester is removed during pretreatment. Subsequent process facilities need not be separate. Process isolation to avoid incompatible combinations of ingredients is a common precaution in plants processing a variety of propellant types."

Description of Process - The proposed selective solvent extraction process is presented in flow chart form in Figure 11. It includes unit operations for size reduction, nitrate ester and binder sol extraction, nitramine and ammonium perchlorate leaching, and crystallization. All unit operations in the proposed reclamation process are designed to be closed-loop processes with solvent recovery. Raw material costs are thereby reduced and effluent discharge streams eliminated. Common, readily available industrial solvents have been selected for use in the process.

The propellant is first shredded into small pieces or chips to obtain high surface-to-mass ratios. This ratio is a major controlling factor in determining the cycle time and efficiency of subsequent extraction and leaching processes.

The next unit operation is an extraction process to remove the nitrate ester, stabilizers, and the unpolymerized fraction of the binder (binder sol) from the propellant. Several selective solvents are identified in Table 6 and have been used in the laboratory for this purpose. They include chloroform and toluene. Methylene chloride has also been used in other applications for nitrate ester extraction. A cocurrent multistage, batch contact method of extraction has tentatively been selected for this unit operation. This method was selected because it offers a high recovery potential and is adaptable to handling of high energy propellants. The shredded propellants would be placed in a closed vessel in contact with the solvents. The mixture would be gently agitated, settled, and the dilute extract removed. Recovery of the solute is increased as the number of stages and the quantity of solvent is increased. The concentration of the extract becomes increasingly dilute in succeeding stages.

The final unit operation is a leaching and crystallization process to remove the nitramine and ammonium perchlorate (AP) from the shredded propellant. A continuous contact, batch leaching process with crystallization and solvent recovery has tentatively been selected for this unit operation. Recycled solvent is continuously introduced into the leaching vessel and

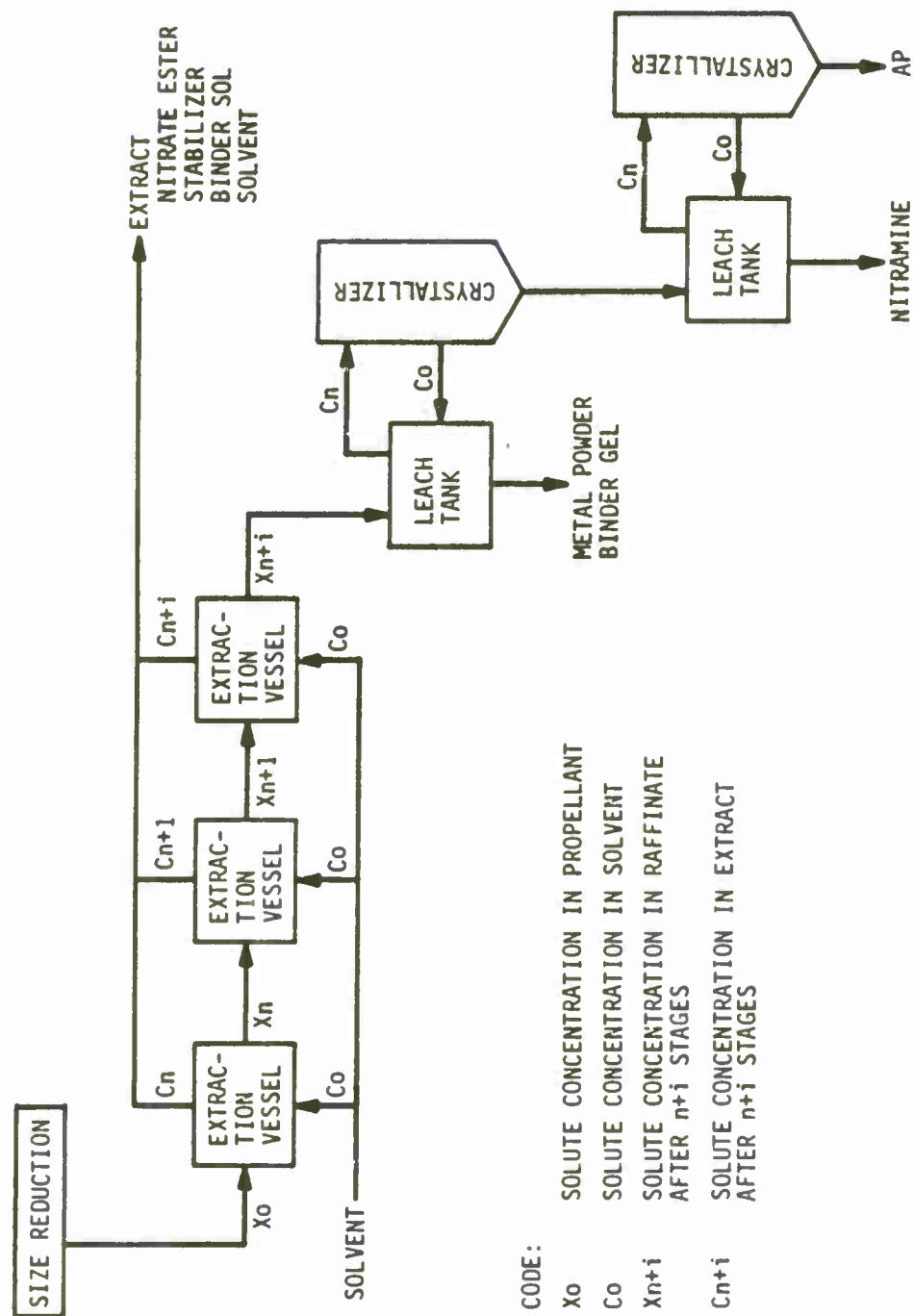


Figure 11. Selective Solvent Extraction Ingredient Recovery Process

TABLE 6

SOLUBILITIES OF SELECTED MINIMUM SMOKE PROPELLANT
CONSTITUENTS AS DETERMINED WITH SOL-GEL
EXTRACTION TECHNIQUES

Solvent	Solute Recovery (%)*					
	Nitramine		Binder Sol			
	RDX	HMX	PEG 2000	PGA	PCP-026	Desmodur N-100
Toluene	2.0	1.3	12.0	102.1	99.8	100.6
Dichloroethane	11.9	2.2	19.4	103.5	100.3	--
Glyme	90.8	39.2	22.5	--	53.3	--
Acetone	100.1	93.8	9.8	100.0	6.7	100.2
Chloroform	2.2	1.4	91.7	102.3	102.9	102.6
Tetrahydrofuran	53.3	--	--	102.9	101.9	--
Hexane	1.0	0.6	0.4	0.2	0.9	0.8
Ethyl Acetate	69.5	31.2	7.1	101.4	11.3	--
Acetonitrile	--	94.4	96.8	--	--	--

*1 g Solute, 25 ml Solvent, 4 Washings

extract continuously withdrawn. The nitramine and AP are removed from the solvent by crystallization and the solvent recovered for reuse. This method was selected because it offers a high recovery potential and an efficient use of the solvent. A two-stage leaching process is required for propellants containing both nitramine and AP. A single stage is required for propellants containing only AP. In the two-stage leaching process, the nitramine and AP are dissolved and removed in acetone or DMSO. Both ingredients are crystallized and the solvent recovered for reuse. The recovered crystals are washed with water to dissolve and remove the AP. After crystallization, the water is recovered as a dilute solution for reuse. The nitramine may be left in a water wet cake for safe handling and storage. The AP may be left as a wet cake or dried depending upon planned disposition. The process would not distinguish between nitramines such as HMX and RDX or between nitrate esters such as NG and TMETN.

The metal powder would be contained in the residual propellant binder residue in this process.

Chemical Reactions - There are no chemical reactions involved in the selective solvent extraction process.

Intermediate and Final Products - The following intermediate products are present in the selective solvent extraction process.

1. Nitramine, oxidizer, solvent solution
2. Nitramine and oxidizer mixed crystals
3. Oxidizer and water solution

The following final products are produced.

1. Nitrate ester, stabilizer, solvent solution
2. Nitramine
3. Oxidizer
4. Metal powder, binder sludge residue

Material Balance - The selective solvent process is defined by the following material balance equations.

1. Nitrate Ester

$$(X_F)(F) = (Y_E)(E) + (Y_R)(R) + (X_N)(N) + (X_A)(A)$$

2. Nitramine

$$(Y_F)(F) = (Y_E)(E) + (Y_R)(R) + (Y_N)(N) + (Y_A)(A)$$

3. Oxidizer

$$(Z_F)(F) = (Z_E)(E) + (Z_R)(R) + (Z_N)(N) + (Z_A)(A)$$

4. Metal Powder

$$(U_F)(F) = (U_E)(E) + (U_R)(R) + (U_N)(N) + (U_A)(A)$$

Where:

- F = propellant feed stock (lb/hr)
- E = extract (lb/hr)
- R = residual sludge (lb/hr)
- N = nitramine produce (lb/hr)
- A = oxidizer product (lb/hr)
- X = nitrate ester concentration (%)
- Y = nitramine concentration (%)
- Z = oxidizer concentration (%)
- U = metal powder concentration (%)

Special Equipment - The selective solvent extraction process uses the following items of major process equipment.

1. Shredder
2. Leaching Tanks
3. Crystallizers
4. Filter
5. Solvent Still

All equipment must be corrosion resistant and compatible with surface ester handling.

Unique Chemical Handling - Handling of nitroglycerin (NG) in its pure state is prohibitive because of its extreme sensitivity. It is normally diluted to a concentration of approximately 70 percent with an inert diluent and stabilizers added for safe storage and handling. The selective solvents used in the extraction process would serve as an inert diluent for interim handling, transfer and storage of the extracted NG. Stabilizers are extracted with the NG. The storage containers would require vapor seals to prevent loss of the diluent by evaporation, however. The NG would be transferred to a less volatile diluent for any long-term storage.

Dry HMX and RDX are very sensitive to ignition by electrostatic discharge. Although processed in a dry powder form, the material is generally transported and stored as a wet cake.

2.1.3 Laboratory Experiments

Laboratory experiments were performed to further expand the data base for the Tompa solvolysis process and the selective solvent extraction process.

Solvolysis - Samples of three polyurethane propellants (PGA-NG-HMX-Al-AP, PEG-NG-HMX-Al-AP, and HTPB-Al-AP) were treated with ethanolamine to evaluate the solvolysis of the binder systems. The NG was removed from the propellants by solvent extraction prior to the solvolysis reaction. Conditions for the solvolysis are summarized below:

Toluene-Isopropanol	1:1
Ethanolamine Concentration	2.0 molar
Propellant-Solvent	30g/100ml
Temperature	20°C
Reaction Time	16 hr

The results of this test are presented in Figure 12. The PGA binder was completely dissolved by the process leaving the HMX, AP, and Al powder in a free flowing slurry. The PEG and HTPB propellants were swollen but not degraded or dissolved by the solvents. Additional treatment for 7 hours at 80°, 90°, and 120°C also failed to produce binder dissolution. It was therefore concluded that the ethanolamine solvolysis process is binder-selective and would therefore have limited application in a propellant ingredient regeneration process.

Selective Solvent Extraction - Four candidate solvents were evaluated for the selective extraction of nitrate esters and several common binder sols in the presence of nitramines, oxidizers, and other ingredients found in most solid propellant ingredients. The solvents evaluated were chloroform, methyl chloroform, toluene, and methylene chloride. The solutes include nitroglycerine, HMX, RDX, AP, and a variety of binder sols. One-gram samples of solute were washed four times with 25 ml of solvent and the solute recovery determined. The results of the tests are summarized in Table 7. As noted in the

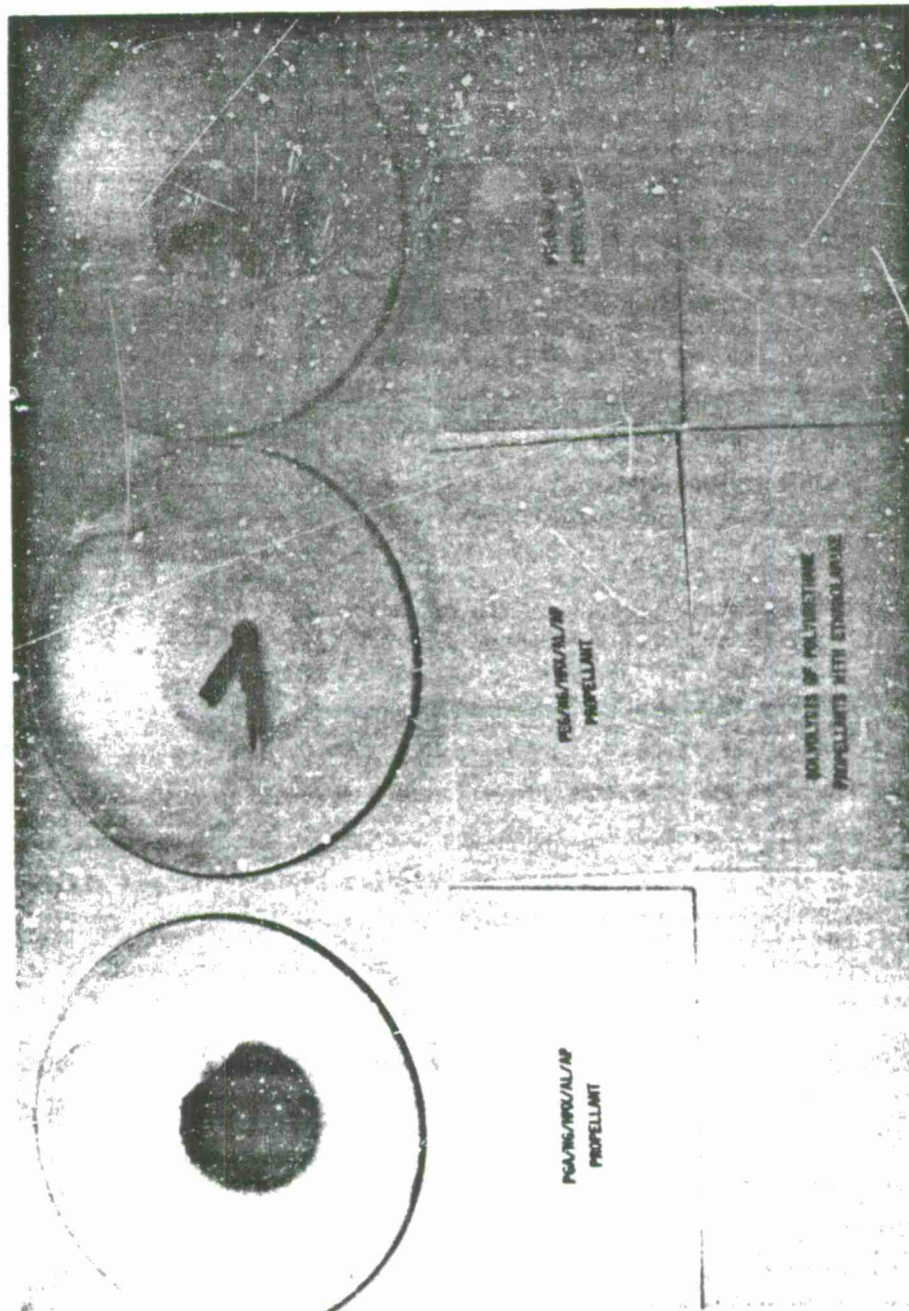


Figure 12. Results of Solvolysis Test

TABLE 7
SOLVENT EVALUATION

Solute	Solute Recovery (%)*			
	Methyl Chloroform	Chloroform	Toulene	Methylene Chloride
• Binder Sol				
• HTPB	100	—	—	—
• CTPB	100	—	—	—
• PEG 2000	—	92	12	—
• PEG 4000	2	—	—	100
• PCP 026	—	100	100	—
• PGA	—	100	100	100
• N-100	100	100	100	100
• BITA	100	—	—	—
• Nitrate Ester				
• NG	100	100	100	100
• Nitramine				
• HMX	1.3	1.4	1.3	1.4
• RDX	—	2.2	2.0	—
• Oxidizer				
• AP	—	—	—	0.5

*1 g Solute, 25 ml Solvent, 4 Washings

table, all four solvents will selectively dissolve nitroglycerine in the presence of HMX, RDX, and AP. Some variation was observed in the ability to dissolve binder sols, especially the polyethylene glycols (PEG).

Two candidate solvents were evaluated for the extraction of HMX and AP. Ternary solubility data were developed for the HMX-AP-acetone and HMX-AP-DMSO systems. These data are presented in Tables 8 and 9 and in Figure 13. As noted in the tables, HMX and AP are soluble in both solvents. The solubility of HMX in DMSO is reduced ten-fold in the presence of AP. The solubility of AP in either solvent was observed to be somewhat insensitive to temperature.

The ignition sensitivities of intermediate products of the selective solvent extraction process were determined. Samples of NEPE-HMX-AP-Al propellant were extracted with chloroform-acetone and chloroform-DMSO to provide representative intermediate product samples. The ignition modes evaluated were impact, friction, electrostatic discharge, and temperature. The results of these tests are summarized in Table 10. Two observations are apparent from these data.

1. Chloroform acts as a solvent and an inert diluent for safe handling of the extracted NG.
2. The dry HMX-AP crystals are sensitive to ignition by impact and friction. The wet cake is electrostatic sensitive due to the flammability of the acetone.

Testing of the DMSO extract was discontinued. The high boiling point and low solubility dependence on temperature exhibited by DMSO made HMX-AP crystallization by evaporation and cooling very difficult. HMX crystallization could be induced by the addition of water, but recovery of AP from the resulting DMSO-water solution becomes even more involved.

2.1.4 Evaluation of Available Reclamation Technology

The potential reclamation methods identified were evaluated based upon the following technical and economic indicators.

1. Technical Feasibility
2. Adaptability
3. Complexity
4. Raw Materials

TABLE 8
TERNARY SOLUBILITY DATA
HMX, AP, ACETONE

Temperature (°F)	Concentration (g/100 ml sol)		Concentration (wt %)*		
	AP	HMX	AP	HMX	Acetone
40	1.63	—	2.06	0.00	97.94
	—	1.70	0.00	2.15	97.85
	2.35	2.87	2.97	3.62	93.41
60	1.60	—	2.02	0.00	97.98
	—	2.29	0.00	2.89	97.11
	2.50	3.11	2.16	2.92	92.91
80	1.55	—	1.96	0.00	98.04
	—	2.20	0.00	2.78	97.22
	2.35	3.54	2.97	4.47	92.56
100	1.68	—	2.12	0.00	97.88
	—	2.54	0.00	3.21	96.79
	2.38	4.11	3.01	5.19	91.80
120	1.68	—	2.12	0.00	97.88
	—	2.94	0.00	3.71	96.29
	2.37	4.64	2.99	5.86	91.15

*Calculated Based on Solution Density of 79.2 g/100 ml.

TABLE 9

TERNARY SOLUBILITY DATA
HMX, AP, DMSO

Temperature (°F)	Concentration (g/100 ml sol)		Concentration (wt %)*		
	AP	HMX	AP	HMX	DMSO
40	47.1	—	37.4	0.0	62.6
	—	**	—	**	**
60	49.7	—	39.4	0.0	60.6
	—	36.8	0.0	29.2	70.8
	47.2	3.1	37.5	2.5	60.0
80	50.4	—	40.0	0.0	60.0
	—	45.6	0.0	36.2	63.8
	48.3	4.9	38.3	3.9	57.8
100	50.7	—	40.2	0.0	59.8
	—	47.9	0.0	38.0	62.0
	47.3	6.1	37.5	4.8	57.7
120	50.7	—	40.2	0.0	59.8
	—	49.1	0.0	40.0	60.0
	42.5	8.5	33.7	6.7	59.6

*Calculated Based on Solution Density of 1.26

**Phase Change at 40°F

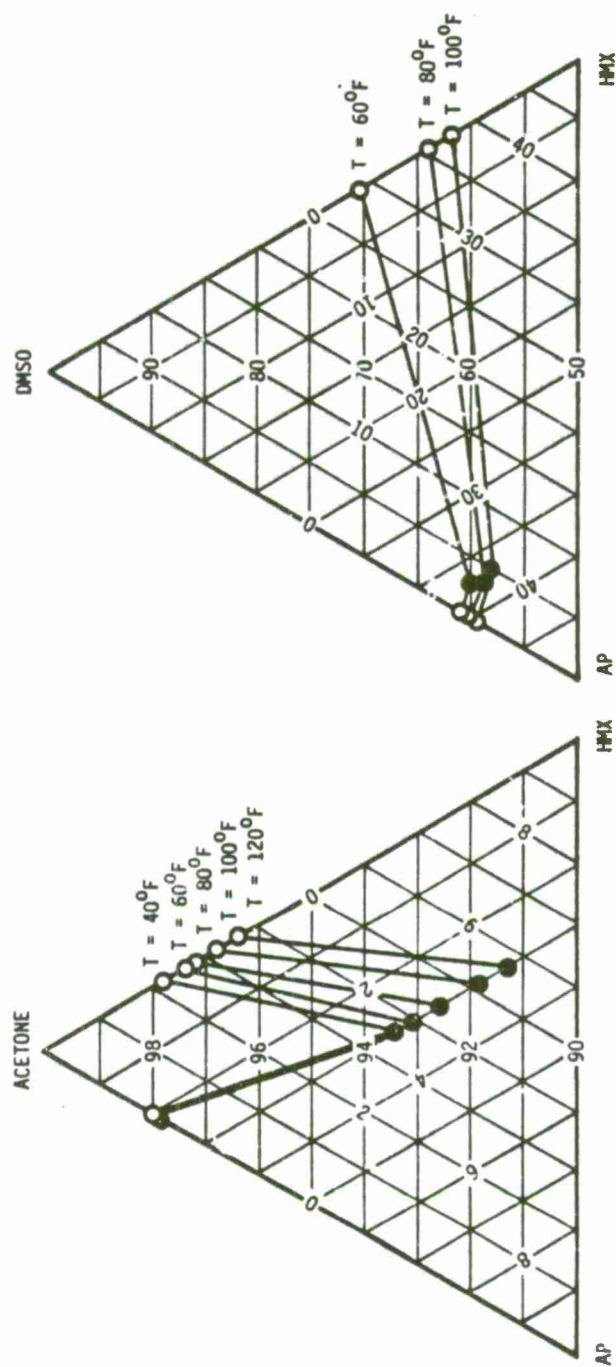


Figure 13. Ternary Solubility Diagram

TABLE 10

IGNITION SENSITIVITY OF INTERMEDIATE PRODUCTS
NEPE/HMX/AP/AL PROPELLANT

Sample Description	Threshold Ignition Level (TIL) ^a			Autotemperature Temperature (°C)	Differential Scanning Calorimeter (°C)
	Impact (cm)	Friction (psi)	Electrostatic Discharge (joules)		
<u>Chloroform Extract</u>					
• Solution	24	100 at 4 ft/sec	1.25	>24	---
• 70% Solvent, 30% Solute					
• Baseline	4.9	50 at 4 ft/sec	4.25	>24	464
• 96% MC, 3% STAB., 1% SOL					
<u>Acetone Extract</u>					
• Wet Cake	11	100 at 6 ft/sec	0.04	>24	---
• 98% Product, 2% Solvent					
• Dry Product	3.5	25 at 4 ft/sec	6.25	>24	503
• 76.7% HMX, 20.8% AP, 0.5% MC					
<u>Binder Baseline</u>					
• 24% CHL, 67% AL, 4% BCL, 4% AP	80	800 at 8 ft/sec	6.25	>24	---

^a0.01 Probability of Ignition
at 300°Y
see First Exotherm

5. Scale-up Capability
6. Safety
7. Environmental Impact

A desirability rating from 0.1 to 1.0 was assigned to each indicator according to the criteria defined in Table 11. Technical feasibility was based on the amount of supporting data available. Adaptability was based on the range of propellant types that the process would accommodate. Complexity was established by the number of unit operations. Process raw material requirements indicate the degree of solvent and chemical consumption. Scale-up capability was based on the uniqueness of the unit operation. Safety considers the degree of hazards associated with the process. Environmental impact was based on the quantity and type of effluent streams. Markets for the reclaimed ingredients or conversion products were not considered in the evaluation since they have not been developed in most instances.

Each process was assigned individual ratings from each technical and economic indicator. These ratings are summarized in Table 12. A composite rating or desirability factor* was then calculated for each process. Ratings varied from 0.25 to 0.82 for the processes evaluated. In the composite propellant disposal processes, the McBride AP recovery process received a low rating, primarily because of the nature of the ammonia solvent and the detonability of ammonia-AP solutions. The McIntosh aluminum powder recovery process was rated low because of economics--costly raw material consumption in the esterification process and high energy consumption in the pyrolysis process. The Sinclair confined space shot process was not felt to be scaleable and had potential safety problems. The Tompa NQ-AP recovery process and the Williams NHC recovery process are restricted to specific propellant formulations and therefore are limited in application.

All high energy propellant disposal processes received a low safety rating since explosive materials (NG, HMX, etc.) are involved. In addition, the Tompa solvolysis process was rated low for adaptability and raw material since it appears to be binder selective and consumes chemicals in the process.

$$*D = \sqrt[n]{d_1 \cdot d_2 \cdot \dots \cdot d_n}$$

TABLE 11

PROCESS EVALUATION CRITERIA

• Technical Feasibility	
• Pilot Plant and/or Production History	1.0
• Laboratory Data	0.5
• Theoretical	0.1
• Adaptability	
• High Energy and Composite Propellants	1.0
• High Energy or Composite Propellants	0.5
• Specific Propellant Formulations	0.1
• Complexity	
• 1 to 6 Unit Operations	1.0
• 7 to 9 Unit Operations	0.5
• >10 Unit Operations	0.1
• Process Raw Materials	
• No Material Consumption	1.0
• Solvent Replacement and/or Make-up	0.5
• Reactive Materials Consumed	0.1
• Scale-up Capability	
• Standard Unit Operation	1.0
• Variation/New Application	0.5
• New Concept	0.1
• Safety	
• Nonhazardous	1.0
• High Pressure, High Temperature or Flammable	0.5
• Explosive or Toxic	0.1
• Environmental Impact	
• No Effluents	1.0
• One or More Nonhazardous Effluents	0.5
• One or More Hazardous Effluents	0.1

TABLE 12
PROCESS EVALUATION

Process	Tech Feas	Adapt	Compl	Raw Mtl	Scale- up	Safety	Envir Impact	D*
<u>Composite Propellants</u>								
McBride - AP Recovery	0.5	0.5	1.0	0.5	0.5	0.1	0.5	0.44
McIntosh - Fire Starter	0.5	0.5	1.0	1.0	1.0	1.0	1.0	0.82
Slurry Explosive	0.5	0.5	1.0	1.0	1.0	1.0	1.0	0.59
AP Recovery	0.5	0.5	1.0	1.0	1.0	1.0	0.5	0.74
Al Recovery	0.5	0.5	1.0	0.1	1.0	0.1	0.5	0.38
Sinclair - Confined Space Shot	0.5	1.0	1.0	1.0	0.1	0.1	0.5	0.42
Tompa - MQ/AP Recovery	0.5	0.1	0.5	1.0	1.0	0.5	0.5	0.48
Tarter/Standard Missile	0.5	0.5	0.5	0.1	1.0	0.5	0.5	0.44
Sidewinder	0.5	0.5	0.5	0.1	1.0	0.5	0.5	0.44
Williams - MHC Recovery	0.5	0.1	0.5	0.5	1.0	0.5	0.5	0.44
<u>High Energy Propellants</u>								
Tompa - Sc'volysis	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.25
Explosive Primer	0.5	0.5	1.0	1.0	1.0	0.1	1.0	0.59
Sol-Gel Extraction	0.5	1.0	0.5	0.5	0.5	0.1	0.5	0.44

$$*D = \frac{1}{n} \int_0^n d_1 \cdot d_2 \cdot \dots \cdot d_n$$

Based on this preliminary evaluation, the following nonincineration disposal methods were identified as the most economical and environmentally acceptable for further evaluation:

1. Composite (Class 1.3) Propellant
 - a. Conversion to a fire starter
 - b. Conversion to a slurried explosive
 - c. Recovery of ammonium perchlorate by aqueous leaching
2. High Energy (Class 1.1) Propellant
 - a. Conversion to an explosive booster
 - b. Recovery of major ingredients by a selective solvent extraction process

The composite propellant disposal methods identified are being evaluated and scaled up in a Manufacturing Technology For Solid Propellant Ingredients-Preparation Reclamation Program funded by the Air Force Wright Aeronautical Laboratories (Contract F33615-81-C-5125). Therefore, only the high energy propellant disposal methods will be evaluated and discussed in the balance of this report.

2.2 BENCH SCALE DEMONSTRATION OF SELECTED DISPOSAL METHODS

2.2.1 Conversion of Class 1.1 Propellant to an Explosive Booster

Ireco Chemicals, a local manufacturer and distributor of explosive boosters, was consulted about qualification requirements for new booster formulations. A variety of explosive geometries and configurations are used by Ireco. The prime configuration considered for a Thiokol explosive booster is 3 in. in diameter and 2-1/2 in. long with a 5/16 in. diameter center perforation for placement of a primacord or cap. The basic requirements for an explosive booster are as follows:

- Safe handling and storage over a temperature range of -40° to +120°F.
- Consistent detonation when initiated with a number 6 blasting cap or a 50-grain primacord over a temperature range of -40° to +120°F.
- Nondetonation when initiated with a 7.5-grain primacord.

It was noted that aluminum foil lined cartridges would be required to prevent nitroglycerin migration.

Handling - In order to evaluate handling characteristics of the Thiokol explosive boosters, samples of a PGA-NG-HMX-AP-Al Class 1.1 propellant were tested to determine the ignition sensitivity over the expected operating temperature range of -40° to $+120^{\circ}\text{F}$. Two common booster materials, Pentolite and TNT, were also tested to provide comparative data. The results of these tests are presented in Table 13. The data include both a 50% ignition level and a threshold ignition level (TIL) based on a 0.01 probability. As noted in Figures 14, 15, and 16, the ignition sensitivity of the Class 1.1 propellant is reasonably stable over the temperature range tested and is generally less sensitive to ignition, based on the TIL, than TNT, and Pentolite.

Storage - Sacrificial stabilizers are added to Class 1.1 propellants in order to control the decomposition rate of the nitrate ester. The safe life of the propellant is determined by measuring the stabilizer depletion rate at various temperatures and extrapolation of this rate to zero stabilizer concentration at which time nitrate ester decomposition proceeds rapidly. The effect of temperature on stabilizer depletion rate and therefore safe life of a typical Class 1.1 propellant is illustrated in Figure 17. As noted, the predicted safe life of the propellant at 100°F is 70 years. An increase in temperature of 20°F (to 120°F) reduces the safe life to approximately 10 years. Cyclic temperature effects would be expected to be cumulative.

Detonation Sensitivity - Nine explosive boosters were tested to determine sensitivity to initiation by primacord. Test results are summarized in Table 14. Initial tests conducted with a 5/16-in. diameter bore in the booster grain were negative. The bore diameter was decreased to 1/4-in. and the tests were repeated. Tests were positive with 50 and 70 grain primacord and negative with 7.5 grain primacord.

Detonation Verification - Six explosive boosters were tested to verify initiation by blasting cap and primacord over the temperature range of -40° to $+120^{\circ}\text{F}$. A 5/16-in. bore diameter was used with the blasting cap initiator and two 1/4-in. diameter holes used with the primacord. The results of these tests are presented in Table 15. All tests were positive. A typical test arrangement is illustrated in Figures 18 and 19 using a blasting cap and primacord for initiation, respectively. A post-test witness plate is shown in Figure 20 indicating booster detonation.

TABLE 13

IGNITION SENSITIVITY DATA FOR
CANDIDATE EXPLOSIVE BOOSTER MATERIALS

Sample	Temp (°F)	Impact		Friction		Electrostatic	
		50% (in.)	TIL** (cm)	50% (lb)	TIL** (lb)*	50% (joules)	TIL** (joules)
Class 1.1 Propellant***	-40	10.77	21	>64	240	>8	6.25
	-20	10.40	21	>64	240	>8	6.25
	0	12.23	26	>64	240	>8	1.25
	+20	9.09	26	>64	240	>8	1.25
	+40	11.10	26	>64	180	>8	1.25
	+60	9.70	33	>64	240	>8	1.25
	+120	9.14	26	63	180	>8	1.25
	-40	31.18	21	>64	100	0.30	0.075
	+60	26.40	13	>64	50	0.08	0.040
	+120	27.60	13	>64	50	0.10	0.060
TNT	-40	>46	26	>64	130	0.38	0.250
	+60	>46	26	>64	50	0.19	0.075
	+120	>46	21	>64	50	0.68	0.250

*Measured at 8 ft/sec

**Threshold Ignition Level, 0.01 Probability

***PGA-NG-HMX-AP-AI

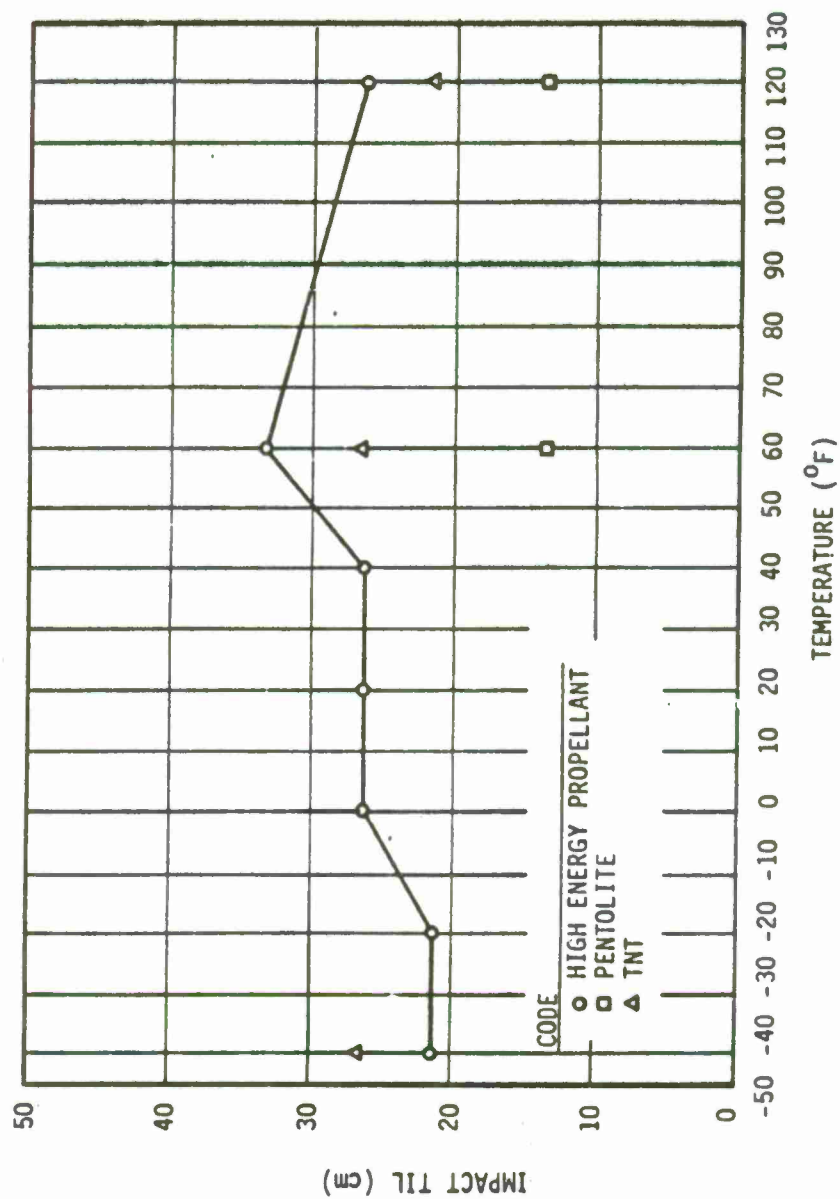


Figure 14. Effect of Temperature on Impact Sensitivity of Explosive Booster Formulations

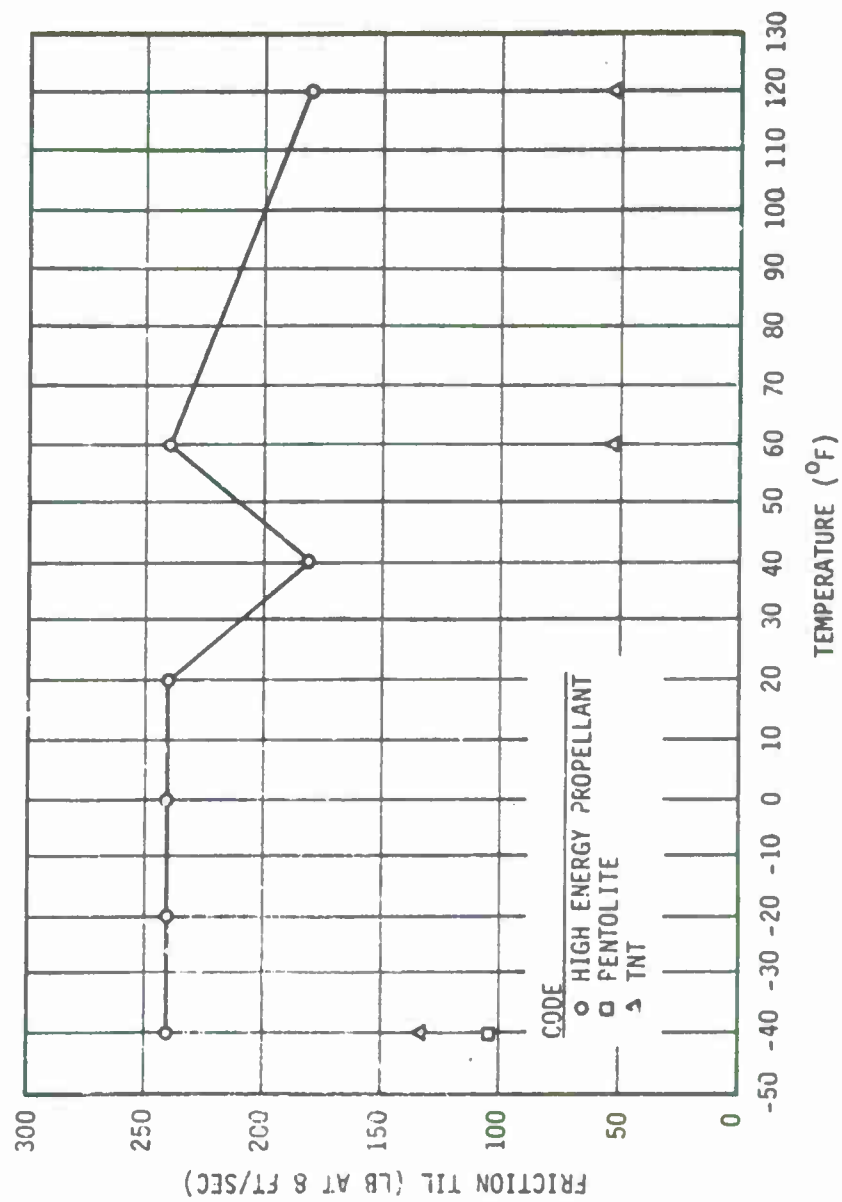


Figure 15. Effect of Temperature on Friction Sensitivity of Explosive Booster Formulations

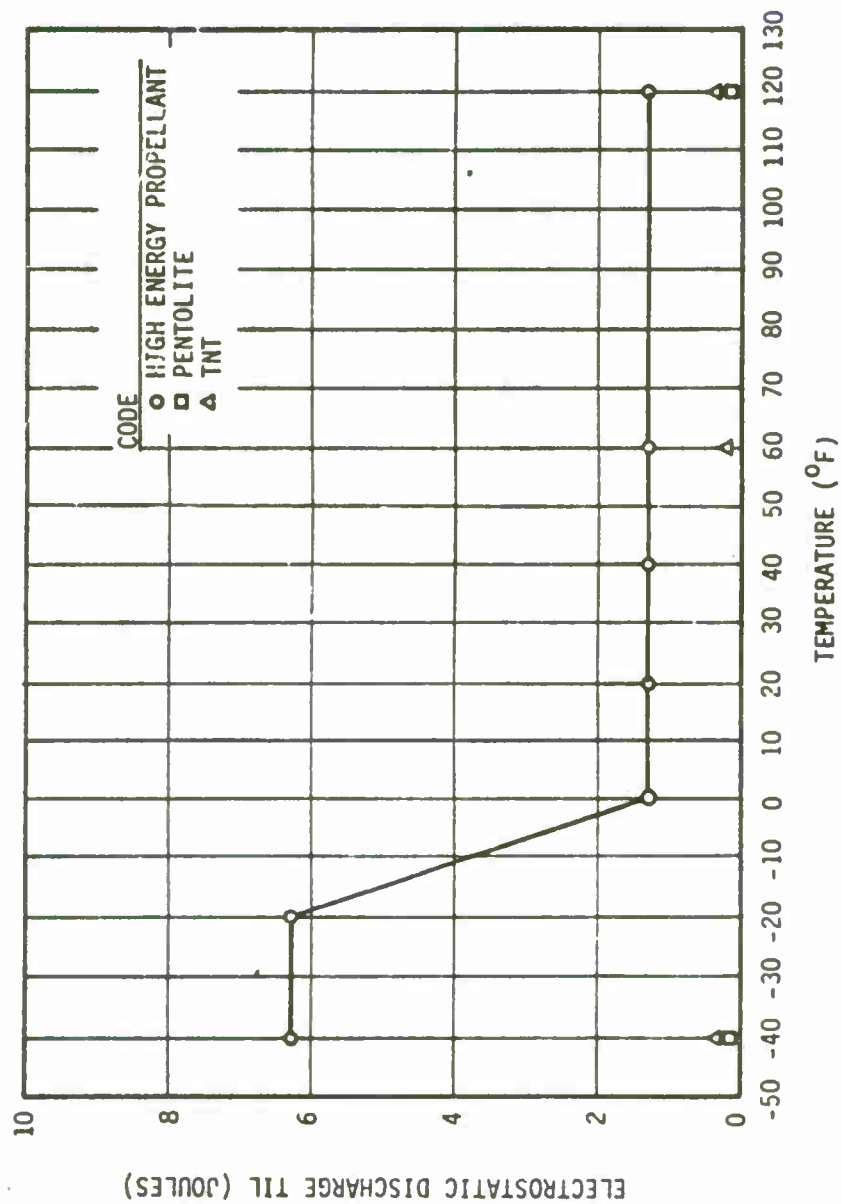


Figure 16. Effect of Temperature on Electrostatic Sensitivity of Explosive Booster Formulations

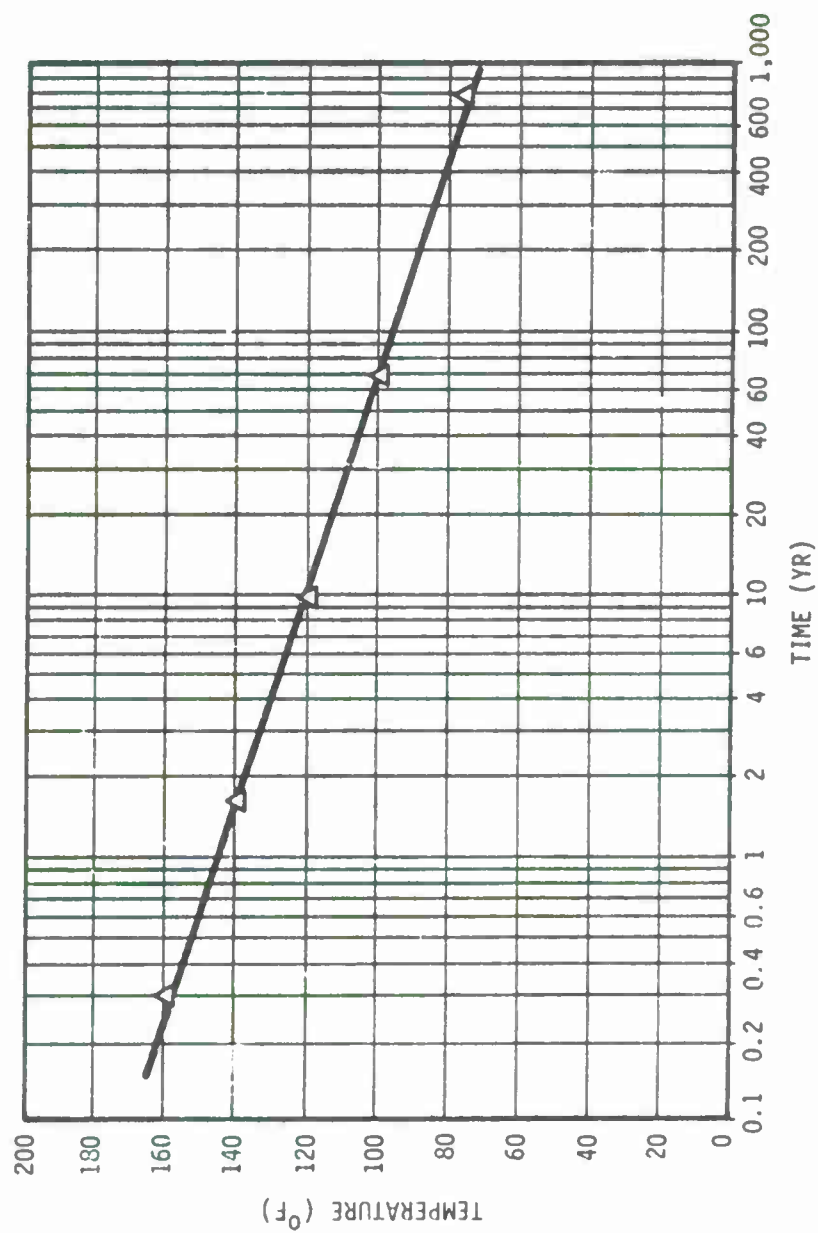


Figure 17. Effect of Temperature on the Safe Life of a Typical High Energy Propellant

TABLE 14

DETONATION SENSITIVITY OF EXPLOSIVE BOOSTER
CLASS 1.1 PROPELLANT*

<u>Test No.</u>	<u>Primacord (gr RDX/ft)</u>	<u>Temp (°F)</u>	<u>Bore Diameter (in.)</u>	<u>Results</u>
1	50	70	5/16	Burned
2	70	70	5/16	Burned
3	70	70	1/4	Detonated
4	70	70	1/4	Detonated
5	50	70	1/4	Detonated
6	50	70	1/4	Detonated
7	7.5	70	1/4	No Reaction
8	7.5	70	1/4	No Reaction
9	7.5	70	1/4	No Reaction

*PGA-NG-FMX-AP-A1

TABLE 15

DETONATION CHARACTERIZATION OF EXPLOSIVE BOOSTER
CLASS 1.1 PROPELLANT*

<u>Test No.</u>	<u>Initiation</u>	<u>Temperature (°F)</u>	<u>Results</u>
1	No. 6 Cap	-40	Detonated
2	No. 6 Cap	+70	Detonated
3	No. 6 Cap	+120	Detonated
4	50 gr Primacord	-40	Detonated
5	50 gr Primacord	+70	Detonated
6	50 gr Primacord	+120	Detonated

* PGA-NG-HMX-AP-A1

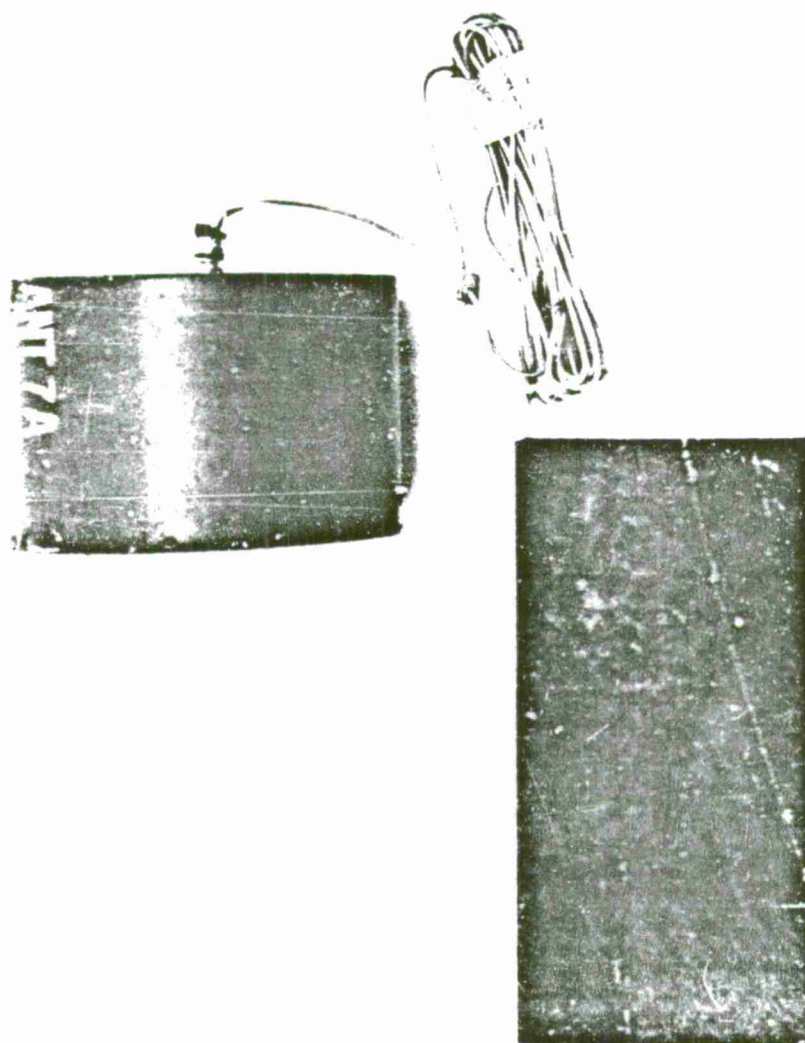


Figure 18. Explosive Booster Initiated with Blasting Cap

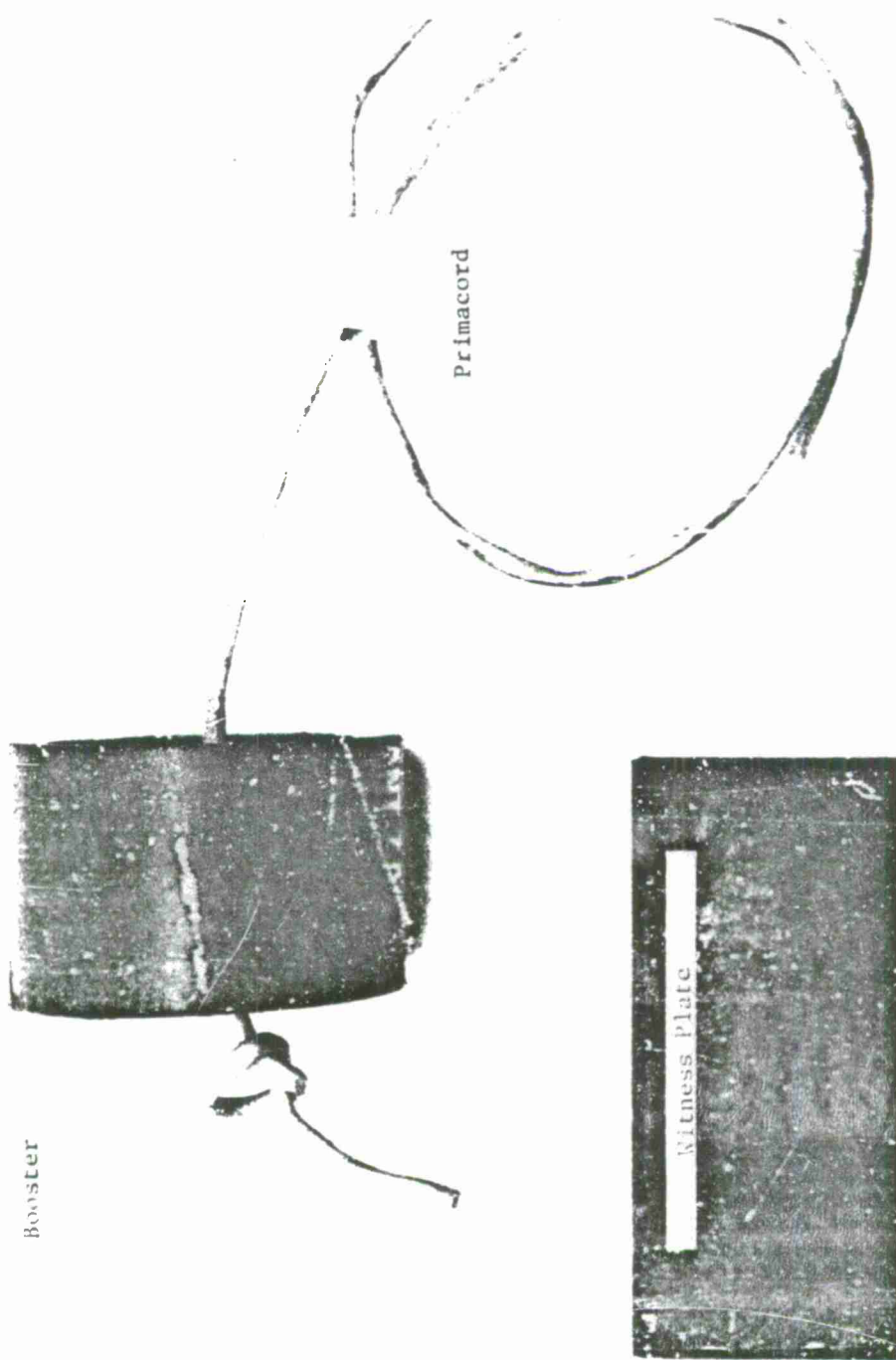


Figure 19. Explosive Booster Initiated with Primacord



Figure 20. Witness Plate after Explosive Booster Test

2.2.2 Selective Solvent Extraction Process

The objective of the selective solvent extraction process is to isolate and recover major ingredients from high energy, Class 1.1 solid propellants, including the following:

- a. Nitrate Ester (NG, TMETN, etc.)
- b. Nitramine (HMX, RDX)
- c. Inorganic Oxidizer (AP, etc.)

Metal powders present in the formulation are retained in the depleted binder residue.

A review of conventional extraction technology was conducted and a basic extraction process selected for nitrate ester, nitramine and inorganic oxidizer recovery. Bench scale tests were conducted with a representative NEPE/HMX/AP/Al* Class 1.1 propellant to provide engineering design and scale up data for each major unit operation. Tests included:

- a. Solvent Evaluation
- b. Extraction Rate
- c. Phase Equilibria

The process design was defined and a process flow chart constructed. The process was modeled on a bench scale to provide proof of principle, determine yield, define product purity and to evaluate ignition sensitivities of intermediate and final products.

2.2.2.1 Review of Conventional Extraction Technology

Four basic extraction processes were considered for nitrate ester, nitramine and oxidizer extractions:

- a. Batch - single contact
- b. Batch - continuous contact
- c. Multistage - cocurrent contact
- d. Multistage - countercurrent contact

A schematic description of these processes is presented in Figure 21. The advantages and disadvantages of each process are summarized in the following paragraphs.

*NEPE = nitrate ester/polyether (polyethylene glycol)

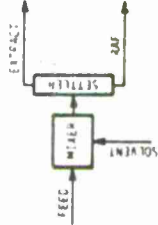
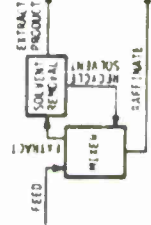
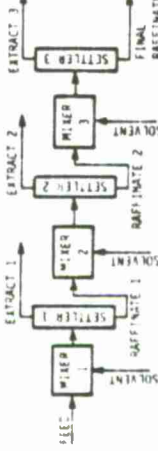
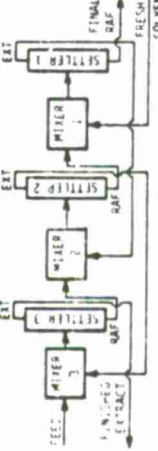
PROCESS	SCHEMATIC	REMARKS		
		SOLVENT REQUIREMENT	YIELD	PRODUCTION RATE
1 BATCH - SINGLE CONTACT		HIGH VOLUME	POOR	BATCH
2 BATCH - CONTINUOUS CONTACT		LOW VOLUME	GOOD	DECREASES WITH TIME
3 MULTISTAGE - COCURRENT		HIGH VOLUME	GOOD	DECREASES WITH TIME
4 MULTISTAGE - COUNTERCURRENT		LOW VOLUME	GOOD	CONTINUOUS

Figure 21. Candidate Leaching Processes

- a. Single Contact Batch - In the single contact batch leaching process, the entire quantity of solvent and propellant are charged into one container, agitated, settled, and the extract withdrawn. The amount of solute extracted is fixed solely by its solubility and the total quantity of solvent used. A relatively large amount of solvent, and hence large leach vessels, are therefore required to attain high extractions. Since the propellant residue is in equilibrium with concentrated extract solution, relatively large amounts of solute at high concentrations are retained. Solute recovery is therefore relatively poor without very efficient dewetting and extensive fresh solvent washings.
- b. Continuous Contact Batch - In this process, the propellant is charged into the leach vessel, solvent continuously introduced and extract continuously withdrawn. The solute is continuously removed from the extract by crystallization and the solvent recovered for reuse. The amount of solute extracted is dependent on the total volume of solvent contacted or, since the solvent is recycled, total contact time. This process provides a more efficient use of solvent than the single contact batch method. Smaller volumes of solvent and smaller leaching vessels are therefore required. The final propellant residue is in equilibrium with a lean extract solution in this case so that solute retention is relatively low. Solute recovery is therefore increased over the single contact batching process. Dewetting and washing requirements are less rigorous. The extraction rate is not constant in this process, however, and the concentration of solute in the extract solution decreases with time as equilibrium conditions are approached.
- c. Multistage, Cocurrent - In this process, fresh solvent is introduced to the propellant in the leach

vessel, the mixture agitated, settled, and the extract withdrawn. The cycle is repeated in successive stages using depleted propellant residue from the previous stage as feed stock. Extraction rate is not constant and the concentration of solute in the extract solution becomes increasingly dilute in succeeding stages. The final propellant residue is in equilibrium with very dilute extract so that solute retention is very low. Total solute recovery is normally very high with this process with minimal dewatering and washing requirements.

- d. Multistage, Countercurrent - In this process, recycled solvent and shredded propellant are introduced to opposite ends of a series of contact stages. Liquid (extract) and solid (propellant residue) phases progress countercurrently from stage to stage through the system. The contacting mixture in each stage is agitated for a designated time period to attain equilibrium, settled and separated. The stages may be operated on a batch basis or continuously. Extract removed from the last stage is in equilibrium with the shredded propellant and therefore concentrated with solute. The propellant residue removed from the opposite end of the system is in equilibrium with the lean, recycled solvent. Solute retention is therefore low and recovery high. Recovery can be increased by fresh solvent washing. Extraction rate is relatively constant in this process and the solute concentration in the extract remains high.

The multistage, cocurrent process was selected for the nitrate ester extraction process. While not as efficient as multistage, countercurrent extraction, the cocurrent process does provide a high yield and minimizes handling requirements for both the propellant and extract solution. Both are essential for nitrate ester containing materials.

The batch-continuous contact process was selected for the nitramine and oxidizer extraction process. This process also provides a high yield and minimizes material handling requirements but also provides a more efficient use of solvent than does the cocurrent process.

2.2.2.2 Nitrate Ester Extraction Process

Evaluation of Candidate Solvents

Four candidate solvents, methyl chloroform, chloroform, toluene, and methylene chloride, were identified and evaluated in paragraph 2.1.3 for the preferential dissolution of nitrate esters. The results of this evaluation and other supplemental physical and chemical properties of each solvent are summarized in Table 16.

The criteria for selection of a solvent is its ability to selectively dissolve the nitrate ester, stabilizers, and binder sol in the presence of other propellant ingredients. A low boiling point is also desired to facilitate its removal by distillation, sparging, etc., in subsequent transfer processes. Low flammability and toxicity are also desirable.

All four solvents evaluated were found to selectively dissolve the nitrate ester. Only two solvents, chloroform and methylene chloride, readily dissolve the polyethylene glycol (PEG) binder sol, however. Boiling points ranged from 39.8° to 110.4°C, flash points from 4.4°C to none, toxicity from moderate to high. Methylene chloride also has a history of application as a solvent and inert diluent for nitrate esters on a production scale.

Methylene chloride was selected as the solvent for nitrate ester extraction in the selective solvent extraction process. The logic used in this selection is summarized below.

- a. Methylene chloride is an excellent solvent for nitrate ester and binder sol.
- b. The solubility of nitramines and inorganic oxidizer in methylene chloride is very low.
- c. It has a relatively low boiling point to facilitate removal from the nitrate ester during subsequent transfer operations.

TABLE 16

Selective Solvent Evaluation
For
Nitrate Ester/Binder Sol Extraction

Solvent	Dissolved		Boiling Point (°C)	Flash Point (°C)	Toxicity		Prior History With NG
	Nitrate Ester & Binder Sol	Nitramine & Oxidizer			Inhalation	Oral	
Methyl Chloroform	Yes, except PEG	No	74.1	None	High	Mod	No
Chloroform	Yes	No	61.3	None	High	High	No
Toluene	Yes, except PEG	No	110.4	4.4	Mod	Mod	No
Methylene Chloride	Yes	No	39.8	None	Mod	Mod	Yes

- d. It exhibits a low flammability.
- e. It is of moderate toxicity.
- f. It has a prior history of usage in nitrate ester processing.

The solvent is also readily available on an industrial scale at moderate cost.

Extraction Rate

Bench scale tests were conducted to define the extraction rate of nitroglycerin, a nitrate ester, from an NEPE/HMX/AP/Al Class 1.1 solid propellant. Propellant chips were placed in contact with methylene chloride and the NG/stabilizer content of the extract solution monitored. The following process variables were evaluated in the tests:

- a. Specific surface area
- b. Solute/solvent ratio
- c. Temperature

The results of these tests are summarized in Table 17 and in Figures 22 and 23. As noted, the extraction rate increases with temperature and specific surface area but is relatively insensitive to the solute/solvent ratio over the range of data evaluated. A contact time of approximately 10 minutes was required to reach equilibrium under optimum conditions of 70°-80°F and a specific surface area of 1,125 in.²/lb.

Extract and Residue Phase Equilibria

The nomenclature used in phase equilibria defines the three components of the extraction system as follows.

Component A	Solvent (methylene chloride)
Component B	Insoluble Solid (binder, HMX, AP, aluminum)
Component C	Solute (NG, stabilizer)

In order to define the system on rectangular coordinates, two concentration terms are used (Figure 24).

N = weight fraction of insoluble solid $\frac{B}{(A + C)}$

x, y^* = weight fraction of solute in the extract and residue, respectively $\frac{C}{(A + C)}$

TABLE 17

NG/Stabilizer Extraction Rate
With Methylene Chloride

Propellant	Specific Surface Area (in ² /lb)	Temperature (°F)	Solute/Solvent Ratio	Time (min)	Extract Concentration (% NG)	Recovery (%)
NEPE/HMX/AP/AL	570*	80	0.046	15	2.85	64.8
				30	3.71	84.4
				45	3.95	89.8
				60	4.07	92.5
				90	4.05	92.1
				120	4.02	91.4
NEPE/HMX/AP/AL	570*	70	0.050	15	2.64	58
				25	3.51	76
				69	3.87	83
				128	3.67	80
				184	4.19	90
NEPE/HMX/AP/AL	570*	70	0.020	16	1.25	65
				29	1.41	75
				64	1.59	82
				127	1.53	80
				215	1.61	85
NEPE/HMX/AP/AL	1125**	70	0.020	20	1.84	91
				30	1.83	93
				40	1.91	93
				50	1.91	95
				60	1.82	93
				120	1.88	92
				180	1.86	91
				240	1.92	96

* 1/8 x 1/16 inch

** 1/8 x 1/32 inch

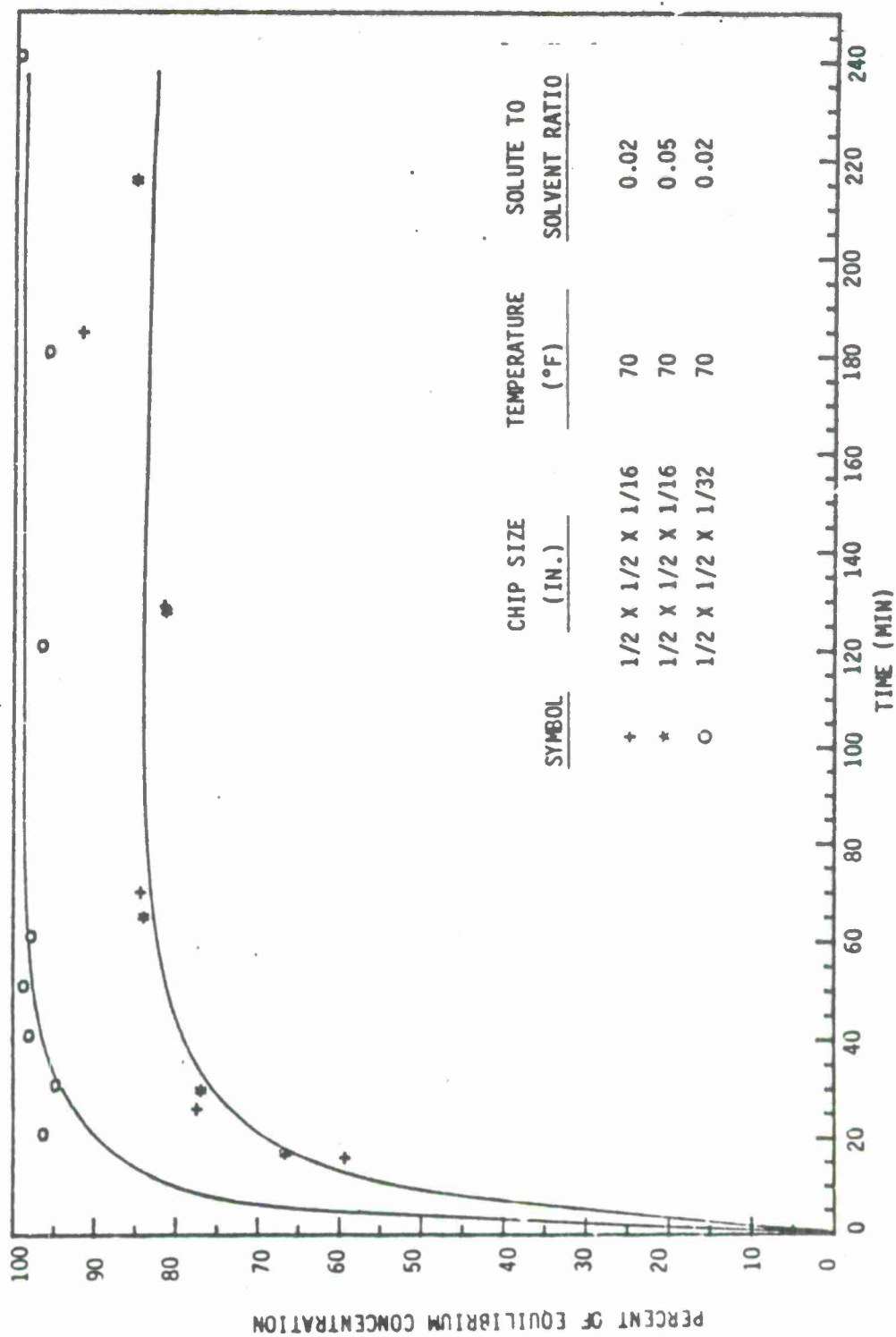


Figure 22. Effect of Chip Size and Solute to Solvent Ratio on the Extraction Rate of NG from NEPE-HMX-AP-AL Propellant

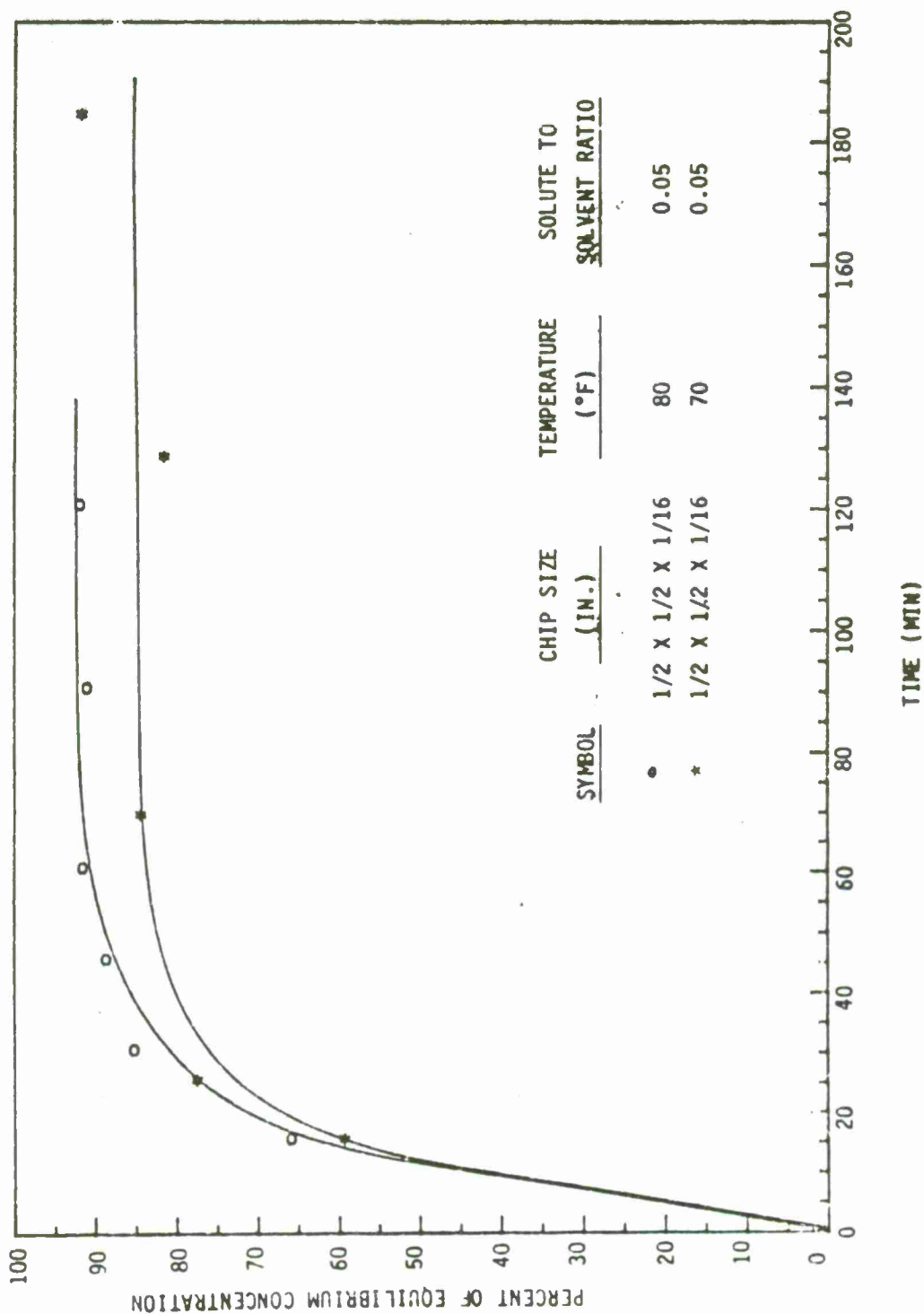


Figure 23. Effect of Temperature on the Extraction Rate of
NG from NEPE-HMX-AP-Al Propellant

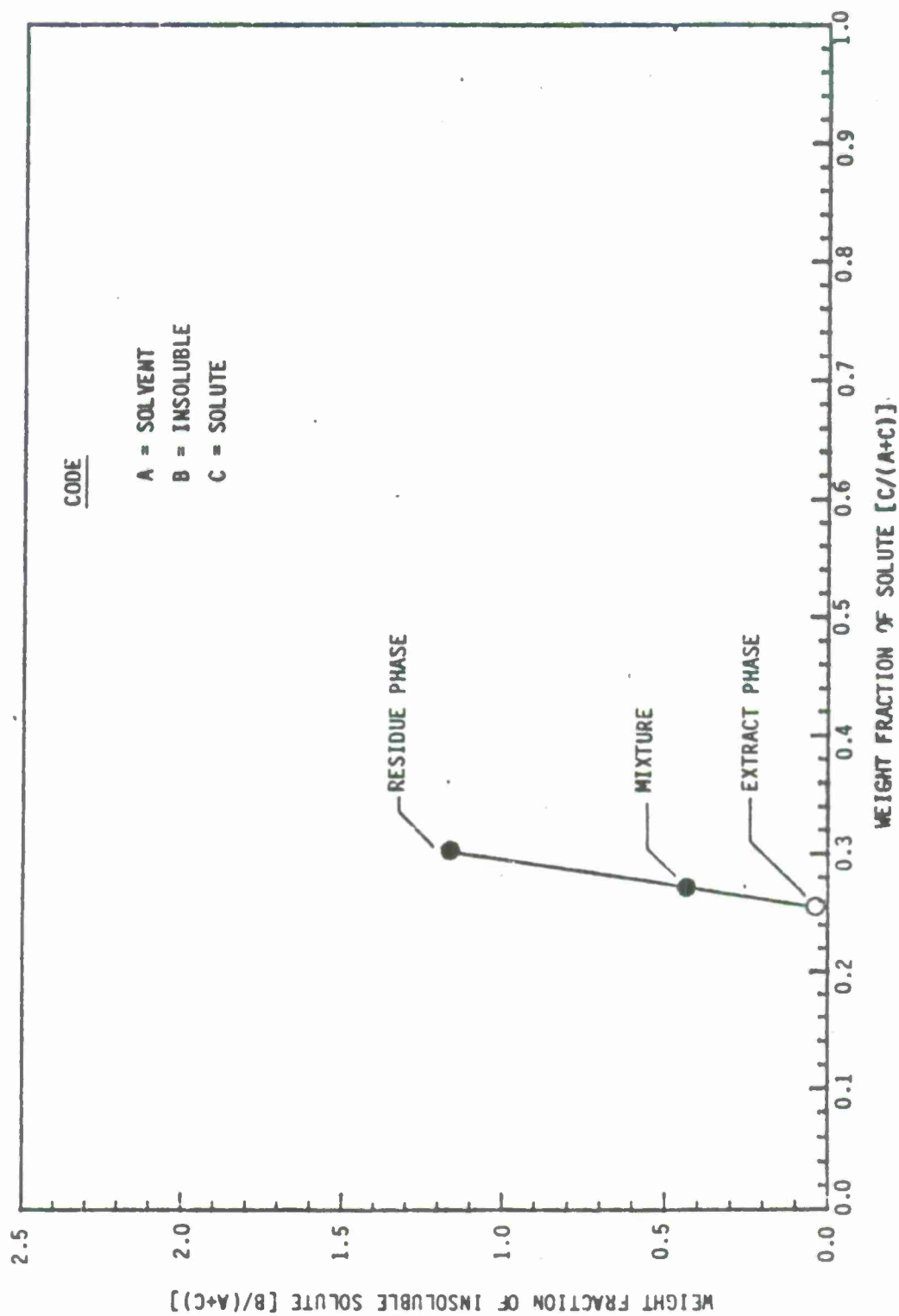


Figure 24. Equilibrium Concentrations for Extract and Residue Phases

A mixture (m, m) of solvent, insoluble solid and solute, if settled and separated, forms two phases. The liquid phase or extract consists of a solution of the solute in the solvent. The concentration of solute in the extract is x and the concentration of insoluble solid in the extract is N . The propellant residue phase consists of insoluble solid, undissolved solute, and residual extract solution. The concentration of solute in the residue is y^* and the concentration of insoluble solid in the residue is N . The upper curve in the equilibrium diagram defines the concentration of the residue phase (N versus y). The lower line defines the concentration of the extract phase (N versus x). The connecting or tie lines indicate equilibrium concentrations of the residue and extract phases.

Bench scale tests were conducted to determine the concentrations of the methylene chloride extract and propellant residue phases in equilibrium with each other. Propellant chips were submerged in solvent in sealed containers and placed in a temperature controlled environment. When the samples reached equilibrium, as determined by extraction rate tests, the extract and residue phases were separated and the solute, solvent, and insoluble solids concentrations determined. Specific surface areas of 570 and 1,125 in.²/lb and solute to solvent ratios of 0.0025 to 0.06 were evaluated.

The results obtained from these tests are presented in Table 18. An equilibrium diagram, constructed from these data, is presented in Figure 25. As previously discussed, the upper curve in the diagram defines the concentration of the residue phase. The lower curve defines the concentration of the extract phase. The connecting of the lines indicate equilibrium concentrations of extract and residue phases. It is noted that:

- a. The equilibrium concentrations of extract and residue phases are predictable.
- b. The equilibrium diagram is insensitive to specific surface area over the range of data evaluated.
- c. The equilibrium tie lines are not vertical indicating that all of the solute is not in solution.

The equilibrium diagram was used (Figure 26) to calculate the number of theoretical, cocurrent contact stages required for the extraction process. Four contact stages are required with a predicted yield of approximately 95%.

TABLE 18

Equilibrium Data for Extraction of NG
With Methylene Chloride

Propellant	Specific Surface Area (in ² /lb)	Temp. (°F)	Solute/Solvent Ratio	Extract Analysis*		Residue Analysis	
				C/(A + C)	B/(A + C)	C/(A + C)	B/(A + C)
NEPE/HMX/AP/AL	570**	70	0.0025	0.0023	0.6 x 10 ⁻⁴	0.0100	0.640
			0.0025	0.0025	0.6 x 10 ⁻⁴	0.0110	0.660
			0.005	0.0049	1.4 x 10 ⁻⁴	0.0110	0.620
			0.005	0.0048	1.0 x 10 ⁻⁴	0.0120	0.670
			0.010	0.0093	1.6 x 10 ⁻⁴	0.0149	0.537
			0.010	0.0093	1.2 x 10 ⁻⁴	0.0155	0.513
			0.015	0.0138	--	0.0205	0.572
			0.020	0.0196	0.9 x 10 ⁻⁴	0.0255	0.586
			0.020	0.0189	2.6 x 10 ⁻⁴	0.0231	0.572
			0.025	0.0234	1.8 x 10 ⁻⁴	0.0324	0.592
			0.030	0.0273	6.1 x 10 ⁻⁴	0.0353	0.607
			0.035	0.0319	8.8 x 10 ⁻⁴	0.0389	0.571
			0.040	0.0355	4.1 x 10 ⁻⁴	0.0445	0.583
			0.045	0.0389	14.1 x 10 ⁻⁴	0.0522	0.579
			0.050	0.0426	18.1 x 10 ⁻⁴	0.0557	0.580
			0.055	0.0464	24.8 x 10 ⁻⁴	0.0605	0.588
			0.060	0.0492	21.1 x 10 ⁻⁴	0.0660	0.593
NEPE/HMX/AP/AL	1125***	70	0.010	0.0094	2.8 x 10 ⁻⁴	0.0180	0.620
			0.015	0.0140	1.7 x 10 ⁻⁴	0.0210	0.630
			0.020	0.0180	9.6 x 10 ⁻⁴	0.0290	0.580
			0.020	0.0180	8.7 x 10 ⁻⁴	0.0290	0.610
			0.025	0.0220	7.2 x 10 ⁻⁴	0.0320	0.590
			0.030	0.0250	24.0 x 10 ⁻⁴	0.042	0.580

* Code

A = solvent

B = insoluble

C = solute

** 1/2 x 1/2 x 1/16 inch

*** 1/2 x 1/2 x 1/32 inch

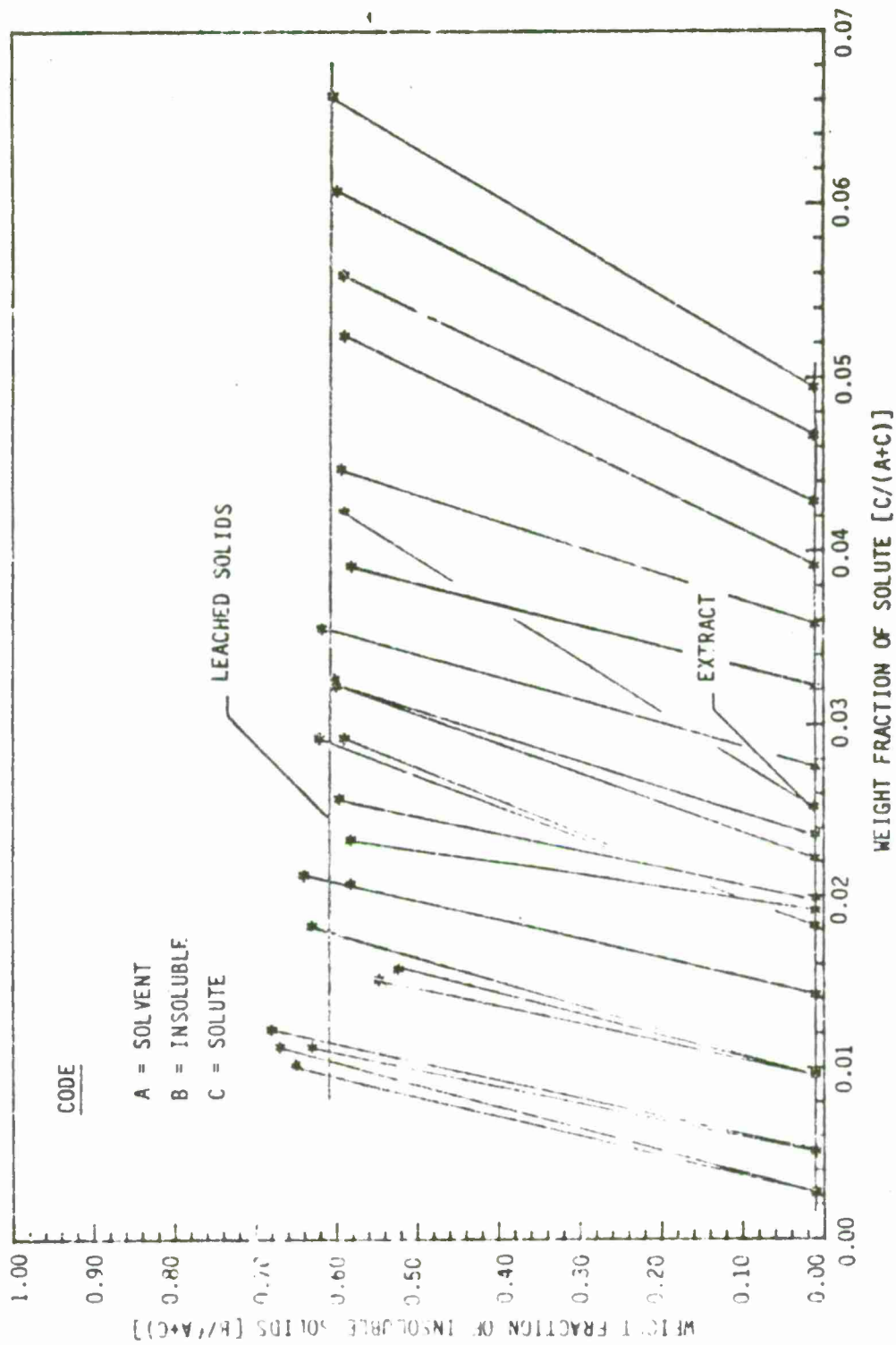


Figure 25. Equilibrium Diagram for Extraction of NG from NEPE-HMX-AP-Al Propellant

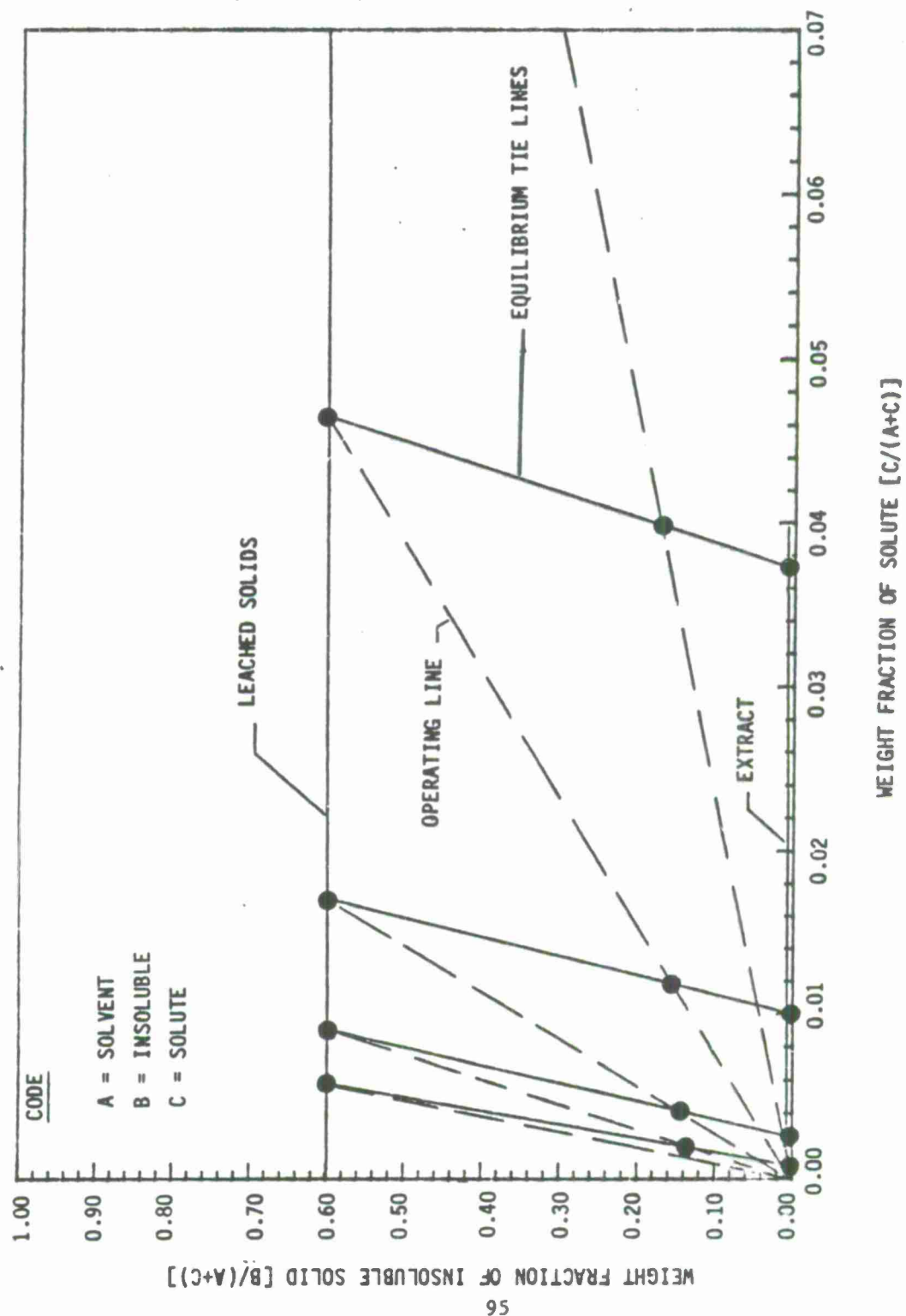


Figure 26. Multistage Cocurrent Extraction of NG from NEPE-HMX-AP-AI

2.2.2.3 Nitramine/Inorganic Oxidizer Extraction Process

Evaluation of Candidate Solvents

Two candidate solvents for nitramine and oxidizer extraction, acetone and DMSO, were identified and evaluated in paragraph 2.1.3. The results of this evaluation together with supplemental physical and chemical properties of each solvent are summarized in Table 19. As noted, DMSO has a much higher solubility for HMX and AP than does acetone. The HMX solubility in DMSO decreases ten fold in the presence of AP, however. The change in solubility with respect to temperature (Ref. 2.1.3) is low for both solvents. DMSO has a much higher boiling point and is less flammable and less toxic than acetone. Acetone, however, has an extensive history as a solvent used in the manufacture of nitramines.

Acetone was selected as the solvent for nitramine and inorganic oxidizer extraction in the selective solvent process. The logic used in this selection is summarized below:

- a. The mutual solubility of HMX and AP in acetone exceeds the individual solubilities.
- b. Acetone has a low boiling point which facilitates evaporative crystallization.
- c. It has a moderate toxicity level.
- d. It has an extensive prior history of usage as a solvent for nitramines.

The major disadvantage of the solvent is its flammability.

Subsequent to the evaluation and selection of a solvent for HMX and AP, a personal contact with the Holston Army Ammunition Plant (manufacturer of HMX) revealed several additional solvents for HMX.

- Dimethyl formamide (DMF), 34 g HMX/100 ml solution
- Cyclopentanone, 8.5 g HMX/100 ml solution
- Cyclohexanone, 5.2 g HMX/100 ml solution
- Dimethylacetamide, 16 g HMX/100 ml solution
- Methylene carbonate, 12 g HMX/100 ml solution
- Dimethyl Cyanamide, 10 g HMX/100 ml solution
- T-butyrolactone, 21 g HMX/100 ml solution

TABLE 19

Selective Solvent Evaluation
For
Nitramine/Oxidizer Extraction

Solvent	Solubility at 80°F (8/100 ml)		Boiling Point (°C)	Flash Point (°C)	Toxicity		Prior History With HMX And/Or AP
	HMX	AP			Inhalation	Oral	
Acetone	2.2	1.6	56.5	-17	Mod	Mod	Yes
DMSO	45.6	50.4	189	95	--	Low	No

This information was received too late to be evaluated in the program, however.

Extraction Rate

Bench scale tests were conducted to define the extraction rate of HMX, a nitramine, and ammonium perchlorate, an inorganic oxidizer, from an "NG-free" NEPE/HMX/AP/Al propellant residue. The propellant residue chips were placed in contact with acetone and the HMX/AP concentration of the extract solution monitored. The following process variables were evaluated in the tests:

1. Process Temperature
2. Solute/Solvent Ratio

The latter variable was controlled by using partially depleted residues for feedstock in consecutive tests.

The results of the tests are summarized in Table 20 and in Figure 27. As noted, extraction rate increases slightly with temperature but is relatively insensitive to the solute-to-solvent ratio over the range of data evaluated. Under the conditions evaluated a contact time of approximately 40 minutes is required to reach the knee of the curve beyond which the recovery rate is much diminished.

Extract and Residue Phase Equilibria

The nomenclature used in phase equilibria was explained in paragraph 2.2.2.1. The definition of terms used in the HMX/AP system is as follows:

Component A	Solvent (acetone)
Component B	Insoluble Solid (binder, aluminum)
Component C	Solute (HMX, AP)

Bench scale tests were conducted to determine the concentrations of the acetone extract and propellant residue phases in equilibrium with each other. "NG-free" propellant residue chips were submerged in solvent in sealed containers and placed in a temperature controlled environment. When the samples reached equilibrium, as determined by extraction rate tests, the extract and residue phases were separated and the solute, solvent and insoluble solids concentrations determined. The results of these tests are presented in Table 21. An equilibrium diagram constructed from these data is presented in Figure 28. The upper curve in the diagram represents the concentration of the

TABLE 20

HMX/AP Extraction Rate With Acetone

Feed Stock	Temperature (°F)	Contact Time (minutes)	Extract Concentration (gm solute/5 ml sol'n)
Fresh Residue (1st Extraction)	70	10	0.097
		25	0.142
		35	0.169
		45	0.187
		120	0.206
		240	0.221
		360	0.231
Once Extracted Residue (2nd Extraction)	70	12	0.078
		23	0.114
		53	0.146
		73	0.165
		203	0.177
		303	0.182
		428	0.186
Twice Extracted Residue (3rd Extraction)	70	10	0.054
		20	0.079
		30	0.102
		40	0.106
		60	0.111
		318	0.114
		410	0.129
Fresh Residue (1st Extraction)	100	10	0.067
		20	0.124
		30	0.168
		45	0.201
		150	0.235
		255	0.260
		330	0.274

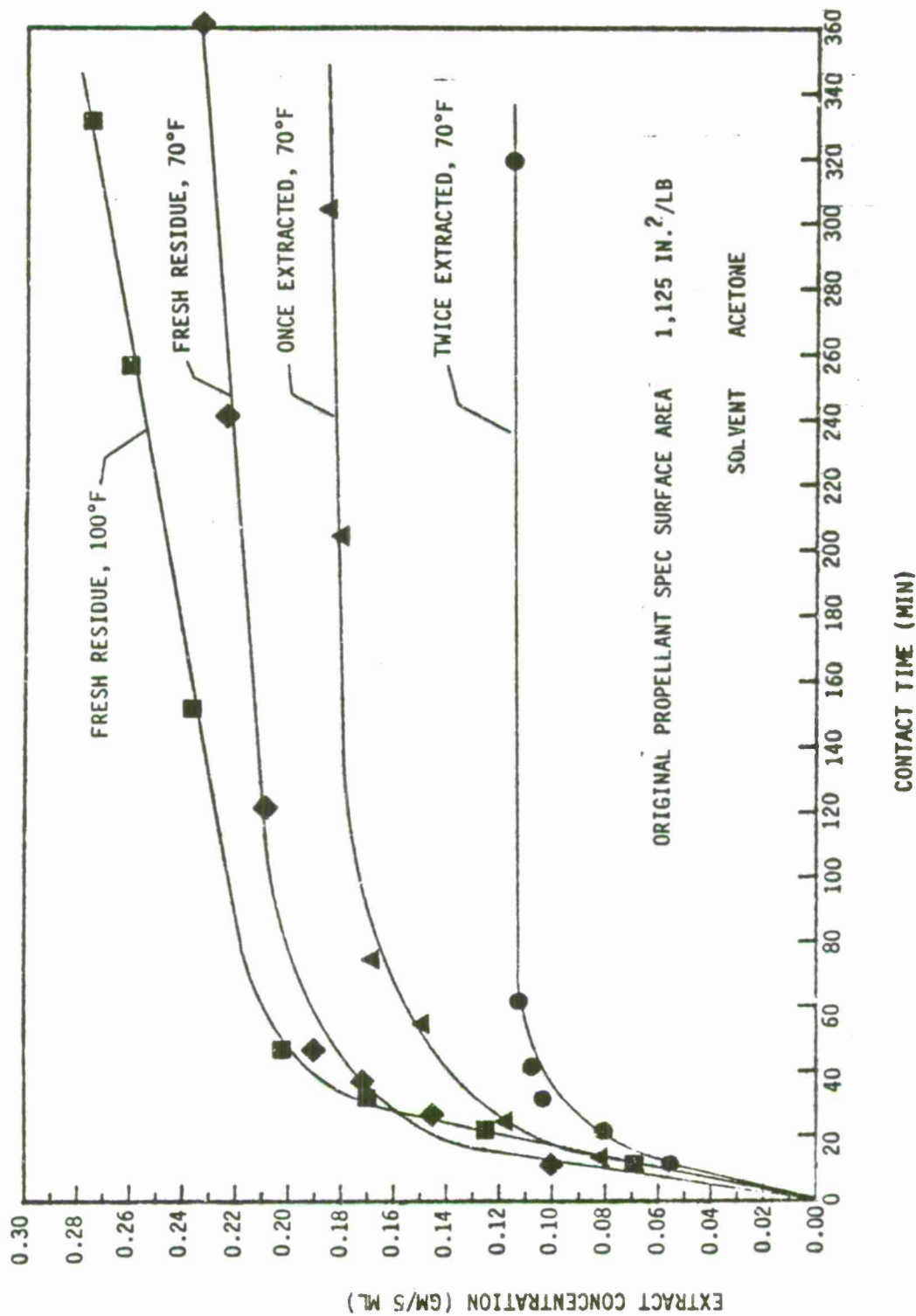


Figure 27. Extraction Rate of AP and HMX from Residue at Different Stages of Total Solute Removal

TABLE 21

Equilibrium Data for Extraction of HMX/AP With Acetone
NEPE/HMX/AP/AL Propellant

Solute/Solvent Ratio	Extract Analysis*				Residue Analysis*	
	C/(A + C)	B/(A + C)	$M_{HMX}/(A + C)$	$M_{AP}/(A + C)$	C/(A + C)	B/(A + C)
.224	0.0639	23×10^{-4}	0.040	0.024	0.402	0.236
.225	0.0616	18×10^{-4}	0.039	0.022	0.416	0.233
.200	0.0607	20×10^{-4}	0.036	0.025	0.388	0.234
.173	0.0584	33×10^{-4}	0.035	0.023	0.372	0.232
.161	0.0552	4×10^{-4}	0.035	0.020	0.312	0.238
.138	0.0480	21×10^{-4}	0.034	0.014	0.294	0.234
.121	0.0427	28×10^{-4}	0.030	0.012	0.273	0.222
.102	0.0367	36×10^{-4}	0.027	0.010	0.248	0.208
.125	0.0359	4×10^{-4}	0.029	0.007	0.223	0.210
.117	0.0343	3×10^{-4}	0.029	0.005	0.211	0.211
.111	0.0327	3×10^{-4}	0.028	0.004	0.195	0.201
.101	0.0310	2×10^{-4}	0.027	0.004	0.175	0.191
.094	0.0297	3×10^{-4}	0.027	0.003	0.162	0.190
.088	0.0291	2×10^{-4}	0.026	0.003	0.150	0.190
.084	0.0285	2×10^{-4}	0.026	0.002	0.139	0.181
.076	0.0277	3×10^{-4}	0.026	0.002	0.124	0.173

*Code

A = Solvent (acetone)

B = Insoluble

C = Solute (HMX/AP)

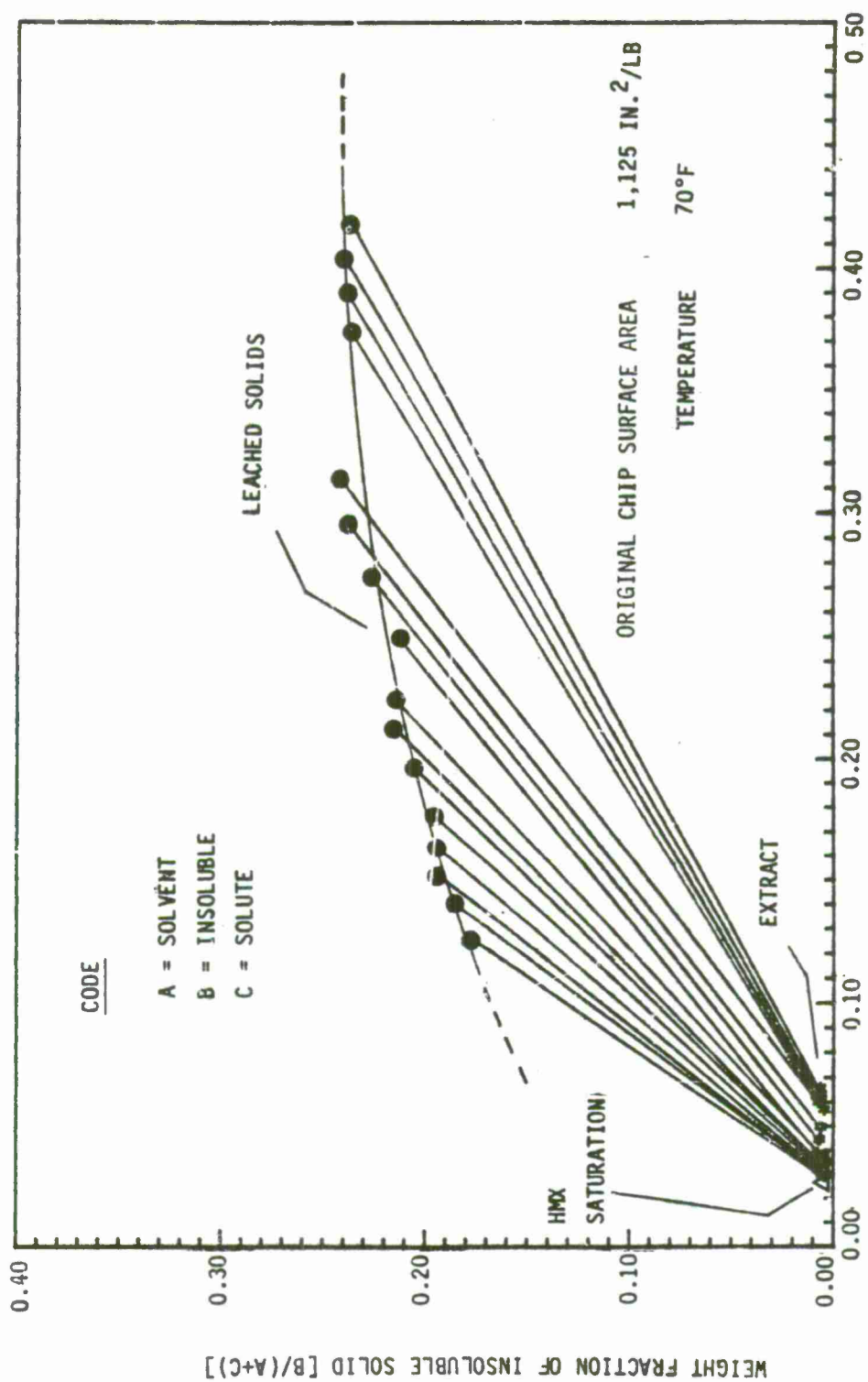


Figure 28. Equilibrium Diagram for HMX-AP Extraction

residue or leached solids phase. The lower curve represents the concentration of the extract phase. Tie lines connect residue and extract solutions in equilibrium with each other. It is noted that:

- a. Equilibrium concentrations of extract and residue phases are predictable.
- b. The equilibrium tie lines are not vertical indicating that all of the solute is not in solution.
- c. The equilibrium tie lines converge at two points on the extract curve indicating a change in the relative solubilities of the two solutes.

The latter phenomenon is best described in Figure 29 where the HMX to AP ratio in the extract is plotted as a function of solute to solvent ratio. At high solute to solvent ratios there is enough of both solutes present to form a mutually saturated solution (HMX/AP approximately 1.5). As the solute to solvent ratio decreases, there is insufficient AP available to maintain mutual saturation conditions and the extract remains saturated with respect to HMX only. The HMX/AP ratio of the extract would therefore be expected to increase with time during the extraction process.

These equilibrium data were used, in Figure 30, to determine the number of theoretical contact stages required for the extraction process. Seven theoretical stages are required with a predicted yield of approximately 95 percent.

2.2.2.4 Process Definition

A summary of the process conditions selected for each major unit operation in the selective solvent extraction process is presented in Table 22. A process flow chart is illustrated in Figure 31.

The propellant is shredded to provide a specific surface area of approximately 1,125 in.²/lb. The nitrate ester is extracted from the propellant with methylene chloride in a four stage, cocurrent extraction process. The extract is concentrated to a 70/30 nitrate ester/solvent mixture and the solvent recovered for reuse. The nitramine and inorganic oxidizer are extracted with acetone in a batch-continuous contact process. The solution is concentrated to form a nitramine, oxidizer, solvent slurry, and the solvent recovered for reuse. The concentrated slurry is filtered and washed with water to separate the two solutes.

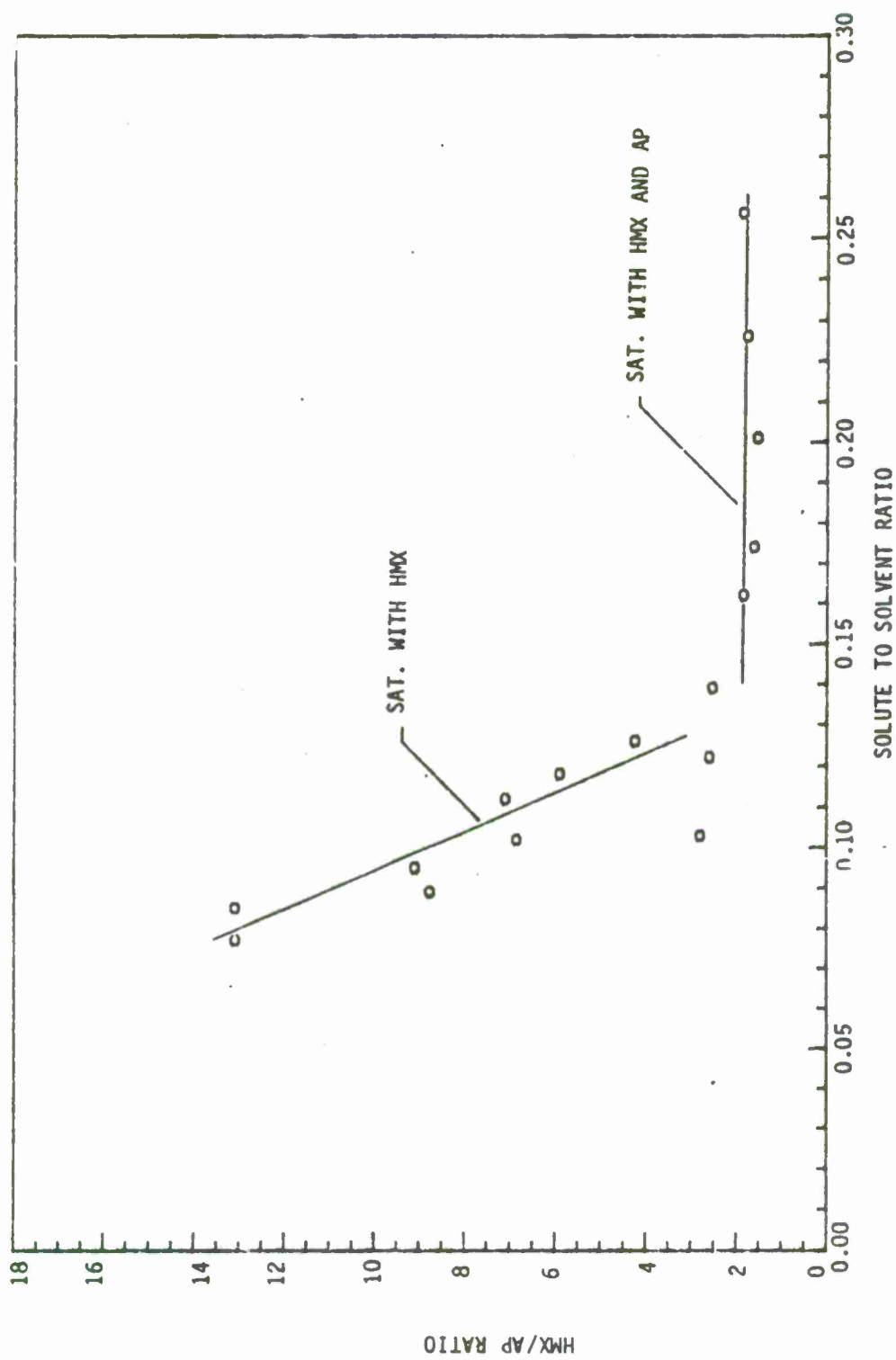


Figure 29. Extraction of HMX-AP from NEPE-HMX-AP-Al Propellant with Acetone

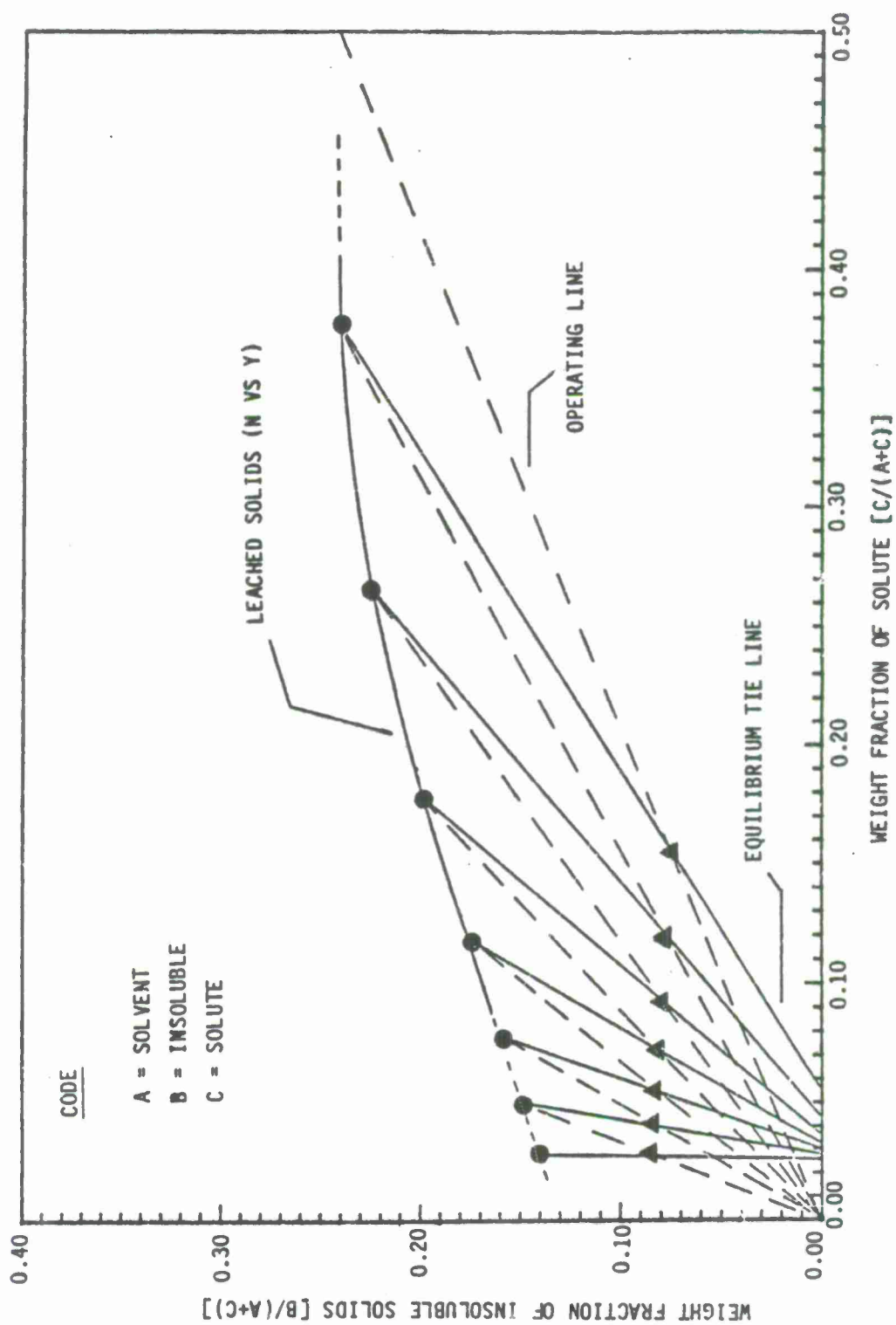


Figure 30. Equilibrium Diagram Contact Stage Construction for HMX-AP Extraction

TABLE 22
Selective Solvent Extraction Process Definition

Nitrate Ester Extraction

• Process	Multistage, Cocurrent
• Solvent	Methylene Chloride
• Solute/Solvent Ratio	0.04
• Process Temperature	70°F
• Specific Surface Area	1125 in ² /lb
• Number of Contact Stages	4
• Residence Time	10 min/stage

Nitramine/Inorganic Oxidizer Extraction

• Process	Batch, Continuous Contact
• Solvent	Acetone
• Solute/Solvent Ratio	0.15 to 0.18
• Process Temperature	70°F
• Specific Surface Area	1125 in ² /lb
• Number of Contact Stages	7
• Residence Time	3 hours

The final products recovered are:

- a. Nitrate ester in inert diluent
- b. Nitramine, water wet
- c. Oxidizer, water wet

The metal powder is retained in the depleted propellant residue.

2.2.2.5 Process Model

Nitrate Ester Extraction

The four stage, cocurrent extraction of nitrate ester from a Class 1.1 propellant was modeled on a bench scale. A 400 gram sample of an NEPE/HMX/AP/Al propellant was extracted with methylene chloride.

An initial solute to solvent ratio of 0.04 was used in the extraction. Four cocurrent contact stages with residence times of approximately 1 1/2 hours were used in the process. Extract and residue phases were separated after each contact phase by decantation and gravity drainage. Samples of the extract from each contact stage were analyzed for composition. The corresponding residue compositions were calculated by material balance. The results obtained from this extraction process are summarized in Table 23. A comparison of the actual and predicted performance of each contact stage, illustrated in Figure 32, shows a reasonably close agreement. A total nitrate ester and stabilizer recovery of 96.7 percent was calculated for the process. A photograph of the recovered ingredients is presented in Figure 33.

Nitramine/Oxidizer Extraction

A batch-continuous contact leaching process for the extraction of HMX and AP from NEPE/HMX/Al/AP propellant was modeled on a bench scale. A 30 gram sample of "NG free" propellant residue, obtained from the nitrate ester extraction process model, was used as feed stock. A continuous flow rate of 6.5 ml/min of acetone was used in order to provide an initial solute to solvent ratio of 0.18. The concentration of HMX and AP in the extract solution was monitored and is summarized in Table 24 and in Figure 34 as a function of time. A recovery of 99.4 percent HMX and 89.4 percent AP was obtained with a contact time of three hours. Note in Figure 35 that the ratio of HMX to

TABLE 23

COCURRENT EXTRACTION OF NITRATE ESTER
FROM NEPE-HMX-AP-AL PROPELLANT

Specific Surface Area (in ² /lb)	Temperature (°F)	Contact Stage	Extract Analysis*		Residue Analysis*		Cumulative Nitrate Ester Recovered (percent)
			C/(A + C)	B/(A + C)	C/(A + C)	B/(A + C)	
1125**	70	1	0.032	6.00×10^{-4}	0.053	0.59	59.4
		2	0.010	3.50×10^{-4}	0.021	0.59	84.4
		3	0.004	2.00×10^{-4}	0.008	0.57	94.1
		4	0.001	0.04×10^{-4}	0.004	0.59	96.7

*Code

A = solvent

B = insoluble

C = solute

** $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{32}$ inch propellant chips

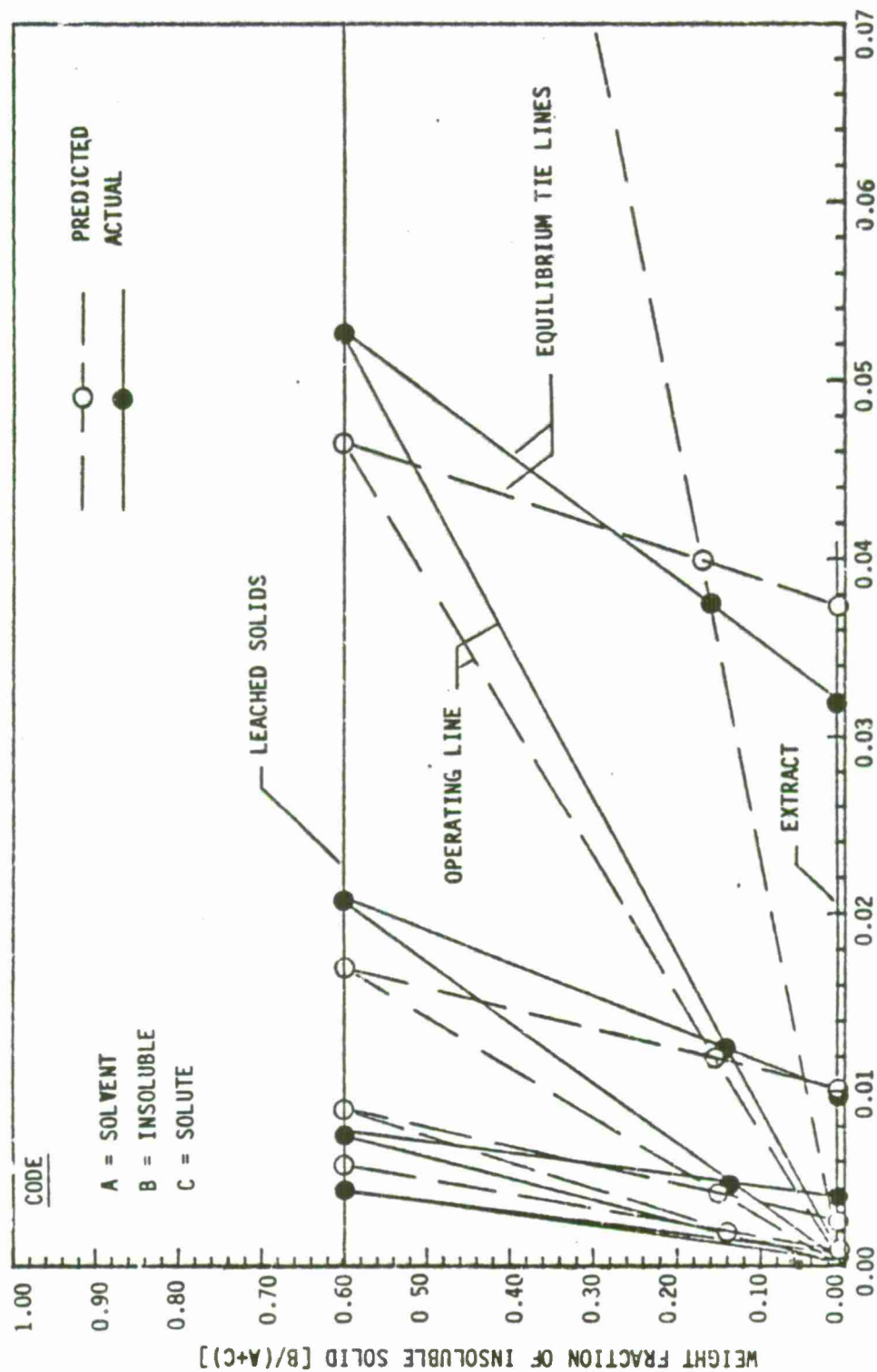


Figure 32. Multistage Concurrent Extraction of NG from NEPE-HMX-AP-Al Propellant

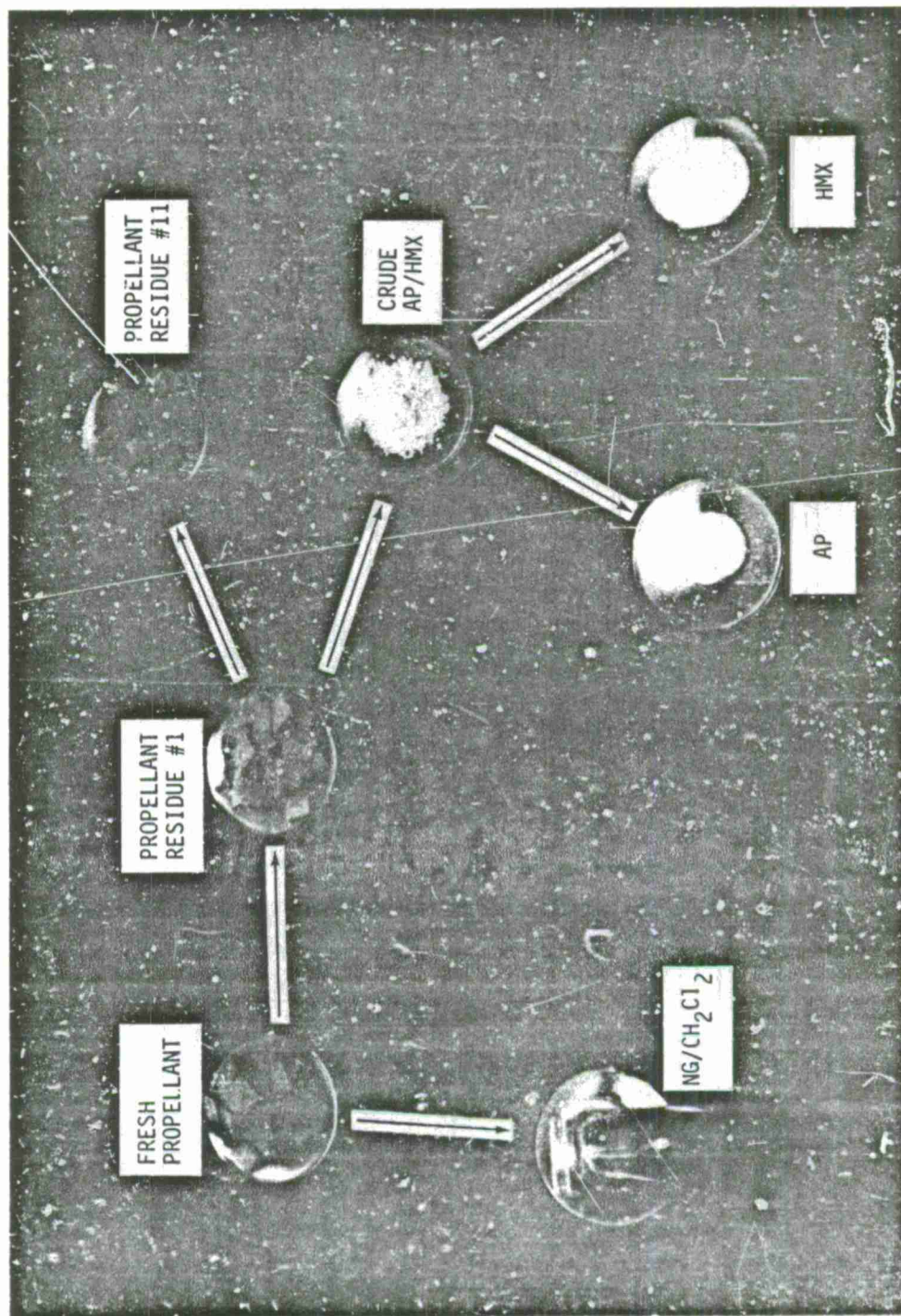


Figure 33. Material Flow in Ingredient Recovery Process

TABLE 24

BATCH-CONTINUOUS CONTACT EXTRACTION
OF NITRAMINE AND INORGANIC OXIDIZER
FROM NEPE-HMX-AP-AL PROPELLANT

Specific Surface Area (in ² /lb)	Temperature (°F)	Time (min)	Cumulative Solute Recovery (%)	
			AP	HMX
1125	70	12	9.6	6.2
		24	21.4	13.6
		36	29.9	19.2
		48	45.2	29.4
		50	56.9	38.8
		62	66.6	48.1
		76	74.6	58.9
		86	77.4	63.7
		98	79.8	69.3
		110	81.4	74.0
		122	83.1	80.5
		134	84.7	87.4
		146	86.1	92.3
		158	87.3	95.6
		170	88.2	97.6
		182	89.4	99.4

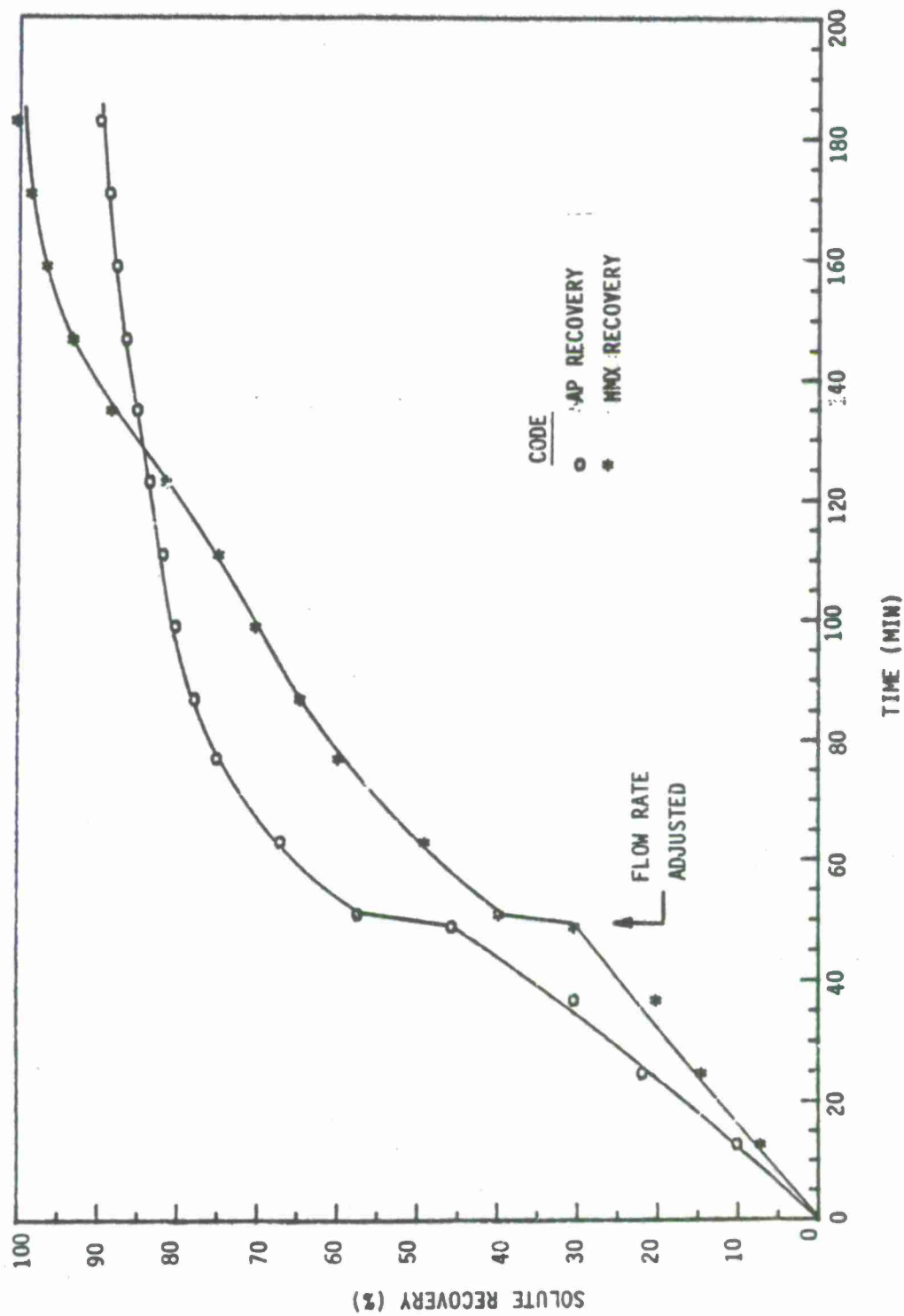


Figure 34. Batch-Continuous Contact Extraction of HMX-AP from NEPE-HMX-AP-A1

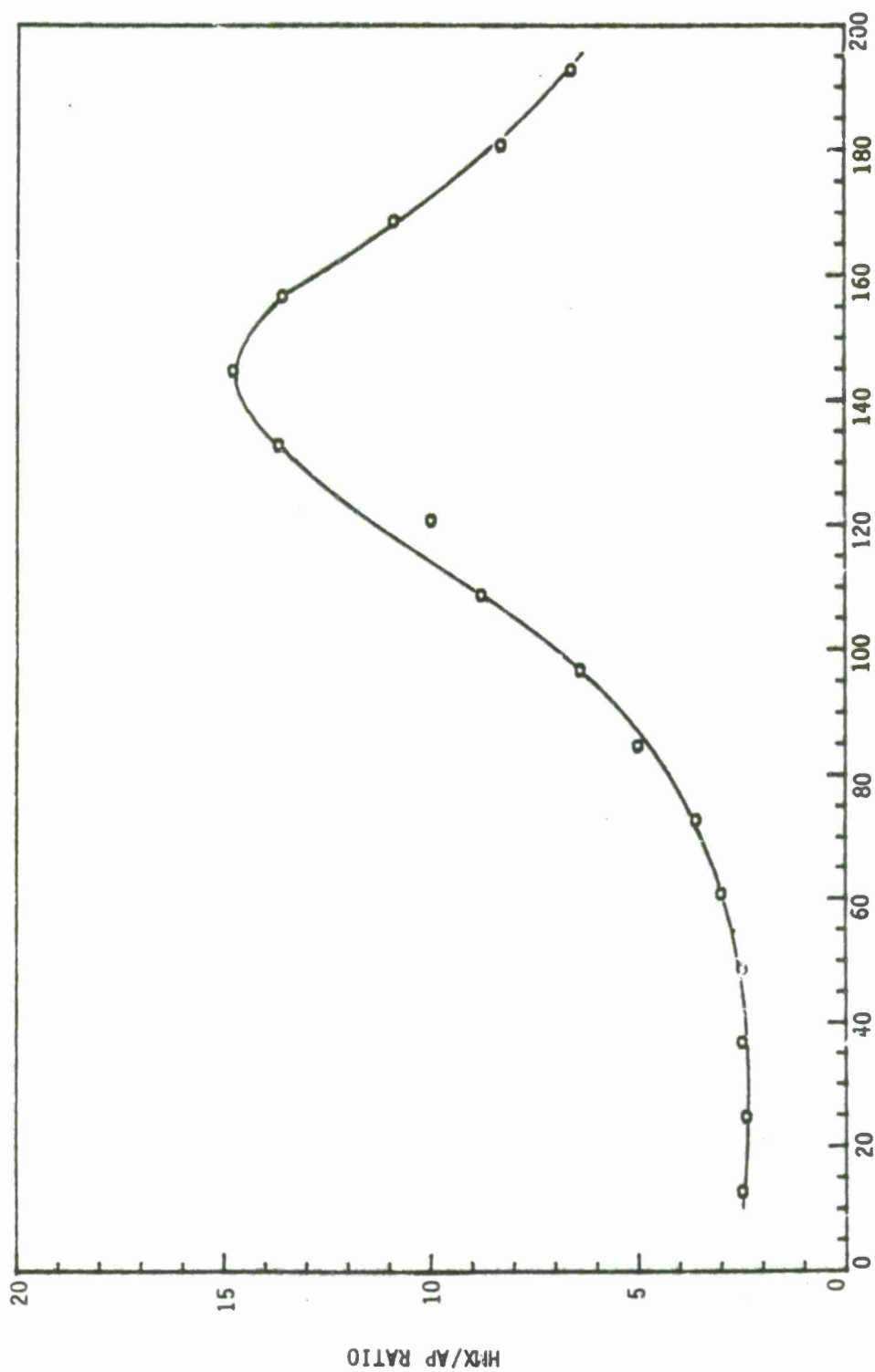


Figure 35. Batch-Continuous Contact Extraction of HMX-AP from
NEPE-HMX-AP-Al Propellant with Acetone

AP extracted varies with time as predicted by previous rate and solubility data. A photograph of the recovered ingredients is presented in Figure 33.

Product Purity

Samples of the NG, HMX and AP reclaimed from the process model were submitted for analysis. The results of this analysis are summarized in Table 25. Specification limits are presented for comparison, where applicable.

As noted, the NG extract contained a total of 96.39 percent NG and stabilizers. The remaining 3.61 percent is attributed to binder sol. The HMX was 96.9 percent pure with a melting point of 273°C, slightly below specification acceptance limits. The recovered AP was 99.17 percent pure with no major traces of impurities as indicated by the emission spectrograph.

All reported analytical values are within specification acceptance limits or sufficiently close to conclude that, with a more thorough washing, reclaimed ingredients offer a source of raw materials of sufficient quality for reuse in solid propellant manufacture and other related applications.

Ignition Sensitivities

Intermediate and final products from the process model were tested for ignition sensitivity to impact, friction, electrostatic discharge, and auto-ignition temperature. The results of these tests are summarized in Table 26. Two ignition sensitive combinations were identified in the process.

1. HMX/AP Wet Cake - The flammability of the acetone used as a solvent in this step makes the wet cake very susceptible to ignition by electrostatic discharge.
2. HMX/AP Dry Cake - The dry mixture of HMX and AP crystals were found to be impact and friction sensitive.

Standard methods of flammable solvent handling, including electrical grounding, explosion proof electrical equipment, vapor tight tanks, and inert gas purge will be employed to minimize the ignition hazard associated with acetone. The HMX and AP will be washed and separated in the wet state to avoid handling the dry HMX/AP mixture.

TABLE 25

RECLAIMED PRODUCT ANALYSIS

	Specification Limits	Reported
<u>NG</u>		
NG (%)	--	95.8
MNA (%)	--	0.43
2-NDPA (%)	--	0.16
<u>HMX</u>		
HMX (%)		
Melting Point (°C)	>98.0	96.9
Acetone Insolubles (%)	>275	273
	<0.05	N11
<u>AP</u>		
Sulfated Ash, as NaClO_4 (%)	<0.9	0.075
Perchlorate, as NH_4ClO_4 (%)	>98.3	99.17
Emission Spec		
Fe (ppm)	--	3.7
Mg (ppm)	--	0.7
Al (ppm)	--	4.5
Cu (ppm)	--	1.5
Ag (ppm)	--	0.7
Na (ppm)	--	10.2
Zn (ppm)	--	3.1
Ti (ppm)	--	2.0
Zr (ppm)	--	1.3
Ni (ppm)	--	0.3
Pb (ppm)	--	1.0
Sr (ppm)	--	0.3
Ca (ppm)	--	16.7
Cr (ppm)	--	0.4
Ba (ppm)	--	16.7

TABLE 26

IGNITION SENSITIVITY SUMMARY

Sample Description	Impact* (cm)	Friction* (psi)	ESD* (joules)	AIT (hours)
Feed Stock				
NEPE/HMX/AP/AL	33	100 @ 8 ft/sec	1.25	24 @ 300°F
NG Extract				
NG/Solvent (70/30)	26	100 @ 4 ft/sec	1.25	24 @ 300°F
Residue No. 1				
Binder/HMX/AP/AL	17	800 @ 8 ft/sec	1.25	24 @ 300°F
HMX/AP Extract				
Intermediate (dry)				
Extract No. 1 (65/35)	11	100 @ 8 ft/sec	6.25	24 @ 300°F
Extract No. 2 (80/20)	3.5	25 @ 8 ft/sec	1.25	24 @ 300°F
Extract No. 3 (88/11)	6.9	50 @ 8 ft/sec	1.25	24 @ 225°F
Extract No. 4 (93/7)	13	100 @ 8 ft/sec	1.25	24 @ 225°F
Final				
Wet Cake (80/20)	11	100 @ 6 ft/sec	0.04	24 @ 300°F
Dry Cake (80/20)	3.5	25 @ 4 ft/sec	6.25	24 @ 300°F
Residue No. 11				
Binder/Al	80	800 @ 8 ft/sec	6.25	24 @ 300°F

* Threshold ignition level (TIL), 0.01 probability.

A third potential ignition hazard is the loss of methylene chloride from the NG extract leaving an NG concentrated residue. Vapor tight seals and storage temperature controls will be employed to preclude solvent loss. Transfer of the NG to diethylene glycol (DEG), a less volatile inert diluent, is optional for long term storage and handling of the NG.

2.3 PILOT PLANT DESIGN

The nature of the processes involved in direct conversion of waste Class 1.1 propellant to explosive boosters and in ingredient recovery are quite different. The boosters are made by simply casting the uncured propellant into small cylinders. This is a manufacturing process in which, except for the exact container, every motor manufacturing facility has experience. Ingredient recovery on the other hand is effected by a chemical process in which the desired propellant components are selectively recovered using solvents.

With this in mind, the philosophy was adopted that routine small sample casting of propellant as performed by all solid rocket motor manufacturers may be considered sufficient pilot manufacturing experience. Thus, if it was decided at some facility to incorporate a booster manufacturing unit into their operations, the full-scale equipment would be selected and installed without any intermediate production or pilot testing.

Nevertheless, the approaches taken in designing the booster manufacturing unit and the ingredient recovery pilot plant were similar. The nature of the materials involved were considered to determine what equipment types were most suitable for the required handling. This included both the physical state of the materials and their hazards characteristics. Then incorporating the bench scale results into the analysis equipment flow diagrams were developed. After finalization of the diagrams, plant capacities and process operating parameters were selected and, in the case of ingredient recovery, a material balance was calculated.

2.3.1 Explosive Booster

Considerations made by any motor manufacturing facility concerning the handling of Class 1.1 propellants are applicable to the manufacture of explosive boosters.

Uncured Class 1.1 propellants are typically high viscosity fluids (3-10 Kp) which are induced to flow by application of a vacuum or by mechanical means. It is essential that the equipment be compatible with these materials. Items to be considered include weld porosity and the elimination of metal to metal contact points.

The benefits of remote, as opposed to attendant, operation must be carefully assessed. Remote operation requires a greater degree of automation and is possibly more expensive but has obvious safety advantages. The authors feel that remote operation for this kind of process is essential from the safety standpoint.

Another major consideration is the propellant casting window or process life. Uncured Class 1.1 propellants typically have process lives of from 30 to 50 hours after mixing has been completed. Process life is defined at Thiokol as the length of time from curative addition to the time the propellant viscosity reaches 40 kilopoise. Beyond that time, the propellant cannot easily be cast by conventional means. Thus, the manufacturing facility must be capable of processing expected quantities of waste propellant well within the casting window. The largest amount of propellant which could be available for casting into boosters at Thiokol is 6,000 lb which would constitute a mix rejected for deficiencies which wouldn't affect booster performance. To process this amount of propellant well within the process life, a casting rate or capacity of 400 lb/hr was selected for the casting equipment.

Finally since this process is one which utilizes waste propellant generated at an established motor manufacturing facility, equipment and facilities already in existence may be suitable for booster manufacture.

With these considerations in mind, a process flow chart was developed and is presented in Figure 36. Mold sets are preassembled, if assembly is required, in anticipation of receiving waste propellant. When waste propellant becomes available, it is transported to the casting building. The transport vessel is presumably the bowl in which the propellant was mixed as the bulk of waste uncured propellant is from either rejected mixes or motor cast excess.

Tooling designed to receive propellant directly from the mix bowl is then used to cast the boosters. The boosters are cured in an oven typically for a 5-day period at 120°F.

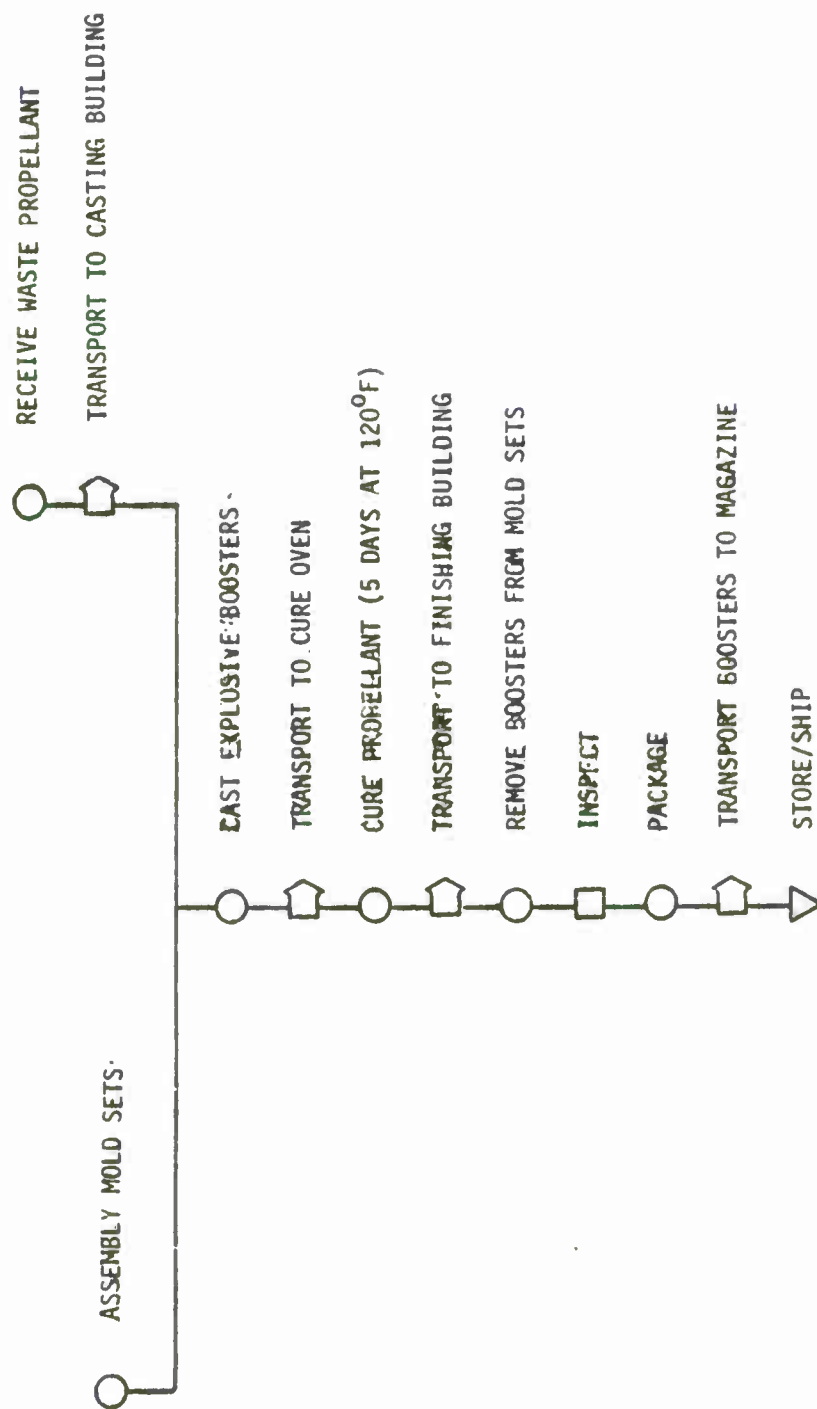


Figure 36. Process Flow Chart for Explosive Booster Manufacture

Following cure the boosters are transported to a finishing building where they are separated from the mold sets and any excess propellant is trimmed. After quality inspection, they are packaged and either shipped or stored.

A detailed tooling and facility design was beyond the scope of the project. Table 27 is a list of the major items necessary for the manufacturing process.

2.3.2 Selective Solvent Extraction Process

The most critical consideration in designing the ingredient recovery process was equipment and facilities compatibility with NG and NG containing materials. General requirements that were considered during the plant design were that the plant be simple, have few moving parts, and be easily cleaned. Other requirements included avoidance of the mating of metal parts, selection of construction materials compatible with NG, and, where welds were necessary, that they be of high integrity in accordance with ASME Unfired Pressure Vessels, Section VIII, Appendix VIII. Location of the facility must be in accordance with the quantity distance provisions of DOD 4145.26M. Compatibility of the facility construction materials with NG is again a requirement. Floors should be lead covered or sealed in a manner to prevent absorption or inclusion of high energy liquid plasticizers such as NG. Special spill containment and clean-up provisions should be considered in the facilities design.

Minimization of inprocess material handling was a goal in designing the plant. Operator contact with NG and the solvents in use is obviously undesirable, and this consideration led to the selection of one leach tank for removing both NG and the solids thus avoiding a transfer step. Consideration should also be given to the special feedstock and product handling and storage requirements in the ultimate plant design.

With the above considerations in mind and using the results of the bench scale demonstration tests discussed earlier, an equipment flow diagram was developed for the pilot plant and is presented in Figure 37.

The whole recovery process can be separated into essentially four operations:

TABLE 27
EXPLOSIVE BOOSTER MANUFACTURE EQUIPMENT LIST

<u>Facilities</u>	<u>Equipment</u>
Casting Building	Casting Apparatus
Oven	Vacuum Pump (if vacuum cast)
Storage Building	Mold Sets
Finishing Building	

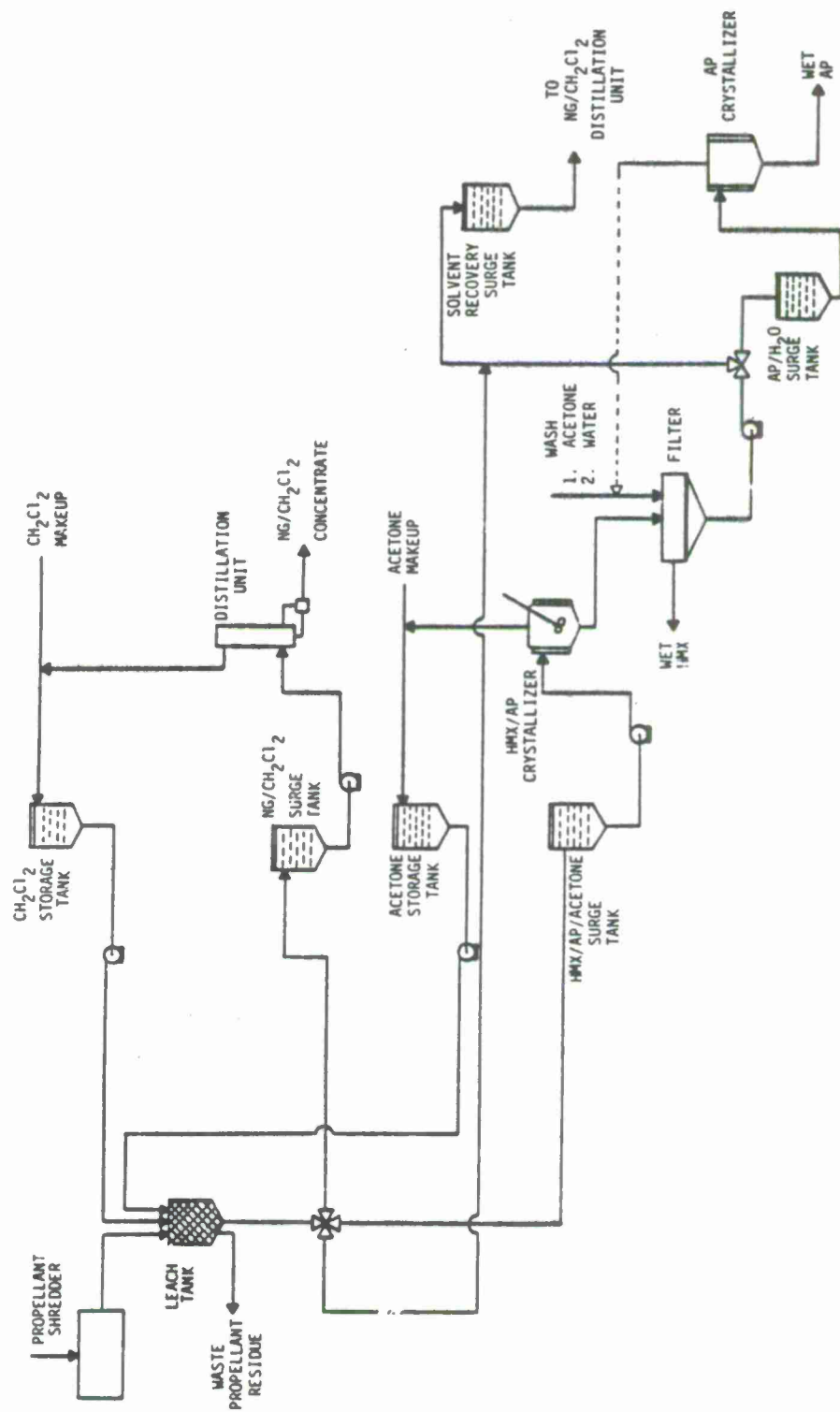


Figure 37. Pilot Plant Design - Selective Solvent Extraction

1. Propellant size reduction to increase the feedstock surface area and hence increase extraction rates.
2. Extraction of NG with CH_2Cl_2 .
3. Extraction of HMX and AP with acetone.
4. Separation of HMX from AP.

The propellant is shredded into a mesh basket which in turn is positioned in the leaching tank. The tank is then charged with CH_2Cl_2 and after 10 minutes the solution is drained into the NG/ CH_2Cl_2 surge tank. This sequence is repeated three times for a total of four solvent contacts.

As soon as the first contact stage is completed, the distillation unit is charged and distillation begun. As solvent is evaporated, condensed and returned to the storage tank, the distillation unit is continuously fed. When all of the solution has been distilled down to a concentration of 70% NG, distillation is ceased and the concentrate is discharged to a suitable container. The total distillation should take between four and five hours.

The next step in the process is removal of HMX and AP from the propellant residue. Since there is still a considerable amount of CH_2Cl_2 held up by the propellant residue in the leach tank, it is contacted briefly with acetone and the resulting solution is diverted to a solvent recovery holding tank to be treated later.

The propellant residue, now only slightly contaminated with CH_2Cl_2 is contacted continuously with acetone for a period of three hours as follows. The acetone is fed from storage to the leach tank, with the bottom outlet valve closed until solvent fills to the desired level. At that point, the valve is opened and solution is drained from, and fresh solvent fed to, the leach tank continuously. When the solution surge tank reaches a predetermined level, the crystallizer is charged and solvent recovery commences. The crystallizer is fed continuously parallel to the leaching process.

Upon completion of the leaching process, the waste propellant residue is drained and can then be washed with water and disposed of in a land fill. The water dilution reduces the flammability hazard due to the solvent vapors. When the HMX/AP/acetone solution has been reduced in the crystallizer to a concentrated slurry it is transferred to a filter. Here the solution portion

of the slurry, which is contaminated with NG, is filtered off and sent to the solvent recovery surge tank.

The next step is a wash of the crystals with a small amount of fresh acetone to remove the last traces of NG. A small amount of HMX and AP is lost in the process. This solution is also sent to the solvent recovery surge tank. The crystals are then washed with hot water to dissolve the AP which is transferred to a surge tank. The wet HMX is discharged from the filter to a suitable storage container. Lastly, the AP is recovered by evaporating off the water to yield a wet cake product.

At some point in the process when the NG/CH₂Cl₂ distillation unit becomes available, the solution in the solvent recovery tank is treated to reduce the solvent loss. The waste left over from this step contains AP/HMX/NG and some solvent and should most likely be burned.

A list of the equipment, their estimated capacities or sizes and materials of construction are presented in Table 28 for a 20,000 lb/yr pilot plant.

Some modifications to this design might become evident upon closer scrutiny of the details. For example, the pump situated between the NG/CH₂Cl₂ tank and the distillation column might be too hazardous an operation. In place of it, the surge tank could be pressurized to transfer the liquid or the tank could be situated above the column to provide for gravity flow. Also, it might be determined that shredding the propellant could safely be done only if the operation is flooded with water. As it turns out, the propellant is quite hydrophobic so that it is quite possible that flooded shredding could be incorporated into the process. The NG/CH₂Cl₂ surge tank would have to be replaced by a phase splitting tank which would take the aqueous phase off the top and return it to the shredding operation. However, the concept of flooded shredding and its impact on the process were not evaluated in any detail.

2.4 INCINERATION

Three types of incinerators are currently in use and/or under development for the disposal of waste explosives, munitions, propellants, and pyrotechnics.

TABLE 28

EQUIPMENT LIST FOR 20,000 LB PROPELLANT/YR
INGREDIENT RECOVERY PILOT PLANT

<u>Description</u>	<u>Quantity</u>	<u>Size/Cap</u>	<u>Material of Construction</u>
Propellant Shredder	1	150 lb/hr	Stainless steel
Tank	1	200 gal	Stainless steel
Tank	3	150 gal	Stainless steel
Tank	1	75 gal	Stainless steel
Tank w/Basket Insert	1	75 gal	Stainless steel
Pump	1	300 gal/hr	Stainless steel
Pump	4	150 gal/hr	Stainless steel
Pump	1	25 gal/hr	Stainless steel
Distillation Unit	1	250 lb/hr	Glass or stainless steel
Crystallizer (batch)	1	1,000 lb/hr	Stainless steel
Crystallizer (batch)	1	60 lb/hr	Carbon steel
Filter (in line)	2	--	N/A
Filter (batch)	1	15 ft ²	Ceramic

1. APE 1236 Deactivation Furnace
2. Radford Rotary Furnace
3. Fluidized Bed Incinerator

The first two furnaces are variations of a rotary kiln incinerator. The latter is a distinct and separate design approach. There are also a number of one of a kind incinerators which have been evaluated but not fully developed. In some instances they are forerunners which have evolved into the current state of the art incineration technology.

2.4.1 APE-1236 Deactivation Furnace

The APE-1236 deactivation furnace was originally developed by the army for disposal of ordnance items which either burn, deflagrate, or detonate. The furnace is currently deployed in approximately 25 Army, Air Force, and Navy installations in the United States and overseas.

Description

The APE-1236 Deactivation Furnace is illustrated in Figure 38. It consists of an unlined, rotating steel cylinder equipped with internal flights for advancement of the combustible material. The rate of advancement is proportional to the pitch of the flights and the rotational speed of the kiln. The incinerator may be oil or gas fired. It normally contains a single combustion stage although an after burner has been added to at least one installation. A temperature gradient exists within the kiln from approximately 1,200°F at the fired end to 500°F at the feed end. The ordnance items are fed to the incinerator by a conveyor belt and advanced in the combustion chamber by the internal flights. The advancement rate is adjusted to provide ignition of the material near the midpoint of the incinerator. Large ordnance items are generally presheared to preclude detonation in the combustion chamber. The feed capacity of the incinerator ranges from 200 to 600 lb/hr depending on the type of material being consumed. Noncombustibles, such as shell casings, are ejected from the fired end of the furnace by a conveyor and are sometimes recycled to insure decontamination. Later models contain, and earlier models are being retrofit with, a cyclone separator and baghouse collector for particulate emission control. A water scrubber has been added in at least one installation.

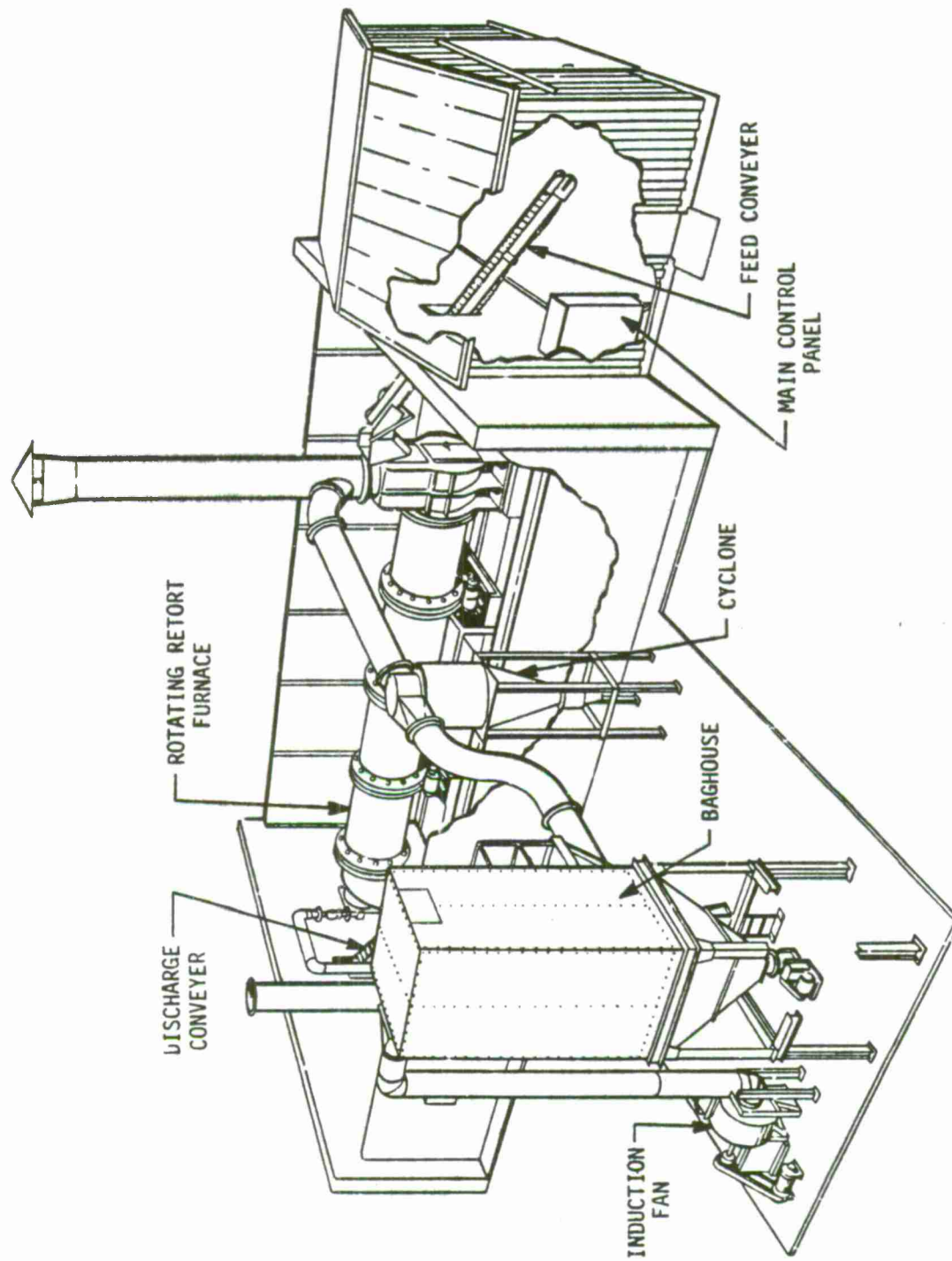


Figure 38. APE 1236 Deactivation Furnace with Air Pollution Control System, Kit E010

An alternate feed mechanism has recently been added to the incinerator for explosive wastes. It consists of a two stage, offset plunger arrangement which precludes prepagation from the furnace to the control room. The incinerator with this modification is termed an Explosive Waste Incinerator (EWI).

Advantages:

1. This method is less expensive than complete ordnance disassembly.
2. A skilled operator is not required.
3. There is a potential for controlled pollution abatement.
4. A regulated rate of feed provides safety.
5. Equipment is simple.
6. Reclamation of steel, brass, and copper is feasible.
7. The potential exists to handle a wide variety of waste munitions, particularly with some equipment modifications.
8. Technology is entirely or largely available.
9. Continuous or semicontinuous processing is possible.

Disadvantages:

1. The section of the furnace where detonations occur must be replaced due to erosion from high-velocity fragments.
2. Auxiliary fuel (gas or oil) is required.
3. Detonation causes noise pollution.
4. There is poor control over temperature.
5. Thermal efficiency is low because of uninsulated walls and recycle of feed material.
6. There are no provisions for control of gaseous emissions such as NO_x .

2.4.2 Radford Rotary Furnace

The rotary kiln application for propellants, explosives, and pyrotechnics (PEP) disposal was investigated extensively on a pilot plant scale (250

lb/hr) by the Radford Army Ammunition Plant (RAAP), Radford, Virginia. Two full-sized kilns (550 lb/hr) were added in January 1977. These facilities are being used for the disposal of bulk waste explosives and propellants.

Description

The Radford Rotary Furnace is illustrated in Figure 39. It consists of a 5-foot diameter by 8-ft long, alumina fire brick lined, rotating cylinder. The units are oil fired and contain a primary and secondary combustion chamber which operate at 1,600° and 1,700°F, respectively. The waste propellant or explosives are metered into the furnace as a water slurry. The slurry consists of approximately 25% ground solids (0.1 inch) and 75% water. The feed rate varies from 250 to 500 lb/hr (dry basis) depending on the explosive waste. The furnace is equipped with a gas cooler and a marble bed water scrubber for pollution control. Normally 8 to 16 hours are required for start up and shut down to avoid damage to the refractory lining.

Advantages:

1. The rate of feed is controlled.
2. This method of incineration is applicable to a wide variety of materials.
3. Kiln rotation provides mixing action for the feed and any ash which builds up; this helps to achieve complete combustion.
4. Water slurry incineration has been shown to be relatively safe.
5. The technology has been proven.
6. The equipment is amenable to modular construction.

Disadvantages:

1. Skilled operators are required.
2. Auxiliary fuel is required.
3. Long start up and shutdown periods are required.
4. There is considerable ash buildup for certain materials such as double-base propellants containing aluminum.
5. Equipment is fairly complex.

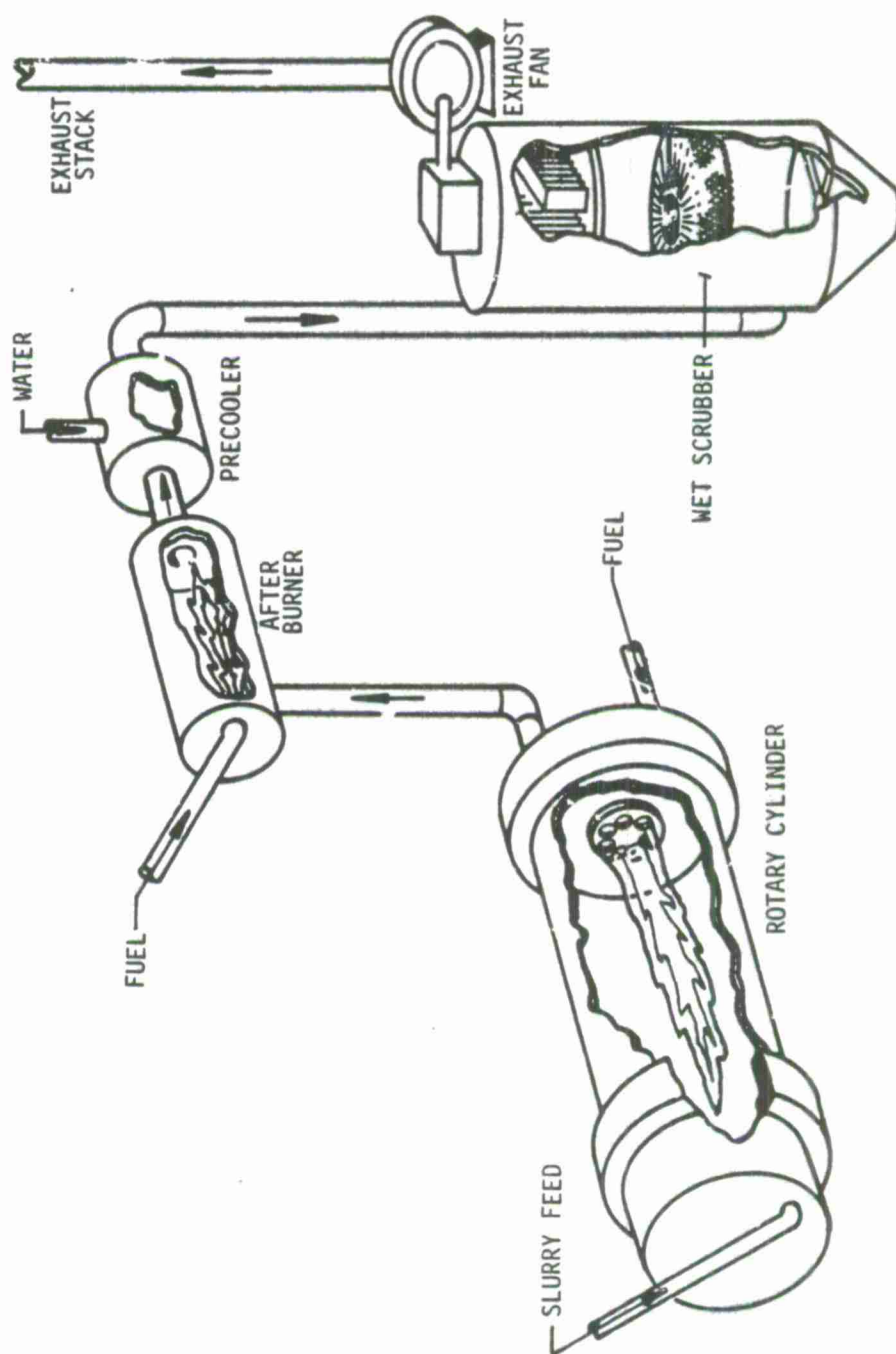


Figure 39. Rotary Kiln Incinerator System

6. Energy is required to convert 3 lb of water to steam for each pound of explosive waste.
7. Size reduction of the feed is required.

2.4.3 Fluidized Bed Incinerator

This approach for incineration of aqueous slurries of explosive materials has been under investigation by the Army since 1971. Initially, Picatinny Arsenal contracted with Esso Research and Engineering Co., Linden, New Jersey, to perform a lab-scale study using a 6-inch-diameter tube. This demonstrated the potential for destruction of several common propellants and explosives. Following the lab-scale work, Picatinny Arsenal decided to pursue a pilot-plant program in-house at Picatinny Arsenal. The program utilized an old vertical draft incinerator which converted to a fluidized bed operation by Process Plants Corporation of College Point, New York. A similar development program is currently underway at Aerojet General Corporation, Sacramento, California, under contract to the Army.

Description

The fluidized bed incinerator is illustrated in Figure 40. It consists of a vertical, 8-ft diameter by 30-ft high chamber, lined with fire brick. The chamber supports an 8-ft (expanded) granular alumina bed. The granular alumina is coated with a nickel oxide catalyst. The incinerator is oil fired and contains a primary and secondary combustion chamber. The primary combustion chamber, containing nickel oxide catalyst, is operated in a reducing atmosphere for conversion of NO_x to elemental nitrogen. Propellant and explosive waste are metered to the incinerator in a water slurry. The Picatinny Incinerator had a capacity of 150 to 250 lb/hr (dry basis) explosives. In addition to the two stage, catalyzed combustion for NO_x reduction, the incinerator was equipped with a cyclone collector for particulate emission control.

Advantages:

1. There is good temperature and air flow control.
2. This method has the potential of emitting very low levels of oxides of nitrogen (NO_x) with no follow-on pollution abatement steps.

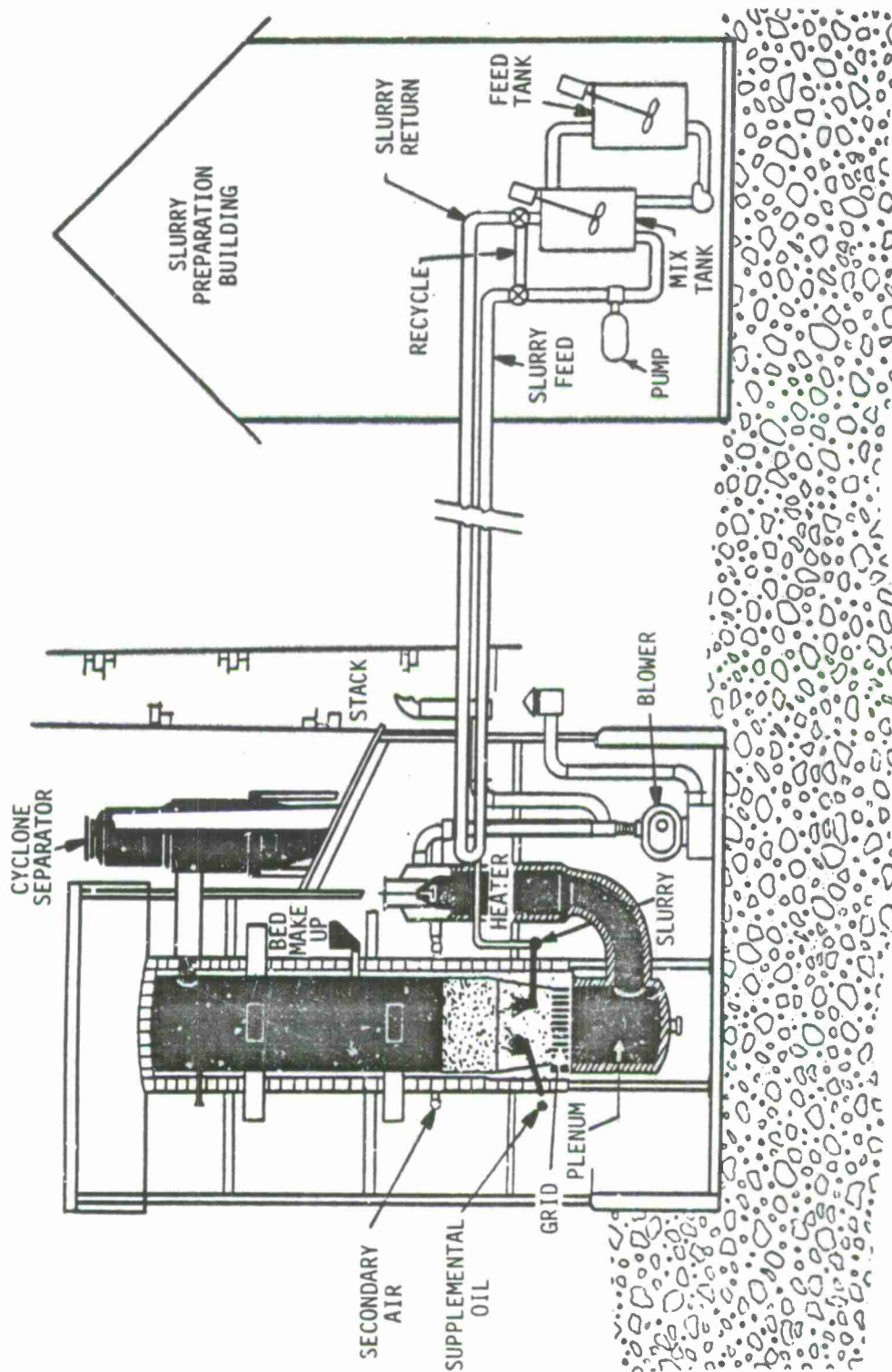


Figure 40. Fluidized Bed Incinerator

3. Minimization of NO_x is accomplished by the combination of catalyst and initial combustion in a reducing atmosphere.
4. The process is contained and controlled.
5. Pollution problems (NO_x) are reduced because only a slight excess of air is required (typically 20%).
6. Retention time is short.

Disadvantages:

1. Complex machinery is used.
2. Construction and maintenance expenses are high.
3. Skilled operators and an engineer are required for operation.
4. A period of time is required before this method reaches operating temperature; likewise, considerable cool-down periods will be required.
5. A supplemental fuel is required.
6. There is a possibility of bed agglomeration.
7. Catalyst lifetimes are unknown.
8. Size reduction of the feed is required.

2.4.4 Miscellaneous Incinerator

Other miscellaneous incineration approaches which have been investigated for disposal of explosive wastes are listed below:

Air Curtain
Closed Pit
Batch Box
Molten Salt
Vortex
Vertical Induced Draft
Wet Air Oxidation

In the wet air approach, oxidation occurs within the liquid phase rather than on the surface of the material being oxidized. Each of these incineration approaches will be discussed briefly. Areas covered will be system description and operation, advantages and disadvantages, and comparisons.

AIR CURTAIN INCINERATOR

The air curtain incinerator (ACI) concept was initiated by E. S. Moore, Jr., of I. E. Dupont de Nemours Co. in 1964. After developing ACI equipment and using a number of ACI units, Dupont elected not to take a patent position. A number of manufacturers offer ACI equipment for sale under a variety of names including "trench burners," "trench incinerators," "open pit incinerators," "pit incinerators," and "air curtain destructors" as well as "air curtain incinerators." The equipment appears to be employed mainly for combustion of trees and demolition of rubbish, pilings, railroad ties, municipal refuse, rubber, plastics, combustible liquids, and certain PEP materials. Wood wastes seem to be its best application. There are conflicting reports about the suitability of ACI equipment for the combustion of rubber materials such as tires, certain plastics and other hydrocarbons, and painted wood. Best results are apparently obtained when the materials are dry and are sized and shaped so there is a considerable surface area exposed for combustion.

ACI has been utilized only to a limited extent for routine disposal of hazardous or toxic liquids, and certain explosive materials.

System Description

An ACI system consists of a motor, a blower, an air manifold ("header") with a slit nozzle or group of nozzles, and a pit or trench. A typical ACI system using an earthen pit is shown in Figure 41. The motor powers the blower; it may be either electric, diesel, or alternately powered. Combustion of the waste occurs in the pit. The pit may be either a temporary (unlined) or crudely lined earthen one or a permanent one constructed with suitable refractory materials and/or metals. A typical commercial ACI unit uses a pit 8-ft wide and 12-ft deep with the length a function of the manifold length; this is usually between 8-ft and 42-ft. The most critical pit dimension parameter seems to be the depth/width ratio which should be about 1.5/2.5. Most designs have walls either vertical or as nearly vertical as is feasible. The top of the pit may either be flush with or above the ground level.

A high air flow from the blower is pumped through the manifold system at a pressure typically equivalent to 0.4 psi. This air flow is then distributed through the manifold along the entire top edge of the longest pit dimension. The air flow is directed against the opposite wall of the pit and

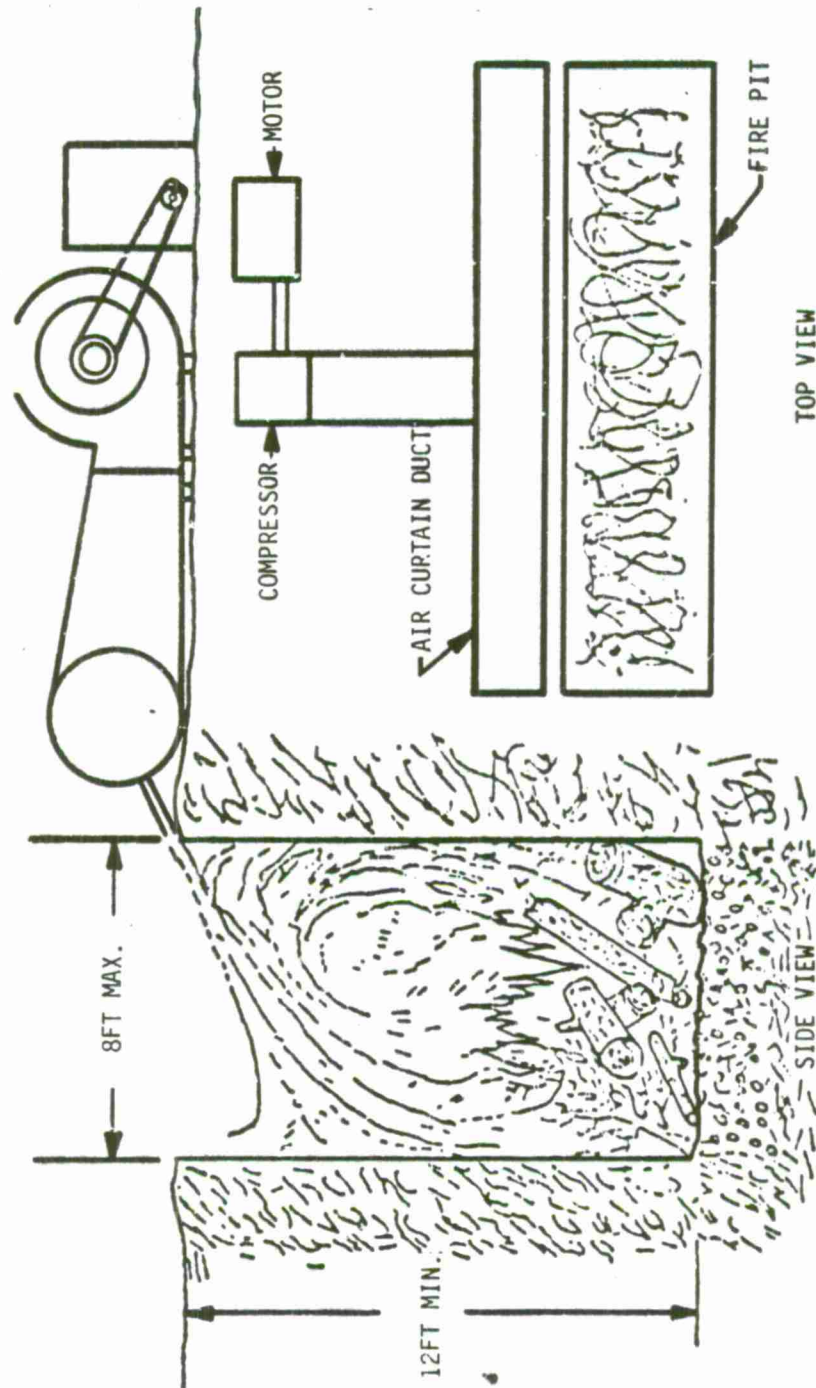


Figure 41. Air Curtain Incinerator

into the lower portion of the pit with usually some provision to adjust the air flow angle. Some units also provide for fan speed adjustment to assist in proper startup. A number of optional features include underfire air with a liquid waste feed system, fly ash arrestor screens, adjustable fan blades (to compensate for altitude variations), high-temperature control shutdowns, solid waste feeding systems, access for ash removal, and trailers and certain modifications to make the units portable.

Operational Principle

The air blower generates a very high flow of air which is blown out of the air manifold at a high velocity, about 100 mph, and directed as a "curtain" of air diagonally across and down into the pit. This air curtain provides a greatly increased amount of air which enhances combustion of the materials in the pit. More importantly, however, it sets up a circular flow in the pit that results in the combustion gases being recirculated through the burning area to burn combustible materials such as particulates, carbon monoxide (CO), and hydrocarbons that would otherwise be emitted. Figure 41 shows the schematic cross section of an operating ACI system. For proper operation, the flames and combustible material should be kept underneath the air curtain. Temperatures in ACI burning pits have shown gradual increases for a number of hours following startup; temperatures as high as 2,500°F have been measured for ACI fires burning wood.

Advantages/Disadvantages

Advantages vs. Open Burning:

1. Conventional open burning is eliminated.
2. Less land is required.
3. Visible emissions of particulates are reduced.
4. Chances for accidental fires are reduced.
5. High air flows cause high burning rates with resulting high capacities.
6. Public Relations of the user organization are enhanced.
7. Carbon Monoxide (CO) and hydrocarbon emissions should be reduced.
8. Odors from burning may be reduced or eliminated.

Advantages vs Other Incineration Techniques:

1. Initial costs are generally lower.
2. Maintenance and operation costs are lower.
3. Operation is probably less critical as regards performance; highly skilled operating personnel are not required.
4. Accidental detonation of PEP should cause only relatively inexpensive damage if a temporary pit is being used.
5. High air flows cause high burning rates with resulting high capacities.
6. Fuel consumption is reduced.
7. There is a potential for batch, semicontinuous, or continuous operation.
8. Equipment can be made portable if a temporary pit is being used.
9. A single motor and blower could provide air to multiple small incineration pits as compared to one large pit, and thus possibly reduce safety hazards.

Disadvantages vs Open Burning:

1. Costs are higher.
2. ACI may be much noisier depending on type of motor used.
3. Energy consumption is higher.
4. ACI may be considered open burning by some regulatory agencies.

Disadvantages vs Other Incinerator Techniques:

1. The potential for pollution abatement of gaseous or aerosol pollutants is small; it may be neither technically nor economically feasible.
2. Operation may be prohibited in certain areas by air pollution regulatory agencies.
3. EPA has indicated the Army's use of ACI for incineration of PEP-contaminated dunnage will be subject to a considerable number of restrictions intended to minimize adverse environmental impacts.

4. Unless care is exercised, the refractory lining in a permanent pit could be broken when feed is dropped into the pit.
5. A temporary pit will probably have a useful lifetime of only a few days to a few months because of abrasion and caving in of the walls. A permanent pit will eliminate the problem of earthen walls caving in, but it will be expensive.
6. The combustion of materials with high ash buildup may cause difficulty in cleaning the pit because of safety problems, possible cooling, etc.
7. Continuous operation is the best mode for minimum environmental effects; consequently, ACI may not be the best suited for disposal of small quantities of PEP.
8. Higher combustion temperatures may result in the formation of more oxides of nitrogen (NO_x).
9. Self-sustained combustion of PEP may require fairly large amounts of PEP that may pose serious safety problems.
10. Sustaining combustion for certain fast-burning PEP items may be a problem.
11. There may be greater problems in feeding PEP safely.
12. High air velocities may blow fine PEP out of the pit prior to combustion.
13. High winds may interfere with normal operations.
14. There may be fly ash problems resulting from feeding, operation, or waste removal.
15. A temporary pit may flood if the water table is too high. A raised pit would eliminate this problem.
16. If the ground is very rocky, it may be difficult and expensive to dig the pit. A raised pit would eliminate this problem.
17. The potential for ground water contamination exists if a temporary pit is used.

CLOSED PIT INCINERATOR

Closed pit incineration has been investigated for burning large quantities of bulk explosives on a batch process by Mason and Hanger-Silas Mason Company at the Pantex Energy Research and Development Administration (ERDA) plant located near Amarillo, Texas. This technique was investigated as an alternative to open burning, which is prohibited in Texas. Concept feasibility was demonstrated and engineering design criteria completed through tests conducted with a full-scale test facility. Explosives tested include TNT and plastic-bonded explosive (PBX) manufacturing wastes.

System Description/Operational Principle

The closed pit incinerator is shown in Figure 42. It was constructed from an old ammunition storage magazine (igloo) measuring 26 ft wide by 26 ft long with a 10 ft inside height. The bulk explosives, typically 1,000 lb, are placed on the dirt floor of the magazine and ignited with a squib. Combustion air is provided by two 10,000 ft³/min fans located on the front of the igloo. These blow over the top of the explosives. The combustion gases then rise and pass through the roof. The first roof is made up of gravel and sand and is intended to act as a filter for particulates. The second roof is metal and is used to protect the incinerator and filter from the weather.

Some laboratory work has been performed using a dirt rather than a sand filter; it has shown that the dirt will reduce the concentration of oxides of nitrogen (NO_x). Dirt has been tried in the full-scale model; however, it had a tendency to cause venting due to the internal pressure blowing holes in the weak spots of the soil filter, allowing unfiltered combustion gases to escape. This resulted from moisture causing soil agglomeration. Future plans include evaluation of various filter materials, measurement of pollutants, and definition of design criteria and operational procedures.

Advantages/Disadvantages

Advantages vs Open Burning:

1. Open burning is eliminated.
2. Less land is required.
3. Visible emissions of particulates are reduced.

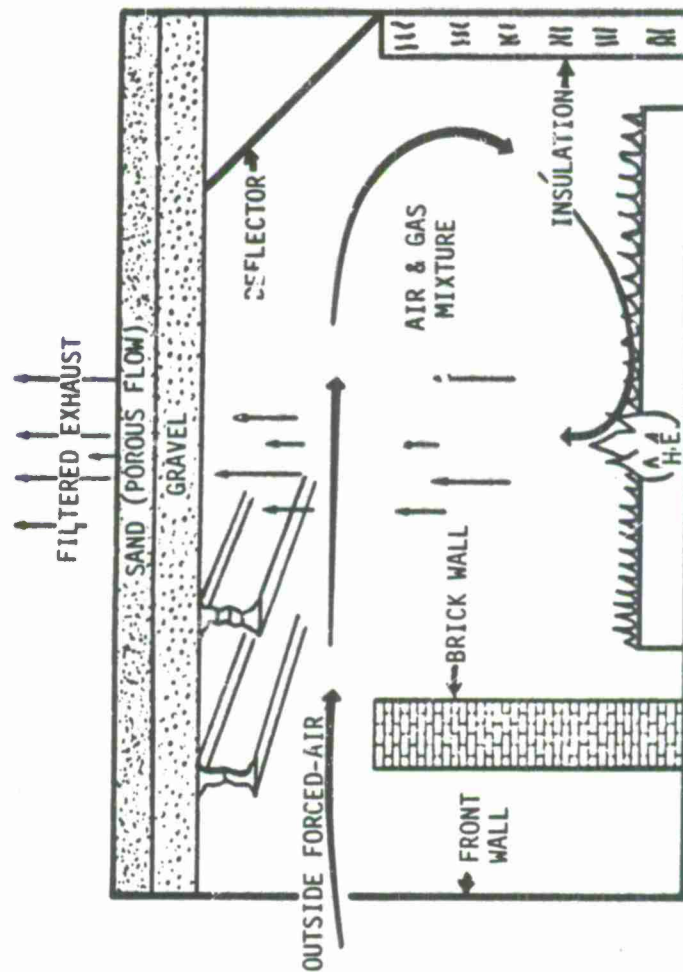


Figure 42. Closed Pit, Batch-Type Incinerator Concept (Side View)

4. Chances for accidental fires are reduced.
5. Public relations of the user organization are enhanced.

Advantages vs Other Incineration Techniques:

1. Initial costs are lower.
2. Maintenance and operating costs are lower.
3. Design and construction are simpler.
4. Operation is probably less critical as regards performance; highly skilled operating personnel are not required.
5. No auxiliary fuel is required.
6. It is possible to burn up to 1,000 lb of PEP material each burn.
7. Accidental detonation of explosives should cause only relatively inexpensive damage.

Disadvantage vs Open Burning:

1. Costs are higher.

Disadvantages vs Other Incineration Techniques:

1. Acceptance by air pollution regulatory agencies in certain areas may be questionable.
2. Continuous operation does not appear feasible.
3. Disposal of filter material could be a potential pollution problem.
4. A short cool-down period is required between burns.
5. The formation of holes or channeling in the filter will lead to emission of unabated effluents.

BATCH BOX INCINERATOR

Status

The batch box incinerator is under development by the Navy Ammunition Production Engineering Center (NAPEC). The batch box incinerator was intended for the disposal of a variety of waste munitions including small arms ammunition up to .50 caliber, pyrotechnics, and contaminated dunnage. The items this furnace is tentatively intended to dispose of are listed below:

Small Arms Ammunition up to .50 Caliber

Small Grenades

Illuminating and Smoke Signals

Cartridge-Actuated Devices

Flares

Grenade, Rocket, and Projectile Fuses

Primers, Igniters, and Blasting Caps

Explosive Fittings

Tracers

An initial prototype furnace was constructed at NAD, McAlester, Oklahoma. This furnace has been tested considerably to determine if it will work according to design specifications. Particulate emission problems are addressed by wet scrubbers or baghouse filters.

System Description/Operational Principle

This is an oil-fired incinerator with overfire air. Figure 43 shows the batch box incinerator's basic features. No. 2 fuel oil and wood dunnage serve as the fuel for deflagrating or detonating the ordnance items fed into the furnace. The contaminated dunnage is placed in the furnace box prior to feeding in the PEP items. The materials to be disposed of are then fed in batches to the furnace through an inclined feed chute. The chute has a pneumatic loading gate located behind a protective barricade; it also has a second pneumatic gate farther down the chute. The chute is equipped with a pneumatic vibrator to assist in moving the material down the chute and onto the burning grate. The grate is power-operated for dumping ashes into a cleanout scrap pan. The exhaust gases resulting from the PEP combustion go through an afterburner and a marble-bed wet scrubber prior to going out of the exhaust stack. The residue or ash from the items burned is manually removed after sufficient accumulation.

Advantages/Disadvantages

Advantages:

1. Some pollution control is achieved by the afterburner and marble-bed scrubber.
2. A skilled operator is not required.
3. Cost is relatively low.
4. Ordnance items do not have to be disassembled.
5. The batch box incinerator will handle a variety of items.

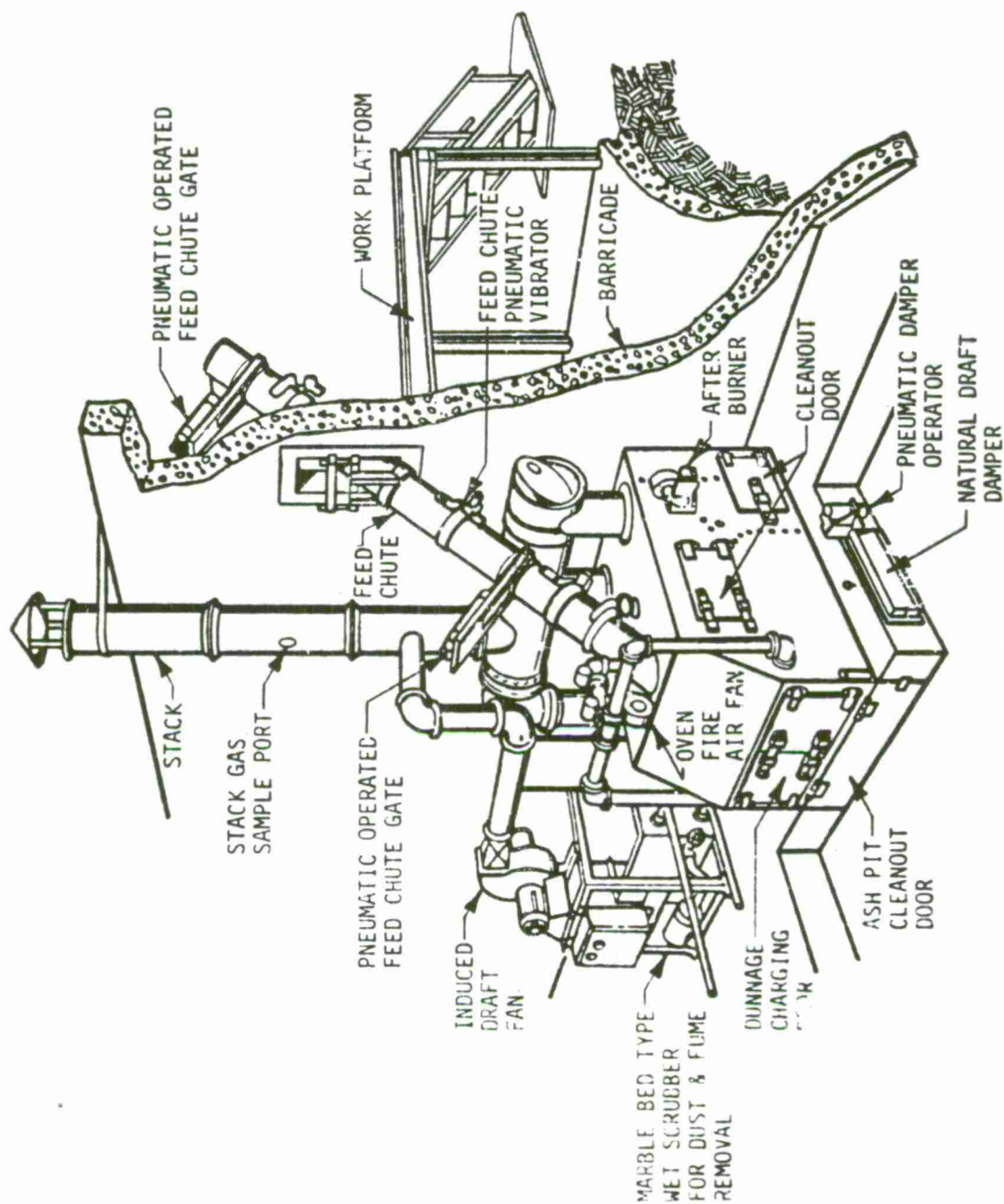


Figure 43. Batch Box Incinerator

Disadvantages:

1. Some auxiliary fuel is required.
2. A cool-down period is required prior to recharging with dunnage.
3. Wall erosion is a hazard if large-caliber (20mm) rounds are detonated.
4. There may be a water pollution problem resulting from the wet scrubber.
5. This incinerator type is not amenable to continuous operation.
6. This method is unsuitable for large quantities of bulk explosives.
7. The potential exists for overloading the furnace.
8. The incinerator must be fed manually.

WET AIR OXIDIZATION

Status

The Naval Ordnance Station (NOS), Indian Head, Maryland, has investigated wet air oxidation (WAO) as an alternative to open burning for the disposal of waste PEP, principally propellants. The original intention was to build a demonstration plant and determine the suitability of WAO for this application rather than to eliminate the open burning problem per se.

System Description/Operational Principle

The wet air oxidation is based on an aqueous phase oxidation of PEP materials using heat and air in a high-pressure reactor. The materials most commonly oxidized in WAO are those which contain a substantial amount of water and cannot easily be concentrated to sustain combustion under conventional burning conditions. Such materials are industrial wastes, waste organic sludges, and sewage sludges of all types. These all oxidize very easily. Fuels that are steam-distillable, and also water insoluble, such as naphthalene, are more difficult to oxidize since practically no oxidation occurs in the gas phase. In any case, the fuel concentration and oxidation conditions must be arranged so there is sufficient water present in the liquid phase to permit the oxidation to proceed and to carry away any insoluble ash remaining after oxidation.

A WAO process may involve many variations, depending on the application. A WAO flow diagram with principal components for a typical continuous liquid-waste system is shown in Figure 44. The process operates as follows: The aqueous waste or sludge to be oxidized (aqueous fuel) is ground under water to 1/4 inch size before entering the storage tank where it is usually preheated to 60° to 80°C. The small particle size is necessary to permit passage of the slurry through openings in the equipment. The waste material is introduced into the system by a positive-displacement high-pressure pump where it joins a metered amount of air supplied by a compressor. The pressure of the system is maintained from 150 to 4,000 psi gage depending upon the fuel concentration. The desired pressure is obtained by setting a back-pressure valve in the gas line located after the gas separator.

The mixture of air and aqueous fuel passes through a series of heat exchangers to increase its temperature to about 200°C, the point at which oxidation will usually proceed spontaneously. During startup, the incoming mixture is heated to the reaction temperature by steam introduced into the heat exchanger. After oxidation is initiated, the heat generated by the oxidation process is utilized to heat the incoming aqueous fuel and air.

The temperature of the reactor effluent can be controlled by regulating the quantity of oxidation products passing through heat exchanger No. 2. To achieve maximum reactor inlet temperatures, all the oxidation products are pressed through heat exchanger No. 2 after which the steam goes to a gas separator. To control reactor inlet temperatures at a lower level, a portion of the reactor effluent stream bypasses heat exchanger No. 2 and goes directly to the gas separator. Here all gases, including steam, nitrogen, and carbon dioxide, are separated from the liquid stream. The liquid fraction carrying any remaining suspended solids goes through heat exchanger No. 1 and a coil in the storage tank, thereby heating the incoming aqueous fuel and air. Such heat recovery may not necessarily be used in systems handling PEP materials because of potential safety hazards. Gaseous streams may be expanded to near-atmospheric pressure in a mixed-gas turbine to recover power if the unit is sufficiently large.

Effluents from the NOS WAO reactor will consist of gaseous and liquid oxidation products, nitrogen from the air feed, and a minor quantity of ash;

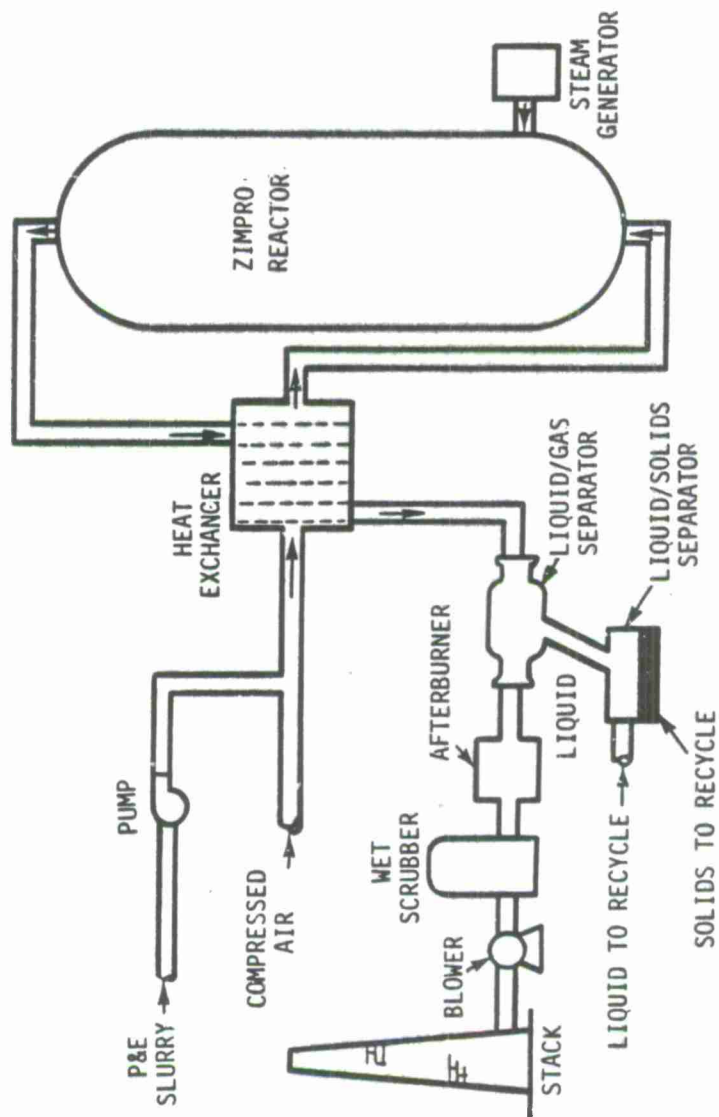


Figure 44. Wet-air Oxidation (Zimpro) Process

they will be cooled by the feed stream in a heat exchanger and then separated into gaseous and liquid streams. The gaseous stream will be treated by an afterburner to destroy CO and residual hydrocarbons; a wet scrubber will then be used to remove nitrogen oxides (NO_x) before they are discharged into the air. The liquid stream, which typically contains a few percent of nitric acid, will be neutralized with ammonia to produce ammonia to produce ammonium nitrate and to precipitate out metal salts as metal hydroxides. The metal hydroxides will be sent to a recovery or disposal operation. The liquid phase will be concentrated by reverse osmosis or some other method to recover an ammonium nitrate solution suitable for sale as a fertilizer. Purified water will be recycled to the slurry preparation stage. The processing will be somewhat more complicated if propellants containing perchlorates as well as nitrates are oxidized.

Some typical materials and their percentage destruction by WAO are listed in Table 29.

TABLE 29

<u>Item</u>	<u>Destruction (%)</u>
Double base casting powder	97.6
OTTO Fuel II	79.5
Modified double-base casting powder	94.8
NOSET-A (Nitrate Ester)	92.5
Trinitrotoluene (TNT)	94.8
Photographic Film	43.7
Shipboard Wastes	60-90

Advantages/Disadvantages

Advantages

1. Following startup, a self-sustained reaction is possible if the feed has a sufficiently high heat of combustion.
2. Heat recovery may be feasible on a large unit (greater than 500 hp); power recovery may be feasible on a very large unit (greater than 1,500 hp).

3. This method is a controlled-temperature process.
4. This method works well with a variety of water mixtures or slurries which would be difficult to incinerate by conventional methods.
5. This method is claimed to eliminate air pollution including nitrogen oxides; there is no fly ash emission.
6. PEP slurries containing as low as 5% solids can be fed into this system.
7. Solids resulting from the process should be inert and possibly disposable as landfill.
8. When the feed heat of combustion is increased rapidly, this system displays an ability to safely absorb large amounts of heat.
9. There is no open flame in this system.

Disadvantages:

1. Complex equipment requires high operator skill.
2. High-pressure equipment used in this system is expensive.
3. Certain propellant ingredients result in very corrosive solutions such as mixtures including HNO_3 , HCl , and HClO_4 ; this may necessitate use of expensive and scarce metals such as titanium or tantalum or various stainless steels (i.e., Hastelloy C).
4. Effluent water may require treatment if all the water cannot be recycled. The required technology for this may not be entirely available.
5. Long retention times are necessary, typically 20-60 min.
6. Some PEP materials are not satisfactorily broken down by wet air oxidation.
7. The degree of oxidation achieved is dependent on the temperature, pressure, solids content, retention time, and chemical composition. It may be difficult

to achieve steady-state operating conditions, especially with varying feed composition.

8. Size reduction of the feed may be required depending on the waste munitions being handled.

VORTEX INCINERATOR

A vortex incinerator, shown in Figure 45, was evaluated by RAAP as part of their initial screening study for incineration using solid propellants and explosives as feeds. The results were unsatisfactory due to settling of solids in the combustion chamber prior to complete combustion of the solids. This type of incineration is usually designed to burn wastes by atomizing the feed and accomplishing combustion of the atomized feed while it is in suspension in the combustion air. Application of a vortex incinerator, therefore, would appear to be limited primarily to liquid wastes.

MOLTEN SALT (FUSED SALT)

A bench-scale feasibility study was conducted on a molten salt incineration process by Atomics International in 1973 and 1974 under contract to NAVORD. The process is shown schematically in Figure 46. The process was successfully demonstrated for burning up to 1-lb samples of Composition B without detonation. The process is also disclosed in a patent issued to Rockwell International. Examples in the patent describe combustion of Composition B and an unspecified propellant using eutectic mixtures of alkali metal hydroxides and carbonates at temperatures between 230° and 525°C. Although all work performed was in batches, a final proposal from Rockwell International showed a semibatch feeding operation using chain buckets.

Advantages/Disadvantages

Advantages

1. Temperature control is easily accomplished, since a molten salt bath acts as a heat sink to help sustain and stabilize combustion.
2. Continuous operation is feasible.
3. A variety of PEP materials can be handled.

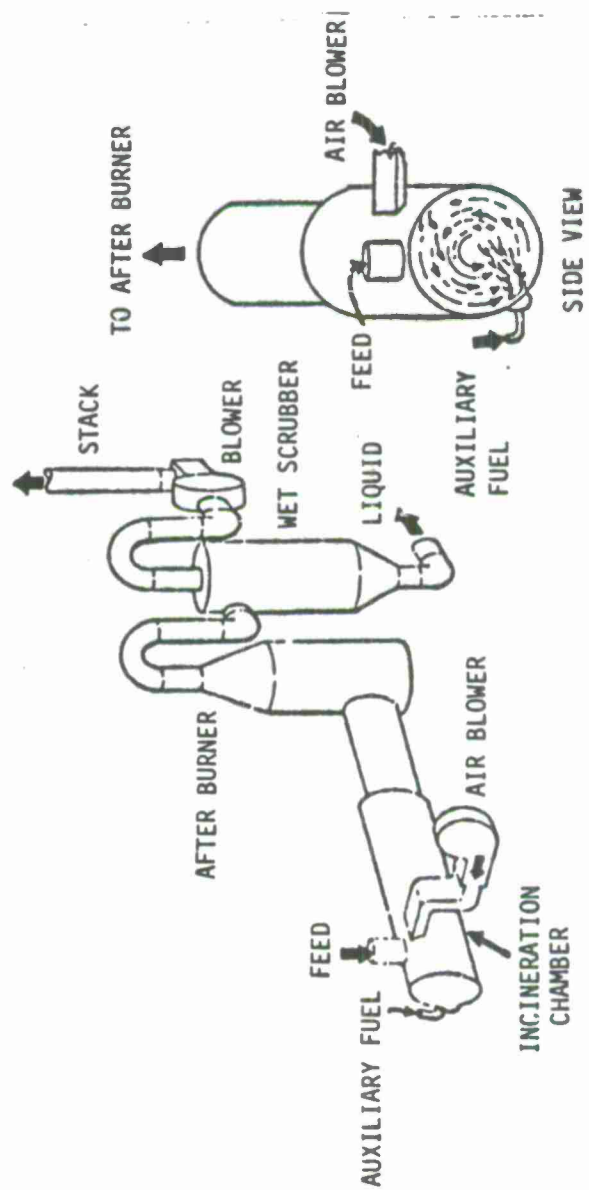


Figure 45. Vortex Incinerator

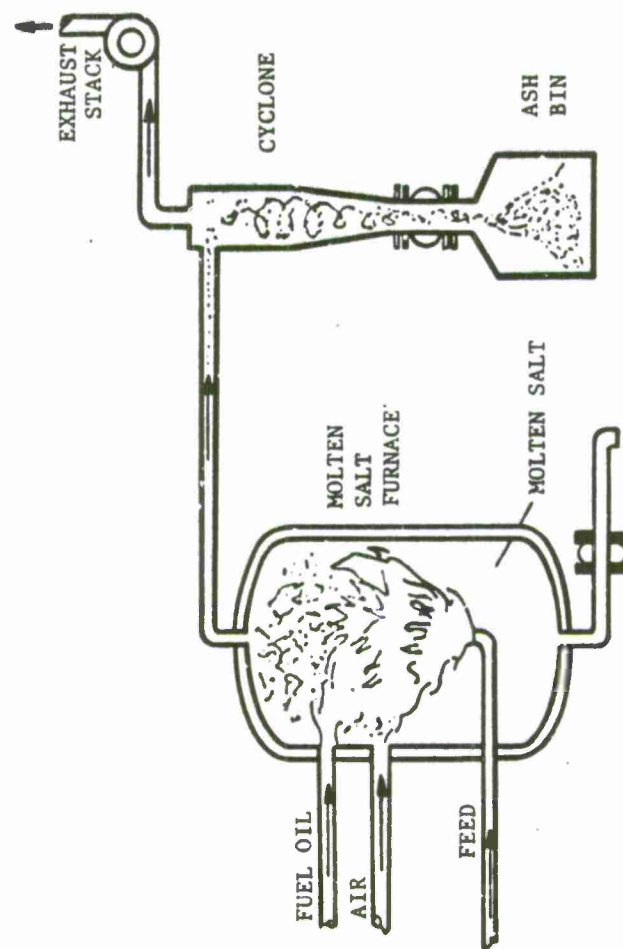


Figure 46. Molten Salt Incinerator (Schematic)

4. The molten salt bath physically retains coke, tar, etc., resulting from decomposition of energetic materials; introduction of an airstream should cause complete burnup of such undesirable by-products.
5. If solid PEP can be fed with few or no diluents, there is a potential for utilization of PEP heat of combustion.
6. This system has an extremely fast heat transfer.
7. A potential exists for molten salts to chemically bind and thereby control the emissions of gaseous pollutants such as sulfur oxides, HF and HCl.
8. The process may possibly be carried out in several modes including combustion in the molten salt with excess air or partial combustion and pyrolysis in the batch followed by complete combustion in an afterburner.
9. Combustion temperatures are low.

Disadvantages

1. There is a considerable amount of equipment required.
2. There is a complicated and long startup and shutdown.
3. This system has a potential for an explosive reaction in the event liquid water comes in contact with molten salt. The latter constraint requires feeding dry PEP materials which complicates the feed process.
4. The PEP materials normally have a lower density than the salt and, therefore, have a tendency to combust on the surface of the salt.
5. The initial and operating cost would be high.

Developmental work on the molten salt approach for PEP incineration was discontinued by NAVSEA several years ago.

VERTICAL INDUCED DRAFT INCINERATOR

This unit, shown in Figure 47, was built in 1955 at Picatinny Arsenal for disposal of explosives dissolved in organic solvents. The unit was later modified to burn aqueous slurries of waste propellants and explosives; tests of this type were run in 1972. The unit was run at a nominal rate of 250 lb/hr TNT using 30 gal/hr of No. 2 fuel oil. Tests were also run using Composition B, HMX and RDX. The unit consisted of a refractory-lined steel furnace (8 ft in depth by 30 ft high), a cyclone dust collector located at the base of the furnace, an induced-draft fan, and a 125 ft high exhaust stack. Air flow was downward through the tower. Two burners were located on opposite sides of the furnace about 8 ft below the top of the furnace. Slurry feed was injected through a steam atomizer about 10 ft below the top of the furnace. The injection lance extended into the center of the furnace and was water-cooled. This type of incinerator is considered to be less efficient than a rotary incinerator. It is also considered outdated. This unit has now been converted to a fluidized bed incinerator discussed in a previous subsection.

2.4.5 Environmental Impact

There are currently no federal or state air regulations directed specifically towards incineration of propellants, explosives, or pyrotechnics. There are, however, a number of applicable air pollution regulations which are primarily directed towards municipal-type incinerators (Table 30).

TABLE 30
FEDERAL AIR EMISSION STANDARDS FOR INCINERATORS

<u>Pollutant</u>	<u>Standard</u>
Particulate	0.08 gr/DSCF (180 mg/DSCM)
Visible	20% opacity

State and regional regulations concerning open burning and incineration are presented in Table 31 for those areas where disposal requirements exist. Particulate standards vary from 0.03 to 0.30 GR/DSCF and visible emissions from 20% (Ringelmann No. 1) to 40% (Ringelmann No. 2) opacity.

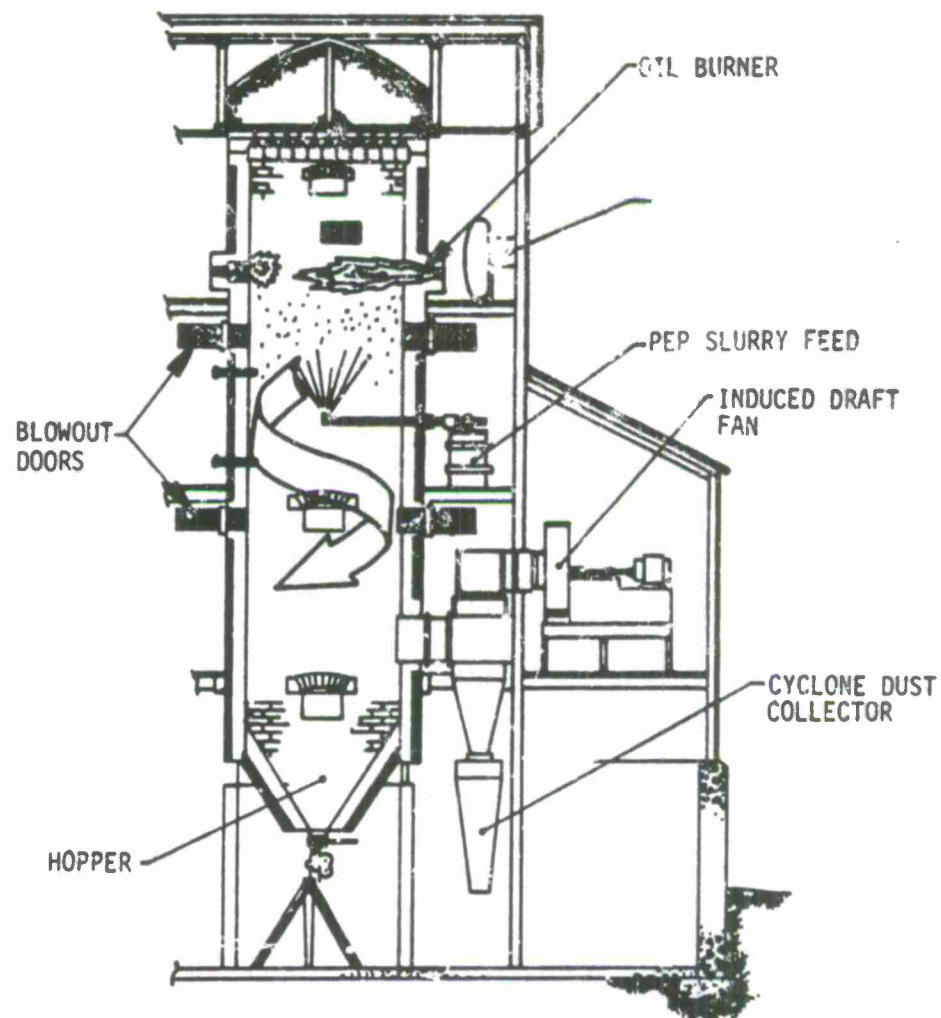


Figure 47. Vertical Induced Draft Incinerator

TABLE 31
STATE AND REGIONAL LIMITATIONS ON THERMAL DISPOSAL
OF WASTE MUNITIONS^a

State	Installation	Open burning ^b	Chamber Type ^b	Particulate Loading	Engineering		Remarks
					Capacity	Singleman No. ^c	
CA	WMS/Concord	R ^d	MC	0.13 gr/dscf	1	1	100 tons/day max. charge rate for incinerator
CA	PMTC/Point Mugu	R ^d	MC	0.2 gr/dscf	1	1	200 lb/hr max. charge rate for incinerator
CA	WMS/Sael Beach	P	MC	0.3 gr/dscf	1	1	100 lb/hr max. charge rate for incinerator
CA	WMC/China Lake	P	MC	0.3 gr/dscf	1	1	
HI	WMC/Lualaba	R ^d	MC	0.20 lb/150 lb charge	2	2	
IN	WMC/Crane	R ^d	MC	0.7 lb/1000 lb flue gas	2	2	
MO	WOS/Indian Head	R ^d	MC	0.01 gr/dscf	1	1	
NY	WAD/Marthorne	R ^d	MC	3.8 lb/ton charge	1	1	50 tons/day max. charge rate for incinerator
NJ	WMS/Berle	R ^d	MC	0.1 gr/dscf	1	1	
OK	WAD/McAlester	R ^d	MC or OP	0.8 lb to 0.13 lb ^h	1	1	250 to 80 lb/hr charge rate
PA	WS/Roosevelt Bds.	R ^d	MC	0.20 lb/100 lb charge	1	1	
SC	WMS/Charleston	U	MC ⁱ	0.75 lb/MRTG	2	2	
TX	WRTAP/McGregor	R ^d	MC ^h	400 kg/m ³ h:	1	1	MC incinerator required unless single-chamber one provides equivalent performance

TABLE 31 (CONT)

STATE AND REGIONAL LIMITATIONS ON THERMAL
DISPOSAL OF WASTE MUNITIONS

State	Installation	Open Burning ^b	Chamber Type ^d	Particulate Loading	Incineration		Remarks
					Opacity	Ringelmann No. e	
OT	11808/Magna	R ^d	See Remarks	350 control	1		Chamber type not specified. Control based on emissions at maximum capacity while control devices are not operating.
VA	WMS/Torkton	U	MC	0.14 gr/dscf	1		
VA	NSWC/Dahlgren Laboratory	U	MC	0.14 gr/dscf	1		
WA	WTS/Keyport	R ^d	MC	0.10 gr/dscf	1		
WV	ABL/Wingo	P	MC	0.12 lb/con	1		200 lb/hr maximum charge rate

P = Prohibited
R = Restricted
U = Unrestricted
MC = Multiple Chamber Incineration

OP = Open Pit Incineration
dscf = Dry cubic feet at standard conditions
gr = Grains
g = Gram(s)

^aAll data from Reference 30 except data for Dahlgren and Mooreville Ponds which were obtained from relevant state clean air laws.

^bInterpreted from the wording in the regulations, not necessarily the policy of the district. Some districts may tolerate open burning even though not permitted by regulations.

^cRingelmann units applicable only to steady or constant rate burn conditions lasting longer than the maximum allowable acceptance period, usually 3 to 5 min. per hour.

^dRequires prior approval from control authority.

^eCorrected to 6 percent O₂.

^fCorrected to 12 percent O₂.

^gInstallation lies in three Air Pollution Control Districts: Inyo, Kern, and San Bernardino.

^hLimit is 0.6 lb at 250 lb, decreasing to 0.15 lb at 90-lb charge.

ⁱApplies to existing units (prior to 1 July 1971).

^jBased on equivalent heat input.

^kMC incinerator required unless single-chamber type provides equivalent performance.

^lNational Primary and Secondary Ambient Air Standards also applicable.

As noted, no consideration is given to gaseous emissions in these standards. Investigators have had the foresight to establish design goals for incinerator emissions, however, which realistically address those gaseous emissions characteristic of propellants, explosives, and pyrotechnics (Table 32).

TABLE 32
EMISSION DESIGN GOALS

<u>Pollutant</u>	<u>Standard</u>
Particulate	200 mg/DSCM
SO ₂	200 ppm
H ₂ S	10 ppm
HCl	50 ppm
NO _x	200 ppm

The standard pollution control devices used on current incinerator designs and their effect on the three major pollutants generated from solid propellants: (a) particulates (metal oxides), (b) HCl and (c) NO_x are summarized in Table 33.

As noted, the APE 1236 deact furnace is equipped with a cyclone separator and baghouse collector. These devices effectively remove particulates and visible emissions and generally meet current state regional and federal standards. No consideration is given to HCl or NO_x emissions, however.

The Radford rotary kiln is equipped with a water scrubber for removal of particulates and HCl although the scrubber is ineffective for NO_x control.

The fluid bed incinerator is equipped with a cyclone separator, two stage combustion and reducing catalyst. This reduces particulate emissions and effectively controls NO_x emissions. HCl emission is not addressed in this system.

Typical performance data for the three major incinerator types are presented in Table 34. The emissions vary, of course, depending upon the type of material being consumed. The data for the fluid bed incinerator were

TABLE 33

POLLUTION CONTROL SUMMARY

Incinerator	Particulates (metal oxides)	HCL	NO _x
Rotary Kiln (APE 1236 Deact. Furnace)	Cyclone Collector Bag Collector	--	--
Rotary Kiln (Radford)	Water Scrubber	Water Scrubber	--
Fluid Bed	Cyclone Collector	--	Two Stage Combustion Nickel Catalyst

TABLE 34

DEMONSTRATED INCINERATION PERFORMANCE

Pollutant	Rotary Kiln		Fluid Bed	
	APE-1236	Radford	Catalyzed	Noncatalyzed
NO (ppm)	--	61-196	47	800
NO ₂ (ppm)	--	0-180	57	840
CO (ppm)	--	--	40	650
CO ₂ (%)	--	2.5-7.6	12	12
HC (ppm)	--	0-82	10	350
SO ₂ (ppm)	--	0-73	--	--
H ₂ S (ppm)	--	0-79	--	--
Particulate (GR/DSCF)	0.09	--	--	--

selected to show the effect of the catalyst under optimum operating conditions. There are, of course, considerable variation in emissions during the test and demonstration program.

It is noted that no single incinerator meets all emission goals with composite and high energy propellants:

- a. Particulates (metal oxides)
- b. HCl
- c. NO_x

The fluid bed incinerator:

- a. Meets particulate limits
- b. Meets NO_x emission goals

The rotary kiln (Radford) incinerator:

- a. Meets particulate limits
- b. Meets HCl emission goals
- c. NO_x emissions are marginal

The rotary kiln (APE 1236) incinerator:

- a. Meets particulate limits

All incinerators meet current state, regional, and federal emission standards, however.

2.5 ECONOMIC ANALYSIS

2.5.1 Introduction

The economic analysis of the ingredient recovery process is unusual in that the goal is not to determine how much it costs to recover the ingredients but how much it costs to dispose of the propellant. The components of the analysis consist of estimation of major equipment costs, raw material costs, labor requirements and overhead factors for various production rates (see Table 35). Summation of these costs result in a calculation of the cost per pound of production. In this estimation, comparison of the cost of final products with other current methods of production is unimportant. The over-

Preliminary Economic Analysis Activities

Preliminary Process Economic Analysis

1. Process Design Inputs
 - a. Raw Material Requirements
 - b. Utility Requirements
 - c. Equipment List
 - d. Labor Requirements
2. Specify Base Case Conditions
 - a. Base Year for Costs
 - b. Appropriate Indices for Costs
 - c. Additional
3. Raw Material Costs
 - a. Base Cost/lb of Material
 - b. Utility Cost
 - c. Total Cost
4. Utility Costs
 - a. Base Cost for Each Utility
 - b. Utility Cost
 - c. Total Cost
5. Major Process Equipment Costs
 - a. Individual Equipment Cost
 - b. Cost Index Adjustment
6. Production Labor Costs
 - a. Base Cost Per Manhour
 - b. Cost Per Area
 - c. Total Cost
7. Estimation of Plant Investment
 - a. Battery Limits Direct Costs
 - b. Other Direct Costs
 - c. Indirect Costs
 - d. Contingency
 - e. Total Plant Investment (fixed capital)
8. Estimation of Total Product Cost
 - a. Direct Manufacturing Cost
 - b. Indirect Manufacturing Cost
 - c. Plant Overhead
 - d. By-Product Credit
 - e. General Expenses
 - f. Total Cost of Product

all objective of the economic analysis is to arrive at comparison of the costs of propellant disposal by the methods under consideration.

Laboratory tests conducted during Phase II indicated that recovery of ingredients from Class 1.1 propellants was technically feasible. A secondary method of utilization of scrap uncured propellant identified was manufacture of explosive boosters. Each of these methods of disposal appear at first hand to be more attractive than disposal by incineration because each conserve materials and furnish an end-product of monetary value. Whether the product value is sufficient to defray the processing cost is a primary question to be answered by the economic analysis and is dependent not only on optimization of the processing method, but the quality and marketability of the final product.

Three methods of disposal were selected for analysis: (1) explosive booster manufacture, (2) ingredient recovery, and (3) incineration. Methods of incineration evaluated were closed systems which appeared to be capable of meeting current federal emission standards.

An initial and necessary step of the analysis was consideration of the amount of high energy waste to be disposed. An examination of Thiokol's Class 1.1 propellant production history indicated a scrap rate of 20,000 to 100,000 lb/yr can be expected. With production of the First Stage Trident motor, Thiokol probably produces more Class 1.1 propellant and subsequently more propellant waste than any other solid propellant rocket motor manufacturer. This limited amount is not much more than would be handled in a pilot-size facility.

Larger quantities of propellant waste can be envisioned in a motor reclamation or demilitarization program. Disposal of the propellant removed from the motors could easily be one to several million pounds.

Based on the above considerations, the selected range of sizes to be evaluated were 20,000, 200,000, and 2,000,000 lb of propellant per year.

2.5.2 Estimation of Costs for the Explosive Booster Process

The base case selected for evaluation of utilization of waste propellant in explosive boosters assumed there would be 20,000 lb of castable propellant

per year. The production rate for casting the boosters was selected to be about 400 lb of propellant cast per hour. Production of explosive boosters consists of casting a detonable propellant into a small cardboard or plastic sleeve capable of holding about 1.2 lb of propellant. A cavity is also formed during casting and curing for insertion of an initiator. This operation is similar to typical sample and subscale casting operations performed in rocket motor manufacturing to obtain and monitor propellant mechanical and ballistic properties. Existing facilities would already be available and the design of what special tooling would be required would be similar to already existing tooling and would not constitute a major design problem.

Factors included in the estimation of the plant investment costs are tabulated in Table 36. The only major equipment would consist of the tooling specially adapted to the casting operation. Since no design was actually made, the cost of similar tooling was used. Tooling for casting 1-lb charges used in ballistic testing was selected as being most nearly similar to what would be required.

Other direct plant investment costs consists of installation costs, piping and instrumentation which normally are included as the battery limit facilities. The factor of 80% of the tooling cost is smaller than is usually used since it was assumed that no new facilities or land development would be required. Another basic item, which would not be available at most facilities but would be needed, would be equipment associated with the packaging and shipping of the product.

Item III, indirect plant investment costs, include such items as the cost for design of tooling and of modification to the existing facilities to accommodate the additional operation.

The total estimated plant investment (fixed capital) of \$186,000 would be a constant for a range of production capacities. The amount of tooling required depends on the working life of the propellant. For example, at a casting rate of 400 lb/hr, a 6,000-lb batch of propellant would require 15 hours to cast. If one reject mix per week were processed (which is extremely unlikely) a total of about 300,000 lb/yr could be cast into boosters and still leave most of the facility utilization time for processing the regular samples and subscale units.

TABLE 36

ESTIMATION OF PLANT INVESTMENT COSTS
FOR MANUFACTURE OF EXPLOSIVE BOOSTERS

	Production Capacity* 20,000-100,000 Lbs Propellant Per Year
I. Major Equipment Costs (tooling)	\$ 60,000
II. Other Direct Plant Investment Costs	48,000
III. Indirect Plant Investment Costs	<u>60,000</u>
IV. Total Direct and Indirect Costs	168,000
V. Overall Contingency	<u>18,000</u>
VI. Total Plant Investment (fixed capital)	186,000

* Operating expenses, not fixed capital vary over the production range.

Factors used in estimation of the product cost are tabulated in Table 37. The direct manufacturing costs normally consist of the cost of the following items: (1) raw materials, (2) direct operating labor, (3) utilities, (4) supervision and clerical, (5) maintenance, (6) operating supplies, (7) laboratory charges, and (8) patents and royalties. In this process Items (1) and (7) are zero and all other items except Item (2), the direct labor, are minimal.

The indirect manufacturing costs, which consists of the fixed charges of depreciation, taxes, insurance, and interest, constitute the major expense. Since the same tooling and installation is capable of processing each of the production levels considered (and more) the indirect costs are a constant.

The plant overhead is a charge to cover the general plant costs not included above and is determined as a percentage of the labor charges included in the direct charges.

The disposal of the propellant was selected as the product or intent of this operation; therefore, the explosive booster was considered as a by-product.

General expenses consist of administration, distribution and sales, and research and development. They are based upon the total manufacturing costs.

The estimated unit product costs determined by consideration of the factors detailed above are shown in Figure 48 as a function of the plant capacity or the pounds of castable propellant disposed of per year. It was estimated that at about 40,000 lb of propellant per year this process would start showing a profit.

By examination of the items in the cost model tabulated in Table 36, it is evident that the product cost would be most affected by changes in the capital or in the by-product credit. To demonstrate the effect of these parameters, the estimated costs were recalculated using (1) a 50% increase in capital and (2) a 25% decrease in by-product credit. The results, shown graphically in Figures 49 and 50 do not greatly affect the basic conclusion that at higher waste levels the process could return a profit. The cost of disposal at the 20,000 lb/yr level is less than other disposal methods as will be shown later.

TABLE 37

ESTIMATION OF PRODUCT COST FOR UTILIZATION OF WASTE
PROPELLANT TO MANUFACTURE EXPLOSIVE BOOSTERS

Production Rate, Klbs. of propellant/year	20	50	100
I. Direct Manufacturing Costs, K\$	7040	14,381	25,893
II. Indirect Manufacturing Costs, K\$	42,780	42,780	42,780
III. Plant Overhead, K\$	<u>2,190</u>	<u>4,464</u>	<u>8,028</u>
IV. By-Product Credit, K\$*	(-) <u>33,900</u>	(-) <u>84,740</u>	(-) <u>169,490</u>
V. Total Manufacturing Costs, K\$	18,110	23,115	92,789
VI. General Expenses, K\$	<u>2,712</u>	<u>6,779</u>	<u>13,559</u>
VII. Total Product Costs, K\$	20,822	16,336	79,230
VIII. Unit Product Costs (\$/lb of propellant)	1.04	(-) .33	(-) .79

* By-product credit: \$2.00/booster.

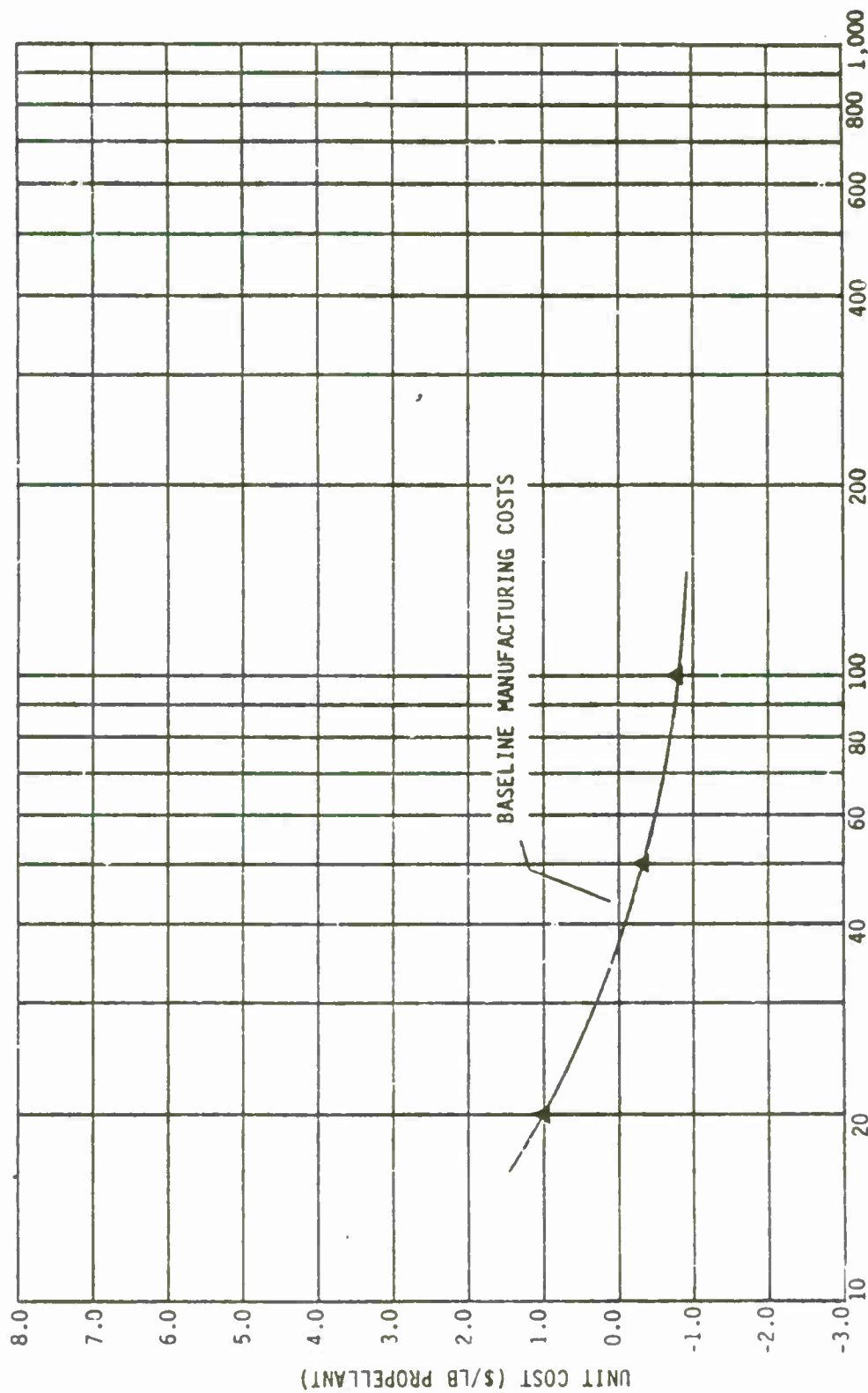


Figure 48. Costs of Explosive Booster Manufacture Using Waste High Energy Propellant

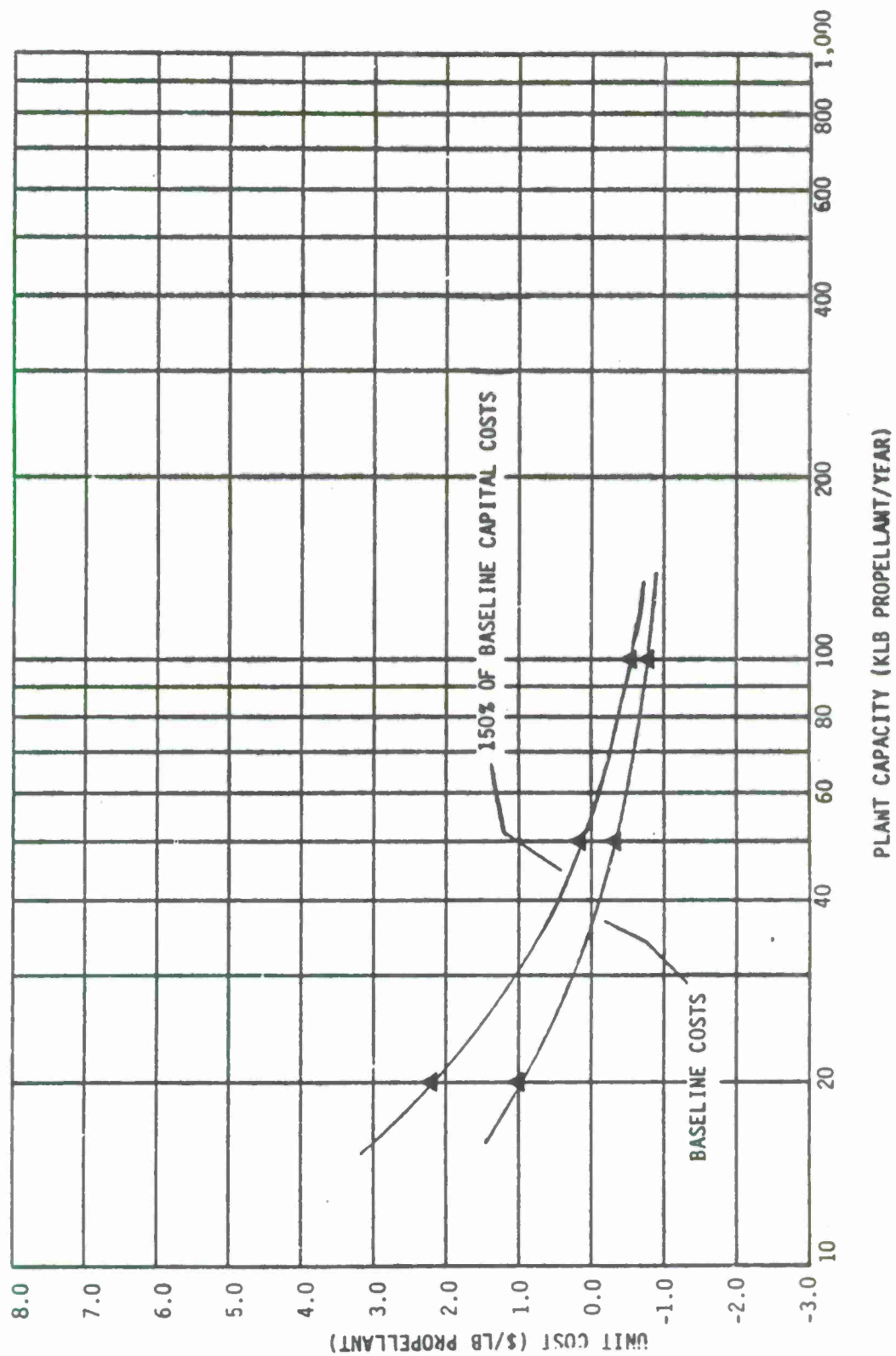
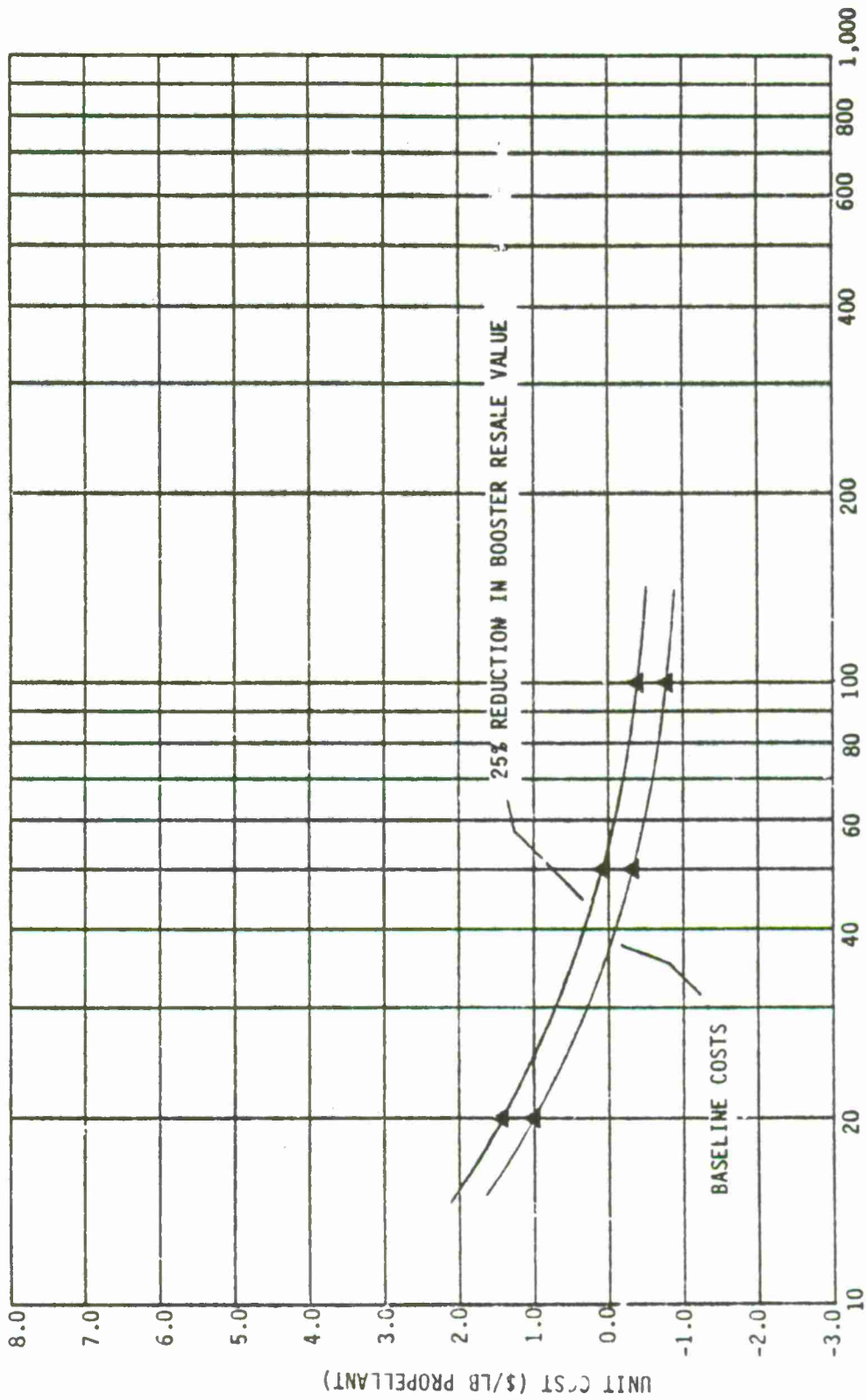


Figure 49. Effect of Capital Cost on the Unit Cost of Explosive Booster Manufacture Using Waste High Energy Propellant



PLANT CAPACITY (KLB PROPELLANT/YEAR)

Figure 50. Effect of Reduced Booster Sale Value on the Cost of Booster Manufacture Using Waste High Energy Propellant

Some basic problems are associated with the acceptability of this method for disposal. Perhaps the greatest is the utilization of propellants with security classified formulations. Perhaps additional ingredients would have to be added to the reject mixes to remove the security classification. A second problem is that this method only processes the castable propellant waste. Some waste would still be created from this process. Other propellant waste generated from machining operations, rejected cured motors, cured samples, etc., would still require disposal; hence, another disposal method would be required.

2.5.3 Estimation of Costs for the Selective Solvent Extraction Process

The calculation of the manufacturing cost for the recovered marketable ingredients was based upon accepted methods of estimation. This analysis demonstrates the basic approach to establishing the plant costs for a process. It presents a flow diagram, a material balance, and a tabulation of the equipment, piping and instrumentation cost, including estimated installation costs. This analysis follows standard preliminary estimating methods which lists major equipment costs and uses factors as developed by Lang,¹ Guthrie,² Haselbarth,³ and others^{4,5} to estimate piping, utility, instrumentation and other costs. Actual data can be used if they are available to make the cost estimates more accurate than can be achieved by using factors above. Cost of site preparation and utilities are characteristic for a given location and will vary from plantsite to plantsite; however, these differences are usually insignificant when compared to the cost of purchase and installation of the processing equipment. A very important element of the estimate is that sufficient detail is given to assure that comparisons be made on an equal basis. The first step in the analysis is the determination of the process design inputs. A prerequisite is the development of the flow

¹Lang, H. J., Series of Articles, Journal of Chemical Engineering, September, October 1947, June-1948.

²Guthrie, K. M., Process Plant Estimating, Evaluation and Control, Craftsman Book Co. of America, Solana Beach, California (1974).

³Haselbarth, J. E., and Beck, J. M., Journal of Chemical Engineering, p. 158 (May-1960).

⁴Cran, J., Journal of Chemical Engineering, p. (April-1981).

⁵Haselbarth, J. E., "Updated Investment Costs," Journal of Chemical Engineering, p. , December 4, 1967.

sheet which indicates the types of equipment and the process flow necessary to accomplish the task. A schematic for the planned pilot plant is presented in Figure 51. A summary of the material balance is given in Table 38. The material balance calculation, based upon the anticipated conversions and separation efficiencies, was developed to determine the equipment sizes and to determine the raw material and energy requirements for the processes.

These values should be adjusted as evaluations better identify the conversions and separation efficiencies actually obtained in pilot plant operations.

After the equipment was sized, the cost of the major equipment was estimated or obtained from vendor quotes. The current cost of equipment, listed in Table 39, was obtained from vendor quotations and catalog prices of actual or comparable equipment. CPI indices published in Chemical Engineering Magazine were used to scale up costs to 1982 dollars where necessary. A power factor was used to scale the costs for the various sized plants given in Table 40.

From the major equipment costs, the plant investment costs, shown in Table 41, were estimated. The factors used in this calculation would be adjusted by each company's historical records and are somewhat dependent upon geographical location and other factors affecting construction costs. Based upon the plant investment costs, the manufacturing costs, listed in Table 42, are calculated. The manufacturing cost is comprised of direct, indirect, and fixed costs.

The direct costs include raw materials, operating labor, supervision, maintenance, operating supplies, and utilities. The raw materials are obtained from material balances of the process. For this calculation, the cost of the raw material is low, as it consists only of makeup of solvent losses. The original charge of solvent would be included in the original investment and is insignificant compared to other capitalized costs.

Operating labor is also obtained from consideration of the preliminary design and the pilot plant operation (Figure 52). While manpower requirements are significantly affected by the degree of automation designed into the operation, average values based on production rates can be estimated

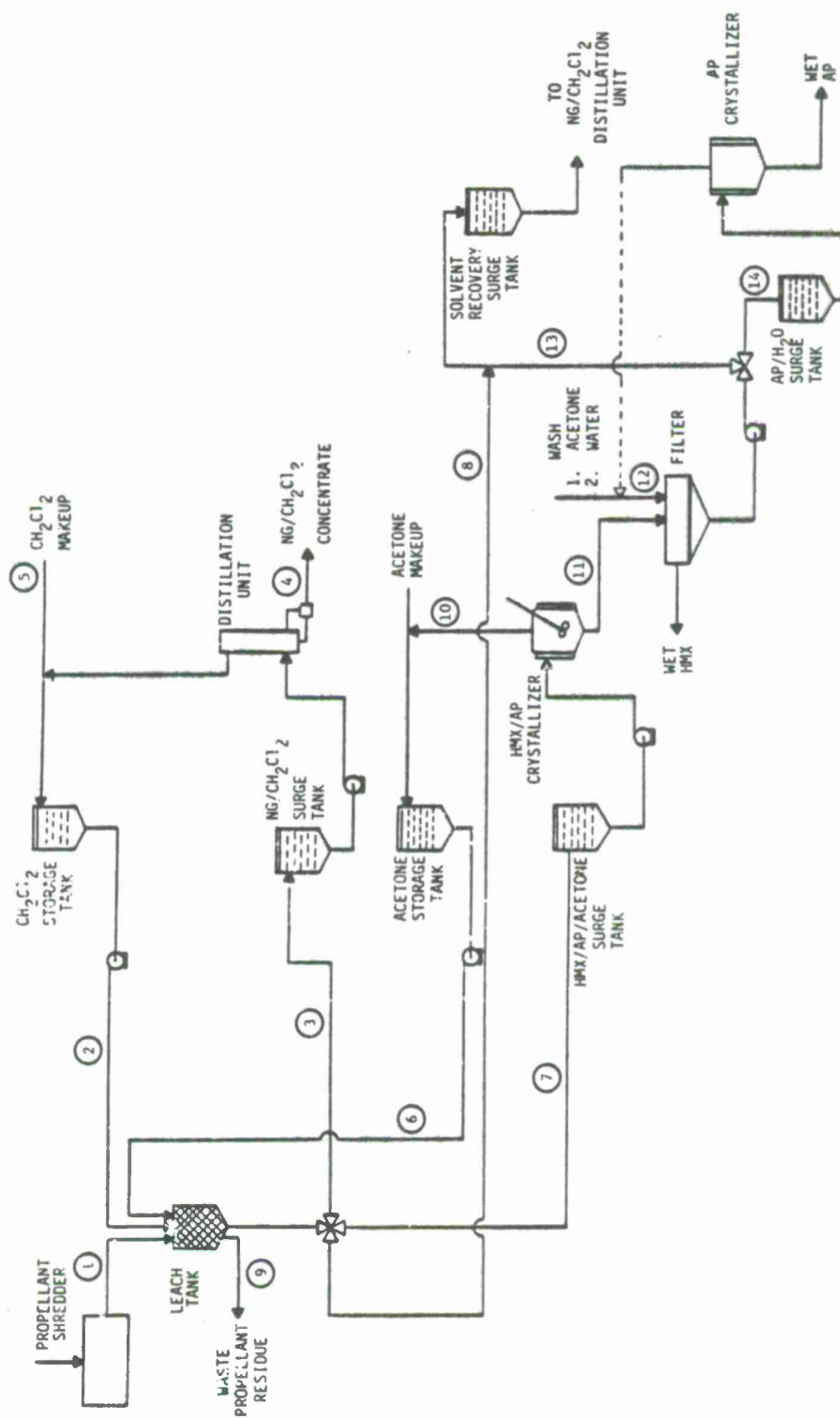


Figure 51. Pilot Plant Design - Selective Solvent Extraction

TABLE 38

MATERIAL BALANCE CALCULATION RESULTS FOR THE PROPELLANT
INGREDIENT RECOVERY PROCESS (P&SIS: 100 LB OF PROPELLANT)

Station	2	3	4	5	6	7	8	9	10	11	12	13	14
NG & Stabilizers	--	17	17	--	--	0.5	0.5	0	0	0.5	0	0.5	0
HNX	--	0	0	--	--	43.3	0.3	0.4	0	43.3	0	2.3	0
AP	--	0	0	--	--	10.4	0.3	1.3	0	10.4	0	1.6	8.
Binder & Aluminum	--	0	0	--	--	0	0	2.6	0	0	0	0	0
CH ₂ Cl ₂	1340	1200	40	--	0	20 ²	120 ³	--	18	2	0	2	0
Acetone	--	--	--	--	2700 ¹	2420	130	180	2370	50	50	95	5
Water	--	--	--	--	--	--	--	--	--	--	100	--	95

¹ 200 lb acetone for wash step to remove CH₂Cl₂.

² 20 lb CH₂Cl₂ not removed in acetone wash step.

³ 110 lb of this recovered in the still so that 10 lb + 20 lb = 30 lb continues into acetone leaching process.

TABLE 39
ESTIMATION OF MAJOR EQUIPMENT COST

	Size On Capacity	Cost (K\$)	
		Standard	NG Adapted
I. Size Reduction			
1. Propellant Shredder	100 lb/hr	50	50
II. CH_2Cl_2 , NG leach			
1. Leach tank w/basket	75 gal.	2.5	3.8
2. CH_2Cl_2 storage tank	150 gal.	2.1	3.2
3. Pumps a.	300 gal/hr	1.0	1.5
b.	25 gal/hr	0.5	0.8
4. Filter	--	0.5	0.8
III. CH_2Cl_2 recovery			
1. Surge tank	150 gal.	2.1	3.2
2. Still w/conditioner and reboiler	250 lb/hr	30	30
3. NG/ CH_2Cl_2 container	50 gal.	1.5	2.3
IV. HMX leach, acetone			
1. Leach tank		Using CH_2Cl_2 tank	
2. Filter	--	0.5	0.8
3. Pump (3)	150 gal/hr	2.4	3.5
4. Surge tank	75 gal.	1.7	2.6
5. Filtrate and CH_2Cl_2 wash tank	150 gal.	2.1	3.2
V. Crystallization of HMX/AP			
1. Crystallizer	1000 lb/hr	30	30
2. Storage	200 gal.	2.5	3.8
VI. Filtration and wash			
1. Filter	15 ft ²	15	23
2. Pump	150 gal/hr	0.8	1.2
3. Wash tank	50 gal.	1.9	2.9
4. AP crystallizer	--	10	15

* 1.5 x Standard Equipment Costs, when required

TABLE 40

SUMMARY OF MAJOR EQUIPMENT COSTS

Operation	Exponential* Factor	Plant Size (lb propellant/yr)		
		20K	200K**	2000K**
Size Reduction	0.60	\$ 50,000	\$199,000	\$ 792,000
NG Leaching w/CH ₂ Cl ₂	0.50	10,100	32,000	101,000
CH ₂ Cl ₂ Recovery	0.60	35,500	141,000	563,000
HMX/AP Leaching w/Acetone	0.50	10,200	32,000	102,000
HMX/AP Recrystallization	0.70	33,800	169,000	849,000
Filtration & AP Recovery	0.60	42,100	168,000	667,000
Total Major Equipment Cost		\$ 182,000	\$ 741,000	\$3,074,000

* Exponential factors are equipment oriented.

** Cost of Plant Size 2 = Cost of Plant Size 1 (Plant Size 2/Plant Size 1)^N

TABLE 41

ESTIMATION OF PLANT INVESTMENT COSTS
(COSTS REPORTED IN K\$)

		% of Equipment Cost	Normal Range	Plant Size, lb prop.		
				20K	200K	2000K
1.	<u>Direct Plant Investment Costs</u>					
1.1	Major Process Equipment	100.0	100	182	741	3074
1.2	Installation	45.0	43-50	82	333	1383
1.3	Process Piping	20.0	19-74	36	148	615
1.4	Instrumentation	11.0	10-19	20	82	338
1.5	Electrical	9.0	9-10	16	67	277
1.6	Process Buildings	10.0	6-10	18	74	307
	(Battery Limits) - Subtotal			354	1145	5994
2.	<u>Other Direct Plant Investment Costs</u>					
2.1	Utilities	30.0	25-48	55	222	922
2.2	General Services, Site Development, etc.	23.0	12-25	42	170	707
2.3	General Buildings	14.0	14-35	25	104	430
2.4	Receiving & Shipping Facilities	24.0	21-25	44	178	738
	(Offsite Facilities) - Subtotal			166	674	2797
3.	<u>Indirect Plant Investment Costs</u>					
3.1	Engineering Overhead	45.0	38-55	82	333	1383
3.2	Normal Contingencies	55.0	44-71	100	408	1691
	(Indirect) - Subtotal			182	741	3074
4.	Total Direct and Indirect Costs			701	2853	11835
5.	Overall Contingency, 30% of 4			210	856	3551
6.	Total Plant Investment (Fixed Capital) - excluding working capital.			911	3709	15386

TABLE 42

ESTIMATION OF PRODUCT COST
(COSTS REPORTED IN K\$)

	Typical % Value	Plant Size, lb prop.		
		20K	200K	2000K
1. Direct Manufacturing Cost				
1.1 Raw Materials	-	15.8	158.0	1580.0
1.2 Operating Labor	-	48.0	76.0	121.0
1.3 Utilities	-	- negligible -		
1.4 Supervision & Clerical % of 1.2	15	7.2	11.4	18.2
1.5 Maintenance & Repairs - % of Fixed Capital	4	36.0	148.0	616.0
1.6 Operating Supplies (% of 1.5)	15	5.4	22.2	92.4
1.7 Laboratory Charge (% of 1.2)	20	9.6	15.2	24.2
Subtotal		122.0	431.0	2451.0
2. Indirect Manufacturing Cost (Fixed Charges)				
2.1 Depreciation, % of Fixed Capital	10	90.0	370.0	1540.0
2.2 Local Taxes, " " "	3	27.0	111.0	462.0
2.3 Insurance, " " "	2	18.0	74.0	308.0
2.4 Interest, " " "	8	72.0	296.0	1232.0
Subtotal		207.0	851.0	3542.0
3. Plant Overhead, % of Labor in 1.2 + 1.4 + 1.5	72	53.0	116.0	322.0
4. By-Product Credit*		-93.4	-933.7	-9337.0
5. Total Manufacturing Cost (1 + 2 + 3 + 4)		289.0	464.0	-3022.0
6. General Expenses				
6.1 Administration, % of Manufacturing Cost (abs. value)	8	23.0	37.0	242.0
6.2 Distribution & Soln., % By-Product Credit (abs. value)	8	8.0	75.0	747.0
Subtotal		31.0	112.0	989.0
7. Total Product Cost (5 + 6)		320.0	576.0	-2033.0
8. Product Cost/lb Propellant		16.00	2.88	-1.02

*
NG = \$5.28/lb
HMX = \$9.08/lb
AP = \$.68/lb

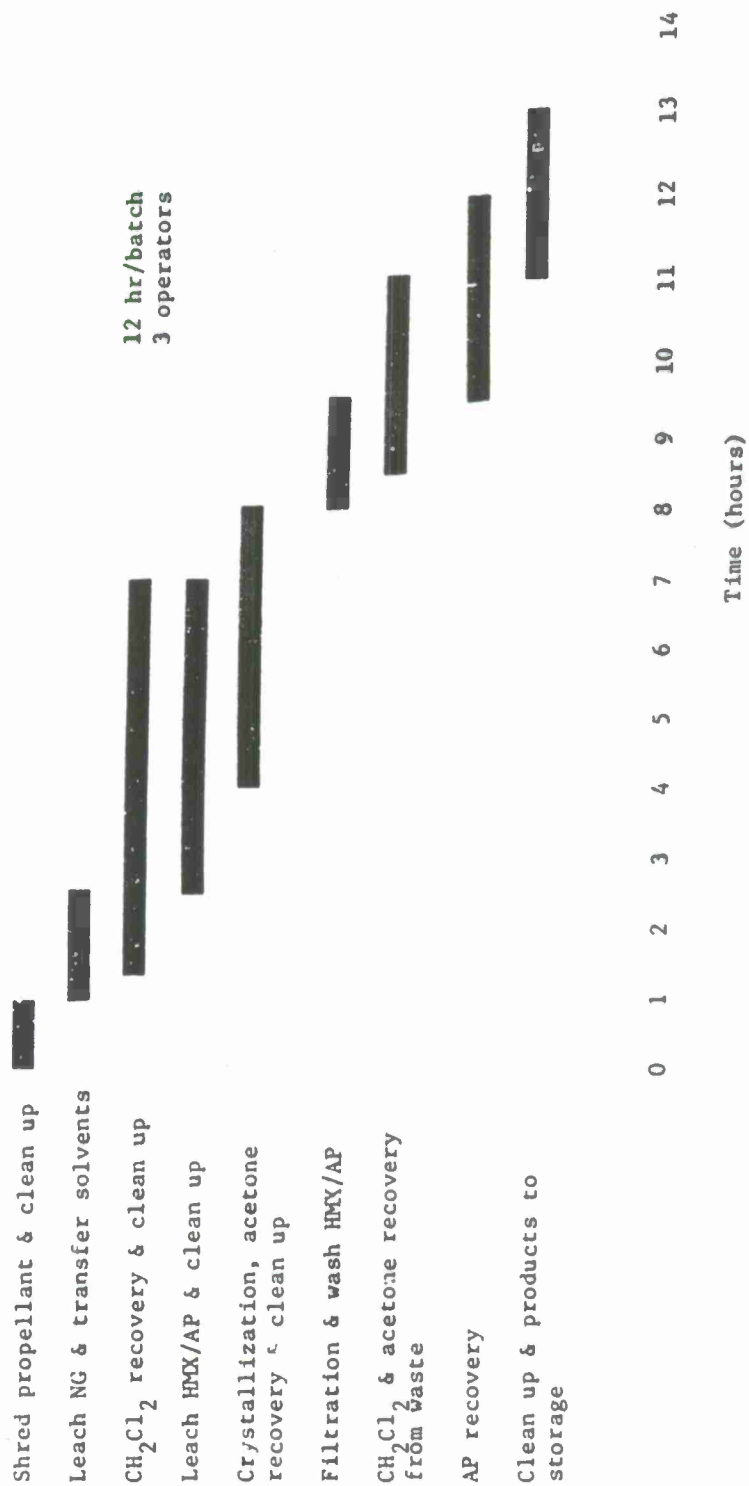


Figure 52. Estimate of Labor Requirements for Ingredient Recovery Pilot Plant

where no actual data exists.⁶ The labor costs estimated in Table 42 are based upon the residence times of the leaching steps and estimated cycle times for the various operations.

Examination of the factors which comprise the manufacturing cost, tabulated in Table 42, are worth considering. Labor costs are significant, especially at lower production rates. Changes in the process may affect the cost of raw materials, labor and utilities as well as the fixed capital investment and each of these factors affect other factors of the calculation. While percentages may vary for preliminary estimates, experience has indicated that, unless the operation is very unusual, the range of values for each factor is quite small. For example, maintenance costs usually range between 2 to 10% per year of the capital cost. A high value is used for processes in which corrosion is high. It has already been experienced⁷ that water solutions of AP are extremely corrosive; therefore, the higher value was used in the example calculation. Other factors such as those listed under indirect and fixed costs are variable from company to company and with geographical location. The goal is to select values which are realistic and form a solid basis for comparison.

The results of these calculations, shown in Figure 53, give the manufacturing cost of disposal of propellant as the plant size varies. This representation accounts for the value of the recoverable ingredients or by-products which have a significant effect.

Since raw material costs are negligible (the waste propellant being free), reduction of the direct operating labor charges would have the most affect on the direct charges. Process improvements which would reduce the major equipment requirements and thus affect the indirect manufacturing costs would have a greater affect on the unit product cost. The most significant factor, however, is the effect of the by-product credit.

This analysis assumes that the ingredients recovered HMX, NG and AP, are salable at the current market prices. Factors affecting this assumption will be discussed later.

⁶Weinberger, A. J., "Calculating Manufacturing Costs," Chemical Engineering, December 23, 1963.

⁷Thiokol Report No. WGT-085, "Additional Study of Crack Initiation in High Pressure Pump Housings at the Motor Case Reclaim Facility," J. B. Millard, 10 June 1963.

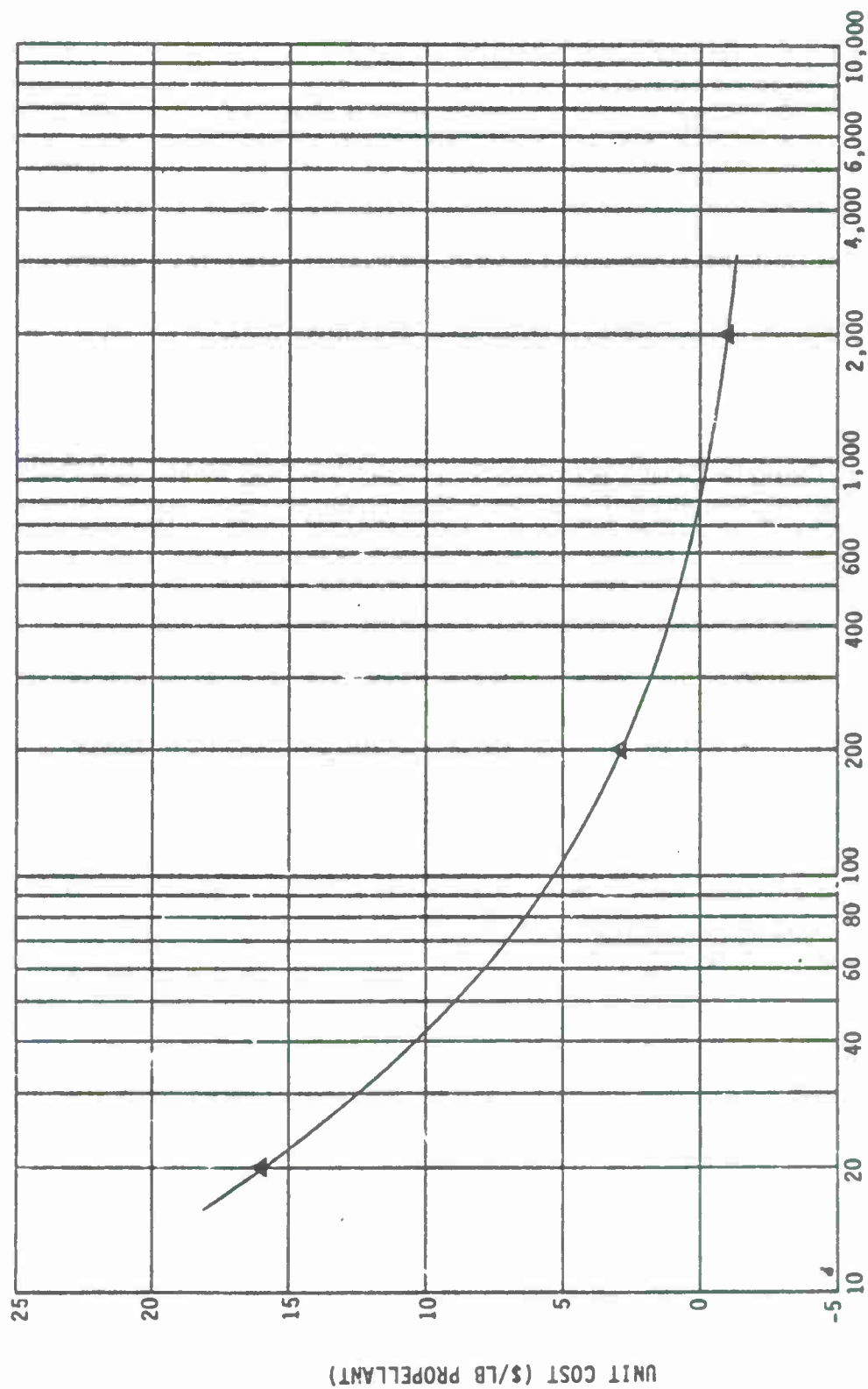


Figure 53. Cost of Baseline Ingredient Reclamation Plant as a Function of Plant Capacity

To demonstrate the affect of these most important parameters on the unit product cost, which is the cost of disposing of one pound of waste propellant, a series of calculations were made to test the sensitivity of the unit cost. Conditions investigated were: (1) decrease and increase of the capital cost by 30%, (2) decrease and increase of the labor cost by 50%, and (3) decrease of the market value of the by-product credit to 75, 50, and 25% of current market value. The results of these calculations are shown graphically in Figures 54, 55 and 56.

The basic conclusion shown by these graphs are that the effect of plant capacity is the most important parameter. For relatively small quantities of propellant, less than 100K lb/yr, the cost of waste propellant disposal by ingredient recovery is estimated to be considerably higher than by incineration methods. Thiokol, one of the leading producers of Class 1.1 propellants, anticipates less than 100K lb waste per year during the next few years. This indicates that replacement of a major solid propellant weapon system would probably be the only circumstance which would generate enough waste to make this process economically feasible.

2.5.4 Estimation of Incineration Costs

Considerable effort has been expended to develop closed incineration systems; such as fluid bed, rotary kiln, and APE 1236 deactivation furnace systems for disposal of propellant and explosives. The successes of these systems have been varied and high maintenance costs appear to be inherent due to the nature of the material burned. Most of these systems have been developed for specialized feed stocks and more development work may be needed to develop feed systems and effluent clean-up systems to make them generally useful.

The cost data use for this analysis were obtained from reports^{8,9} and from communication with personnel at the Ammunition Equipment Directorate, Tooele Army Depot, Tooele, Utah. These data were used primarily to develop current estimates of the major equipment costs and of labor requirements and capacities. Cost estimating methods previously described were then

⁸Tech Report AD-064124, Part 1 of 2, 1974, "Fluidized Bed Incineration for Disposal of Propellant and Explosives," R. Scola and J. Santos.

⁹Scola, R., Santos, J. S., "Fluidized Bed Incinerator for Disposal of Propellants and Explosives," AARDCOM, Dover, N. J., October 1978, pp 129.

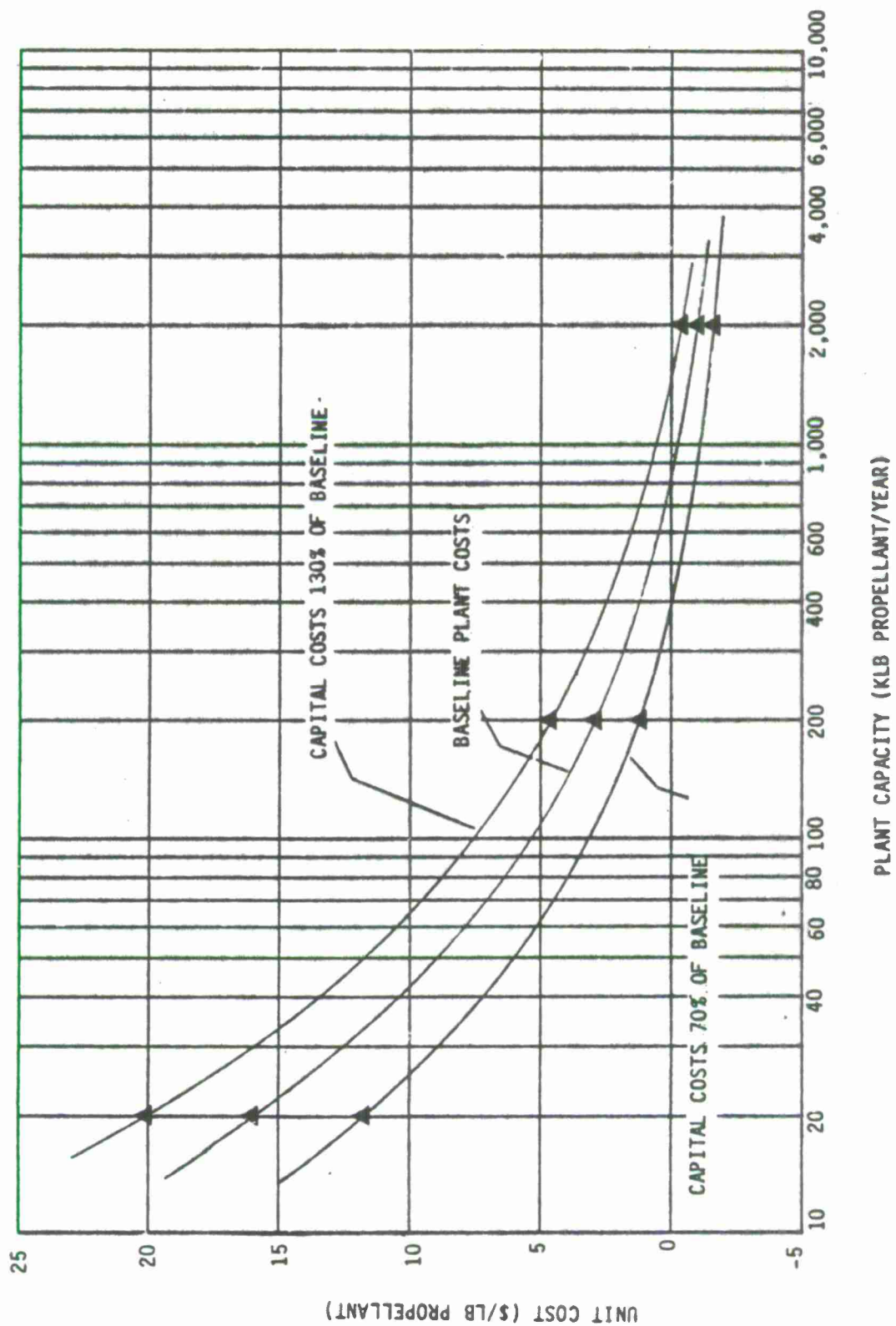


Figure 54. Effect of Capital Costs on the Unit Cost of Ingredient Reclamation from High Energy Propellant

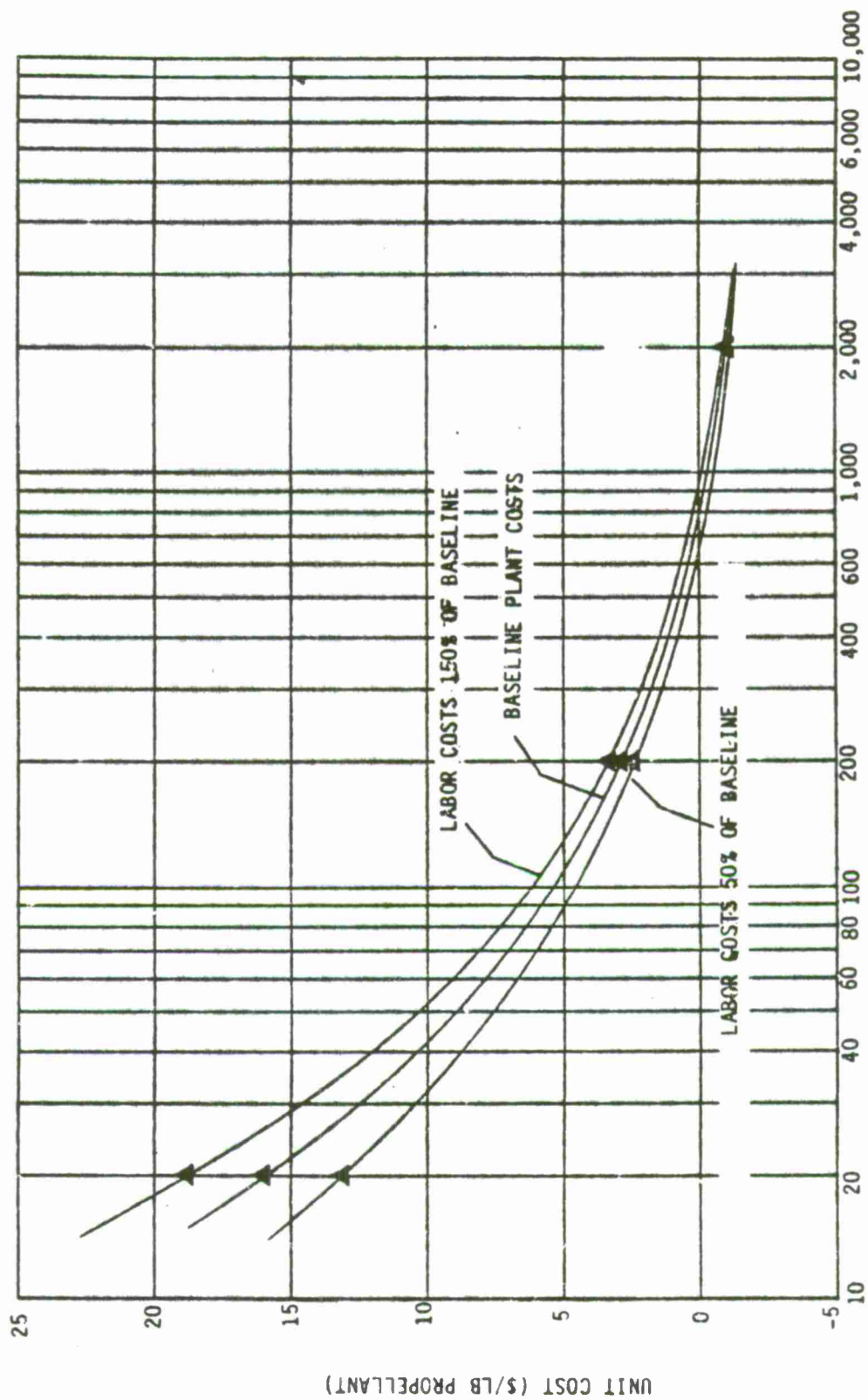


Figure 55. Effect of Labor Costs on the Unit Cost of Ingredient Reclamation from High Energy Propellants

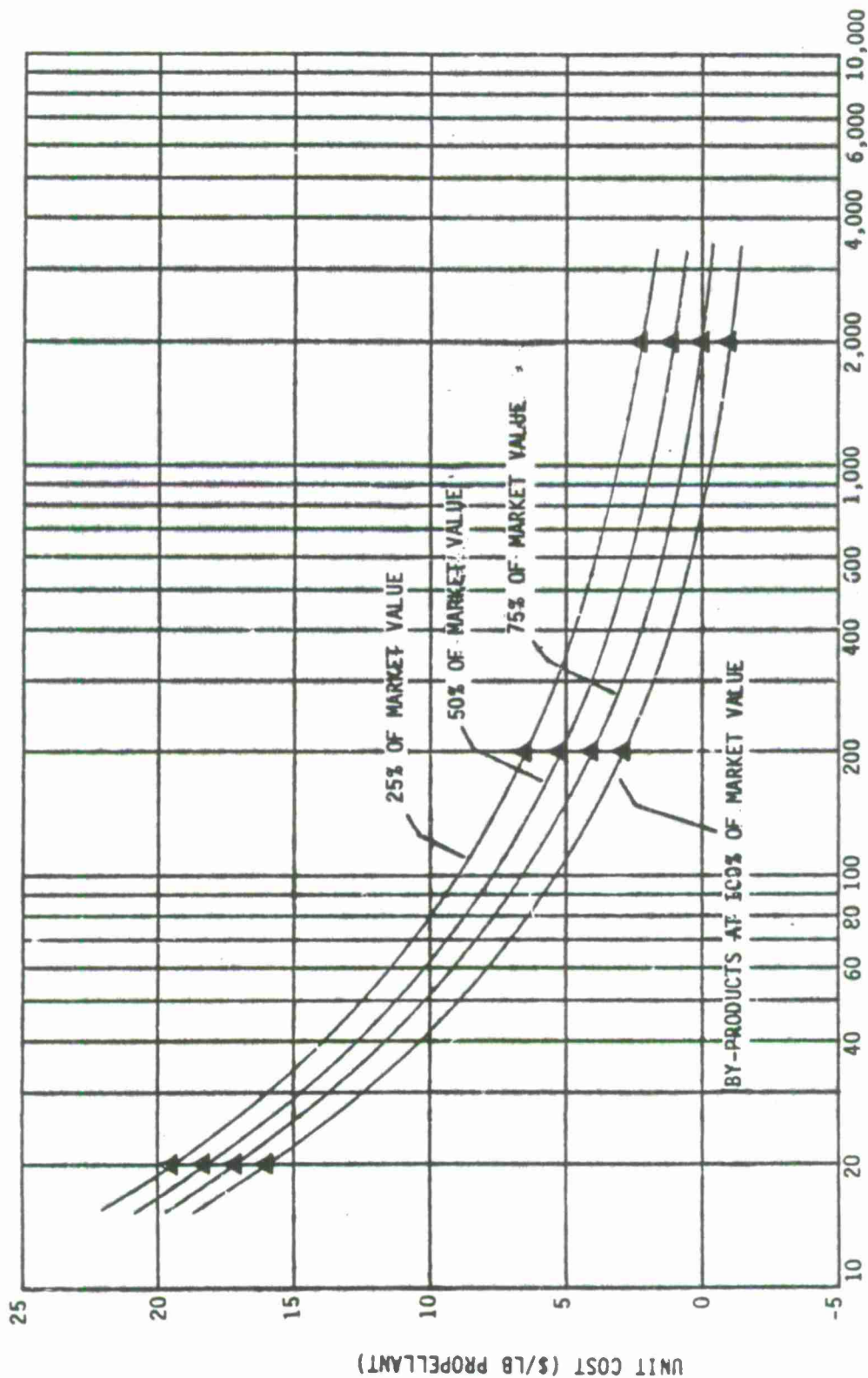


Figure 56. Effect of By-product Credit Reduction on the Unit Cost of Ingredient
Reclamation from High Energy Propellant

used to develop unit costs for disposal of HE propellant at various capacities. The results of these calculations are listed in Table 43. The cost calculated for comparison for the deactivation furnace at Tooele is believed to be more accurate because the data are current and were received first hand. The agreement between this cost and the cost developed from data in the Scola and Santos report gives confidence to the analysis of the data and the resulting estimation.

The incinerator capable of handling 400,000 lb of propellant per year (on a 200 operating days/year schedule) is the smallest unit currently available. The capital investment cost for lower capacities than 400,000 lb/yr is therefore identical. At these lower capacities the operation would be intermittent with operating labor decreasing as capacity decreases. The results of these calculations are shown in Figure 57.

2.5.5 Comparison of the Cost Estimations of Methods of High Energy Waste Disposal

Each of the cost estimates previously described used the same basis for comparative purposes. Products produced in the manufacture of explosive boosters and in ingredient reclamation were treated as by-products to keep the final unit product cost defined as the cost for disposal of one pound of propellant. A comparison of the results of the analysis are summarized in Figure 58.

These results show that utilization of the propellant in explosive boosters is the most economical method. Ingredient reclamation, although technically feasible, is economically feasible only where very large quantities of propellant are available. Since the capital costs were depreciated over a ten year period, this method is less attractive if the projected term of operation were less than ten years. Incineration methods are shown to be economically more feasible than ingredient recovery in the intermediate range of capacity and extrapolation of the curve applicable for prediction of costs at lower capacities.

2.6 CONCLUSIONS

The alternate use of waste Class 1.1 solid propellant as an explosive booster is technically feasible and economical on an intermediate production

TABLE 43
BASELINE INCINERATOR COSTS

	Plant Size (klb/yr)		
	100*	200*	400
Rotary Kiln (Scola & Santos)			1800
Incinerator Cost	\$ 880,000	\$ 880,000	\$ 880,000
Unit Cost (\$/lb)	2.84	1.63	0.99
APF 1236 Deactivation Furnace			0.50
Incinerator Cost		1,165,000	
Unit Cost (\$/lb)		1.24	
Fluidized Bed (Scola & Santos)			
Incinerator Cost	1,078,000	1,078,000	1,467,000
Unit Cost (\$/lb)	3.01	1.61	0.90
			0.34

* intermittent operation of 400 klb/yr units.

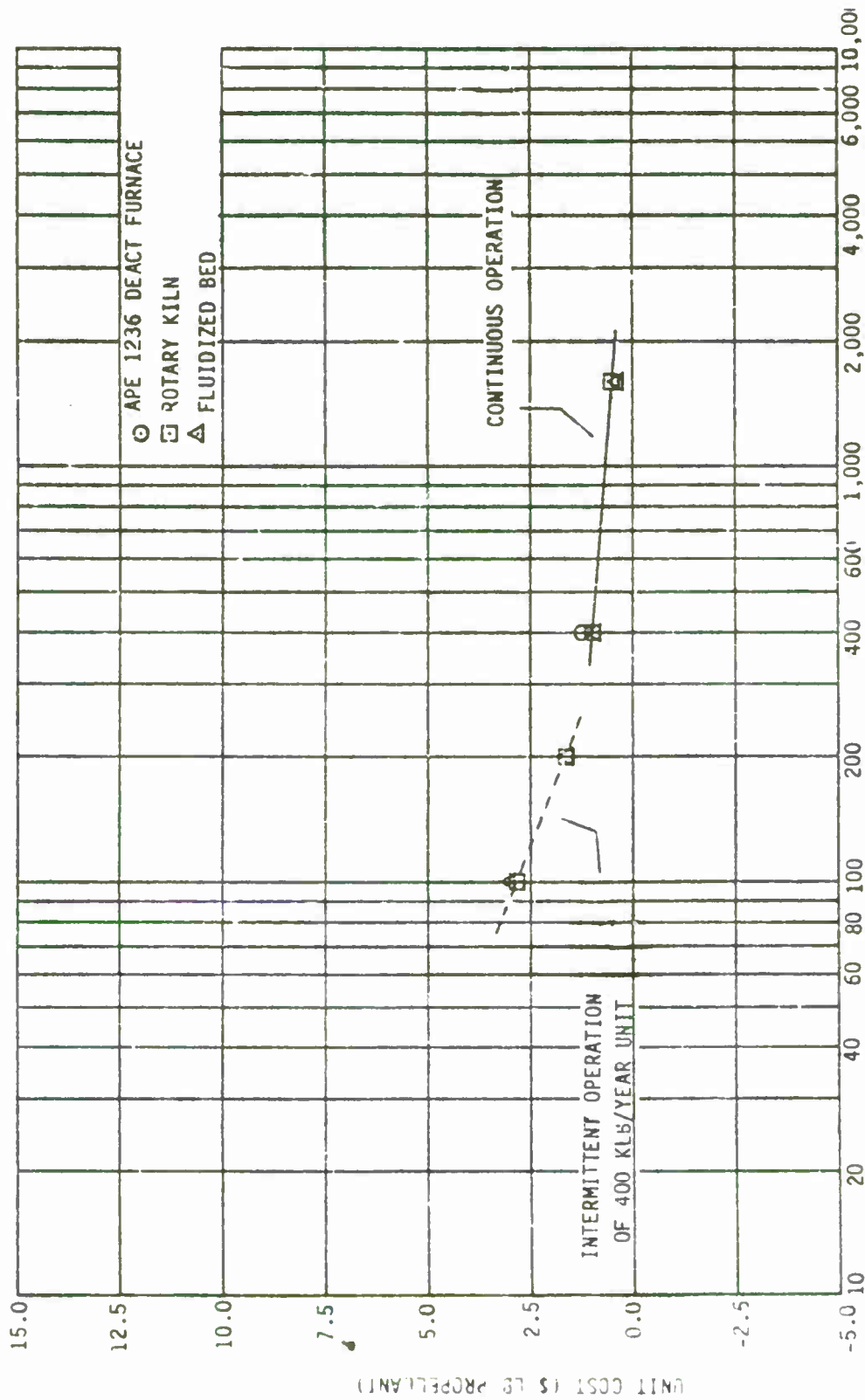
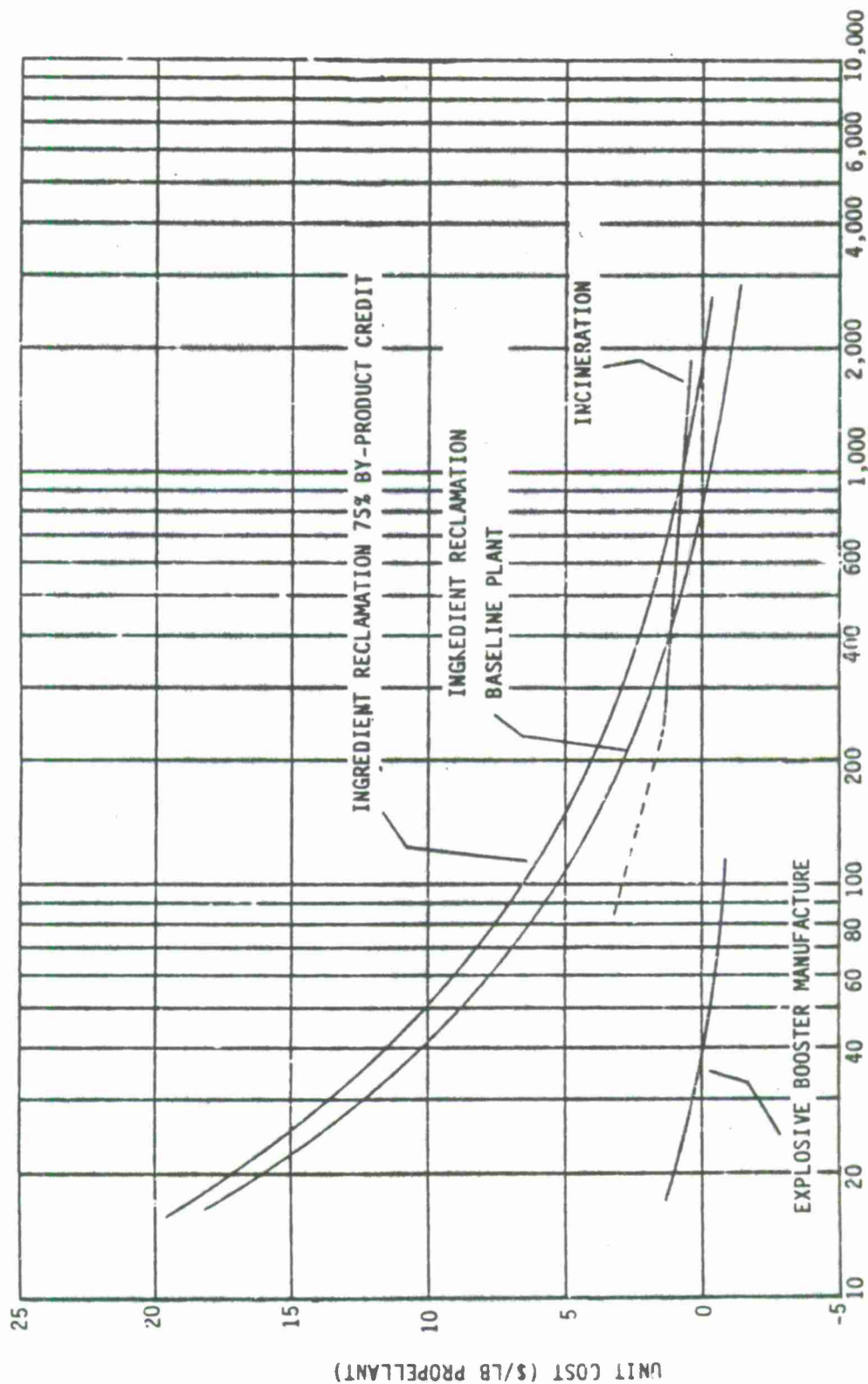


Figure 57 Costs of Incinerating Explosive Materials in Fluidized Bed and Rotary Kiln Incinerators



PLANT CAPACITY (KLB PROPELLANT/YEAR)

Figure 58. Comparison of the Costs of High Energy Propellant Waste Treatment by Incineration, Explosive Booster Manufacture, and Ingredient Reclamation

scale of approximately 40,000 to 50,000 lb/yr. The classification of many Class 1.1 propellant formulations prohibits distribution to the industrial sector however, and thereby restricts application of this disposal concept.

Reclamation of major ingredients from Class 1.1 solid propellants by a selective solvent extraction process is technically feasible, but economical only on a comparatively large production scale in excess of 400,000 lb/yr. The economics of this disposal method are very sensitive to the recovered ingredient market. The production scale necessary for economical implementation of this disposal method exceeds projected waste Class 1.1 propellant quantities for most manufacturers. Economical operation of an ingredient reclamation facility would therefore be restricted to specialized applications such as large motor demilitarization programs.

Incineration of waste Class 1.1 solid propellants has been demonstrated on full scale incinerators. Incineration appears to be economical only on a large scale in excess of 400,000 lb/yr which, as previously noted, exceeds projected waste Class 1.1 propellant quantities for most manufacturers. Small, intermediate size incinerators which address cured and uncured propellant and propellant contaminated wastes (rags, plastics, disposable tools, etc.) and their characteristic emissions are not available.

In summary, open pit burning remains the most simple and cost effective method for disposal of intermediate quantities of Class 1.1 solid propellants. The alternative would involve large capital investments for either an ingredient reclamation facility or an incinerator and operation of the facility on a low capacity, inefficient and costly basis.

2.7 RECOMMENDATIONS

It is recommended that the selective solvent extraction process be scaled up to the pilot plant level in order to:

- a. Optimize the process
- b. Develop markets for the reclaimed ingredients
- c. Update the economic projections
- d. Provide a design for a large scale plant

The large scale plant design may be modular in concept to facilitate transfer to various motor demilitarization sites.

It is recommended that a low cost, intermediate size incinerator be developed which would:

- a. Be compatible with projected waste propellant quantities.
- b. Accommodate all types of hazardous wastes associated with propellant manufacture including:
 - 1. Cured propellant
 - 2. Uncured propellant and premixes
 - 3. Propellant contaminated wastes
 - 4. Scrap raw materials
- c. Address total emissions characteristic of solid propellants, including:
 - 1. Particulates (metal oxides)
 - 2. NO_x
 - 3. HCl

This would provide a more economical and environmentally acceptable means of disposal by incineration than the present state of the art allows.

It is recommended that alternate use and application concepts for disposal of waste Class 1.1 solid propellants be pursued due to the simplicity and inherent low costs associated with this approach. Two specific concepts which surfaced late in the program but which appear promising are:

- a. Conversion of waste Class 1.1 propellant to a warhead explosive booster.
- b. Utilization of detonation energy of Class 1.1 propellant to synthesize industrial diamonds.

The first method avoids the security problems associated with distribution of explosive boosters containing classified formulations to the industrial sector. The second method provides on-site disposal and a readily marketable by-product.

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GLOSSARY

AMMONOLYSIS	Degradation and dissolution of a propellant binder with ammonia
BINDER SOL	Soluble, unpolymerized fraction of propellant binder
BINDER GEL	Insoluble, polymerized fraction of propellant binder
SOLVOLYSIS	Chemical degradation and dissolution of a propellant binder
TALIANI TEST	Test for compatibility of a material with a nitrate ester

LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS

ACI	Air curtain incinerator
Al	Aluminum powder
AP	Ammonium perchlorate
BITA	Butyl imine adduct of trimesic acid
C-4	91% RDX, 9% Plasticizer
CTPB	Carboxy Terminated Polybutadiene
Desmodur N-100	Polyisocyanate
DMSO	Dimethylsulfoxide
DSCF	Dry standard Cubic Foot
DSCM	Dry standard cubic meter
EA	Ethanol amine
Gr	Grain
HEMAP	Hydroxyethyl-Methylaziridino-Propionate
HMX	Cyclo-tetramethylene tetranitramine
HTPB	Hydroxy terminated polybutadiene
MAPO	Methyl aziridinal phosgene oxide
Mg	Milligram
MNA	n-methyl-p-nitroaniline
2-NDPA	2-nitrodiphenylamine
NEPE	Nitrate ester polyether
Ng	Nitroglycerine
NHC	n-hexylcarborane
NQ	Nitro guanidine
PBAN	Polybutadiene-acrylonitrile
PCP	Polycaptolactone
PEG	Polyethylene glycol
PEP	Propellants, Explosives and Pyrotechnics
PETN	Pentaerythritol Tetranitrate
PGA	Polydiethylene Glycol Adipate
RDX	1,3,5-tetranitrazo-cyclohexane
THF	Tetrahydrofuran
TIL	Threshold Ignition Level
TMETN	Trimethylolethane Trinitrate
TNT	Tri nitrotoluene
WAO	Wet Air Oxidation

