

FINAL REPORT

EVALUATION OF TREATMENT,
STORAGE AND DISPOSAL TECHNIQUES
FOR IGNITABLE, VOLATILE
AND REACTIVE WASTES

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LIST OF TABLES

<u>Table</u>	<u>Page</u>
1.1 Summary of Treatment, Storage and Disposal Practices	1-3
3.1 Comparison of Estimated Emission Using Best Available Techniques and MATES	3-3
3.2 VCM Concentrations Found in PVC Sludges	3-18
3.3 Summary of Treatment, Storage and Disposal Technology for Water Pollution Control Sludge from PVC Production	3-22
3.4 Vinyl Chloride in Wastewater Treatment Sludge	3-42
3.5 Nitrobenzene in Waste Tars	3-51
3.6 Chlorobenzene in Distillation Residue	3-62
3.7 Costs Associated with Stripping of Nitrobenzene Wastes	3-71
3.8 Nitrobenzenes in Column Bottoms	3-73
3.9 Crude Oil Processing Capacity of U.S. Refineries	3-75
3.10 Major Petroleum Products Produced by U.S. Refineries in 1974	3-79
3.11 Comparison of Refinery Waste Disposal Methodologies Used in 1973 with Those Projected for 1983	3-83
3.12 Generation Rates and Volume Distribution of 17 Waste Streams From the Petroleum Refining Industry	3-84
3.13 Water Quality Estimates of Typical Effluents Sent to DAF Systems from API Separators	3-89
3.14 Oil Concentrations and Removal Efficiencies for 14 DAF Systems	3-90
3.15 Percentages of Oil, Water, and Solids in DAF Float	3-93
3.16 Calculation of Specific Gravity of DAF Float	3-94
3.17 Concentrations, Generation Rates, and Minimum Toxicity Levels of 28 Elements Found in DAF Scum	3-95
3.18 Comparison of Daily Generation Rates for 28 Elements in DAF Float With Their MATE Values	3-97
3.19 The Hazards of 27 Chemicals Found in DAF Influent	3-98
3.20 National Fire Protection Association Indices for Hazards of 27 Chemicals Found in DAF Influent	3-99
3.21 Treatment/Disposal Strategies for DAF Float at Eight Petroleum Refineries	3-101
3.22 Current and Projected Percent Use of Several Methods for Managing DAF Scum	3-105

List of Tables (Continued)

<u>Table</u>	<u>Page</u>
3.23 Summary of the Data From a Study of the Effects of Land Treatment API Separator Sludges	3-110
3.24 Summary of Environmental Effects of Disposal Methods for DAF Float	3-120
3.25 Summary of Potential Emission Levels from Disposal Methods for DAF Float	3-121
3.26 Summary of Costs of Disposal Methods for DAF Float	3-122
3.27 Production of Water Pollution Control Sludge From the Electroplating and Metal Finishing Industry (Job Shops)	3-126
3.28 Metal Hydroxide Wastes in Water Pollution Control Sludges From the Electroplating Industry (1975)	3-126
3.29 Criteria for Public Water Supplies	3-129
3.30 Summary of Treatment, Storage, and Disposal Technology for Water Pollution Control Sludge From the Electroplating and Metal Finishing Industry	3-130
3.31 Treatment Methods Used by Fifty Job Shops to Separate Solids From Treated Wastewater	3-131
3.32 Estimated Centrifuge System Capital and Operating Costs for Three Different Size Electroplating and Metal Finishing Model Plants	3-134
3.33 Summary of Estimated Contractor Hauling, Treatment, and Disposal Charges for Electroplating and Metal Finishing Waste Destined for Land Disposal	3-139
3.34 Cyanides in Wastewater Treatment Sludge	3-142
3.35 Chromium in Wastewater Treatment Sludge	3-143
3.36 Comparison of Plating Sludge Metallic Constituents With State of Illinois Criteria	3-144
3.37 Waste Streams Generated by Typical Woven Fabric Dyeing and Finishing Plant	3-147
3.38 Woven Fabric Dyeing and Finishing Sludge Chemical Composition	3-150
3.39 Drinking Water Limit for Metals and Chlorinated Organics	3-152
3.40 Summary of Treatment, Storage, and Disposal Technology for Wastewater Treatment Sludge from Woven Fabric Dyeing and Finishing Operations	3-154
3.41 Estimated Installed Costs for Various Types of Pond Liners	3-157
3.42 Summary of Major and Minor Elements in Sludge	3-161

List of Tables (Continued)

<u>Table</u>	<u>Page</u>
3.43 Chlorinated Organics in Wastewater Treatment Sludge	3-162
3.44 Comparison of Wastewater Treatment Sludge with State of Illinois Criteria	3-163
3.45 Typical Formulation Changes to Achieve a Variety of Coatings	3-167
3.46 Paint and Coatings Manufacture Summary of Total Wastes in 1974	3-168
3.47 Estimated Pigment Usage by Paint Industry, 1972	3-172
3.48 Estimated Resin Usage by Paint Industry, 1972	3-175
3.49 Estimated Drying Oil Usage by Paint Industry, 1972	3-176
3.50 Estimated Solvent Usage by Paint Industry, 1972	3-177
3.51 Estimated Miscellaneous Materials Usage, 1972	3-178
3.52 Toxicity of Raw Materials Used in Surveyed Paint Plants	3-179
3.53 Process Liquid Wastes from Solvent-Thinned Trade Sales Paint Manufacture	3-185
3.54 Contents of Li-SO ₂ Battery	3-188
3.55 Potential Air Releases from Li-SO ₂ Battery Disposal	3-190
3.56 Comparison of Hazardous Nature of Li-SO ₂ Cell Components	3-193
3.57 Cost Estimates for Various Disposal Methods	3-201
3.58 Cost-Benefit Comparison of Landfill With and Without Prior Incineration	3-203
3.59 Li-SO ₂ Scrap Cell Treatment and Disposal	3-204
4.1 Typical Solvents and Selected Properties	4-3
4.2 Solvent Consumption by Selected Industries	4-4
4.3 Charges Levied for Treatment and Disposal of Wastes, Oils and Chemicals in Denmark	4-16
4.4 SOCM I Secondary Emission Sources and Estimated Emissions	4-19
4.5 Applicable Control Methods	4-27
4.6 Secondary VOC Emission Reductions by Various Control Techniques or Methods	4-29
5.1 Percentage Distribution of Commercial Explosives Use	5-3
5.2 Examples of High and Low Explosives	5-6
5.3 Common Ingredients of Dynamite	5-7
5.4 Typical Composition of Dynamite	5-13
5.5 Waste Waters Generated in LAP Operations	5-35

List of Tables (Concluded)

<u>Table</u>	<u>Page</u>
5.6 Nitrate Treatment Methods	5-40
5.7 Bulk PEP Sold to Commercial Users	5-58
6.1 Summary of Contacts with Selected State Agencies	6-10
6.2 Summary of Telephone Contacts with Selected IRV Waste Disposers	6-11
A.1 Damage Incidents Involving Land Disposal of Volatile Wastes	A-2
A.2 Definitions of Volatility, Ignitability and Reactivity Used In This Report	A-4
A.3 Comparison of Vapor Pressures and Toxicities of Selected Chemicals	A-7
C.1 Waste Streams Chosen for Study	C-4

Table of Contents (Concluded)

	<u>Page</u>
APPENDIX C Selection of Ignitable, Reactive and Volatile Waste Streams	C-1
C.1 Method for Selection of Waste Streams	C-1
C.2 Waste Streams for Further Study	C-3
C.2.1 Organic Chemicals and Plastics Manufacturing	C-5
C.2.2 Petroleum Refining	C-5
C.2.3 Electroplating and Metal Finishing	C-5
C.2.4 Textile Manufacturing	C-6
C.2.5 Paint Manufacturing	C-6
C.2.6 Primary Batteries	C-6
C.2.7 Commercial Explosives	C-6
C.2.8 Military Explosives	C-7
APPENDIX D Updating Costs	D-1

1.0 EXECUTIVE SUMMARY

1.1 PROGRAM OBJECTIVE

Section 3004 of the Resource Conservation and Recovery Act of 1976, required EPA to issue regulations establishing standards for the operation of hazardous waste treatment, storage and disposal facilities.

The purpose of this project is to begin to develop an information base to support development and implementation of methods for treating, storing and disposing wastes exhibiting the characteristics of ignitability, reactivity and volatility.

Information contained in this report is intended as input to the initial set of regulations due to be issued in April 1980 by the EPA Office of Solid Waste, and to subsequent fine tuning and closing of gaps in the regulations. Input is also provided for post-regulatory activities such as writing permits for hazardous waste sites and enforcing the regulations.

The project was directed toward identification of best available treatment, storage and disposal alternatives for waste streams selected for their ignitability, reactivity or volatility, or combination of all three. Further criteria included toxicity, volume of waste generated, originating industry and waste form.

Ignitable, reactive and volatile wastes create special problems such as fires, explosions and harm to human life and the environment during handling and disposal, and in the post-disposal environment. The properties of ignitability, reactivity and volatility overlap so that most wastes investigated had more than one of the properties, and some had all three. A significant proportion of hazardous wastes listed in Section 3001 regulations have these properties, although data has not been developed to determine the actual quantity of ignitable, reactive and volatile wastes produced.

For this study, alternatives for each waste stream were identified, primarily by a review of current industrial practices, to determine

the average and best techniques in use for disposing of each one. Final determination of best available technologies were based on the following criteria:

- Proven technology
- Relatively low operation and maintenance cost
- Potential for recovery of valuable materials
- Overall cost and effectiveness.

Thirteen waste streams were selected as representative of all ignitable, reactive and volatile wastes. A summary of treatment, storage and disposal practices identified in the investigations for these 13 waste streams is shown in Table 1.1. Landfill is the current practice most often employed, while incineration with land disposal of residue is the best technology most often used. The cost of using incineration on the plant site would be about four times that of simple landfill for most of the wastes investigated. However, the cost of incineration can be significantly reduced, in many cases, by having wastes incinerated by off-site waste disposal contractors. Avoiding financial burden of purchasing and operating an incinerator will mandate consideration of off-site contractor disposal of waste, particularly for small plants.

1.2 APPROACH

Tasks performed in conducting the project follow in chronological order:

- Development of a working definition of volatility
- Assembly of a list of ignitable, reactive and volatile waste streams, and selection of waste streams for study
- Studies of waste streams to determine current and best treatment, storage and disposal methods
- A study of solvent use and recovery in industry
- A study of treatment, storage and disposal of wastes from explosives manufacture
- Evaluation of options for regulating ignitable, reactive and volatile wastes.

Table 1.1 Summary of Treatment, Storage and Disposal Practices

Waste Streams	Current Practices	Best Available Technology	Most Environmentally Sound Practice
Wastewater treatment sludge from polyvinyl chloride production	Landfill	Incineration with HCl recovery, land disposal of residue	Salt deposit disposal
Chlorobenzene still bottoms	Landfill	Incineration with HCl recovery, land disposal of residue	Chlorinolysis
Nitrobenzene still bottoms	Disposal in sealed steel drums in landfill	Rotary kiln incineration with NO _x control and heat recovery Land disposal of residue	Steam distillation, alkali hydrolysis followed by catalytic reduction. Disposal of nitrophenols in landfill
Tars from aniline production	Land application of sludges from biological treatment of combined plant wastes	Rotary kiln or multiple hearth incineration with NO _x control and land disposal of residue. Heat recovery potential is good	Steam stripping followed by incineration of product. Biological treatment of bottoms
Sulfur sludge from parathion manufacture	Rotary kiln or multiple hearth incineration with SO _x scrubbing. Land disposal of stabilized scrubber sludge and incineration residues. Potential for heat recovery	Same as current practice	Sulfur recovery, composting organophosphates with lime
DAF skimmings from petroleum refining	Landfill	Rerefining	Rerefining

Table 1.1 Summary of Treatment, Storage and Disposal Practices (Continued)

Waste Streams	Current Practices	Best Available Technology	Most Environmentally Sound Practice
Process liquid wastes from solvent-thinned trade sales paint manufacture	Landfill	Recovery with land disposal or incineration of residue	More complete recovery with land disposal or incineration of residue
Wastewater treatment sludges from woven fabric dyeing and finishing in the textile industry	Discharge to unlined lagoon	Sludge dewatering, disposal in approved landfill	Encapsulation, disposal in secure landfill
Wastewater treatment sludge from electroplating	Landfill	Sludge dewatering disposal in landfill	Sludge dewatering, encapsulation, disposal in secure landfill
Lithium-sulfur dioxide battery	Landfill	Mechanical disassembly with incineration; SO ₂ , NO _x scrubbing, and disposal of residue	Disassembly, recovery of components for reuse
Red water from TNT production	Open burning	Concentration/incineration with caustic scrubbing and land disposal of ash	Same as best available
Bulk propellents, explosives, pyrotechnics	Open burning	Incineration with caustic scrubbing and land disposal of ash	Same as best available
Pink water from load, assemble and pack operations	Carbon adsorption evaporation, burning	Incineration with caustic scrubbing and land disposal of ash	Same as best available

1.3 CONCLUSIONS

The definition of volatility was developed early in the project and used throughout. Further consideration of vapor pressure cutoff points should be made to reflect how the definition is likely to be applied. If it is ultimately used to determine the methods for disposal of a substance, then the basis for the cutoff points should be strengthened, and application of the definition to mixed wastes should be further investigated.

The 13 waste streams studied are indicative of all ignitable, reactive and volatile waste streams generated. The best available technologies are expected to have little environmental impact, but may pose a significant financial burden on industry. Emissions are estimated for implementation of each best available technology and are compared with Minimum Acute Toxicity Effluents (MATE's) for the critical chemical constituent of each waste stream (Cleland and Kingsbury, 1977). Best available technologies meet draft 3004 regulations and would result in emissions meeting the MATE goals for pollutant concentrations for protection of human health and the disposal environment.

Recovery is the most environmentally sound technique for handling waste solvents. Recovery is generally applicable for solvents as long as an economic incentive exists.

While much research and development effort to control environmental emissions at explosive manufacturing facilities has been made by the military, implementation by military or commercial manufacturers has not occurred. Open burning is commonly practiced for disposal of many explosive wastes and, although it is not an environmentally sound practice, practical alternatives have not yet been developed.

Recommendations for further study are given in Chapter 2.

2.0 RECOMMENDATIONS

The objectives of this project were to study ignitable, volatile and reactive wastes and identify treatment, storage and disposal technologies and recommend best available practices where the data and analysis support such recommendations. From these analyses, recommendations for regulating these wastes were devised. Additional studies of treatment, storage and disposal methods were performed for explosives and solvents, while a definition of volatility was developed and used for this project. Coupled with the definition of ignitability and reactivity previously proposed by the EPA Office of Solid Waste, these definitions formed the basis for determining whether a waste stream was ignitable, volatile, or reactive.

Very specific waste streams, such as chlorobenzene still bottoms, were chosen for study so that specific technologies could be identified, which allowed a more detailed evaluation of costs and environmental impacts.

Technologies for each waste stream were classified into one of three most prevalent categories: current practices; best practices as used by at least one operating facility; and most environmentally sound practice. Most environmentally sound practice for a given waste was chosen by identifying developing technologies and technologies being used for similar wastes and assessing feasibility and cost for implementing the technology and environmental releases associated with its use.

2.1 REGULATORY APPROACH

Once this study was underway, it became apparent that regulating these wastes would be more difficult than originally thought. JRB developed some ideas for regulation in the course of the study. Although this activity was not part of the study, these ideas are offered for EPA consideration.

Some general approaches may be suggested for regulating the treatment, storage and disposal of ignitable, volatile and reactive wastes. Some of the problems that have made regulating these wastes difficult are:

- Developing definitions for ignitability, reactivity and volatility that are precise enough to be used for regulatory activities, while retaining meaning that reflects its hazard or nonhazard in treatment, storage and disposal scenarios.
- Developing quantitative levels at which wastes are proven to be hazardous or nonhazardous.
- Lack of accurate quick and inexpensive means for testing actual waste streams.
- Diversity of waste specific technologies applicable to these wastes.

Since ignitability, reactivity and volatility are properties of wastes they describe how wastes behave under given conditions. Much research has been and is being done to describe waste behavior and to promote a better understanding of what makes wastes hazardous during and following treatment, storage and disposal.

However, many of these conditions are site- or process-specific, increasing the difficulty of thorough analysis of waste behavior.

Additionally the properties of ignitability, reactivity and volatility overlap, further increasing the difficulty of setting limits exclusively for each property to determine whether or not a waste should be handled or disposed in a particular manner. However, once each property is defined and acceptable levels for each are established, any one level is envisioned to be cause for violation. Therefore, if a waste is either ignitable or volatile or reactive according to established definitions, then the waste would be subject to regulation.

A summary of the regulatory approach recommended by JRB as a result of this study is as follows:

- A dollar per quantity tax on generators of these wastes.
- Storage of IRV wastes, as long as the purpose is to stockpile wastes to decrease unit costs of recovery; decrease unit costs

of transporting wastes to a treatment, storage or disposal facility, or wait for more favorable short term market conditions of wastes or recovered components or products.

- Cutoff levels for ignitability, reactivity and volatility to determine appropriate means for handling wastes. For example, for levels below the cutoff level, landfill, land treatment or lagoon disposal would be allowed.
- Setting volatility cutoff levels which incorporate vapor pressure and toxicity.
- Setting ignitability levels as determined by flash point.
- Defining reactivity by known constituents of wastes or lacking this information, the production process which uses reactive raw materials or produces a reactive product.
- For wastes with combinations of these properties, consider using a combination of each level for determining appropriate handling and disposal.

The purpose of this approach is to emphasize removal of ignitable, reactive and volatile properties of wastes by the generator and de-emphasize the activities required of disposal site owners and operators to ensure environmentally adequate disposal of these wastes.

2.1.1 Proposed Tax on Generators

The EPA regulatory program should address the following in its initial stages:

- Do these wastes have value?
- Can they be partially reused in the generating process?
- Can increasing process control and generally tightening the generating process substantially eliminate generation of wastes with these properties?

More than half of the studied waste streams had a component or components that appear to be worth recovering and reusing or converting into useful products. Other studied wastes probably would be recovered if a higher value were placed on their ignitable, volatile and reactive

components. Therefore one regulatory approach would be to assign a negative value or "tax" in dollars per unit to wastes having these properties which leave the generating process for disposal. Conversely, a tax incentive could be offered to processes who now generate these wastes, but who make process changes to reduce or eliminate such discharges.

This approach would have several favorable aspects:

- It would encourage efforts by industry to find ways to reuse these wastes.
- It would provide incentive to industry to handle these wastes in a manner that is both environmentally sound and cost effective.
- It would provide rules that could be applied evenly to all waste generators.

An example of a tax on generators would be a base charge of so much per pound of waste with additional charges for ignitability, volatility and reactivity, which is similar to user charges levied on industrial facilities by municipal sewer authorities.

2.1.2 Storage

Implementation of the tax on generators may create the need for storage of wastes or recovered waste components. Although we recognize that storage of wastes has created some problems due to improper storage in the past, we feel that a tradeoff is needed to allow industry some leeway in determining the most economic method for handling their wastes. The problem arises because of the many low volume and intermittent wastes, such as still bottoms and tank cleanings, that may not justify immediate treatment or recovery. This is due to the high costs for purchasing process equipment with the capacity to treat the waste in a short time period and then allowing the equipment to stand idle until another batch of waste is ready for processing. Storage of wastes is currently regulated under RCRA Section 3004 which requires that facility owners or operators who store wastes for longer than 90

days must comply with RCRA Section 3010 notification and Section 3005 permit application requirements in order to qualify for interim status as a waste treatment, storage or disposal facility. No change in these requirements would be necessary to carry out this approach.

Although storage of many reactives such as explosives may not be feasible, storage of most ignitables and volatiles can be performed in an environmentally safe manner. Storage may allow a generator to:

- plan the continuous utilization of waste processing equipment,
- decrease unit costs of transporting wastes, because partial loads of each waste batch are eliminated,
- recover and store waste components until market conditions are more favorable.

Means of monitoring these practices may include agreement on a maximum time limit for storage between EPA and the generator, leaving open the possibility of extending the storage period beyond the 90 day limitation currently in the regulations subject to notification and permit application requirements mentioned previously, if the generator can demonstrate good faith to EPA's satisfaction. The hazardous waste manifest system will serve as a check to determine when and if the waste is transported.

2.1.3 Summary and Example

These recommendations are given to suggest a possible approach for regulating these wastes. An example may help illustrate the recommended approach.

One type of waste studied in this report was still bottoms from production of several organic chemicals. This type of waste may be ignitable, volatile, reactive or combinations of all three depending on many parameters such as:

- materials used in the process
- operating conditions of temperature, pressure, feed rate

- manner in which waste is removed (determines whether waste is liquid, semisolid or solid)
- purity of raw materials
- direct vs. indirect heating.

Wastes may be removed periodically, such as during plant shutdown. If the recommended regulatory approach is followed, the generator must decide whether to pay the tax or remove or recover waste constituents. However, if the tax on generators were promulgated, the generator would probably first investigate alternatives which would reduce the tax on his waste. Some of these alternatives may include:

- substituting feedstock materials that are not ignitable, volatile or reactive
- altering operating conditions such as temperature pressure and feed rate to reduce levels in wastes
- optimizing waste removal operation for reduction in these properties.
- increasing the purity of raw materials in the process to decrease wastes
- decreasing purity of the product to decrease wastes
- using indirect heating to prevent waste caused by degrading the product due to overheating.

Once the generator has reduced his tax by altering the proces, he then has the option to use recovery methods to further decrease the tax. Some of the alternatives he may consider would be the following:

- solvent extraction to recover a portion of the waste that is reusable in his process
- exchange with another generator whose waste may be more easily recovered
- set up central treatment or recovery process in conjunction with other generators.

After the previous options are considered, he may still have a tax on his waste, though it may be substantially reduced. Disposal of

the waste in a relatively inexpensive manner such as in a sanitary landfill is likely to be an acceptable alternative based on previously established cutoff levels for volatile, ignitable and reactive constituents in wastes destined for landfill, which are further discussed in Section 2.2. If the wastes do not meet landfill criteria, then means such as thermal pretreatment may be used to allow acceptance in a landfill.

The example is only for illustration purposes. Many approaches may be feasible with other types of waste.

We feel that the approach outlined in this section would encourage recovery and reuse of wastes without unduly penalizing industry. It allows even-handed treatment of all facilities, using procedures that are relatively simple. It also allows EPA to set standards that are restrictive enough to prevent environmental damage, while not too restrictive to force facilities to close without having a reasonable chance to successfully handle their own ignitable, volatile and reactive waste problems.

2.2 CUTOFF LEVELS FOR IGNITABILITY, VOLATILITY AND REACTIVITY

The following discussion stems directly from the evaluation performed in this report. Although the purpose of the study was not to set cutoff levels or to derive them from the data presented in this report, we feel that cutoff levels are a viable approach for regulating these wastes and we recommend that cutoff levels be established for these wastes. The data presented herein may provide an information source which would aid in such future regulatory activities.

2.2.1 Cutoff Levels for Ignitability and Volatility

Cutoff levels are recommended as a means of determining whether or not a waste may be allowed in a landfill, land treatment facility or lagoon. These may be similar to the one for ignitability, which has been set at a flash point of 60°C (140°F). If the proposed tax

on generators is implemented, it is believed that less pressure will be placed on owners and operators of waste facilities to take the initiative in removing ignitability and volatility properties from waste.

Based on the development of the working definition of volatility used in this report, we recommend that a cutoff level for volatile wastes be based on volatility and toxicity. Toxicity levels may be based on the EPA extraction procedure. Volatility levels may be based on vapor pressure. Although we recognize that vapor pressure does not describe all of the mechanisms for release of volatile substances, it does provide a relatively simple means for testing and evaluating wastes, while approximating simple release mechanisms. Vapor pressure is a property that can be measured by generators, transporters, disposers and the EPA. Additional parameters such as solubility or molecular weight may be justified for disposed site evaluation purposes. As part of developing the working definition of volatility for this report, cutoff levels were set. However, additional research is required before use of these cutoff levels is made in activities outside the scope of this report.

2.2.2 Reactivity

Reactivity is difficult to define as precisely as other properties of wastes, such as ignitability. Therefore, we recommend that reactivity of a waste be determined by the presence of reactive work constituents, if they are known. Reactive materials may be listed by groups, such as explosives, strong oxidizing agents and alkali metals, for determining reactivity of a waste. Alternatively, wastes from production processes using reactive raw materials or producing a reactive product may be considered reactive unless the waste was produced with no contact with reactive materials.

Reactive wastes may require evaluation on a case-by-case basis to insure safe disposal.

2.2.3 Combinations

Many wastes studies in this report were found to have properties that were combinations of ignitable, volatile and reactive. Few had

only one of these properties. Therefore, a means of taking into consideration each of these properties and applying criteria that reflects actual potential for hazard due to all three properties may be needed.

A means for accomplishing this may be to use the tax on generators with additional charges for ignitability, volatility and reactivity.

2.3 RECOMMENDATIONS FOR FUTURE STUDY

The following recommendations stem directly from the work done. In the course of conducting this study, some areas were identified which appeared to deserve greater attention than was possible within the broad scope of this study. These areas fell into two general categories. First there were those that required further research such as sampling and analysis or visits to industry to develop data that would serve to bring those technologies identified as most environmentally sound into greater usage. The following are descriptions of possible future research areas that fall into these categories.

2.3.1 Data Development

Detailed data on properties of waste streams were not always available and development of this data was not within the scope of this project. The waste streams studied are complex and are usually made up of one or more subwaste streams, each with differing properties. In most cases, information on general characteristics of wastes are available. For example, it has been reported that distillation residue from chlorobenzene manufacture is made up of 10 percent chlorobenzene, 89 percent polychlorinated resinous material, and less than 1 percent dichlorobenzene. A further analysis of polychlorinated resinous material would have been necessary to provide a more accurate reading of waste stream properties which would help identify more precisely potential problems that could result from treatment, storage and disposal of this waste. However, future studies are recommended to not just characterize waste streams, but to develop data for properties that could help determine whether problems will be encountered with specific treatment, storage and disposal techniques. Some of the properties of waste streams

may include flash points, vapor pressures, toxicities and reactivities.

For some wastes, detailed costs for treatment, storage and disposal were not available in literature. It is recommended that initial capital requirements and annual costs (such as financing, taxes, insurance, operations and maintenance) be developed by such means as contacting equipment vendors and industry where detail is lacking.

Further contact with waste generating industries is recommended to help identify process changes, equipment cleanup and housekeeping practices, effects of production start-up and shut-down and production of off-specification products. Once these are identified, in-process changes could be recommended to reduce waste quantities or hazards associated with the waste.

A working definition of volatility was developed to attempt to relate a physical property of wastes to release mechanisms encountered in treatment, storage and disposal facilities. The working definition was used in this study to define volatile wastes. The definition and information describing the basis for its development is given in Appendix A. Resource limitations prevented development of a means for applying the definition to mixed wastes and laboratory procedures for testing it. Further investigation is recommended to complete the definition.

Quantification of expected environmental releases from disposal facilities was attempted using minimum acute toxicity effluent (MATE) values developed under a recent EPA study (Cleland and Kingsbury, 1977). Though this was a first-cut attempt, it appears that a marked improvement in this approach can be made only by modeling facilities. Although many models exist, using this approach was not within the scope of this study. The first need would be the ability to model a treatment, storage or disposal facility to the degree that releases could be estimated from disposal of a particular waste. The next need would be the ability to model the release mechanisms of substances from a mixed waste stream so that release estimates of different compounds from the same waste stream could be made. Finally, the ability to model interactions between mixed wastes, including compatibility, would have to be developed.

Incineration is one of the best available techniques for many of the waste streams studied. However, two waste streams, stack gases and residues are produced during incineration. Specific technologies have been recommended in this report for scrubbing stack gases resulting from incineration of each waste. Removal of pollutants in stack gases necessitates disposal of collected material. Specific information on disposal of this waste as well as residues from incineration were not found for the waste streams studied. Further data development efforts may be necessary to fully assess potential impacts of these wastes.

Some waste streams were found to be treated, stored or disposed some distance from where they were generated. In general, waste disposal contractors were employed for this purpose. In many cases, tracking the specific waste streams to offsite disposal contractors and identifying particular treatment, storage and disposal techniques used there for each waste stream was very difficult. Reasons are that specific waste streams are frequently mixed with other specific waste streams and with general plant wastes such as waste paper and wood before being sent to an offsite disposal contractor. Offsite contractors typically use their own analytical laboratories to determine appropriate treatment, storage and disposal methodologies. Therefore, the waste stream's origin as used to denote waste streams in the bulk of this report may not have much meaning to an offsite contractor. This problem is being addressed in an ongoing EPA project to subcategorize wastes by the physical and chemical characteristics that will be meaningful for offsite disposal contractors and further evaluate exemplary disposal techniques and their costs.

2.3.2 Increasing Acceptance of Most Environmentally Sound Technologies

Further investigation of the refining of scum oils from dissolved air flotation of oil refinery wastes may help identify ways for reusing a larger portion of this waste stream in the production process. Further identification of chemical and physical properties of residues from dissolved air flotation may help identify specific alternatives for disposal.

Investigation of in-process changes for solvent-thinned trade sales paint manufacture may increase the reuse of spills, and out-of-date and off-specification paints in the production process, reduce solvent consumption and increase solvent recovery. Each of these practices could result in dollar savings to the manufacture as well as decrease negative impacts to the environment from disposal of these substances.

The process of chlorinolysis has been used for many years to convert chlorinated hydrocarbon wastes, especially from pesticide manufacture, to saleable products such as carbon tetrachloride. This process has not been applied to distillation residue from chlorobenzene manufacture. However, further investigation would lead to a determination of the feasibility of recovering carbon tetrachloride from this waste stream.

Investigation of the separation and reuse of nitrobenzene contained in column bottoms from its manufacture may result in savings to the manufacturer from both recovery of the nitrobenzene product and reduction of volume and hazard associated with the column bottom waste stream. A three-step stripping procedure involving steam distillation, alkali hydrolysis and catalytic reduction is recommended for further study.

In the past, concentrated red water from trinitrotoluene (TNT) production has been reused by a few paper manufacturers as a source of sulfite liquor. Further investigation of this practice may help identify further markets for this waste and allow economic comparison with other alternatives such as incineration.

These specific recommendations and recommendations for future study represent JRB's overall assessment based on studies of specific waste streams. Although this study was meant to be a technical assessment, it is believed that portions of the study may provide information for future regulation and permitting activities. The study may also provide information for study of other similar industrial wastes.

3.0 WASTE STREAM STUDIES

This chapter presents the results of the studies of 10 waste streams. For each waste the studies included analysis of the literature and an evaluation of treatment, storage and disposal techniques. The discussion below includes a short description of production processes and waste stream characteristics, a description of current, best available, and most environmentally sound treatment, storage and disposal techniques, and an assessment of the technological, cost and environmental impact associated with implementation of the best available technology for each waste stream. Three additional waste streams are part of the explosives study in Chapter 5.

Information on production processes and waste stream characteristics was obtained from the current literature, through discussions with knowledgeable plant personnel, and from regulatory agencies.

Treatment, storage and disposal alternatives were then identified. Current and best available practices were defined as those currently being used by waste stream generators, with current practice being the one most often used. The most environmentally sound practice given usually involved transferring technology used in other industries. In some cases, practices that have been proposed, but not yet implemented by industry, have been given as most environmentally sound. Where techniques used off the plant site differ from those used by plants to handle their own wastes, the differences are discussed. In almost all cases, techniques used on a plant site were found to be the same as those used by disposal contractors. Further discussion of contract waste disposal sites, and a listing of sites contacted, is given in Chapter 6.

Assessments of engineering feasibility, cost analysis and environmental impact were made for the method determined to be the best available technique for treating, storing and disposing of each waste stream. Nearly all techniques determined to be the best available are currently in use in at least one waste-generating facility.

Environmental impact of implementing best available treatment, storage and disposal techniques was assessed by comparing estimated emissions of air, water and land to corresponding minimum acute toxicity effluents (MATE's) given in Cleland and Kingsbury, Multimedia Environmental Goals for Environmental Assessment, 1977. Table 3.1 compares estimated emissions from implementing best available technologies for the 13 specific waste streams. MATE's are concentration levels of specific pollutants. These concentrations were judged to be appropriate for preventing certain negative effects on the environment or determined to represent limits achievable through technology. In many cases, a MATE value was not given for a component of the waste stream. Therefore, only estimates of low, medium or high emissions could be given with a corresponding dash mark where the MATE value would normally appear.

In most cases, properties of key chemical constituents in the waste stream were used to estimate emissions. For example, a key constituent for determining waterborne emissions from landfill disposal of chlorobenzene still bottoms was the solubility of chlorobenzene, which is 0.0488g in 100g of water at 30°C. Therefore, even though solubility will increase with increasing temperature, it is estimated that roughly 49 mg can be dissolved in 0.1l of water at 4°C, or about 490mg/l. This establishes an emission of chlorobenzene to water for estimating purposes.

3.1 SULFUR SLUDGE FROM CHLORINATOR UNIT IN PARATHION MANUFACTURE

Production of parathion, an insecticide, is included in the Standard Industrial Classification Manual, 1972 (SIC 2879) as part of agricultural chemical manufacturing. The total amount of parathion produced annually is not known. What is known is that approximately $117,621 \times 10^3$ pounds of cyclic organophosphorus insecticides are produced annually, of which parathion is the most widely used. However, 10 percent of the amount produced is sulfur sludge.

Table 3.1 Comparison of Estimated Emissions Using Best Available Techniques and MATES
(Cleland and Kingsbury, 1977)

Waste Streams	Component of Major Interest	Best Available Technology	Emissions For Major Component			MATES For Major Component					
			Air Mg/m ³	Water Mg/l	Land µg/g	Air, Mg/m ³		Water, Mg/l		Land, µg/g	
			Health	Ecology	Health	Ecology	Health	Ecology	Health	Ecology	
Wastewater treatment sludge from PVC production	Vinyl Chloride	Incineration with HCl recovery, land disposal of residue.	.02	<38	<76	2.6	-	38	>100	76	200
Chlorobenzene still bottoms	Chlorobenzene	Incineration with HCl recovery, land disposal of residue.	0.001	<488	<0.2	350	-	5.3 x 10 ⁶	100	11,000	0.2
Nitrobenzene still bottoms	Nitrobenzene	Rotary kiln incineration with NO _x control and heat recovery. Land disposal of residue.	<5.0	<1.0	<2.0	5.0	-	75	1.0	150	2.0
Tars from aniline production	Nitrobenzene	Rotary kiln or multiple hearth incineration with NO _x control and land disposal of residue. Heat recovery potential is good.	<5.0	<1.0	<2.0	5.0	-	75	1.0	150	2.0

Continued-----

Table 3.1 Comparison of Estimated Emissions Using Best Available Techniques and MATES
(Cleland and Kingsbury, 1977) , Continued

Waste Streams	Component of Major Interest	Best Available Technology	Emissions For Major Component			MATES For Major Component					
			Air Mg/m ³	Water Mg/l	Land µg/g	Air, Mg/m ³		Water, Mg/l		Land, µg/g	
			Health	Ecology	Health	Ecology	Health	Ecology	Health	Ecology	
Sulfur sludge from parathion manufacture	Sulfur	Rotary kiln or multiple hearth incineration with SO _x scrubbing. Land disposal of stabilized scrubber sludge and incineration residues. Potential for heat recovery.	Low	Low	Medium	-	-	-	-	-	-
	Organo-phosphates		Low	Low	Medium	-	-	-	-	-	-
DAF skimmings from petroleum refining	Low specific gravity oils	Rerefining	Low	Low	Low	-	-	-	-	-	-
Process liquid wastes from solvent-thinned trade sales paint manufacture	Solvents and pigment residues	Recovery with land disposal or incineration of residue.	Medium	Medium	Medium	-	-	-	-	-	-

Continued-----

Table 3.1 Comparison of Estimated Emissions Using Best Available Techniques and MATES
(Cleland and Kingsbury, 1977), Continued

Waste Streams	Component of Major Interest	Best Available Technology	Emissions For Major Component			MATES For Major Component					
			Air, Mg/m ³	Water, Mg/ℓ	Land, μg/g	Air, Mg/m ³	Water, Mg/ℓ	Land, μg/g	Health	Ecology	Health
Wastewater treatment sludges from woven fabric dyeing and finishing in the textile industry	Chlorinated organics and heavy metals	Sludge dewatering, disposal in approved landfill.	Low	Low	Medium	-	-	-	-	-	-
Wastewater treatment sludge from electroplating	Cyanide	Sludge dewatering disposal in steel drums in approved landfill.	<5.0	<0.5	<0.025	5.0	-	0.5	0.025	1.0	0.05
	Chromium		<0.001	< 0.25	<0.5	0.001	-	0.25	0.25	0.5	0.5
Lithium-sulfur dioxide battery	Lithium metal	Mechanical disassembly with incineration; SO _x , NO _x scrubbing, and disposal of residue.	<1	<1	<1	0.022	-	0.33	0.38	0.7	0.75
Red water from TNT production	Alpha TNT	Concentration/incineration with caustic scrubbing and land disposal of ash.	Low	Low	Low	-	-	-	-	-	-

Continued-----

Table 3.1 Comparison of Estimated Emissions Using Best Available Techniques and MATES
(Cleland and Kingsbury, 1977), Continued

Waste Streams	Component of Major Interest	Best Available Technology	Emissions For Major Component			MATES For Major Component					
			Air ³ Mg/m	Water Mg/ℓ	Land μg/g	Air, Mg/m ³	Water, Mg/ℓ	Land, μg/g	Health	Ecology	Health
Bulk propellents, explosives, pyrotechnics	Many explosive compositions	Incineration with caustic scrubbing and land disposal of ash.	Low	Low	Low	-	-	-	-	-	-
Pink water from load, assemble and pack operations	Spent Activated Carbon	Incineration with caustic scrubbing and land disposal of ash.	Low	Low	Low	-	-	-	-	-	-

3.1.1 Manufacturing Process and Waste Stream Characterization

Parathion (o,o-diethyl, o-4-nitrophenyl, phosphothionate) is an insecticide manufactured under several trade names, and by several different manufacturers. Monsanto and American Cyanamid produce the greatest amounts (Noyes, 1977). Parathion is manufactured by combining phosphorus pentasulfide with ethanol to form diethyl-diethio-phosphoric acid, which is chlorinated to form parathion. The reaction product from the mixing of phosphorus pentasulfide and ethanol is processed through a chlorinator. In the chlorinator, sulfur forms microspheres; these can encapsulate both the starting material and the chlorination product. The simple schematic shown in Figure 3.A illustrates the manufacturing process (Process Research, Inc., 1977).

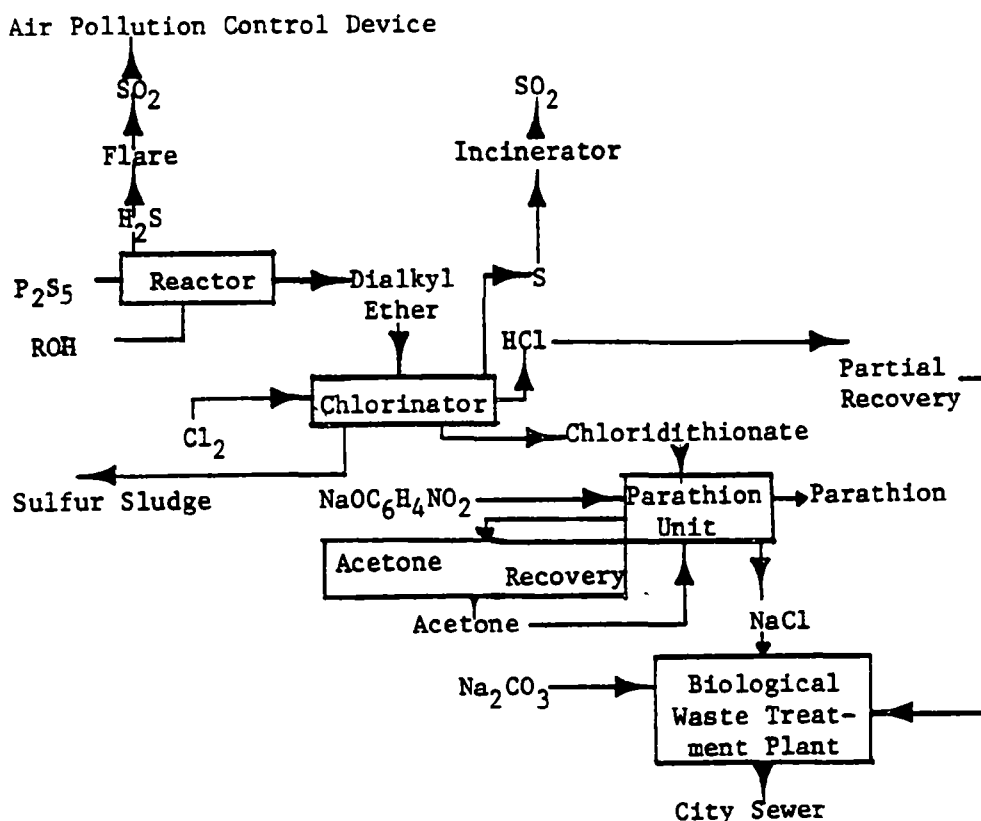


Figure 3.A Parathion Manufacturing Process

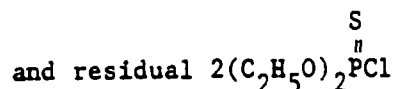
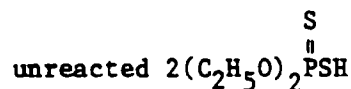
There are two manufacturing by-products of parathion: Hydrochloric acid (HCl) from the chlorinator unit, and sulfur dioxide (SO₂) from both the reactor and the chlorinator. At some facilities, HCl from the chlorinator is partially recovered for reuse: what is not recovered becomes part of the aquatic waste stream. Recovery of SO₂ as elemental sulfur from gaseous waste streams is widely practiced in industry. Recovery of SO₂ from the parathion manufacturing process is probable although no information was found to verify the practice.

Segregatable waste streams include the following:

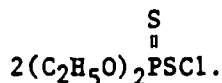
1. Sulfur sludge from chlorinator unit. This waste stream is normally incinerated.
2. Hydrochloric acid from the chlorinator unit. This by-product is normally recovered using quench tanks. Unrecovered HCl is mixed with the other plant waste streams prior to biological pretreatment.
3. Sodium Chloride waste from parathion unit. This waste stream is mixed with the other aqueous process wastes for biological pretreatment prior to disposal in municipal sewers.
4. Scrubber effluent from reactor process. If SO₂ recovery is not practiced, hydrogen sulfide (H₂S) from the reactor is incinerated and emitted as SO₂. To meet air pollution standards, an air pollution control device, such as a wet scrubber, is used to collect the SO₂. Scrubber effluent is an aqueous waste stream and is pretreated for disposal in municipal sewers along with other aqueous process wastes.
5. Acetone wastes from parathion unit. Waste acetone is recovered continuously for reuse in the parathion unit. The process used for recovery of acetone is not identified.

Although little information is available concerning details of the parathion manufacturing process, it is assumed that a fair amount of variability exists. Two patents for the manufacture of parathion exist, one by Monsanto and another by American Cyanamid (Noyes, 1977). For this reason, there is probably industry-wide variability. Additional variability of the waste could stem from problems in production, such as incomplete reactions and inconsistencies in the chemicals used in each batch.

Sulfur sludge from the chlorinator unit contains approximately 93 percent sulfur and 7 percent organophosphates. Precise identification of the organophosphate constituents is not available in literature. However, it can be estimated that the organophosphate contains:



Another probable intermediate product is:



In the chlorinator, elevated temperature and pressure contribute to the formation of numerous intermediate products, but instability of the products outside the chlorinator makes them of little consequence in waste streams.

Organophosphates are highly toxic compounds, and sulfur has a flashpoint of approximately 66°C (Merck, 1976). The potential toxicity of the waste stream led to its inclusion in this study. Parathion is highly toxic, with an LD₅₀ of 3.6-13 mg/kg, and it is possible that the organophosphates in the sludge might contain similar toxic properties (Merck, 1976). There is no information currently available on the toxicity, stability, or volatility of these intermediate products. Using general information on the product and the individual elements can allow for estimating the intermediate properties. Organophosphates are generally considered to be quite volatile compounds.

3.1.2 Treatment Alternatives

Parathion manufacturers and the organic chemicals industry in general are reluctant to divulge any information concerning their hazardous waste disposal methods. Information is available concerning

the methods currently used for disposal of parathion sulfur sludge, but it is not known whether treatment is performed on-site or off-site. American Cyanamid, for instance, incinerates some of their process wastes on-site. The remainder of their wastes are incinerated off-site, and we have been unable to identify which of these wastes contain parathion sulfur sludge (American Cyanamid, personal communication, 1979).

The present method for treatment of parathion sulfur sludge is incineration (PRI, 1977). Incinerators for the treatment of sulfur sludge can be either a rotary kiln type or a multiple hearth incinerator. They are equipped with air pollution control devices such as wet gas scrubber systems to cut down the otherwise high emissions of SO_2 . SO_2 control during the incineration is often difficult and expensive. It is difficult to control the SO_2 emission in an environmentally acceptable manner, even with a wet gas scrubber. Incineration is very efficient in reducing the volume of waste to be disposed and will reduce the toxicity of the waste by oxidation. A major disadvantage to use of incineration as a treatment method for sulfur sludge is the high quantity of energy required to maintain complete combustion of waste products. $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$ is an exothermic reaction; however, a large quantity of heat is still required to maintain consistently high temperatures for the period of time necessary to completely break down the waste. Energy could be recovered from the incinerator in the form of heat or steam, lowering net energy requirements. No evidence of this practice was found.

Another disadvantage to incineration of sulfur sludge is that sulfur emissions mandate use of extensive air pollution control technology for SO_2 removal. Typical air pollution control devices are lime/limestone scrubber systems, which meet current standards, but generate considerable calcium sulfite containing waste requiring stabilization prior to disposal as landfill.

Incineration represents the best available technology for this waste stream. From an environmental and engineering standpoint incineration (combined with air pollution control equipment) is an acceptable means of disposing of this sulfur sludge.

3.1.3 Disposal Alternatives

Sulfur recovery from the sludge is less energy intensive and more regenerative than incineration (PRI, 1977). This process is a conceptual design only and to our knowledge has not been implemented at an existing plant. This alternative is a five-step process which separates sulfur for recovery, then detoxifies the organophosphates for ultimate disposal. The first step involves taking sludge from the chlorinator unit to a steam heated sedimentation tank operating at 125°C (12°C above the melting point of sulfur). This treatment melts the sulfur component of the waste stream and decants the insoluble organophosphate compounds in the stream. The sulfur stream then proceeds to the ultra-filtration unit, a membrane separation system which removes organic compounds with a molecular weight of 150 or greater from the sulfur stream. The sulfur passes through the membrane at a hydrostatic pressure up to 10 atmospheres. The organophosphates removed in the first step are cooled to ambient temperature, then refiltered with a cartridge filter to remove any sulfur retained in the phosphates. The molten sulfur is cast into solid, pure bricks which are cooled and then are ready to be sold. Organophosphate material is mixed with lime, which partially detoxifies the phosphates, and is composted for final disposal. Detoxification of the organophosphates is further accomplished, in time, by bacterial degradation. Figure 3.1 illustrates the recovery process.

In addition to having recovered a salable product, sulfur recovery reduces the total volume of waste for disposal by 93 percent and eliminates expensive incineration as a disposal mechanism.

It is not known whether incineration is performed on- or off-site, nor is there information as to the feasibility of sulfur recovery being performed on- or off-site. Consequently, methods of treatment discussed previously apply to both on-site and off-site treatment.

3.1.4 Storage Alternatives

Current information available concerning the treatment, storage and disposal of parathion sulfur sludge provides no insight into the use of storage in handling this waste stream. It is presumed that none

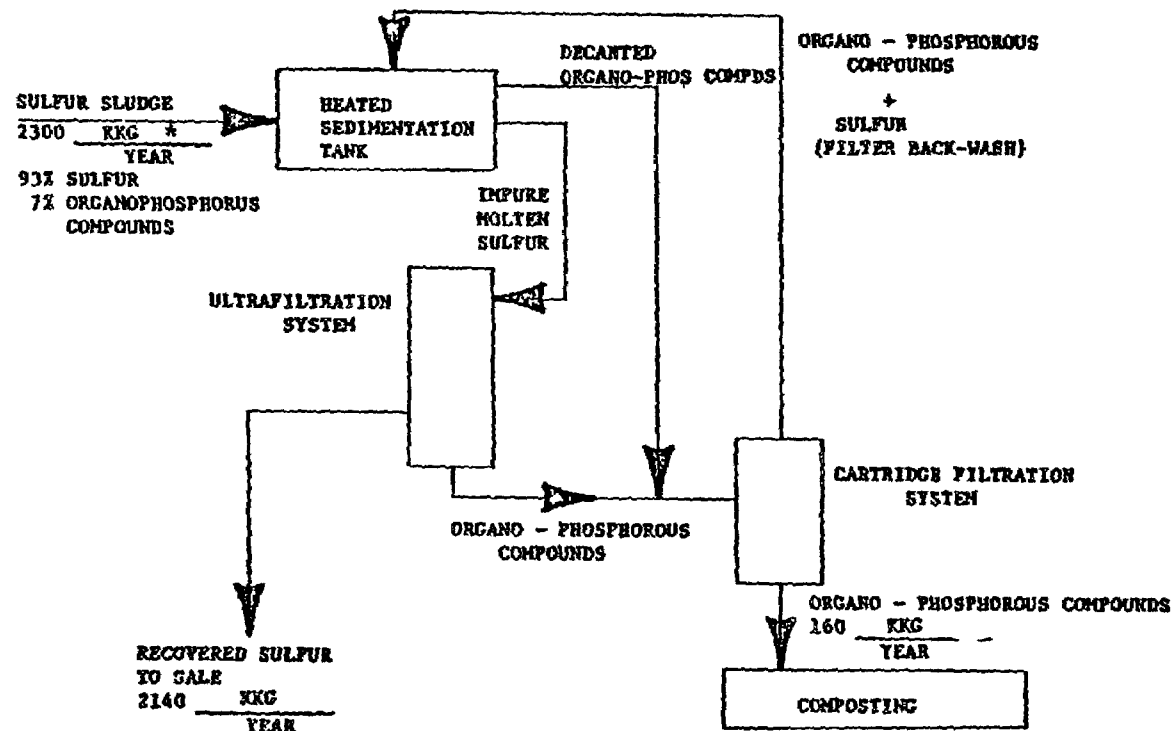


Figure 3.1 Process for Recovery of Sulfur from Chlorination Unit Sulfur Sludge from Parathion Manufacture (PRI, 1977)

* Design Figure

of the waste streams are stored for longer than 90 days, other than the sludge that is collected from chlorination and transported directly to the incinerator without significant storage periods. Should a sulfur recovery system be employed, it would presumably operate on a continuous feed basis, thereby providing only for emergency storage. If the sludge was stored temporarily, sealed vessels would be necessary.

Other than disposal of residues from incineration, direct disposal without incineration is not practical for this waste stream.

3.1.5 Recommended Techniques

Sulfur recovery of parathion sulfur sludge is the recommended treatment technology for handling this waste stream since the only burden it places on the environment is composting the organophosphates. It also eliminates the energy and air pollution burden of incineration, which is the best available technology and is the treatment currently in use. Sulfur recovery has a low functional energy demand, a marked contrast to incineration. However, additional research is necessary for implementation of this technology as further discussed in the following section. We recommend that an industry or expert review be conducted on this technology.

3.1.6 Engineering, Cost and Environmental Evaluation of Sulfur Recovery from Parathion Sulfur Sludge

The following equipment would be required for sulfur recovery of a typical parathion sulfur sludge waste stream:

- Sludge pump - 3 l/min
- Sedimentation tank - 6,000 l
- Sulfur pump - 9 l/min
- Ultrafiltration system - 10 l/min
- Organophosphorus pump - 2 l/min
- Sulfur pump - 8 l/min
- Cartridge filter - 2 l/min
- Sulfur conveyors - 900 kg/hr
- Organophosphorus storage tank - 2,500 l

Although the system described for using sulfur recovery technology appears to be feasible, it has not been tested in either a working or pilot study situation.

Currently, we have been unable to determine the willingness of industry to accept sulfur recovery. If the system is easily operable and cost effective, there is reason to believe that the process would be accepted by the four parathion manufacturers. Marketability of sulfur would play a large part in determining acceptability.

The following is a cost evaluation of sulfur recovery (PRI, 1977):

1. Estimated Installed Capital Cost

Basis: 7.67 kkg/day of sulfur sludge

<u>Equipment Item</u>	<u>Capacity</u>	<u>Estimated Cost</u>
Sludge Pump	3 l/min	\$ 14,600
Sedimentation Tank	6,000 l	45,700
Sulfur Pump	9 l/min	8,900
Ultrafiltration System	10 l/min	4,400
Organophosphorus Pump	2 l/min	13,100
Sulfur Pump	8 l/min	8,900
Cartridge Filter	2 l/min	13,100
Sulfur Conveyors	900 kg/hr	44,000
Organophosphorus Storage Tank	2,500 l	14,600
<hr/>		
Subtotal		\$167,300
Engineering @ 10 percent		16,700
Contingency including freight @ 20 percent		<u>33,400</u>
Total		\$217,400

2. Annual Fixed Charges

Depreciation	\$217,400 @ 10%/yr	\$ 21,700
Interest	\$217,400 @ 10%/yr	21,700
Insurance and Taxes	\$217,400 @ 4%/yr	<u>8,700</u>
Total Annual Fixed Charges		\$ 52,100

3. Direct Operating Cost

Raw Material	\$ 53,300	
Utilities	\$ 94,800	
Maintenance $0.04 \times 217,400$	8,700	
Direct Labor $7200 \times 9.0 \times 1.5$	<u>97,200</u>	
Annual Direct Operating Cost		\$254,000
Annual Composting and Leachate $160 \text{ kkg} \times \$9.00 \text{ per kkg}$		<u>1,500</u>
Total Annual Cost		\$255,500
Recovered Materials:		
Sulfur @ \$58.00/kkg		
$58 \times 0.7 = 40.60 \times 2140 \text{ kkg}$		<u>-86,900</u>
Net Total Annual Cost		\$168,600

4. Cost Per kkg Product $\$168,600 \div 20,000 \text{ kkg}$ \$ 8.43

5. Cost Per kkg Waste $\$168,600 \div 2,300 \text{ kkg}$ \$73.30

6. Impact on Product Cost

(Market value of 1 kkg product = \$1,918)

$\text{Cost/kkg} \div \text{Market value/kkg} = \$8.43 \div \$1,918$ 0.44%

There are no foreseeable releases to the environment from the sulfur recovery system. The small amount of organophosphorus residue is detoxified to some extent with lime and then biologically treated by composting. Ultimate disposal of organophosphorus residue can lead to possible movement of phosphorus in the environment, but phosphorus is not considered a hazardous substance. Regardless of the variability

of the waste stream, there will be no resultant variability of the environmental impact due to the sulfur recovery system.

MATE values were not available for sulfur or organophosphorus portions of the waste stream. Low air emissions from incineration will occur, based on the high temperatures and long retention times provided by rotary kiln or multiple hearth incineration. SO_x is efficiently removed by wet lime/limestone scrubbing. Medium values for water and land emissions will occur, based on the high volume of sludge which must be stabilized and disposed. Although sludge components are not highly toxic, the high volume generated is expected to have some environmental impact on water and land in the disposal area.

Estimated emissions from sulfur recovery are based on limited information which indicates at most a slight impact on land and water from composting of the organophosphorus portion of the waste stream.

In summary, we feel that controlled incineration is an acceptable treatment for sulfur sludge, but the associated environmental burdens make it less desirable than sulfur recovery. Sulfur recovery is heavily dependent upon the solubility of elemental sulfur. Therefore, further testing and research is needed to determine the sulfur market and engineering feasibility of the recovery system.

Our discussions with Monsanto and American Cyanamid proved unsuccessful in discovering why they do not recover sulfur or reveal their views on the recovery technology. Sulfur disposal is a major problem, which leads one to conclude that recovery should be an encouraging option to the industry.

3.2 WASTE WATER TREATMENT SLUDGE FROM POLYVINYL CHLORIDE PRODUCTION

Production of polyvinyl chloride, a plastic, is included in SIC 282.

3.2.1 Manufacturing Process and Waste Stream Characterization

Polyvinyl chloride (PVC), which consists predominantly of the repeating structure ($\text{CH}_2\text{-CHCl-}$), is produced from vinyl chloride monomer (VCM). All polymerizations in the United States are batch operations. PVC is currently manufactured by four basic processes: suspension, emulsion, bulk and solution polymerization. Each process has different discharge characteristics.

Total annual PVC production in 1976 was about 2.34×10^6 kkg (2.56×10^6 tons). Total 1976 vinyl chloride waste from the PVC manufacturing industry was about 554.9 kkg (611.8 tons) (EPA, 1978b). Table 3.2 illustrates the processes used and the total estimated vinyl chloride process waste generated from each polymerization technique.

Of the four major polymerization processes available, the suspension process accounts for 79 percent of total production. The process flow is shown schematically in Figure 3.2.

In the suspension method, VCM is dispersed as small droplets into a stabilized suspending medium consisting of water and small amounts of proprietary suspending agents. The suspension is then heated in the presence of catalysts (such as organic peroxides). After the desired degree of polymerization is achieved, the suspension is stripped free of monomer, blended with other batches, washed, centrifuged, and dried. Some plants strip within the reaction vessel, therefore high pressures and moderate temperatures will be experienced. The effluent stream from centrifugation contains the majority of the plant wastes, including significant amounts of very fine polymer.

Table 3.2 VCM Concentrations Found in PVC Sludges

No.	PVC Sludge Identification	Weight Percent Solids		VCM Concentration,* ppm by weight	
		As Collected	After Filtration	Wet Sludge	Dry Solids
<u>Plant 1</u>					
1	Freshly centrifuged sludge [†]	34	42	150	360
2	Fresh combination sludge ^{††}	--	55	210	380
3	Sludge from full truck ^x	35	41	520	1260
4	Sludge freshly discharged from truck ^y	34	42	90	200
5	Sludge after disposal and doze	36	41	90	200
<u>Plant 2</u>					
6	Sludge collected during discharge from truck ^y	17	40	7	20
<u>Plant 3</u>					
7	Sludge collected during discharge from truck ^y	30	60	90	130

* VCM analysis of wet (filtrated) sludge by GC-FID analysis of THF extract. Also calculated on a dry solids basis. 360 ppm = 360 µg/g = 0.36 mg/g = 0.036 weight percent.

† Sludge collected at PVC plant directly from centrifuge discharge tube.

†† Sludge collected at PVC plant from partly filled truck loader.

x Sludge collected at PVC plant from full truck loader.

y Sludge collected during landfill disposal.

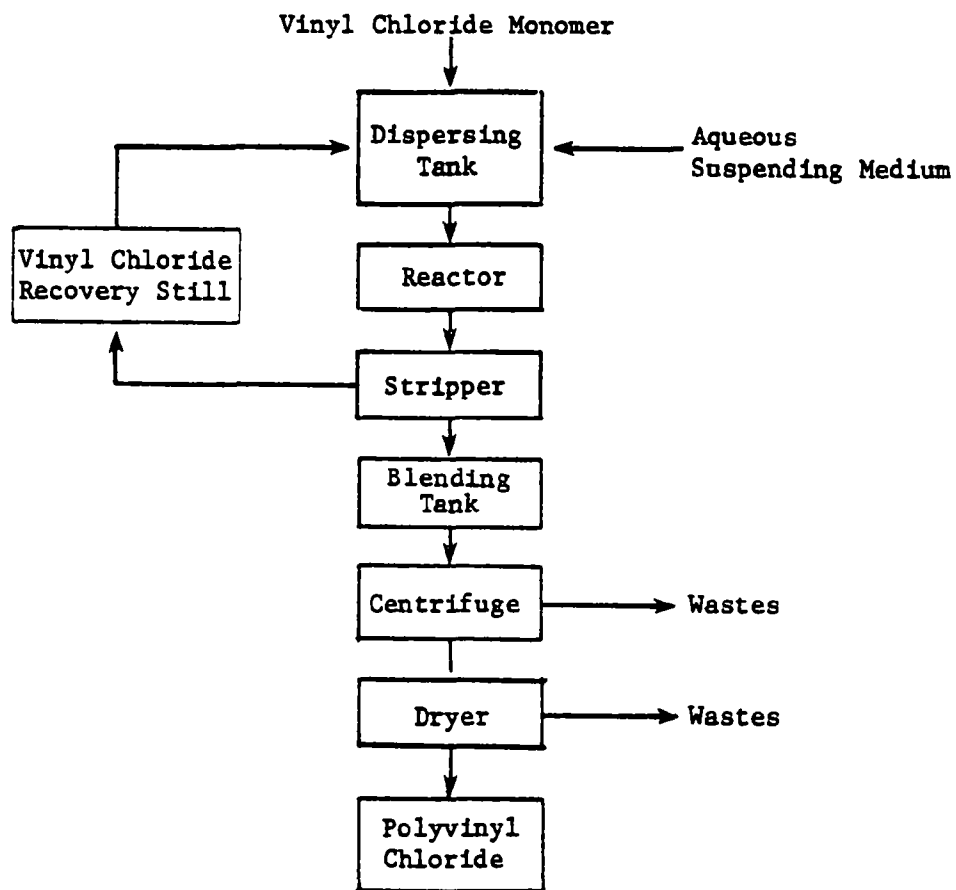


Figure 3.2 Suspension Process for Polyvinyl Chloride Production

The typical PVC manufacturing plant includes the following operations, common to all four production processes:

- receiving and storing of VCM and catalysts
- polymerizing of VCM, which includes measuring, charging and reacting
- stripping and recovery, which includes reactor blowdown and recovery, and slurring handling and storage
- centrifugation or filtration
- drying
- pneumatic conveying and storage of the product
- packaging and shipping
- blending
- wastewater treatment.

Centrifugation and wastewater treatment in the PVC production process results in by-product wastes containing suspended solid matter and vinyl chloride monomer (VCM). The effluent stream from centrifugation contains the majority of the contaminants from the process. Impurities in the effluent stream consist of small amounts of various polymerization processing aids, such as suspending agents, surface-active agents, free radical catalysts or initiators, unreacted monomer and significant amounts of very fine particles of the polymer product. In addition to these contaminants, there may be small amounts of phenol, sodium phenolate, and sodium hydroxide, which could come from purification of the monomer. It is possible that chlorinated organic solvents, such as carbon tetrachloride and chloroform, which are included in the starting mixture to arrest the polymerization at any desired point, also may find their way into the effluent streams. Nevertheless, the entrapped VCM in the waste treatment sludge is of primary concern in this study.

Suspension polymerization is the most widely used method for the manufacture of PVC. However, for production of co-polymers, emulsion and solution polymerization are employed to a significant extent. There has been little change in vinyl resin manufacturing methods and technology over the past 20 years, and no drastic changes are anticipated in the foreseeable future. Therefore, characteristics of the

waste stream may not be expected to change to any significant degree in the future. Wastewater and resulting treatment sludge volumes may increase with an anticipated increase in total U.S. production of vinyl resins in the near future.

3.2.2 Treatment Alternatives

Levels of treatment, disposal and storage technology which are, or may be, applicable to the water pollution control sludge waste stream generated by PVC production are summarized in Table 3.3. The most prevalent current technology for water pollution control sludge is contractor disposal in off-site landfills. It is practiced by about 85 percent of the industry. The best available technology currently in use is rotary kiln incineration. Best available technology suggested by related industries is incineration with recovery of by-products, which are heat and HCl.

The technologies applicable to water pollution control sludge are employed by both industry and waste disposal contractors.

3.2.2.1 Current Practices

As stated previously, most PVC manufacturers currently dispose of the stripped sludge in off-site landfills, which involves no treatment. However, controlled incineration is being used at some plants.

Controlled incineration represents a technology that is universally practiced in the plastics industries. The two areas of concern related to vinyl chloride waste incineration are incinerator air pollution and incinerator and gas scrubber corrosion. Hydrogen chloride is the major toxic material released when vinyl chloride waste is burned, and it is also a main factor in corrosion of firebox and pollution control equipment. These problems may be overcome by proper design and operation and by equipping the incinerator with an emission control device such as one of the following: an electrostatic precipitator, a baghouse, or a catalytic or thermal afterburner. Presently, state regulations are such that monitoring and control are the rule on all incineration equipment. PVC plants still lacking in these

Table 3.3 Summary of Treatment, Storage and Disposal Technology for Water Pollution Control Sludge from PVC Production

	Current Practices	Best Available Technology	Technology Suggested by Related Industries
Treatment		Rotary kiln incineration	Incineration with recovery of heat and HCl
Storage	Steel drums, storage tanks	Waste container with safeguard	Encapsulation, cementation
Disposal	Landfills, burial operations	Secured landfills	Salt deposit

features anticipate equipping or replacing their equipment to meet air pollution standards.

3.2.2.2 Best Available Technology

Rotary kiln incineration was selected as best available technology because of potential broad applicability, demonstrated performance and ability to handle a variety of physical forms of waste. It can incinerate combustible solids, liquids, gases, sludges and tars. With the addition of highly efficient secondary abatement equipment such as scrubbers and precipitators, rotary kiln incineration would be a very useful method for disposing of highly volatile waste such as PVC sludge. The basis for use as best available technology was the destruction of PVC waste sludge in a test study performed at the 3M Company Chemolite plant (EPA, 1977a). The sludge selected for this study contained 42 percent water and 26 percent solids, primarily vinyl chloride. The waste was found to contain 220 ppm of residual VCM and insignificant quantities of other organic compounds on a wet weight basis. No trace elements were found at concentrations high enough to cause concern about emissions of toxic metals at the feed rates used in the tests.

The incinerator was operated at full capacity (about 1 ton/hr) and achieved a combustion efficiency of 99.9 percent. The gaseous emission rates of chlorinated organics for these tests were determined to be 0.02 mg per cubic meter of effluent gas. This compares to a federal EPA emission standard for PVC manufacturing processes of 33 mg/m³ (10 ppm by volume). Evidently, incineration of PVC would not present an environmental hazard when combustion efficiency is maintained relatively high (99.9 percent).

The 3M Company Chemolite incinerator system consists of a rotary kiln primary chamber, a secondary combustion chamber and a wet scrubbing system for air pollution control. The plant facility has a rated capacity of 23 million Kcal/hr (90 million BTU/hr). A schematic of a rotary kiln facility is shown in Figure 3.3.

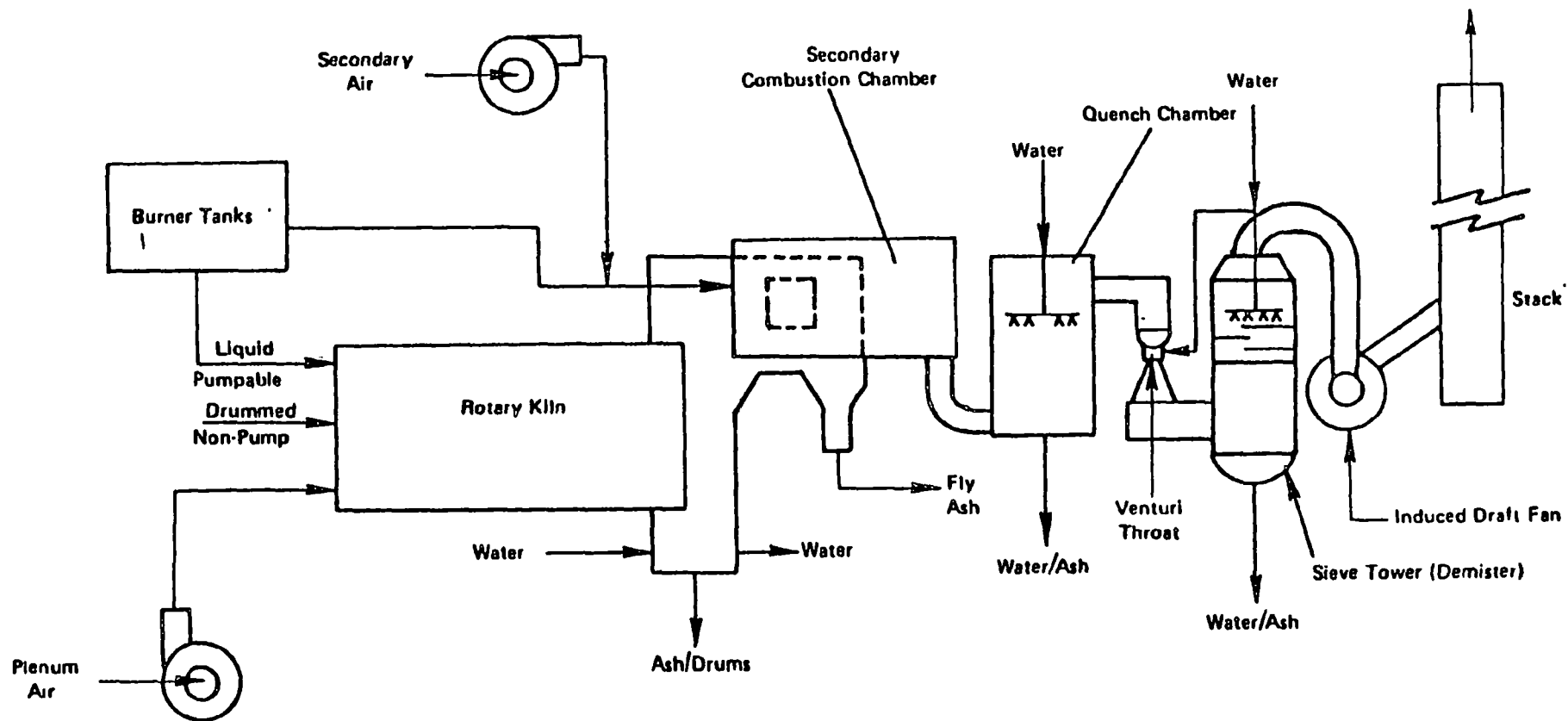


Figure 3.3 Schematic of Rotary Kiln Facility (EPA, 1977a)

The rotary kiln is fired with liquid waste fed through a burner at the front of the kiln. Non-pumpable wastes are left in drums and fed into the rotary kiln by the drum feed system. The rotary kiln is normally operated at a temperature range of 815-870°C (1300-1600°F). The average solids detention time of combustion gases within the kiln is roughly two seconds. The rotational speed of the kiln is usually set at 0.2 to 0.3 rpm. At the downstream end of the kiln, an ash handling system quenches and collects ash and burned-out drums from the incinerator which are loaded together into trucks and transported to an on-site landfill.

Gases from the kiln flow through a mixing chamber to the secondary combustion chamber. The secondary combustion chamber is designed to burn uncombusted gases and particulate matter from the rotary kiln. It is fired with pumpable PVC waste and/or No. 2 fuel oil, depending on the characteristics of the PVC waste being incinerated in primary combustion. The secondary combustion chamber is generally operated at 980°C.

Gases from the secondary combustion chamber are cooled with water in the quench elbow and quench chamber. They then follow through a high energy Venturi scrubber where particulates are removed. A demister removes entrained water particles from the combustion gases which then flow through an induced draft fan and are exhausted to the atmosphere through the stack.

Water streams discharged from the scrubber system, demister and ash handling system are combined into a single wastewater stream. The wastewater is acidic, and is neutralized with an alkali and sent to a central wastewater treatment system.

3.2.2.3 Methods Suggested by Related Technology

Thermal oxidation processes have been used to treat gaseous emissions from incineration of PVC wastes for some time. Other methods are activated carbon adsorption and the scrubbing (usually wet) of waste gas streams, techniques that are generally uneconomical

and inefficient (Moore, 1975). Oxyphotolysis of vinyl chloride has been studied but not yet proven in a commercial application. When the volume of waste gas streams is low, refrigerated vent coolers have been found useful for limiting emissions, but this approach entails high operating costs and is not very efficient (Gothesman, 1974). A thermal oxidation process developed by Nittetu Chemical and Engineering, Ltd., of Tokyo, Japan, not only can control vinyl chloride emissions, but also can recover energy and by-product HCl (Ezaki, 1971; Santoleri, 1973). The Nittetu process is based on the thermal sub-X (submerged exhaust) system for quenching the exhaust gases by direct contact of the gas with liquid. The submerged exhaust system quenches hot gases without the need for a heat exchanger surface (Naidel, 1973). Figure 3.4 shows a process which disposes of chlorinated hydrocarbons with recovery of up to 20 percent hydrochloric acid, which can be further concentrated for sale or reuse.

The waste sludge, together with combustion air and auxiliary fuel (if required), are introduced into the oxidation chamber by an externally atomized nozzle, horizontally fired by a vortex burner. Hot oxidation chamber exhaust gas is then discharged through an alloy downcomer tube into an acid-brick lined steel tank (sub-X quench tank). Gas is cooled to saturation temperature and then discharged into the scrubbing towers for hydrogen chloride or chlorine removal. Up to 20 percent HCl can be recovered with or without the heat exchanger. Exhaust from the tower, saturated with water vapor and almost free of hydrogen chloride, can be discharged directly into the atmosphere. However, there are also traces of hydrogen chloride vapor and chlorine which pass through the tower and require further scrubbing. The gases are scrubbed by an alkaline solution in a tower placed directly above the absorption tower before they are discharged to the atmosphere. This scrubbing tower is also packed with the Tellcrette material. Stack gases contain less than one part per million by volume of HCl and 10 parts per million by volume of chlorine. This is well within existing pollution codes.

A system utilizing heat recovery is shown in Figure 3.5.

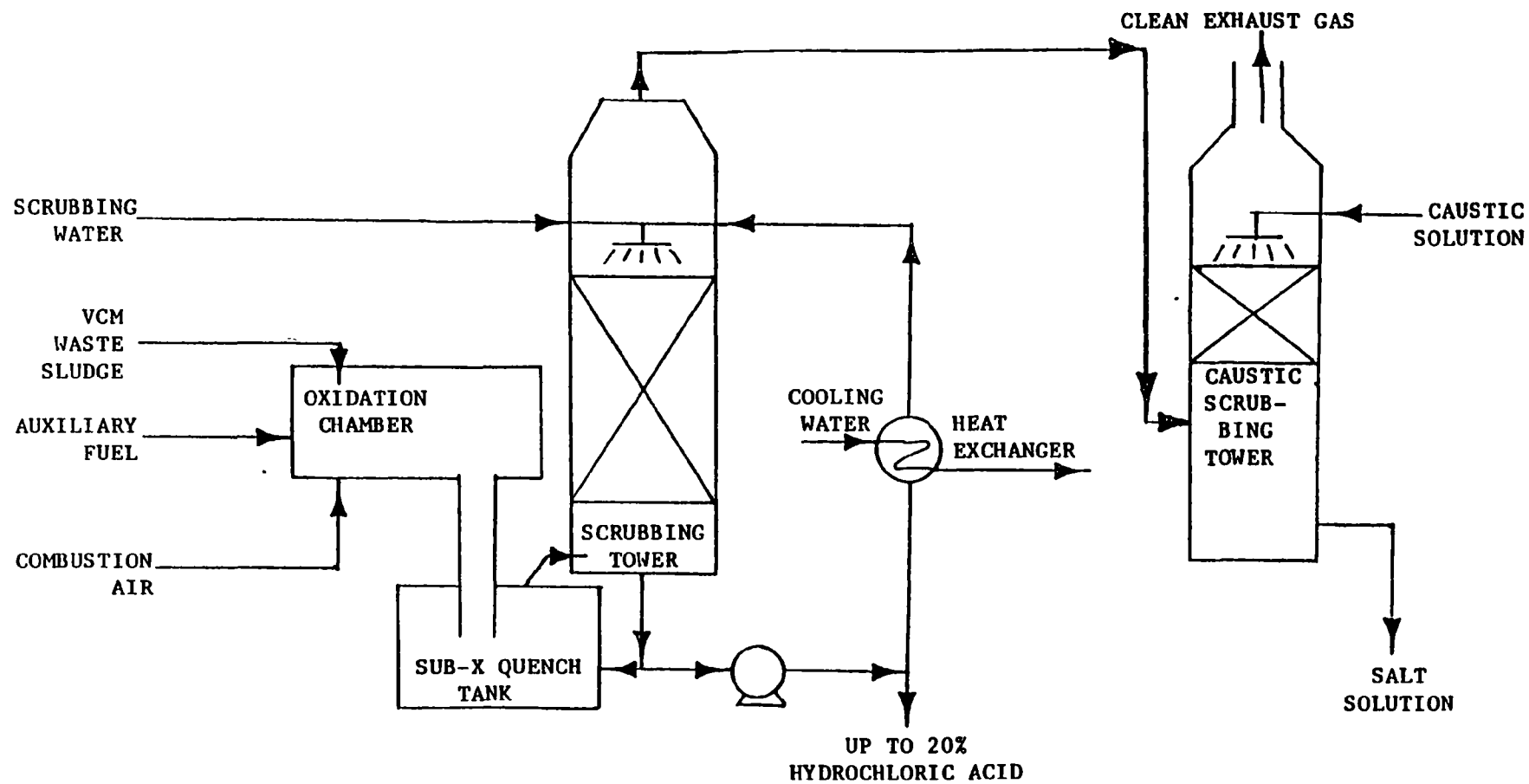


Figure 3.4 Sub-X Type VCM Waste Sludge Cleaning and Acid Recovery System (Kainey, 1976)

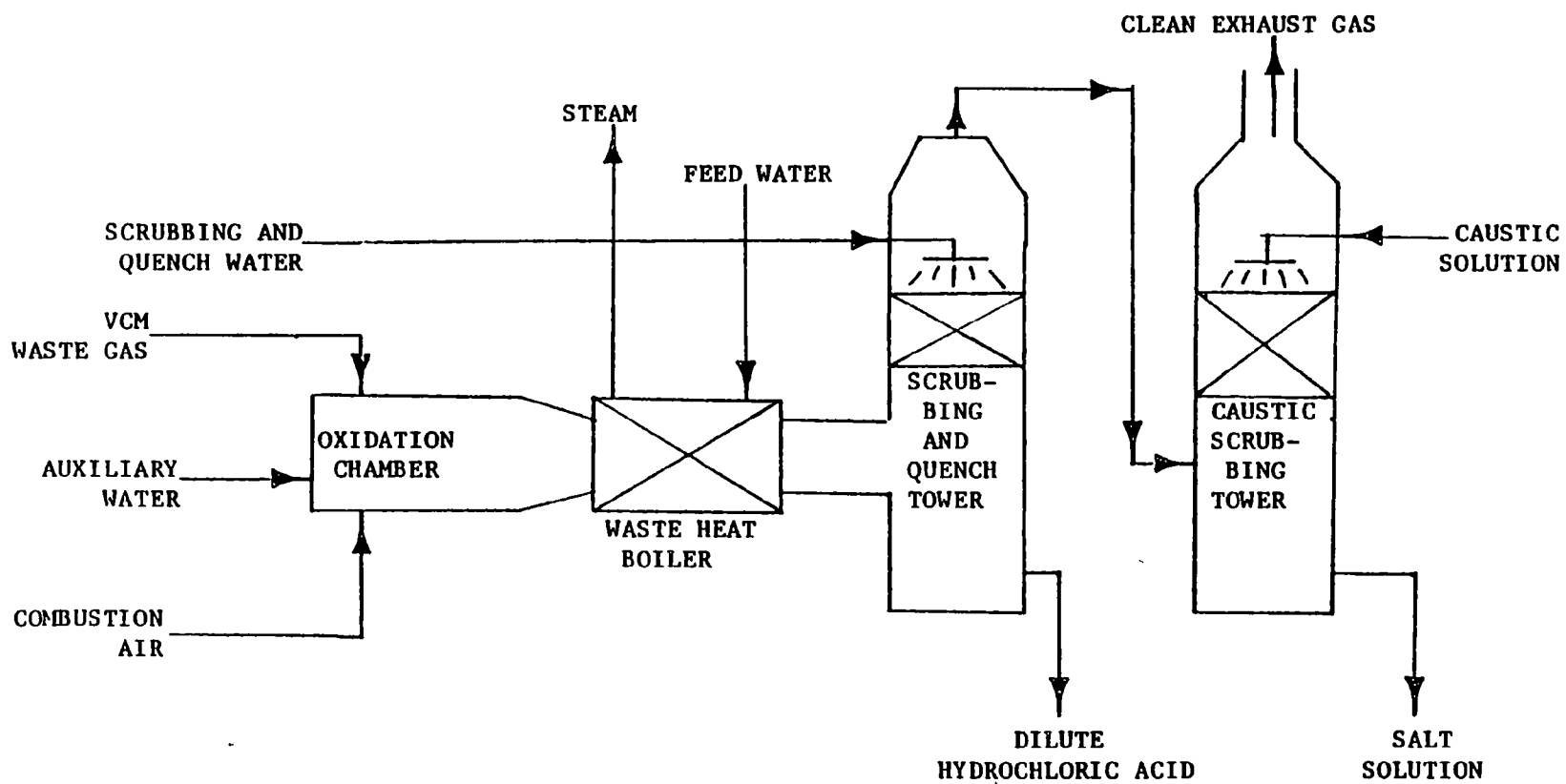


Figure 3.5 VCM Waste Sludge Cleaning and Heat Recovery System (Kainey, 1976)

3.2.2.4 Methods Suggested by Related Technology

If permanent storage is required, encapsulation and cementation are two related techniques which could be applied to storage of vinyl chloride sludge. Encapsulation involves permanent sealing of a material and its container in another impervious container of plastic, glass, or other material unaffected by the waste material. This container may in turn be sealed within a durable container made of steel, plastic, concrete, or other material of sufficient thickness and strength to resist physical damage during and subsequent to burial. It may also involve the use of above ground silos.

Cementation involves fixation or immobilization of toxic materials to permit easier handling and reduce the possibility of leaks. Examples of the cementation processes which have been developed and are applicable for storage in a permanent disposal facility are discussed in the following.

Weismantel reports that Chemfix, Inc. (Pittsburgh, Pennsylvania) and Crossford Pollution Services, Ltd. (Sole, England) have each developed processes that are now being used commercially to harden residues into inert rock-like materials said to be safe for use in landfill. The Chemfix process uses soluble silicates to fix the wastes. The Crossford process converts the waste into a monomeric mixture which polymerizes at the landfill site within three days to a rock-hard solid. TRW, Inc. (Redondo Beach, California) is also reported to be working on a polymeric sludge solidification scheme (Weismantel, 1975).

A process developed by K. Tuzaka is designed to convert industrial waste such as sludges and cyanide-containing waste to innocuous solid blocks. This is done by incorporating a coagulant into such industrial wastes, kneading the mixture, press-shaping the kneaded mixture, sealing the outer periphery of the shaped article by means of concrete coating, and aging and solidifying the sealed block. The resulting innocuous solid blocks may be utilized for reclamation or construction.

J. R. Connor has developed a process in which an aqueous solution of an alkali metal silicate setting agent causes the silicate and setting agent to react. This converts the mixture into a consolidated, chemically and physically stable solid product that is substantially insoluble in water and in which pollutants are entrapped in the solidified silicate so that the waste material is rendered nonpolluting and fit for long term storage and disposal (Connor, 1974).

3.2.3 Storage Alternatives

3.2.3.1 Current Practices

At present, waste sludge from PVC production is being stored on land in storage tanks and/or waste containers prior to being transported for ultimate disposal or treatment. Usage of these methods is determined by volume of waste, type of waste, pumpability and cost. Pumpable waste can be stored either in a tank or waste container, while nonpumpable waste storage is limited to waste containers. Costs dictate usage of waste containers for storing small volumes.

Steel drums and other waste containers used with or without plastic liners provide some long-term containment and are the most convenient storage and transportation mode for relatively small quantities of potentially hazardous wastes. The most obvious problem with this method is the eventual decay of the steel drum. Rate of decay information for PVC sludge in drums has not been found. Unless disposed in approved or secured landfills, future release of drum contents to the environment is likely. Research performed to date has not identified whether or not disposal in steel drums in a secure landfill will result in releases to the environment. However, it is believed that by assuming a slow release over a long period of time, a broad estimate can be made.

Another problem associated with storage tanks and waste containers is emission of toxic gases to the air. Air pollution incidents at waste storage facilities have been cited in an EPA study. Problems can be avoided by implementing good design and operational practices, which are described in the following discussion.

3.2.3.2 Best Available Technology

In many states, regulations governing the storage of hazardous wastes are part of general hazardous material regulations. The guidelines applied to hazardous waste disposal are also applied to waste storage facilities. In many states, waste storage is not specifically mentioned in regulations. However, storage tanks or waste containers and handling procedures are described at the time engineering plans for a waste disposal facility are submitted for state review and approval. The following items also should be considered in plans for handling and storing hazardous wastes such as PVC wastewater treatment sludge:

- Storage rooms for PCV waste storage containers should be dry, well ventilated and fireproof
- Signs should be placed on the storage building, a fence should surround the site and doors should be kept locked
- Fire fighting equipment and appropriate safety devices (respirators, etc.) should be prominently placed. The fire department should be aware of quantities and characteristics of stored materials
- Emergency instructions relevant to the materials stored should be prominently displayed
- Frequent inspection is desirable.

Storage cannot be used as an ultimate disposal method because of deterioration of containers. Deteriorating containers must be replaced promptly. A polyurethane foam method for plugging leaking containers can be used on a temporary basis. This will assure safety while providing containment until permanent repair or replacement can be made. Container materials which are commonly used and available include steel, rubber-lined steel tanks, nonreactive plastic-lined steel drums and plastic-lined concrete cases. Containers to be buried may be further protected by additional inert casings.

Storage of waste with hazardous volatile components such as VCM is a potential source of air pollution. Careful selection of original storage container material and size, proper filling and sealing, regular inspections of the storage facility and prompt replacement of old, deteriorating containers should permit safe, long term storage. In

addition, those containers which require venting must be equipped with a vapor recovery system.

Aqueous waste streams from PVC production are treated in various ways at different PVC plants. Typical treatment practices employed are chemical addition, followed by primary clarification and activated sludge treatment. Primary clarification concentrates the solids content of the waste, while wastewater is typically discharged to the municipal waste treatment system or a surface stream. Chemical coagulants are added prior to primary clarification and the precipitated materials are physically removed by sedimentation and centrifugation. The final waste material is a water-based sludge ranging from about 15 percent solids from sedimentation to 40 percent solids from centrifugation. Physical properties vary from water-like, thin slurries to thick pastes approximately the consistency of a concrete premix.

EPA studies in the spring of 1974 at six PVC plants show concentrations of VCM in sludge ranging from less than 1 ppm to 3,520 ppm in wet sludge and from less than 1 ppm to 4,200 ppm in dry sludge. Most of the samples contained greater than 10 ppm on either a wet or dry basis. These fluctuations may reflect changing plant production schedules, which affect production rates and product mixes (PVC homo-polymer types, PVC copolymer types, ratio of homo-polymer to copolymer, etc.). Table 3.3 shows VCM concentrations found in PVC sludges in another EPA study (EPA, 1976a). There are also insignificant amounts of various polymerization processing aids in the sludges. The chemical composition of the sludge includes 1 to 3,520 ppm VCM, 200 ppm PVC solids, 2 percent ash, and very low concentrations of heavy metals (EPA, 1976a).

Vinyl chloride, which can volatilize from PVC wastewater treatment sludge, is a colorless, flammable gas under normal temperature and pressure. It has high volatility with a vapor pressure 2,660 mm Hg at 25°C, boiling point 13.9°C. VCM polymerizes in light or in the presence of catalyst. On combustion, it is degraded into hydrogen chloride, carbon monoxide, carbon dioxide and traces of phosgene (Cleland and Kingsbury, 1977). Pure VCM is considered a severe fire and explosion hazard when

vapors are exposed to heat and flame. At about 450°C, vinyl chloride begins to decompose, forming small amounts of acetylene. Vinyl chloride is slightly soluble in water and soluble in alcohol and ether (Kirk-Othmer, 1967).

Employees of PVC production plants must not be exposed to vinyl chloride at concentrations greater than 1 ppm, averaged over an eight hour period, according to the Occupational Safety and Health Administration (OSHA). Also, no employee may be exposed to concentrations greater than 5 ppm, averaged over 15 minutes or less. An estimated 20,000 workers, past and present, have been exposed to vinyl chloride in manufacturing plants.

Toxic effects associated with vinyl chloride exposure include narcosis from acute exposure and low grade liver and kidney damage from chronic low exposures. Low exposure effects are similar to those from exposure to other halogenated aliphatic hydrocarbons. In addition, vinyl chloride disease, or anacroosteolysis, has been observed among workers exposed to vinyl chloride. This disorder is characterized by degeneration of bones in the fingers accompanied by interference in peripheral nerve response and diminished blood circulation. Anacroosteolysis has been associated primarily with physical contact with PVC and high levels of VCM (Dinman et al., 1971). This disorder has become well documented in PVC epidemiological studies. Anacroosteolysis appears to be a toxic effect unique to vinyl chloride compared to other aliphatic chlorohydrocarbons. The multi-tumor response and appearance of liver angiosarcoma in experimental animals at lower exposure levels is similar to the cancer response reported in PVC/vinyl chloride workers (EPA, 1978b).

When spilled on the skin, rapid evaporation of vinyl chloride can cause local frostbite. At concentrations over 500 ppm, this chemical has a slightly toxic action and irritates the eyes, and it is considered to be a primary irritant for skin and mucous membranes. Acute vinyl chloride toxicity in humans is rare since toxicity is not clearly perceptible below 1,000 ppm. At 1,000 ppm, humans exhibit slight anesthesia, drowsiness, slight visual disturbances, faltering gait, numbness and tingling of the extremities (EPA, 1978b).

Carcinogenic activity of VCM has been confirmed in several species of rodents at 250 ppm and is associated with both sub-acute and chronic low-level exposure when the experimental period was long enough to permit tumors to appear. Tumors found in mice were primarily lung tumors, mammary carcinomas and angiosarcomas (malignant haemangioendotheliomas) of the liver. Angiosarcomas of the liver and other organs, zymbal gland carcinomas and nephroblastomas occurred in exposed rats. Preliminary studies have suggested that VCM also produces subcutaneous angiosarcomas in the offspring of rats that have been exposed during pregnancy (Viola et al., 1975).

In view of the extreme rarity of angiosarcoma of the liver in the general human population, observation of the 16 cases in workers exposed to VCM during the polymerization process is evidence of a casual relationship (Viola et al., 1971). The appearance of hepatic angiosarcoma in experimental animals and the discovery of the rare lesion in PVC/vinyl chloride workers underscores the predictive value of experimental animal toxicology (Maltoni, 1974).

3.2.4 Disposal Alternatives

3.2.4.1 Current Practices

Burial operations and landfill are widely used in the plastics industry for hazardous wastes which are not incinerated. These wastes are essentially wastewater treatment sludges, such as those from PVC production, and hazardous nonflammable solids. Burial and landfill locations include both public and private landfills.

At the present time most, if not all, of these sludges are discarded at municipal or privately owned landfills. Typically the sludges are transported to the landfill or burial site in pressure-controlled tank trucks or open-bed trucks and dumped into bulldozer-prepared pits or trenches 0.6 to 3 or more meters deep. They are then covered with compacted layers of trash and soil to a depth of 0.3 to 1 meter or more.

The problem with these disposal methods is that PVC sludges disposed at landfills may still contain sufficient VCM to constitute a

potential health hazard when the gaseous VCM escapes. An EPA study reported that VCM air concentrations on the order of 1.0 ppm can occur at normal breathing heights (1.5 meters) above ground level at these landfills as long as 24 hours after PVC sludge deposits are covered and VCM air concentrations as high as 0.37 ppm can occur in residential or public access areas adjacent to these landfills. The study also found that about 0.1 to 0.3 ppm of VCM present in air at landfills where PVC sludges have been disposed for several years (EPA, 1976). Monitoring of VCM concentrations in leachate or runoff water from landfill has not been conducted. However, it is possible that components of PVC sludge, such as one or more of those listed in Section 3.2.2 may find their way into ground and surface waters.

3.2.4.2 Best Available Technology

At the present time, secured landfills are the best available land-filling techniques considered adequate to prevent environmental damage to air, and to ground and surface waters.

Secure landfilling would require the following:

1. The composition and volume of each extremely hazardous waste is known and approved for site disposal by a permitting agency.
2. The site is geologically and hydrologically acceptable for extremely hazardous wastes, including the following criteria:
 - soil or soil liner permeation rate of less than 10^{-7} cm/sec
 - water table well below the lowest level of the landfill
 - adequate provision for diversion and control of surface water.
3. Provision is made for monitoring wells, rain water diversion and leachate control and treatment.
4. Records are made of burial coordinates to avoid any chemical interactions.
5. Registration of the site is performed for permanent record of its location once filled.

The typical landfill techniques presently practiced for disposal of hazardous waste include surface adsorption, direct landfill, isolation, burial and subsurface injection. Each of these techniques results

in underground emplacement of wastes. The type of cover materials vary with the disposal technique which, in turn, is determined by the type of waste. Surface adsorption and direct landfill require only a relatively shallow cover of impermeable material, whereas subsurface adsorption and isolation burial need deeper underground placement of waste materials. In isolation burial, the wastes are commonly surrounded and covered by an impermeable layer of soil.

Relatively isolated impermeable soil conditions exist in many areas of the country. If impermeable soil is not available, then clay, special concrete, asphalt, plastic and other liners and covers are available to accomplish similar containment and isolation of the hazardous wastes.

Figure 3.6 shows a typical design for a secured landfill using impervious liners (Lindsey, 1975). The impervious cover protects the waste from rainfall and also prevents continuous escape of gases, which may create other problems of pressure build-up and catastrophic release. These problems can be corrected by installing gas venting equipment at the landfill. Gas vents have been used successfully to prevent underground migration and subsequent emission of pollutants in areas adjacent to the disposal site (Pacey, 1975).

Either subsurface injection, surface adsorption, or consignment burial may also be used as the disposal method. In the event that soil covers or liners are not adequate to control emissions of toxic gases from the VCM waste, waste pretreatment alternatives (encapsulation, chemical fixation, neutralization, etc.) may be used.

The cost of secure landfill disposal varies with the burial techniques employed. Isolation burial in a separate grid cell or subsurface injection would cost about \$9 to \$12 per ton (1977) of wastes while disposal of materials by surface adsorption costs about \$3 to \$8 per ton (1977) (EPA, 1978b). Factors contributing to cost distinctions from site to site include the available land and its value, geological and meteorological conditions, state design requirements for secure

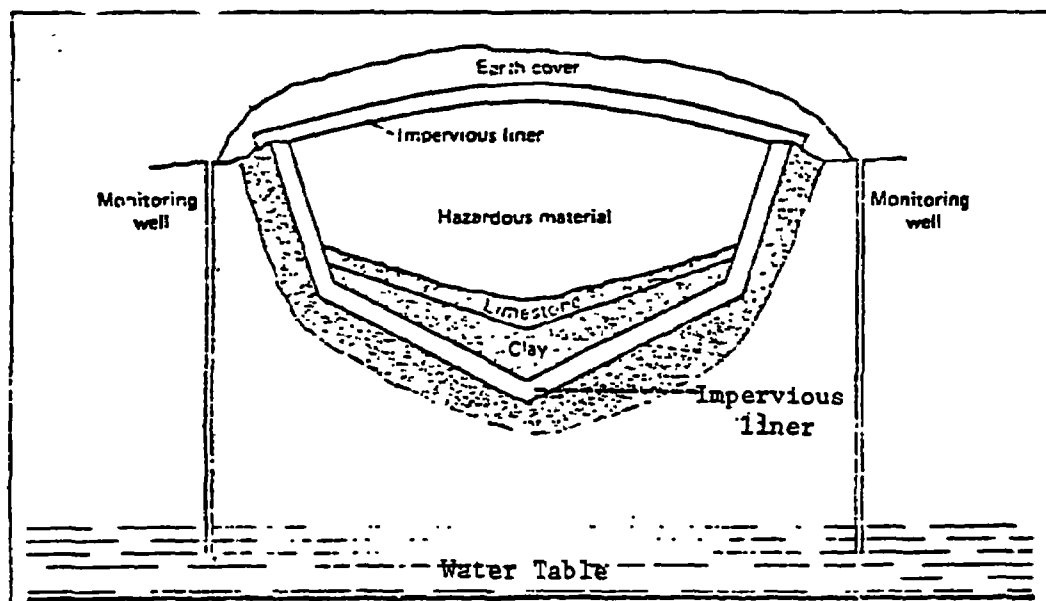


Figure 3.6 Secure Landfill Configuration (Lidsey, 1975)

landfills, labor rate and equipment costs, the available market and volume of waste processed, and types of cover materials used.

3.2.4.3 Methods Suggested by Related Technology

A category of ultimate disposal which is similar to, yet quite different from deep well disposal, is salt deposit disposal. This technique may be applicable for the disposal of wastewater treatment sludge from PVC production industries.

A process developed by D. A. Shock provides a method by which predominantly organic waste materials of a highly toxic or noxious nature, such as mustard gases, nerve gases, harmful biological agents, phenols and the like, may be permanently disposed in a safe manner. Basically, and in its broadest aspect, the method involves mixing of a toxic organic waste material with an oil-base fluid material which is compatible with the waste material and forms a pumpable slurry.

The oil-based material contains appropriate jelling agents which impart thixotropic properties to the slurry, or at least ensure that the mixture will be in a solid state upon standing. The slurry may be transported to, and allowed to solidify in, a location which is inaccessible to human and animal life, and is isolated from contact with useful mineral deposits. The physical and chemical properties of the slurry are such that underground cavities may be utilized for permanent disposition of the material if desired (Shock, 1965).

3.2.5 Engineering, Cost and Environmental Evaluation of Rotary Kiln Incineration of PVC Sludge

The best available technology for treatment of PVC sludge, rotary kiln incineration, has been used successfully for this waste stream. The incinerator must be equipped with a secondary combustion chamber align scrubber to meet air emission regulations. Waste streams from wet scrubbers must be treated prior to recirculation or discharge. Combustion residues include ash and burned out drums, which previously contained nonpumpable sludge. These materials are not considered

hazardous due to low heavy-metal content and thus could be used as landfill. Industry acceptance of this technique depends largely on the added costs. This method does not recover salable materials or heat from the waste stream, which would otherwise provide an added incentive to the industry. Costs might be more acceptable if they were shared among plants, using an off-site waste disposal contractor's rotary kiln for this waste stream.

As an alternative, the Nittetu process is designed to recover heat and salable HCl, eliminating the waste stream from the wet scrubbing system of the rotary kiln. However, several mechanical problems remain to be solved and tested with PVC sludge before this process can be considered as the best available. For example, the interface between the oxidation chamber and the acid tower will be subjected to continual hot-cold temperature swings, which the refractory would be able to withstand in an acid liquid environment. A special interface has been developed by Trane Thermal Company for this application. The acid towers are constructed with acid-brick within a lined steel tower, and the tower internals are usually made from inert materials such as graphite or ceramic. Materials for the caustic scrubbing tower must be able to withstand both acid and hypochlorite corrosion. If caustic is used in the acid tower, the material selection must also take this into consideration.

3.2.6 Recommended Treatment and Disposal Techniques

The most favorable treatment and disposal techniques for treatment of wastewater treatment sludge from PVC production is the Nittetu process. The rationale for selection of this process is that not only can it control vinyl chloride emissions to meet existing pollution codes, but also it can recover energy and by-product HCl. The process developers also claim that it produces no by-product residues to be collected and disposed. To date, it is estimated that about 30 installations using the Nittetu process have been designed and built in the United States for chlorinated hydrocarbon waste disposal. Of these, a few are installed for disposal of vinyl chloride sludge

(Santoleri, personal communication, 1979). The problems associated with the Nittetu process include high costs of incineration equipment, fuel, and operations and maintenance. Another drawback of this process is that in the event of equipment breakdown, there is no back-up system to assure adequate protection from exposure to vinyl chloride emissions.

One major problem in the combustion of wastes is associated with the introduction of waste materials into the combustion chamber. Major problems with liquid injection are those presented by high viscosity and solid particles in the sludge from the wastewater treatment plant. To overcome these problems, an externally atomized nozzle developed by Trane Thermal Company is utilized. This type of nozzle operates at low pressure, minimizing the problems of pumping liquid wastes.

In the heat recovery process shown earlier in Figure 3.4, the waste heat boiler uses hot gases being discharged from the oxidation chamber to generate steam. Equipment downstream from the boiler can be either an acid tower or a sub-X quench tank (Kaing, 1976). Because of the acid and chlorine environment in the boiler, corrosion of the boiler tubes is the major problem for this system (Hung, 1975). Corrosion problems observed during startup and shutdown can be mitigated by setting and following proper operational procedures.

Recovered HCl has a quality comparable to commercial technical grade HCl, and has a composition as follows: chlorine, 10 ppm; water, 60 ppm; and organics, 10 ppm. It was also claimed that by modifying this system, recoveries of HCl from 20 percent up to 100 percent could be attained (Ezaki, 1971; and Naidel, 1976).

The process developer also claims that use of a vortex burner permits operation at very near to stoichiometric levels with essentially complete combustion, ensuring complete destruction of wastes due to high heat release characteristics. Therefore, little residue is produced in the combustion chamber, minimizing collection and desposition problems.

Rotary kiln incinerator capital and operating cost estimates were reported for a system of the size tested at 3M Company and for a much smaller system, more nearly matching the requirements of the average individual PVC manufacturing facility. Results of these estimates are shown below:

	3M System	Smaller System
Incinerator Capacity (Metric Tons/yr)	6,696	335
Estimated Capital Investment (\$)	7,780,000	3,900,000
Estimated Operating Costs (\$/Metric Ton)	582	1,767

The capital investment is based on March, 1976 dollars which is represented by an Engineering News Record Construction Cost Index of 2,322 (EPA, 1977).

Capital investment includes equipment costs, site preparation, engineering and contingency. Operating costs include labor, overhead, taxes and insurance as well as interest on equipment purchases.

Table 3.4 compares estimated vinyl chloride emissions for landfill incineration and salt deposit disposal. Due to potential air, ground water and surface water pollution, direct land disposal of wastewater treatment sludge from PVC production is not recommended. Rotary kiln incineration of this waste stream can result in air emissions of chlorinated organics at 0.02 mg/m^3 of effluent stack gas, assuming optimum operation of the incinerator. This can be compared to a minimum acute toxicity effluent (MATE) for health of 2.55 mg/m^3 for vinyl chloride, which is conservative, since less toxic chlorinated organics may be present in the stack gas emission (Cleland & Kingsbury, 1977).

The wastewater stream from the wet scrubber must undergo pH adjustment and biological or physical/chemical treatment prior to discharge. Although no data were available from the 3M facility, only traces of organics are expected in the waste stream, and the MATE for health of 38 mg/l would be met easily.

Table 3.4 Vinyl Chloride in Wastewater Treatment Sludge

Estimated Emissions

		Current Practice	Best Available	Transfer of Technology
Media MATE VALUES		Landfill	Incineration with HCL scrubbing	Salt deposit disposal
Air, mg/m ³	Health 2.55	1 part per million	0.02	<2.55
	Ecology N.G.			
Water, mg/l	Health 38	High but probably <38	Approaching Zero	<38
	Ecology >100			
Land, ug/g	Health 76	>76	<76	<76
	Ecology 200			

Solid residue from incineration would be disposed as landfill and would not contain organics, meeting the MATE of 76 µg/g for land disposal.

Information on emissions from salt deposit disposal was not available from the literature, but it is assumed that the waste would be isolated so that MATEs for air, water and land would be easily met.

3.3 TARS FROM ANILINE PRODUCTION

Anilines are used in dyes, as pharmaceuticals, photographic chemicals, rubber accelerators, antioxidants, herbicides and fungicides. Aniline is also called aminobenzene, phenylamine, and aniline oil. The industry code for anilines is found within SIC 2865.

3.3.1 Manufacturing Process and Waste Stream Characterization

Aniline is processed in two ways: the reduction of nitrobenzene and the aminolysis of chlorobenzene (Ottinger et al., 1973). The method utilizing nitrobenzene reduction is used for 95 percent of all aniline production. Seven chemical companies manufacture anilines, and three of these manufacture for captive use (Lowenheim and Moran, 1975). Captive use is estimated to consume between 47 and 60 percent of the 279,000 kkg of anilines manufactured annually (Ottinger et al., 1973). This amount is expected to escalate because of increased production of isocyanate which uses aniline in its synthesis. Figure 3.7 illustrates the mechanism for production of aniline by way of nitrobenzene reduction (Lowenheim and Moran, 1975).

No by-products were found in the nitrobenzene reduction process.

Segregatable waste streams include the following (Lowenbach and Schlesinger, 1978):

- Waste from the separator which consists of aniline, carbon monoxide, hydrogen, methane and nitrobenzene. No information is available indicating the percentage of each component in the waste stream
- Volatile components from the distillation column which contain an unknown amount of cyclohexamine, volatile amines and water
- Still bottoms from the distillation column, frequently referred to as tars, which contain unknown amounts of aminophenol, azepin, diphenylamine, nitrobenzene, phenylenediamine, and nitrogen-containing high molecular weight polymers
- Extraction column residue containing aminophenol, aniline, nitrobenzene, phenylenediamine and water-soluble amines.

The concentration of each component is not known.

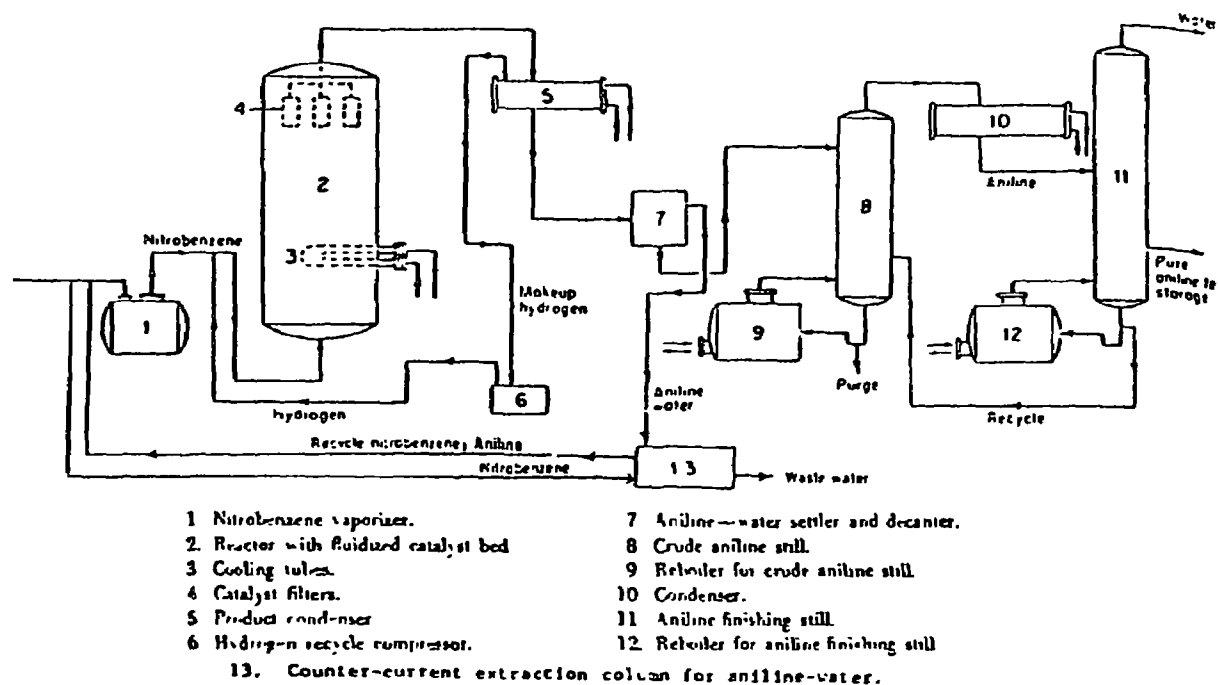


Figure 3.7. Catalytic Vapor-Phase Hydrogenation of Nitrobenzene

Aside from equipment malfunctions, the aniline process appears to produce little variability in the waste streams. However, the waste streams from reduction of nitrobenzene differ greatly from the waste stream from aminolysis of chlorobenzene. The nitrobenzene reduction mechanism, since it is used for almost all of the aniline manufactured in the United States, will be covered in detail.

Anilines are hazardous in that they are highly explosive and have a flash point of 76°C (International Technical Information Institute, 1976). The aniline vapor forms an explosive mixture with air and it can ignite in a violent reaction with HNO_2 . The TLV for aniline is 5 ppm and it is highly toxic when absorbed through the skin, inhaled or swallowed. Nitrobenzene, which vaporizes easily, is also a very toxic component of the waste stream.

3.3.2 Treatment Alternatives

Most commonly, aniline manufacturers use a combination of physical/chemical and biological treatment for wastes. Most manufacturers also combine all aniline processing wastes, including tars, for treatment. The analysis of waste treatment practices is further complicated because most aniline manufacturers also manufacture nitrobenzene and therefore the wastes from both processes are combined. Figure 3.8 shows the types of biological treatment used for aniline manufacturing wastes (Lowenbach and Schlesinger, 1978).

Best available treatment for tar residues from aniline manufacture is incineration. The hazardous nature of the waste stream has caused biological treatment problems when combined with liquid wastes from production facilities. These problems are associated with the toxic materials in the waste stream killing the bacteria that comprise the treatment process. Rotary kiln or multiple hearth incinerators are effective for aniline distillation residue. Tests on the tar substance show it to have a median heat value that would be well-suited to incineration and other thermal destruction techniques. It is not known if aniline wastes are incinerated directly; however, nitrobenzene wastes are incinerated as are aniline wastes after they have been stripped.

MAJOR U.S. NITROBENZENE/ANILINE MANUFACTURERS¹

MANUFACTURER	NAME PLATE CAPACITY NITROBENZENE ANILINE (Million pounds/year)	NPDES NO.	MEANS OF WASTEWATER TREATMENT ²
First Mississippi Corporation Pascagoula, Mississippi	135 100	MS 0001791	Neutralization, equalization, stripping, activated carbon adsorption.
American Cyanamid ³ Willow Island, West Virginia	60 50	WV 0000787	Aerated lagoon, biological contact, clarification, sludge handling.
E.I. duPont de Nemours & Co. Beaumont, Texas	310 230	TX 0004669	Equalization, aerated lagoon, activated sludge, activated carbon adsorption.
E.I. duPont de Nemours & Co. Gibbstown, New Jersey	200 130	NJ 0004219	Organic extraction, stripping, neutralization, equalization, clarification.
Mallinckrodt, Inc. Raleigh, North Carolina	--- --- ⁴	NC 0003338	Equalization, stabilization pond, activated sludge, clarification, chemical treatment (odor control), stabilization pond, land application.
Mobay Chemical Corporation New Martinsville, West Virginia	135 100	WV 0005169	Neutralization, clarification, equalization, activated sludge, activated carbon adsorption.
Rubicon Chemical, Inc. Catskill, Louisiana	75 60	LA 0000892	Subsurface disposal.

¹Chemical Marketing Reporter, January 7, 1974, May 24, 1971, August 30, 1976 and communications with industry; as cited in Directory of Chemical Producers - U.S.A.

²Data collected from EPA Organics and Plastics 308 Response (1976), BPI Master File Listing. Note: This listing represents all unit treatment processes in use for all nitrobenzene/aniline manufacturing effluents, however, it is not the intention of this listing to necessarily imply an ordering of unit processes. Furthermore, segregated process streams are typically combined with other manufacturing wastes at each facility, making a detailed description of wastewater treatment facilities from publicly available information impossible.

³American Cyanamid facility in Bound Brook, New Jersey has been on stand-by since 1974; nitrobenzene capacity: 85 million pounds/year; and aniline capacity: 60 million pounds/year. This plant is due to come on-line in 1978.

⁴Production figures are unavailable for this aniline manufacturer. Note: Nitrobenzene is not produced at this facility.

Figure 3.8 Biological Treatments Used by Major U.S. Aniline Manufacturers

Related technology in other industries suggests stream stripping as a possible alternative for treatment of aniline tars (Lowenbach and Schlesinger, 1978). An aqueous phase stripper can be used to separate the waste. The product from the stripper contains 50 percent aniline by weight which would be incinerated leaving a bottom product containing 0.2 percent aniline for biological treatment. The advantages to this system are that it reduces the quantity of waste for incineration and leaves the waste requiring biological treatment low in toxic aniline concentration. A more detailed discussion of stream stripping is given in Section 3.5.

Reference to the use of off-site contractors for treating tar residues were not found; however, differences are not expected between on-site and off-site practices.

3.3.3 Storage Alternatives

Storage techniques with particular application to aniline tar residues were not found.

3.3.4 Disposal Alternatives

Presumably sludges from wastewater treatment are disposed either on or off-site, although there is no literature on the subject.

Rubicon Chemical, Inc. of Louisiana currently practices off-site deep well injection as a means of disposing of their nitrobenzene and aniline wastes. Deep well injection is a proven hazardous waste disposal alternative. However, few areas of the United States are underlain with geological formations which permit environmentally safe deep well injection. Therefore, their capacity to handle large volumes of wastes may be more appropriately used for wastes for which no other reasonable disposal alternatives exist.

Secure landfill may be a viable alternative for off-site disposal of the waste stream, although no information was found on this practice.

3.3.5 Recommended Techniques

Drawbacks for biological treatment of aniline tars include the difficulty of acclimating biological organisms to the waste stream. The stability of the treatment system varies with the waste loading, and the treatment system must handle seasonal variations in loading. Many of the organic compounds in aniline tars are volatile. If treated in a lagoon or stabilization pond these compounds will vaporize and be released into the atmosphere. Many lagoons and stabilization ponds are inadequately lined for hazardous wastes and can allow seepage of these compounds into the ground water system. It is often difficult to treat different waste streams in the same lagoon system and, as mentioned previously, they are not entirely effective in treating wastes such as aniline tars.

Incineration, as discussed for other waste streams, has a number of associated environmental burdens. An ordinary incinerator has the burden of requiring much energy to burn most wastes efficiently, particularly those with low organic content. Also, disposal of the ash residue and scrubber wastes from incineration creates an additional burden. This burden is lessened when anilines are incinerated, because this medium heat value allows recovery of energy in the form of steam or hot water. With the use of air pollution control devices the air pollution burden from incineration of aniline wastes is decreased; however, even with the use of flue gas scrubbers, some NO_x emissions will reach the atmosphere. Venturi scrubbers are the most common gaseous air pollution control devices. The liquid scrubber effluent will require biological treatment before disposal to the publicly owned treatment works (POTW) or surface discharge.

Steam stripping presents a lower environmental burden than incineration or biological treatment of tarry wastes. Biological treatment and incineration are both used in steam stripping aniline tars. However, steam stripping cuts the burden on each of these systems, since it halves the waste load handled by the biological treatment system, thus increasing its effectiveness and incineration is only required for half the amount of wastes, thus halving NO_x emissions.

Deep well injection is a burden predominantly to the ground water environment due to the problems of seepage. Minimal amounts of volatile components could be emitted to the atmosphere during the transportation and injection process. Under ideal conditions, contamination of ground water can be prevented, but cracks in the geologic formation and any minor faulting can lead to contamination of a ground water aquifer system. Also there is an explosion hazard associated with injection of aniline wastes, since they can explode under certain environmental conditions.

3.3.6 Engineering, Cost and Environmental Evaluation

The engineering and cost evaluation for incineration and steam stripping is given in detail in Section 5.5. The evaluation is applicable to aniline tars as well as nitrobenzene distillation residue.

Table 3.5 shows a comparison of estimated emissions of nitrobenzene, a key component in aniline tars, with MATE values.

Biological treatment in a lagoon can cause many components of the tar residue to be volatilized into the atmosphere. Lagoons and stabilization ponds can often lead to ground and surface water contamination because of seepage and leaching. However, many components of the waste stream degrade readily into simpler, less harmful compounds when exposed to air and light. Therefore, biological treatment is potentially more effective for aniline waste than for other similar waste streams, provided aniline concentrations are not too high.

Incineration of aniline tars creates small impact on air pollution through the release of NO_x to the atmosphere. There is an impact on water pollution due to the use of a wet scrubber to abate the air pollution problem. The largest impact is that of energy usage to operate the incinerator. High energy demands of incineration play an important role in evaluating the benefits of incineration. Energy demand can be minimized with common heat recovery techniques. Another environmental impact of incineration is from disposal of ash residue in secure landfills after incineration. Although the waste stream has been

Table 3.5. Nitrobenzene In Waste Tars

Estimated Emissions

		Current Practice	Best Available	Transfer of Technology
		Land application of sludges from biological treatment of combined plant wastes	Rotary kiln or multiple hearth incineration	Steam stripping followed by incineration of product. Biological treatment of bottoms
Media	MATE VALUES			
Air, mg/m ³	Health 5.0	> 5.0	< 5.0	< 5.0
	Ecology N.G.			
Water, mg/l	Health 75	> 1.0	< 1.0	< 1.0
	Ecology 1.0			
Land, ug/g	Health 150	> 2.0	< 2.0	< 2.0
	Ecology 2.0			

detoxified, the ash must be properly disposed in a sanitary landfill which is designed to abate ground and surface water problems.

The environmental impact of steam stripping is the same for the total impact of both biological treatment and incineration.

The environmental impact of deep well injection is on ground water. The possibility of ground water contamination is always present with this method of disposal.

In summary, steam stripping appears to be the best method for disposing of aniline tars. The explosive hazard of the waste stream makes it imperative that reliable procedures are used in the disposal of this waste. Although, in our literature review, we found no recording of damages due to explosions during aniline waste disposal.

3.4 DISTILLATION RESIDUE FROM CHLOROBENZENE MANUFACTURE

Production of chlorobenzene, also called benzene monochloride, monochlorobenzene and phenyl chloride, falls into SIC 2865. Chlorobenzenes are used as solvents in lacquers, paints and waxes, and also as intermediates for dyes (ITII, 1976).

3.4.1 Manufacturing Process and Waste Stream Characterization

More than 70 million gallons of chlorobenzene are produced annually at 12 U.S. facilities (A.D. Little, 1973). The process of chlorobenzene manufacture is shown in Figure 3.9. Chlorobenzene is manufactured by reacting benzene in the presence of iron catalysts; gaseous chlorine is bubbled into the reactor and the reaction is kept at 50°C to produce crude chlorobenzene. Crude chlorobenzene is actualized, settled and separated. Fractionation produces mono- and dichlorobenzene. It is the residue from the fractionation towers which produce the hazardous waste stream (PRI, 1977).

There are two by-products from chlorobenzene manufacture. One is dichlorobenzene and the other is HCl (PRI, 1977). Dichlorobenzene is collected from the settling tanks and is recovered from the sludge. HCl is a product of the scrubbers from the reactors. HCl is a by-product insofar as it is emitted from the incinerator as a gas and sent to a quench tank, where it is recovered in a gas scrubber.

There are six segregatable waste streams from chlorobenzene manufacture (PRI, 1977). They are:

- hydrochloric acid from scrubber effluent
- dichlorobenzene sludge from settling tanks
- benzene and water from fractionation towers
- benzene and chlorobenzene from fractionation towers
- chlorobenzene and dichlorobenzene from fractionation towers
- polychlorinated aromatic resinous materials from fractionation towers.

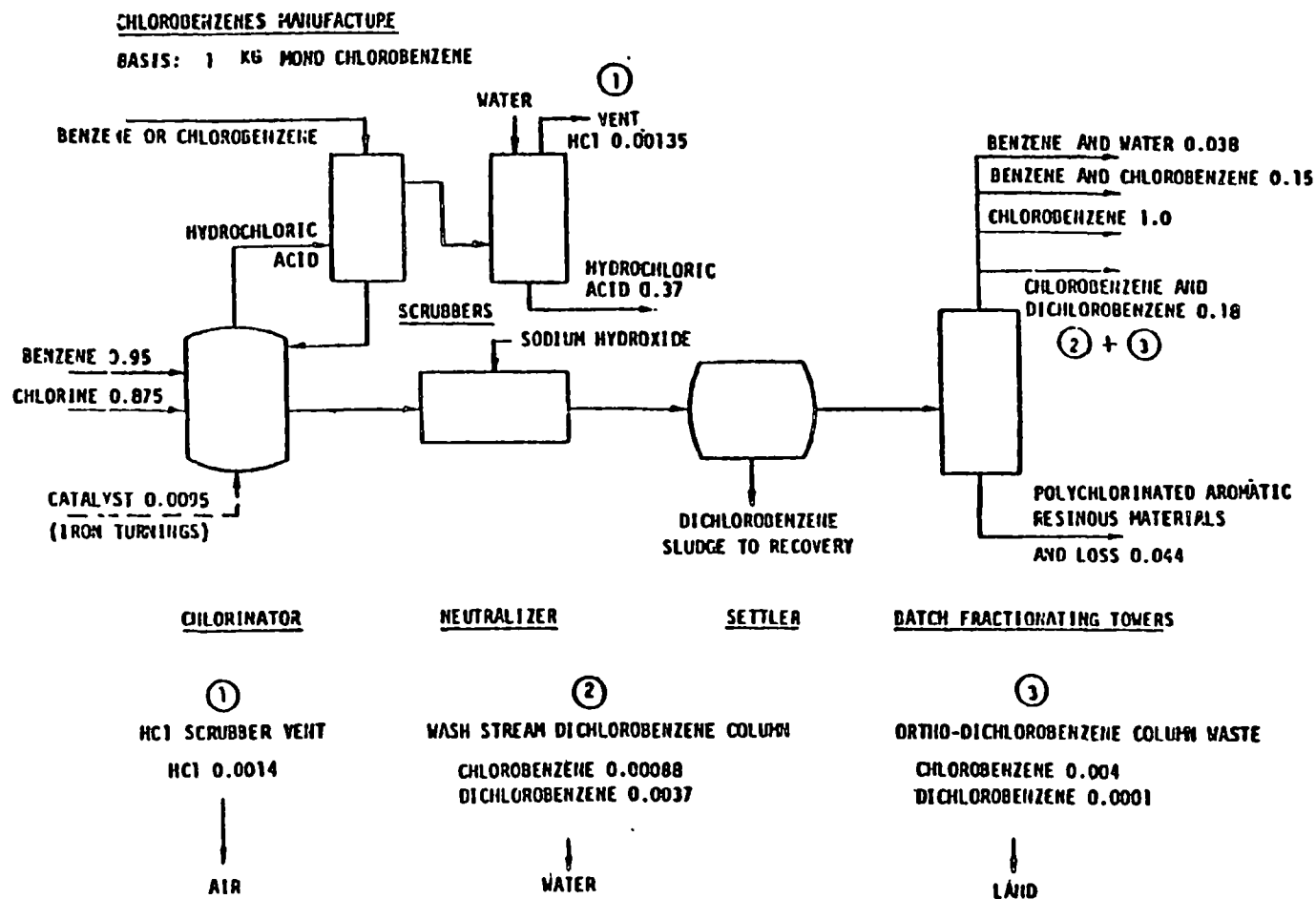


Figure 3.9 Chlorobenzene Manufacturing Distillation Residues From Batch Fractionating Towers (PRI, 1977)

For every kg of chlorobenzene manufactured, 0.372 kg of HCl is generated. Most of the HCl is collected in water from the scrubber used to collect waste material from the reactor. Less than 0.002 kg of HCl is vented to the atmosphere per kg of chlorobenzene. It is not known whether the HCl effluent is recovered for sale or reuse.

Dichlorobenzene sludge from the settling tank is collected and recovered.

Benzene and water are components of one of four waste streams from the fractionation tower with 0.038 kg of benzene and water waste generated per kg of chlorobenzene produced.

Benzene and chlorobenzene from the fractionation tower are generated at the rate of 0.15 kg per kg of chlorobenzene manufactured.

Chlorobenzene and dichlorobenzene from the fractionation tower are generated at the rate of 0.18 kg for each kg of chlorobenzene manufactured. The waste stream is from both the dichlorobenzene and ortho-dichlorobenzene column. The dichlorobenzene waste stream is deposited with the water effluent from the plant. Ortho-dichlorobenzene waste stream is deposited in landfills.

Polychlorinated aromatic resinous materials from the fractionation towers are generated at the rate of 0.044 kg for each kg of chlorobenzene produced. Ten percent of the waste stream is chlorobenzene, approximately 89 percent is composed of polychlorinated aromatic resinous materials and less than one percent is dichlorobenzene (PRI, 1977).

No information is currently available which discusses the variability of the manufacturing process. Variation in production methods used by the different chlorobenzene manufacturers would result in variability in the waste streams. Variability would probably be expressed as variation in the orientation of the waste components rather than variations in the components themselves.

Chlorobenzene distillation residue is considered a hazardous waste because of the volatile nature of the polychlorinated aromatic material in the residue (A. D. Little, 1973). Chlorobenzene, itself,

is ignitable with a flash point of 28°C. In Dangerous Properties of Industrial Materials, chlorobenzene is viewed by Sax as being mildly toxic, with inhalation toxicity ratings of acute local, 1; acute systemic, 2; chronic local, 2; chronic systemic, 2.

3.4.2 Treatment Alternatives

3.4.2.1 Current Practices

Landfill disposal predominates in the industry. There is no currently practiced treatment technology being used for chlorobenzene distillation residues (Sax, 1975). There are isolated instances of incineration of chlorobenzene wastes which are discussed as the best available technology (Diamond Shamrock, Inc., personal communication, 1979).

3.4.2.2 Best Available Technology

The best available treatment for chlorobenzene distillation residue is incineration (Sax, 1975). Incineration can be practiced both on-site and off-site. Incinerators used for distillation residue are the rotary kiln type and can be equipped for hydrochloric acid and energy recovery. Rotary kilns burning chlorinated hydrocarbons have a specially constructed boiler and are not preheated because of potential corrosion problems. Controlled incineration of chlorinated hydrocarbons converts all chlorine to HCl. Rotary kiln incinerators are generally adapted with a wet gas scrubber system to control air emissions.

Incineration has the advantage of efficiently reducing the volume of waste to be disposed and reduces the toxicity of waste by oxidation. Depending on the employment of a HCl recovery unit or energy recovery process, the system has a high energy demand. (The controlled incineration of chlorinated hydrocarbons is achieved by high temperature, high water content and low oxygen, yielding a high concentration of HCl.) (Eden, 1978). HCl recovery is possible if the incinerator only burns chlorinated wastes. However, rotary kilns operate most effectively on a continuous feed system, and would have to handle more than the chlorinated distillation residue from a typical manufacturing facility.

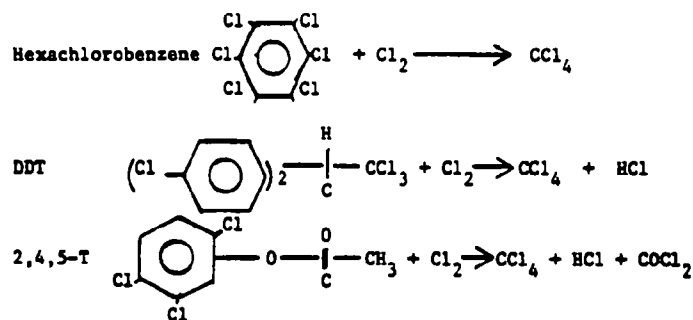
A facility recovering HCl from incinerating chlorobenzene distillation residue has not been found, although the method is practiced in the plastics industry and appears applicable to this waste stream. HCl recovery is accomplished by controlled combustion, i.e., the gases are caught in the scrubber and recovered from the scrubbing and quench tower. Landfilling of ash residue can be performed either on- or off-site.

Energy can be recovered from the incinerator in the form of steam or heat regardless of the type of waste incinerated. Energy from the burning of chlorinated waste can be recovered by taking gases discharged from the oxidation chamber to generate steam in a waste heat boiler.

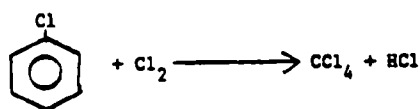
3.4.2.3 Most Environmentally Sound Technology

Chlorinolysis has been used for other similar waste streams as an effective treatment for chlorinated pesticide wastes, such as DDT and 2,3,5-T (trichlorophenoxy acetate acid) (Landreth and Rogers, 1974). Chlorinolysis has been used to convert chlorinated hydrocarbon wastes to soluble products, mainly carbon tetrachloride (CCl_4). Waste chlorinated hydrocarbons and chlorine are placed in a nickel-stainless steel reactor and under controlled temperature and pressure are converted to CCl_4 . By-products are formed depending on the chemical composition of the waste stream. Reactor conditions are either high pressure and low temperature, or high temperature and low pressure. Stoichiometrically, four to eight chlorines are added for each carbon molecule. At 500°C and 200 atm of pressure in the presence of excess chlorine, the chlorine-hydrocarbon bonds are broken and carbon is recombined with chlorine forming CCl_4 (A. D. Little, 1976). If hydrogen is present in the waste, as in the case of chlorobenzene distillation residue, then HCl is formed. If oxygen is present in the waste, carbonyl chloride is formed as a by-product.

The behavior of hexachlorobenzene, DDT and 2,4,5-T under chlorinolysis have been studied extensively. The reaction sequence for each of these is listed below:



Behavior of chlorobenzene in chlorinolysis is postulated below:



Currently, there are several chlorinolysis facilities in operation. Chlorinolysis is discussed as an on-site treatment, since many facilities are operated by organic chemical manufacturers. Diamond Shamrock both manufactures chlorobenzenes and operates a chlorinolysis facility. They have, however, never tried to convert chlorobenzene distillation residue. In the early 1970's, Diamond Shamrock conducted a pilot study on converting hexachlorobenzene distillation residue. They found that the residue contained 80 percent hexachlorobutadiene and 20 percent hexachlorobenzene. Upon chlorinolysis, 95 percent of the hexachlorobutadiene was converted, but the hexachlorobenzene fraction was not efficiently converted. The kinetics of the hexachlorobenzene reaction were such that conversion was too slow to consider incorporation into that plant process (Diamond Shamrock, personal communication, 1979).

It is not known whether these results indicate the possible behavior of chlorobenzene distillation residue in chlorinolysis. The polychlorinated resinous material of the distillation residue could interfere with effective chlorinolysis.

A primary purpose of chlorinolysis has been to detoxify pesticide wastes, but a major disadvantage to this method of treatment is that sulfur in concentrations of 20 ppm or greater will poison catalysts in the reaction system. For this reason, wastes cannot contain sulfur compounds.

Success of chlorinolysis as a waste treatment method is critically dependent on the solubility of CCl_4 . Currently, CCl_4 appears to be marketable, making chlorinolysis a cost-effective treatment alternative. Eighty-five percent of the CCl_4 manufactured is used for the manufacture of Freon. There are several operating chlorinolysis facilities: Diamond Shamrock has a 5 ton/day reactor; Hoechst-Uhde has a 10 kg/hr reactor and is planning a 50,000 ton/year facility. Diamond Shamrock focuses on the chlorinolysis of aromatics while Hoechst-Uhde works mainly with aliphatic compounds and operates at 400°C lower temperature than the Diamond facility.

All of the treatment alternatives discussed in this section apply to on-site as well as off-site treatment, although no reference was found for a facility using off-site treatment.

3.4.3 Storage Alternatives

No reference was found for storage of chlorobenzene distillation sludge.

3.4.4 Disposal Alternatives

Landfills are the current method used for handling polychlorinated resinous material from chlorobenzene distillation towers. Landfills are the prevalent method for disposal of distillation sludge. There is no evidence to suggest that any special handling of the waste at the landfill is used (Diamond Shamrock, personal communication, 1979).

3.4.5 Other Environmental Pollution Control Problems

Two major environmental burdens are associated with the incineration of chlorobenzene distillation residue: air pollution problems and the disposal of incinerator residues. To meet both federal and state environmental regulations, air pollution control devices must be used with incineration. Rotary kilns most commonly use gas and wet scrubbers to control air emissions. Incineration of chlorobenzenes causes some problems in that the HCl formed is highly corrosive to a rotary

kiln and attention must be focused on the design and strength of the equipment. Ash residue disposal causes a second environmental burden. Ash residue from all the wastes incinerated are generally sent to a landfill for disposal.

Chlorinolysis has not been used on this waste stream, therefore any environmental problems associated with chlorinolysis treatment of polychlorinated resinous material wastes have not been documented.

3.4.6 Engineering, Cost and Environmental Evaluation of Incineration Techniques and Chlorinolysis as Applied to Chlorobenzene Distillation Sludge

The following equipment is required for incineration of chlorobenzene distillation residue.

- auto-cycle feeding system:
 - feed chopper
 - pneumatic feeder
 - slide grates
- rotating cylinder
- ash burner
- auto burner
- scrubber system
- exhaust fan
- stack
- fly ash sludge collector
- after burner chamber
- pre-cooler

Incineration of chlorobenzene distillation is a feasible treatment technique. Industry is currently using this method of treatment and it is, therefore, judged to be acceptable to them.

Recovery of HCl in conjunction with incineration would require the use of the following additional equipment:

- quench tank
- wet scrubber to remove effluent

Recovery of HCl is a feasible, well-demonstrated process. It is not known if HCl recovery has been tried during incineration of chlorobenzene distillation residue nor whether industry would accept this additional control. If the incinerator is used only to burn chlorinated waste, it appears likely that HCl recovery would be widely accepted.

Lack of detailed information makes an engineering evaluation of chlorinolysis speculative.

The cost of landfilling chlorobenzene distillation residue at a sanitary landfill is \$17.00/kg, while the cost for using a chemical landfill is \$77.00/kg (Diamond Shamrock, personal communication, 1979).

Cost evaluation for incineration of chlorobenzene distillation residues is based on 1977 data for a 1,400 kg waste stream of residue per year. The incinerator has a 195 kg/hr capacity:

\$205,000	Installed capital cost
\$ 49,200	Depreciation value/year
\$ 5,000	Utility cost/year
\$ 8,200	Maintenance/year
\$ 73,000	Labor/year
<hr/>	
\$135,400	Total annual cost

This capital annual cost works out to \$0.97 per kg of waste (Diamond Shamrock, personal communication, 1979).

Costs for incineration with HCl recovery would be the same as those cited above excepted for additional costs for the quench tank.

No cost information was found for chlorinolysis.

Table 3.6 compares estimated emissions of chlorobenzene in distillation residue with MATE values. Environmental release factors for incineration of chlorobenzene distillation residue are given for emissions to air, water and land. Emissions from the incinerator to the atmosphere are expected, even though scrubbers used with the rotary kiln meet current air pollution standards. Emissions are mostly particulates and HCl. Emissions to air were estimated based on 99.9 percent

Table 3.6 Chlorobenzene In Distillation Residue

Estimated Emissions

		Current Practice	Best Available	Transfer of Technology
Media MATE VALUES		Landfill	Incineration with HCL recovery, land disposal of residue	Chlorinolysis
Air, mg/m ³	Health 350	Medium (<350)	0.001	Not Known
	Ecology N.G.			
Water, mg/l	Health 5,300	>100 <5,300	<100	Practically Zero
	Ecology 100			
Land, ug/g	Health 11,000	>11,000	<0.2	Practically Zero
	Ecology 0.2			

combustion efficiency, 99.8 percent scrubber efficiency and 40 percent excess air.

As residue is the only other environmental problem associated with incineration, and the ash material is disposed in landfills. There would be relatively little hazard associated with the ash from incineration of polychlorinated resinous material, and it does not represent a great danger to surface and ground water. Scrubber effluent is sent for neutralization prior to disposal in the POTW. With pretreatment the environmental burden is lessened. Emissions to air from landfill are based on a vapor pressure of 10 mm Hg at 22°C for chlorobenzene. Emissions to water and land were based primarily on solubility of chlorobenzene, which is 49 mg/100 ml of water at 20°C. References for environmental releases of hazardous substances to the environment due to chlorinolysis were not found. Such releases are expected to be quite small.

In summary, the currently practiced method for disposal of polychlorinated resinous material, landfill, may not be environmentally acceptable due to such things as toxicity, solubility and mobility in a landfill environment. Incineration, with or without HCl recovery, is a recommended means of disposing of this waste stream. Recovery of HCl or energy coupled with incineration helps offset costs making the technique more acceptable to industry. Chlorinolysis converts the waste stream to a salable product, increasing its acceptability. Chlorinolysis has not been tested for polychlorinated resinous material, as most of the studies have been for toxic substances such as DDT, Agent Orange and other materials that are difficult to dispose. Since chlorinolysis facilities are currently in use, we recommend that chlorinolysis be examined as a means for treating chlorobenzene distillation residue.

3.5 HEAVY END WASTES FROM NITROBENZENE COLUMN BOTTOMS

The SIC code for nitrobenzene is found in 2865 (SIC, 1972).

3.5.1 Manufacturing and Waste Stream Characterization

Nitrobenzene is an organic intermediate from aniline. Annual production, by seven manufacturers, amounts to 140,000 metric tons (1978). Nitrobenzene is manufactured by introducing benzene into a reaction vessel, followed by mixed acid. Mixed acid is approximately 55 percent sulfuric acid (H_2SO_4), 35 percent nitric acid (HNO_3) and about 10 percent water. Reaction occurs at a temperature of 45° to 95°C . The mixture is separated into an upper phase (nitrobenzene) and lower phase (spent acid) in a liquid contacting vessel. Nitrobenzene is then purified by distillation. Figure 3.10 diagrams the manufacture of nitrobenzene (PRI, 1977).

There are no by-products in the manufacture of nitrobenzene. Segregatable waste streams include the following:

- spent acid
- washer wastes
- column wastes

Spent acid from the reactor is captured from the liquid-liquid separator and sent to a sulfuric acid concentrator for recovery. Recovered acid is reused in the manufacturing process. From the flow diagram, we have assumed that all of the nitric acid is used in the reaction and none is discharged in the waste stream.

Washer wastes from the washing step preceding the column wastes consist of approximately 0.00004 kg of nitrobenzene for each kg of nitrobenzene manufactured and 0.025 kg of sodium sulfate/carbonate 350 tons total ($\text{Na}_2\text{SO}_4/\text{H}_2\text{CO}_3$) (PRI, 1977). This effluent is discharged with other aquatic effluents for primary treatment and disposal in POTW.

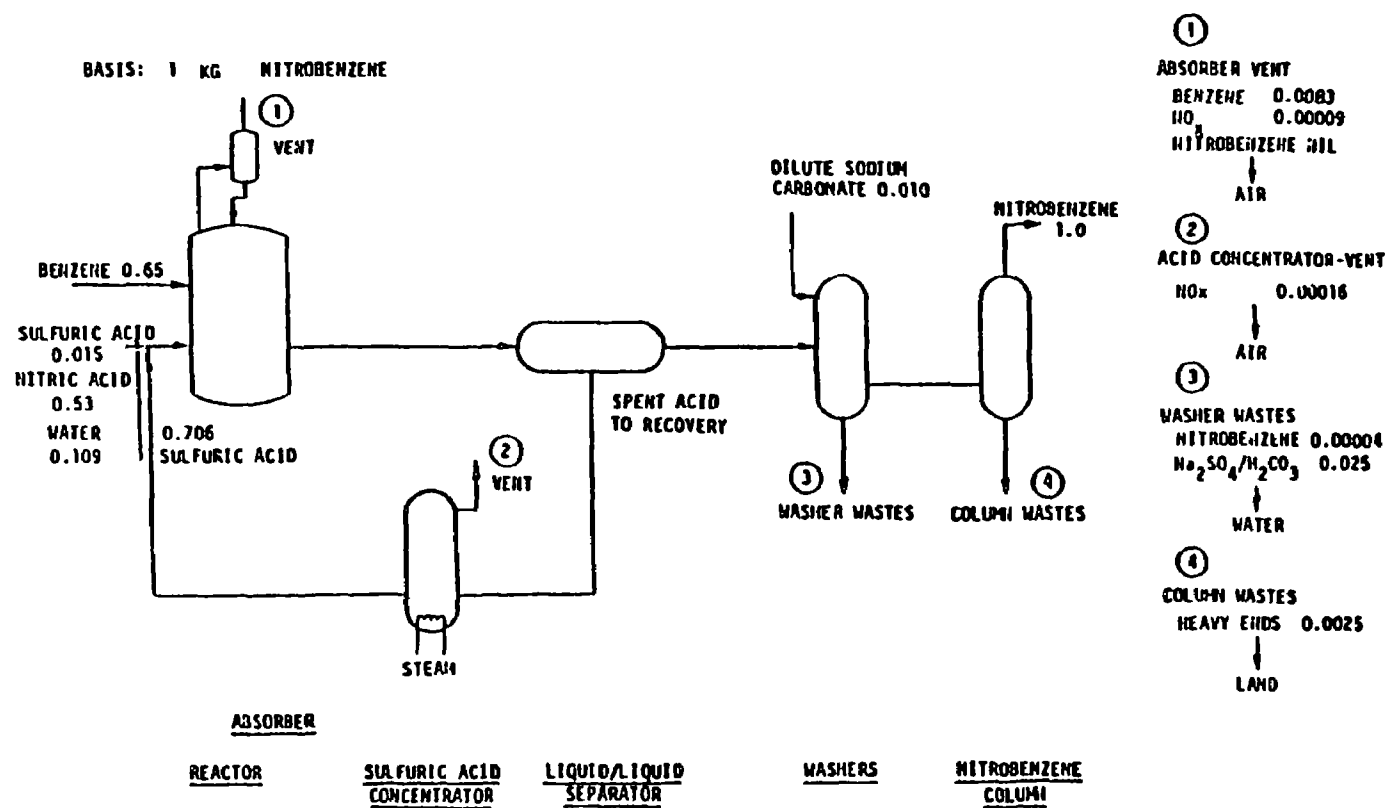


Figure 3.10 Nitrobenzene Manufacture (EPA, 1977b)

Column wastes consist of still bottom or heavy ends from the purification process. Exact composition of these heavy ends is unknown, but 0.0025 kg of heavy ends is generated for each kg of nitrobenzene.

The manufacture of nitrobenzene appears to be a very controlled process with little room for chemical variability within the process. No variability is expected in the composition of heavy ends.

Chemical composition of heavy ends from the purification column is not known, although it can be hypothesized that nitrobenzene, benzene and various forms of sulfate and nitroso compounds would be present.

Nitrobenzene is a volatile and toxic chemical with Sax toxicity ratings of: acute local, u; acute systemic, 3; chronic local, u; and chronic systemic, 3 (Sax, 1972). On the basis of the chemical constituents of the waste stream, this waste stream is categorized as volatile. The waste is considered highly toxic due to the nitro-substituted aromatics expected to be in the heavy ends.

3.5.2 Treatment Alternatives

Treatment of nitrobenzene heavy ends is not currently practiced either on-site or off-site.

The best available treatment for heavy ends is incineration. Incineration, either performed by itself or in association with heat recovery, is most commonly carried out in rotary kiln incinerators with scrubbers to capture the NO_x emissions. Because of large amounts of nitrogen in the waste stream, there is a large potential for heat recovery. For every kg of nitrobenzene heavy ends incinerated, 5,990 kcal of energy can be recovered (PRI, 1977). At a facility producing 20,000 kkg of nitrobenzene, 200 million kcal of heat can be recovered (PRI, 1977). At a facility producing 20,000 kkg of nitrobenzene, 200 million kcal of heat can be recovered annually. Heat, or energy, can be recovered as steam for reuse.

A three step procedure involving steam distillation and alkali hydrolysis, followed by catalytic reduction, has been suggested as a means of treating nitrobenzene heavy ends. This stripping procedure is outlined in Figure 3.11 (PRI, 1977). Steam distillation of the heavy ends will strip off any nitrobenzene present. Nitrobenzene stripped off in the distillation step will reenter the processing line. Column bottoms are presumed to contain m-, o-, and p-dinitrobenzene. The m-dinitrobenzene is separated from the other isomers by adding a 5 to 10 percent caustic solution at 90-100°C. Ortho and para isomers are converted to the corresponding nitrophenols and removed as soluble salts. These alkali salts and the alkaline solution are disposed in a landfill, in lined drums. m-Dinitrobenzene is a salable product and can be sold at this point or reduced in a catalytic reactor to produce m-nitroaniline or m-phenylenediamine. Aqueous phenylenediamine can be used in this form for dye preparation or can be further purified by distillation.

No indication was found of the percentage of treatment practiced on-site versus off-site for this waste stream.

3.5.3 Storage Alternatives

No alternatives were found for storage of nitrobenzene purification column heavy ends. It can be assumed that storage in steel drums is used for low volume wastes until a truck load is accumulated. This storage procedure is adequate for short-term storage, but not for long-term.

3.5.4 Current Disposal

The current method for disposal of nitrobenzene heavy ends is to bury them in a secured landfill in sealed steel drums (PRI, 1977). Three hundred fifty tons of heavy ends are disposed in this manner annually. Landfill sites can be located either on- or off-site, although no indication of an actual split was found.

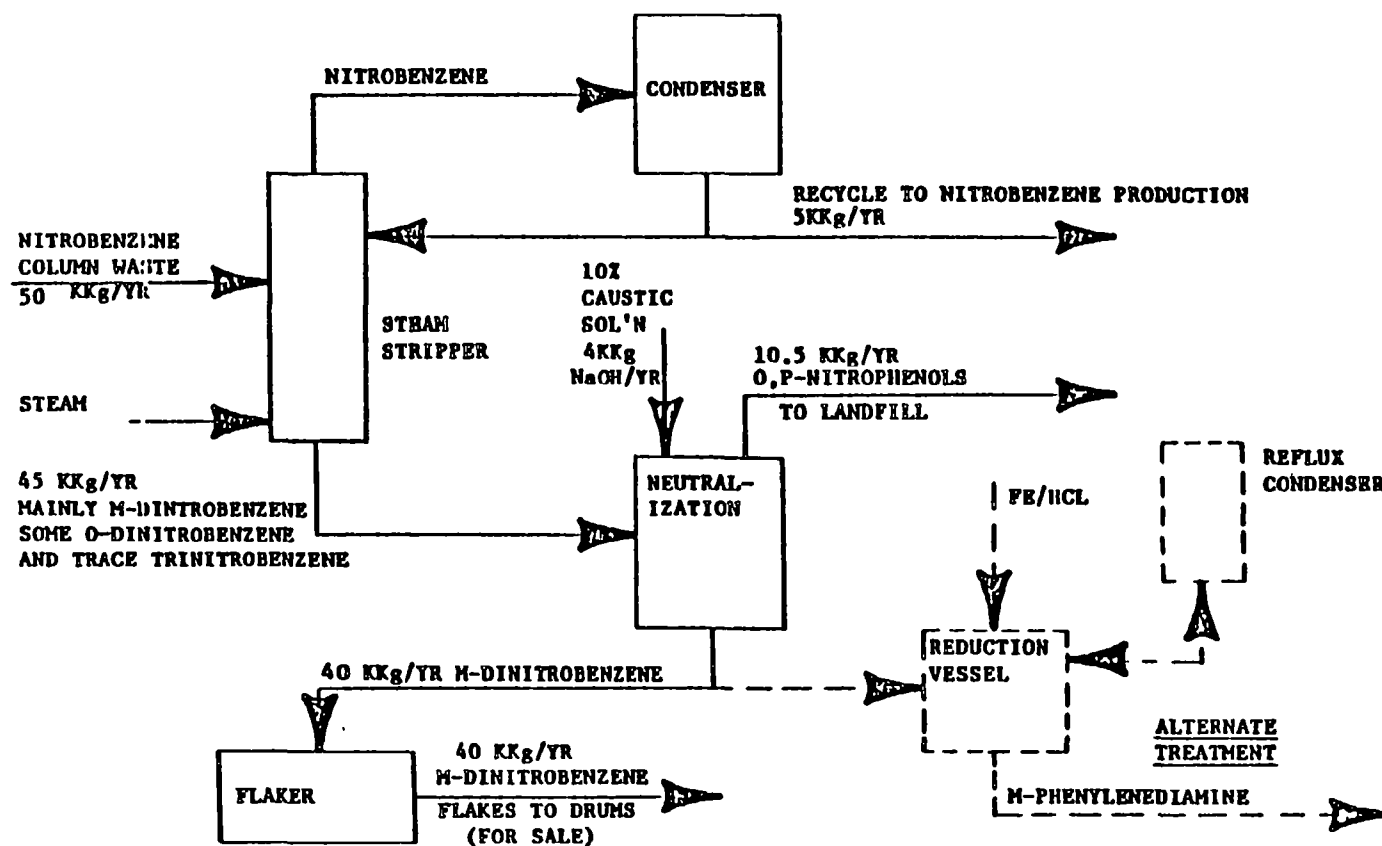


Figure 3.11 Nitrobenzene Stripping of Heavy Ends from Purification Column in Nitrobenzene Manufacture

3.5.5 Other Environmental Pollution Controls

There are three environmental burdens associated with use of incineration as a treatment alternative: air emissions, scrubber effluent and landfill of ash residue. Air emissions from the incineration of nitro-aromatic compounds are high in NO_x . To reduce these emissions, wet scrubbers are used to collect the NO_x . The second problem is disposing of the scrubber effluent which, commonly, goes through pretreatment at the site and is then disposed with other aquatic effluents into the POTW. Ash residue from incineration is disposed in landfills located either on- or off-site. Energy recovery is not thought to be widespread among facilities incinerating nitrobenzene column bottoms.

The only environmental burden from nitrobenzene stripping is the disposal of the nitrophenols in a landfill. Approximately 73.5 kkg of nitrophenols would have to be landfilled annually if nitrobenzene stripping was universally practiced in industry, and a primary concern is potential leakage of nitrophenols from drums. Nitrobenzene stripping was the most environmentally sound treatment technology found for nitrobenzene column bottoms. Phenols provide a special hazard to ground water because of the difficulty in removal by treatment and their low waste threshold.

3.5.6 Engineering, Cost and Environmental Evaluation of Acceptable Alternatives for Nitrobenzene Column Bottoms

Equipment required and costs for incineration of nitrobenzene column bottoms are the same as those for chlorobenzene distillation residues given in Section 3.4.6. The amount of waste is too small to consider separate incineration equipment for nitrobenzene heavy ends.

Equipment requirements for nitrobenzene stripping are as follows:

- holding tank
- holding tank pump
- steam stripper
- stripper condenser

- decanter
- caustic treat tank
- decanter/condenser pump
- stripper bottoms pump
- treat tank waste pump
- flaker.

Nitrobenzene stripping is a fairly simple chemical system. It is not known how readily industry would accept this treatment alternative, and the costs might diminish their interest. Nitrobenzene heavy ends do not represent a high volume waste stream. Costs associated with nitrobenzene stripping are given in Table 3.7.

Incineration of nitrobenzene heavy ends would have some environmental impact. Although air pollution control devices are used, there are still some NO_x emissions to the atmosphere from heavy ends incineration. Effluent water from the scrubber is sometimes discharged to a holding pond prior to pretreatment. In ponds, toxic substances can be leached to both surface water and ground water. Table 3.8 compares estimated emissions of nitrobenzene in column bottoms with their MATE values.

For nitrobenzene stripping, landfill of the alkaline nitrophenol solution represents the only significant impact on the environment. Landfill in steel drums is regarded as a relatively safe method for disposal of hazardous waste. Use of lined drums or encapsulation in more durable containers would be preferred. Environmentally, nitrobenzene stripping is a more acceptable treatment, highlighted by recovery of a valuable waste stream component and the volume reduction of the waste stream prior to disposal.

In summary, incineration is more acceptable treatment at the present time because of existing facilities and industrial acceptance. Nitrobenzene stripping may be a more environmentally acceptable treatment alternative but will require further testing and investigation before it can be fully evaluated and successfully implemented.

Table 3.7 Costs Associated with Stripping of Nitrobenzene Wastes

1. Estimated Installed Capital Cost

Basis: 0.167 kkg/day of nitrobenzene column waste

<u>Equipment Item</u>	<u>Estimated Cost</u>
Hold Tank, 760 ℓ	\$38,750
Hold Tank Pump, 8 ℓ/m	3,200
Steam Stripper, 50 cm dia x 4.5 mH	44,100
Stripper Condenser, 160 ℓ/m	7,400
Decanter, 560 ℓ	7,300
Caustic Treat Tank, 760 ℓ	38,750
Treat Tank Pump, 40 ℓ/m	3,360
Decanter/Condenser Pump, 20 ℓ/m	3,210
Stripper Btms Pump, 40 ℓ/m	3,360
Treat Tank Waste Pump, 40 ℓ/m	3,360
Flaker	8,760
<hr/>	
Subtotal	\$161,600
Engineering at 10 percent	16,200
Contingency including freight at 20 percent	32,400
Total Estimated Installed Capital Cost	<u>\$210,200</u>

Table 3.7 Costs Associated with Stripping of Nitrobenzene Wastes
(Continued)

2. Annual Fixed Charges

Depreciation \$210,200 @ 10%/year	\$21,000
Interest \$210,200 @ 10%/year	21,000
Insurance and Taxes \$210,200 @ 4%/year	8,400
Total Annual Fixed Charges	<u>\$50,400</u>

3. Direct Operating Cost

Raw Material - 50% NaOH 4 kkg @ \$160 =	\$640
Utilities	1,800
Maintenance - $0.04 \times \$210,200 =$	8,400
Direct Labor - 4,200 MH x \$9.00 x 1.5 =	<u>56,700</u>
Annual Direct Operating Cost	\$67,540
Annual Disposal Cost	<u>2,500</u>
Total Annual Cost	\$120,440
Recovered Materials - m-Dinitrobenzene 40 kkg @ \$790 x 0.7 = Nitrobenzene 5 kkg @ \$510 x 0.7 =	\$22,120 1,780 <u>-23,900</u>
Net Total Annual Cost	\$96,540

4. Cost Per kkg Product - $\$96,540 \div 20,000 =$ \$4.83

5. Cost Per kkg Waste - $\$96,540 \div 50 =$ \$1,930

6. Impact on Product Cost

(Market value of 1 kkg product = \$510)
Cost/kkg \div Market Value = $\$4.83 \div \510 0.95%

Table 3.8 Nitrobenzenes in Column Bottoms

Estimated Emissions

		Current Practice	Best Available	Transfer of Technology
Media MATE VALUES		Disposal in sealed steel drums in secure landfill.	Rotary kiln incineration with NO _x control and heat recovery. Land disposal of residue.	Steam distillation, alkali hydrolysis followed by catalytic reduction. Disposal of nitrophenols in landfill.
Air, mg/m ³	Health 5.0	<5.0	<5.0	<5.0
	Ecology N.G.			
Water, mg/l	Health 75	<1.0	>1.0 <75	<1.0
	Ecology 1.0			
Land, ug/g	Health 150	<2.0	<2.0	<2.0
	Ecology 2.0			

3.6 DAF FLOAT FROM PETROLEUM REFINING INDUSTRY

As defined by the Standard Industrial Classification (SIC 2911), a petroleum refinery is a complex combination of interdependent operations engaged in converting crude oil into more than 2500 products including liquefied petroleum gas (LPG), gasoline, kerosene, aviation fuel, diesel fuel, a variety of fuel oils, lubricating oils, asphalts and cokes, and feedstocks for the petrochemical industry.

3.6.1 Industry Description

Crude oil is the major raw material processed in a refinery. The chemical composition of crude oil varies widely depending on its source. It is largely a mixture of paraffinic, naphthenic, and aromatic hydrocarbons containing varying amounts of sulfur, nitrogen, oxygen and inorganic ash. However, over 3,000 different chemical compounds may also be present. The chemical composition of the crude oil being processed will partially determine the product slate from a particular refinery. For example, a paraffinic crude oil will tend to produce better lube oil stocks than a naphthenic crude oil and is thus the favored feedstock for that product.

As of 1 January 1979, the processing capacity of the United States petroleum refining industry was 2.73 million cubic meters (17,169,909 barrels) per day. According to the Oil and Gas Journal, (1979) the petroleum refining industry has been expanding at the rate of about four percent a year. Table 3.9 presents historical data on the growth of the U.S. petroleum refining industry. Future growth rates may depend largely on the Federal government policy on importing crude oil versus importing refined products.

One trend in this industry is increasing dependence on imported crude oils. In 1971 only about 270,000 cubic meters (1.7 million barrels) per day of imported crude were consumed (Dickerman et al., 1977) while in 1978 over 1,290,000 cubic meters per day (8.1 million barrels per day) were used (Geotimes, 1979). Foreign crude accounts for nearly half of all oil refined in the U.S.

As of 1 January 1979, 153 companies comprised the U.S. petroleum refining industry. These companies operated 289 refineries in 41 states

Table 3.9 Crude Oil Processing Capacity of U.S. Refineries

<u>Year*</u>	<u>Capacity Per Calendar Day</u>		<u>Growth Over the previous year (Percent)</u>
	<u>hm³</u>	<u>Thousands of Barrels</u>	
1967	1.662	10452	-
1968	1.771	11142	6.6
1969	1.832	11523	3.4
1970	1.932	12155	5.5
1971	2.016	12681	4.3
1972	2.081	13087	3.2
1973	2.128	13383	2.3
1974	2.260	14216	6.2
1975	2.360	14845	4.4
1976	2.397	15075	1.5
1977	N.G.	N.G.	N.G.
1978	2.678	16846	N.G.
1979	2.730	17170	1.9

*As of January 1 of the year indicated

N.G. = Not Given

Source: Oil and Gas Journal, Annual Refining Issues

with most of the refining capacity found near the coasts. There is considerable variation in the size of refineries, and their production rates range from 500 cubic meters per day to more than 64,000 cubic meters per day (Oil and Gas Journal, 1979). Approximately one third of U.S. refineries capacities of less than 1,600 cubic meters per day (10,000 bb/day). These refineries represent only 2.5 percent of total industry capacity. Refineries capacities greater than 24,000 cubic meters per day (151,000 bb/day) represent about 9 percent of U.S. refineries and account for 43 percent of total industry capacity. Total annual employment of the industry in 1974 numbered approximately 140,000, and total industry-wide sales were \$28.9 million (Statistical Abstracts, 1979). Texas has the greatest concentration of refineries, with a total of 54 facilities representing 18.7 percent of the national total. California has 39 refineries and Louisiana, Illinois, Kansas, Oklahoma, Pennsylvania and Wyoming each have 10 or more (according to the Oil and Gas Journal 1979). Refining capacity of individual states roughly parallels the number of facilities. Sixty-four percent of all U.S. refineries, or a total of 158 refineries, were constructed between the years 1944 and 1970 (Rosenberg et al., 1976).

3.6.2 Manufacturing Processes

Processes involved in the manufacture of refined petroleum products involve distillation, absorption, extraction, thermal and catalytic cracking, isomerization and polymerization. Figure 3.12 is a flow diagram illustrating the sequence in which these processes interact to produce refined products. Few refineries, if any, employ all of these processes, and some processes are designed for a particular crude oil. Larger refineries use most of the processes shown. American refineries usually use more processes than foreign refineries, since they concentrate on gasoline production, while European refineries generally concentrate on production of heating fuels which are more easily produced than gasoline. Complex American refineries generally produce a minimum of residual oil. Fuel oil for the U.S. East Coast comes predominantly from Caribbean refineries with minimum facilities for gasoline production.

Approximately 2,500 products are produced wholly or in part from

Figure 3.12 Representative Flow Diagram for a U.S. Refinery (Bombaugh et al., 1976)

petroleum. Most of these products are blends of several refinery streams. Table 3.10 lists the major petroleum products and their production in 1974.

Refinery products vary widely with location, climate, and season. In winter, there is higher demand for heating fuel oils. Winter gasoline also must contain a higher percentage of volatile products to enhance cold weather starts. Summer weather requires reduction in volatile components to decrease chances of carburetor vapor lock and to minimize evaporation losses.

The petroleum refining industry also provides raw materials for the petrochemical industry. Petrochemical feedstocks supplied by refineries include olefins, LPG, and aromatic compounds. In addition, naphtha is cracked in a thermal cracking process to produce ethylene. Ethylene production is performed in both refineries and petrochemical plants. Petrochemical feedstocks accounted for only about two percent of the refining industry's production in 1973 (Dickerson et al., 1977).

As the size of a refinery increases, so does the number of products produced, and the processing operation becomes more flexible. The production rate of each product can be varied significantly with relatively minor changes in refinery processing conditions. Hydrocarbon fractions can be shifted from one product to another to meet product demands. Many refineries have crude capacities of less than 800 cubic meters (5,000 barrels) per day. Economic operation of these small refineries is possible only through production of specialty items, lube oils, or asphalts.

The major trend in the industry is the increase in production of gasolines, especially non-leaded, high-octane gasolines. Expansion of processing units that produce high-octane blending stocks, such as catalytic reforming units, can also be anticipated to meet this growing demand.

3.6.3 Petroleum Refining Waste Stream Characterization

The petroleum refining industry produces gaseous, solid, and liquid wastes. Air emissions make up by far the largest potential source of

Table 3.10 Major Petroleum Products Produced By U.S. Refineries in 1974
(Bombaugh et al., 1976)

<u>Product</u>	<u>Volume Percent of Total Refinery Products*</u>
Gasoline	49.0
Kerosene	1.2
Jet Fuel,	
Naphtha type	1.5
Kerosene type	4.9
Distillate Fuel Oil	20.4
Asphalt	3.4
Residual Fuel Oil	8.2
Marketable Coke	1.3
LPG	2.4
Petrochemical Feedstocks	2.8
Other (Fuels, misc.)	4.9

*Based on total U.S. production

contamination from the industry. The major gaseous wastes emitted are particulates, hydrocarbons, carbon monoxide, sulfur oxides, and nitrogen oxides.

The major liquid effluents are oil and grease in condensed steam from various processes, cooling water from various processes, tank cleaning wastes, spent chemicals, waste caustics containing cresylic acids and sulfides from gas treating, oil spills and lead waste.

Solid wastes include fines from cracking units, coke fines, iron sulfide, clay filtering media, and sludges from tank cleaning operations, oil-water separators, and biological processes. Spent catalysts not worth processing for recovery of valuable components are an intermittent solid waste stream. Typical components of waste catalyst streams are aluminum, cobalt, nickel and titanium compounds.

3.6.4 Treatment Alternatives

Treatment and disposal methods used by the industry are contingent upon the nature, concentration, and quantities of waste generated. They are further affected by geographic conditions, transportation distances, disposal site hydrogeologic characteristics, and regulatory agency requirements.

One of the primary references consulted for this section was a study conducted for the EPA Office of Solid Waste in 1974 titled "Assessment of Hazardous Waste Practices in the Petroleum Refining Industry" (Rosenberg et al., 1976). The study included a survey of 16 refineries representing 18 percent of U.S. crude capacity. The survey included visits to refineries and sampling and analyses of wastes.

Another major reference is a study conducted for the American Petroleum Institute titled "The 1976 API Refinery Solid Waste Survey" (API, 1978). This was a survey of 78 refineries representing 57 percent of the U.S. crude refining capacity. Information was received on 28 air flotation units in the industry while analytical data on 18 units were tabulated. Some comparisons of the API study and the EPA study

show higher amounts of oil and solids in air flotation units, and varying metals content as shown in the following in metric tons per year:

	<u>API Study</u>	<u>EPA Study</u>
Oil	12,000	9,000
Solids	28,000	11,000
Oil & Solids	40,000	20,000
Arsenic	0.001	0.1
Cadmium	0.02	0.0003
Chromium	5.32	8.4
Copper	0.43	0.4
Lead	0.23	0.5
Mercury	0.003	0.03
Nickel	0.17	0.001
Selenium	0.003	0.1
Vanadium	0.13	0.003
Zinc	5.88	6.3
Total Metals	12.2	15.8

Some of the differences are explained as follows:

- Many refineries added air flotation systems in the period 1974-1976 adding oil and solids to the waste stream.
- Different data bases were used to derive this information.

The differences in the two studies are not great enough to substantially change this discussion of DAF float. If the API study were used as a major reference, an even greater emphasis would be placed on petroleum rerefining as best available technology, due to the increase in oil content of the waste and the increase in crude oil prices since the study was written.

3.6.4.1 Current Practices

The technology of treating refinery wastewater streams is well established. Basic water cleanup processes commonly found in refineries are oil/water separation, sour water stripping, suspended solid sedimentation, acid base neutralization and biological oxidation. Although many compounds are present in the liquid effluent from refinery processes, they are generally eliminated or reduced to an acceptable level before the water is discharged from the refinery.

Solid wastes from petroleum refineries are generally landfilled or incinerated. Spent catalysts are usually disposed in landfills.

In 1973, 51 percent of petroleum refinery wastes were disposed in landfills, 40 percent by lagooning, 7 percent by land spreading and 1 percent by incineration. Approximately 44 percent of refinery wastes were managed on-site, and 56 percent were hauled by private contractors to off-site disposal locations. Of refinery wastes handled on-site, 38 percent were disposed of by landfilling, 41 percent by lagooning, and the remainder by landspreading and incineration (Rosenberg et al., 1976). Table 3.11 compares waste disposal methods used in 1973 with those projected for 1983. This table illustrates two trends expected for the industry—a move to more on-site disposal and much greater emphasis on landspreading at the expense of lagooning. Table 3.12 shows generation rates and distribution of 17 categories of solid and liquid wastes produced by the industry in 1974. Many of these waste streams are especially hazardous because ignitable, volatile, and reactive chemical mixtures have been concentrated in them.

Figure 3.13 shows a relatively complex system for handling wastewater streams. Unit operations involved vary from refinery to refinery depending on local requirements. All refineries can be expected to have an API separator to separate oil and soluble solids from effluent. Dissolved air flocculators (DAFs) are more compact than API separators and are becoming commonplace. Many newly designed DAF units have been installed in the past few years. Biological oxidation units are less common and there are only one or two activated carbon bio-oxidation

Table 3.11 Comparison of Refinery Waste Disposal Methodologies Used in 1973 With Those Projected for 1983
(Rosenberg et al., 1976)

Disposal Procedure	1973			1983			Net
	Onsite (%)	Offsite (%)	Total (%)	Onsite (%)	Offsite (%)	Total (%)	Change (%)
Landfilling	16.8	34.3	51.1	24	20	44	-7
Lagooning	18.3	21.4	39.7	12	7	19	-21
Incineration	0.8	0	0.8	3	0	3	+2
Landspreading	<u>8.4</u>	<u>0</u>	<u>8.4</u>	<u>34</u>	<u>0</u>	<u>34</u>	+26
Total	44.3	55.7	100.0	73	27	100.0	
Net Change				+29	-29		

Table 3.12 Generation Rates and Volume Distribution of 17 Waste Streams
From the Petroleum Refining Industry

Waste Stream	Generation Rate (Wet Weight) Met Tons/Year/ 1000 BPSL *	Percent Of Total Waste Generation	Generation Rate (Dry Weight) Met Tons/Year/ 1000 BPSD *	Percent Of Dry Waste Generation	Frequency of Generation
Slop Oil Emulsion Solids	11.5	4.99	1.38	0.40	Continuous
Silt From Storm Water Runoff	2.8	1.21	2.0	0.58	Batch
Exchanger Bundle Cleaning Sludge	0.9	0.39	0.33	0.10	Turnaround
API Separator Sludge	9.02	3.91	2.2	0.64	Batch
Non-Leaded Tank Bottoms	25.4	11.02	46.0	13.42	Batch
Crude Tank Bottoms	0.14	0.06	0.17	0.05	Batch
Leaded Tank Bottoms	0.14	0.06	0.75	0.22	Batch
Dissolved Air Flotation Skimmings	66.15	28.69	3.64	1.06	Continuous
Kerosine Filter Clays	1.02	0.44	0.93	0.27	Batch
Lube Oil Filter Clays	13.2	5.72	215.6	62.90	Batch
Neutralized HF Alkylation Sludge	4.1	1.78	21.7	6.33	Batch
Spent Lime From Boiler Feedwater	71.0	30.79	28.9	8.43	Continuous
Waste Bio Sludge	6.3	2.73	0.8	0.23	Continuous
Once Through Cooling Water Sludge	16.9	7.33	12.6	3.68	Batch
Cooling Tower Sludge	0.12	0.05	0.029	0.01	Continuous
FCC Catalyst Fines	1.86	0.81	5.45	1.59	Continuous
Coke Fines	0.008	0.01	0.28	0.08	Batch
Totals	230.558	99.99	342.759	99.99	

*Source: Tarnay and Krishnan, 1978

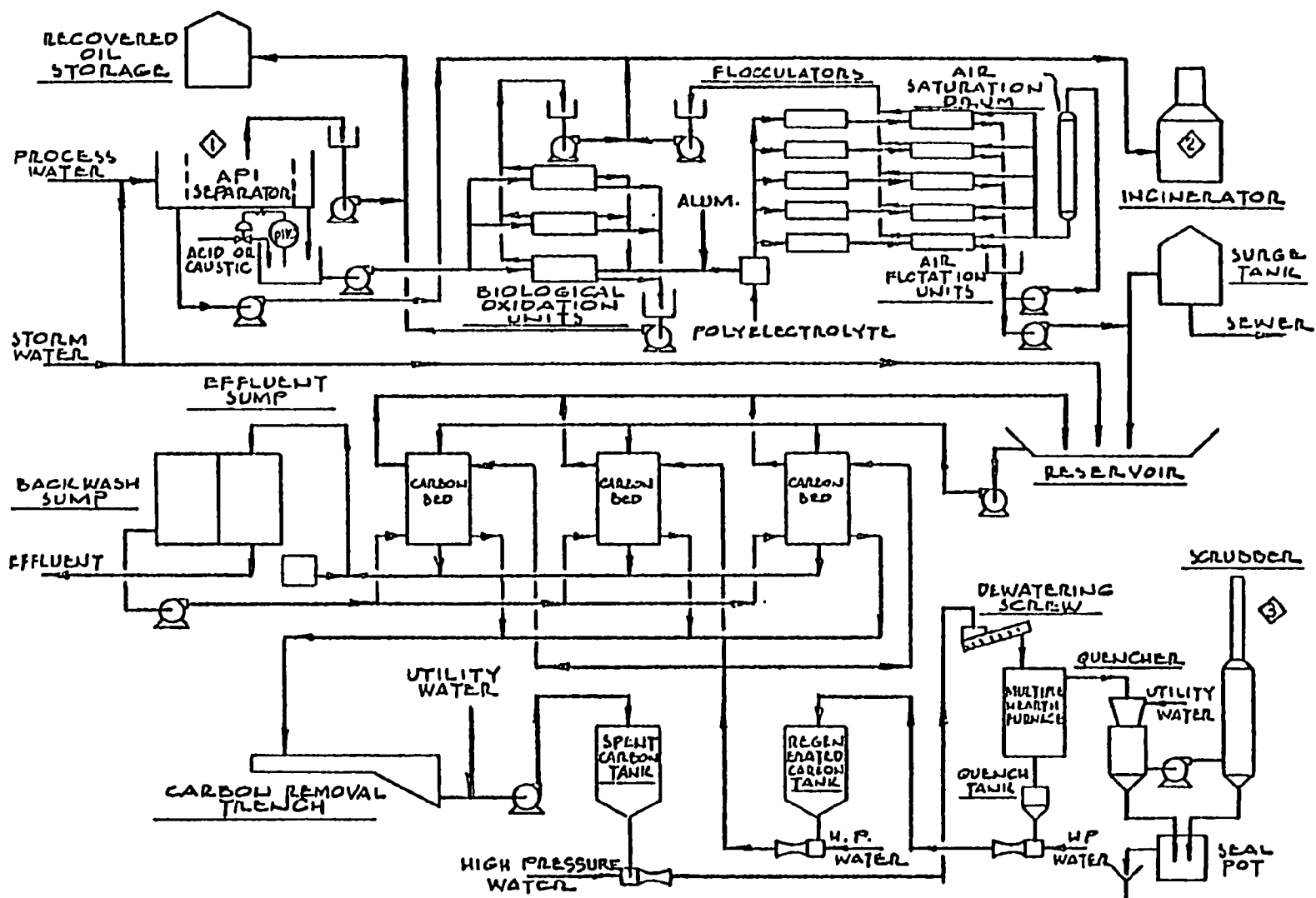


Figure 3.13 Idealized Wastewater Treatment System (Sims, 1974)

units presently in service. The maximum rate through these wastewater systems is limited by the capacity of the biological oxidation and air flotation units.

DAF skimmings present a special problem to the industry because they contain a number of highly volatile, ignitable, and reactive chemicals or mixtures in varying quantities. A discussion of the hazards associated with this wastestream follows.

3.6.5 Special Problems Associated with DAF Systems

In a DAF system, air is first dissolved in the wastewater under pressure (2.1 to 4.9 kg/cm²). Air bubbles are then released from the liquid by reducing the pressure to atmospheric level. For smaller systems the entire flow can be pressurized. For larger systems only a portion of the effluent is pressurized, and this portion is then mixed with the unpressurized main stream just prior to entering the flotation tank.

As air bubbles rise through the wastewater in the system, oils and insoluble particles are carried upward to the water surface where they form a dark, oily froth. This float is skimmed off on a continuing basis and either disposed or returned to the API separator for oil recovery. Heavier tars and particles settle to form a sludge which is usually discarded. Wastewater from the DAF system either is sent to tertiary treatment systems (e.g., carbon adsorption) or is discharged into streams or municipal sewers. Figure 3.14 is a schematic drawing of a typical DAF system.

Petroleum refineries generate about 66.15 metric tons of DAF float annually for every thousand barrels of oil refined each day (Tarnay and Krishnan, 1978). For a typical 32,000 cubic meter (200,000 barrels) per day refinery this amounts to 13,230 metric tons per year. Assuming that refineries process an average of 14.4 million barrels of crude oil a day (85 percent of their total capacity as of 1 April 1979), 952,560 metric tons of DAF float will be produced in the United States this year.

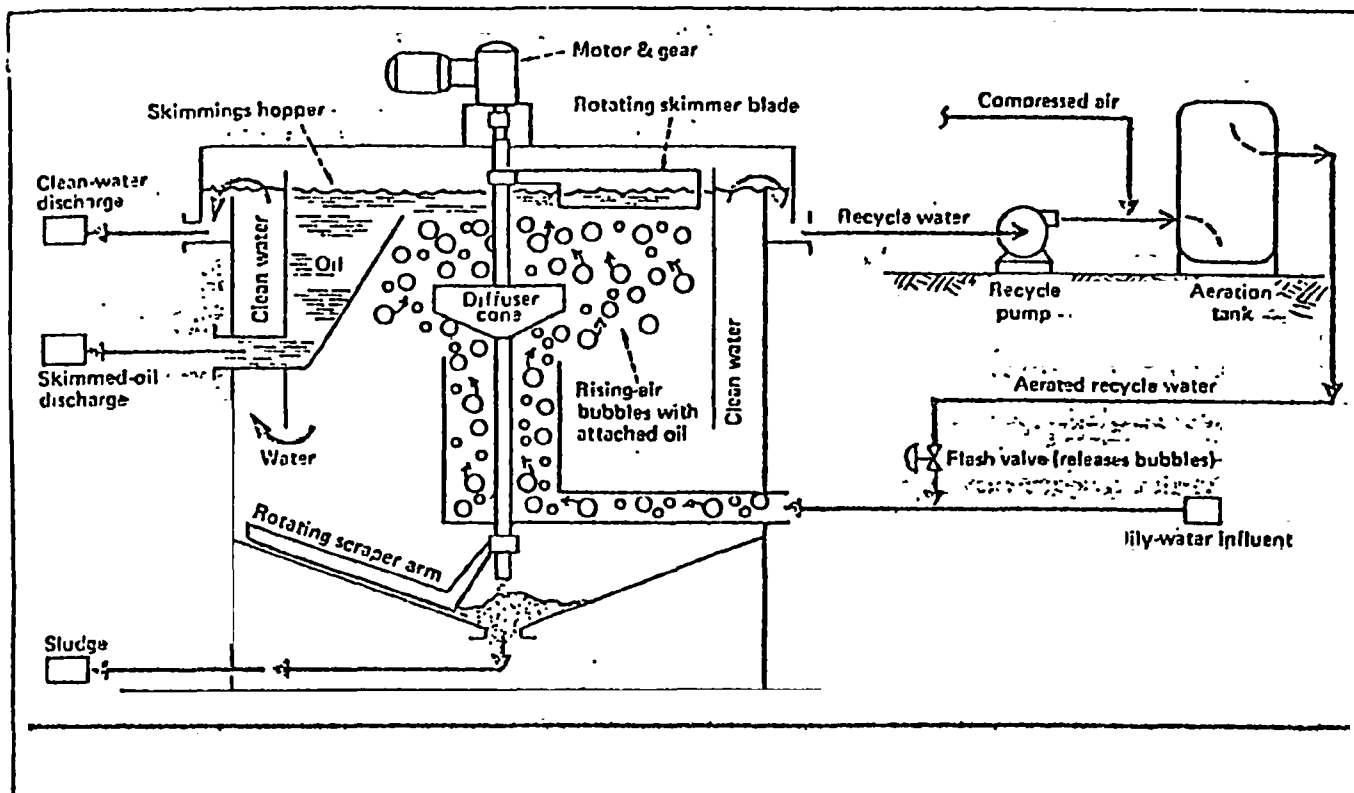


Figure 3.14 Typical Dissolved Air Flotation System (Ford and Elton, 1977)

The quantity and composition of float produced at each refinery depends primarily on two factors: the nature of the influent wastestream and the operation of the system. Generally, float volume is 0.2 percent to 2.5 percent of the influent volume (American Petroleum Institute, 1969). DAF system influents usually come directly from API separators. Table 3.13 summarizes water quality estimates on a typical API separator effluent. As the concentration of oils and solids in the DAF system influent wastestream increases, so will the quantity of float. This observation is supported by Table 3.14. The composition of the float depends on the waste stream mix of the refinery and thus on the types of crude, the processes, and the product mix used. These factors also influence the nature of API separator influents. Consequently, both the quantity and composition of DAF system influents and effluents are highly variable.

Operating conditions also affect froth generation. Principal operation variables are:

- residence time
- air-to-solids ratio
- depth of scraping
- use of chemicals

Residence time in the DAF system for wastewater is generally 10 to 40 minutes. As the residence time increases, more froth is generated per unit of influent.

The air-to-solids ratio in the system is generally 0.01 to 0.03. As the air-to-solids ratio increases so does the amount of solids in the float, producing a thicker, more dense float. The thickness of the scum layer will be approximately inversely proportional to the square root of the air-to-solids ratio (Bratby, 1977).

The depth of scraping is usually 5 mm to 200 mm, but will depend on the thickness of the scum layer and the adjustability of the DAF unit. The greater the depth of scraping, the greater both the proportion of water in the skimmings and the amount of float collected.

**Table 3.13 Water Quality Estimates of Typical Effluents Sent to DAF Systems
From API Separators (Bombaugh, 1976)**

	EXPECTED CONCENTRATIONS (ppm)		
	<u>Minimum</u>	<u>Maximum</u>	<u>Average</u> *
BOD	1	1,180	413
COD	69	3,080	1,170
Solids			
Suspended		1,950	480
Dissolved	83	15,180	2,630
Alkalinity	14	2,620	600
pH	6.8	9.5	8.2
Oil	3	870	140
Phenols	0.5	335	76
Sulfide	0.2	240	30
Phosphorus	0.5	6	3
NH ₃ (N)	21	1,000	480

Water is greater than 98 volume percent of the total flow.

*Assumes 85% efficiency of the API separator which may be a high estimate.

Table 3.14 Oil Concentrations and Removal Efficiencies For 14 DAF Systems

<u>Configuration</u>	<u>Chemicals</u>	<u>Influent oil mg/ℓ</u>	<u>Effluent oil mg/ℓ</u>	<u>% removal</u>	<u>Oil * Removed mg/ℓ</u>	<u>Calculated percentage of oil in float **</u>
Circular	No	170	52	70	118	7
Circular	Yes	125	30	71	95	6
Circular	Yes	100	10	90	90	6
Circular	Yes	133	15	89	118	7
Circular	Yes	94	13	86	81	5
Circular	Yes	1,930	128	93	1,802	†
Circular	Yes	580	68	88	512	32
Rectangular	Yes	105	26	78	79	5
Rectangular	Yes	68	15	75	53	3
Rectangular	Yes	638	60	91	578	36
Rectangular	Yes	153	25	83	128	8
Rectangular	Yes	75	13	82	62	4
Rectangular	Yes	61	15	75	46	3
Rectangular	Yes	360	45	87	315	20
AVERAGE		328	37	83	291	11
MINIMUM		61	10	70	46	3
MAXIMUM		1,930	128	93	1,802	†
RANGE		1,869	118	23	1,756	†

Source: Ford and Elton, 1977, except as noted

*Calculated by subtracting the oil concentration of the effluent from the oil concentration of the influent.

**Calculated from "oil removed" by assuming a float generation rate of 1.5 ℓ of float per 100 ℓ of influent and a float density of 1.077.

†Value calculated was over 100 percent which indicates that the float generation assumption cannot be valid for this case.

Coagulents such as lime, alum, ferric salts, and polyelectrolytes are commonly used to improve floc formation. They will increase both the density and the quantity of float produced.

Depending on these factors, oil and solids removal efficiencies for DAF systems can range from about 70 to 90 percent. Table 3.14 is a list of removal efficiencies for 14 DAF systems. Although this data is insufficient for purposes of statistical inference, it appears that addition of chemicals does significantly improve removal efficiency. The system's configuration has little effect.

As research on DAF system operation and chemical flocculants progresses, the average oil removal efficiency should improve. With this improvement will come higher scum generation rates. In addition, more refineries are turning to DAF systems as a means of treating oily wastewater. These trends clearly point to increasingly larger amounts of waste DAF float in the future.

3.6.5.1 DAF Float Composition

Table 3.15 gives measured percentages of oil, water, and solids for eight samples of DAF float. The percentage of oil in this table supports values calculated for Table 3.14. For the sake of consistency, values given by Rosenberg et al. and Tarnay and Krishnan will be used in all subsequent calculations requiring float composition estimates. These values are:

- 82 percent water
- 12.5 percent oil
- 5.5 percent solids

Given these approximations of float composition, the specific gravity can also be estimated. This is shown in Table 3.16.

Little or no information is available on the composition of the oil or the concentrations of organic chemicals in DAF float. Concentrations of inorganic constituents, primarily metals, are described in Section 3.6.5.2.

3.6.5.2 Potential Hazards of DAF Float

Two components of DAF float that present a significant hazard to the environment are oils and trace constituents. Based on a DAF float generation rate of 66.15 metric tons per year per 1,000 barrels refined per stream day (BPSD), of which 12.5 percent is oil, approximately 8.27 metric tons of DAF scum oil is produced annually for every 1,000 barrels of oil refined. With a refinery capacity of 17 million BPSD (as of 1 April 1979), the industry could generate up to 40,600 metric tons of oil this year. Assuming a weight of 7.11 barrels per metric ton (based on a specific gravity of .8871 for the oil) this amounts to 1 million barrels per year. By comparison, the 1976 Argo Merchant spill was 178,600 barrels. Admittedly, the industry does not produce at 100 percent of their capacity, but even at the more reasonable estimate of 85 percent capacity, 850,000 barrels would be generated annually. A typical 200,000 BPSD refinery would have to dispose of 10,000 barrels of waste oil from their DAF system alone.

It is difficult to judge how hazardous the oils in DAF float are because of the lack of data on their composition and variability. It can be assumed that DAF scum is a mixture of light and heavy fractions. Certainly, some of the oils are volatile and ignitable, and some may be carcinogenic (see Table 3.2). Little else is known for certain. Additional studies are needed to focus on this problem, especially in light of the large quantities indicated.

Substances present in DAF float in trace amounts can present potential hazards despite low concentrations because of ignitable, volatile, and toxic properties. Trace substances include inorganic metallic compounds as well as solvents and organic compounds.

There is considerably more data on concentrations of metals in DAF scum than there is on organic compounds. Table 3.17 gives concentrations of 28 elements found in DAF scum. Using a solids generation rate of 3.64 metric tons per year per 1,000 BPSD, calculations of annual production nationwide and at a "typical" (200,000 BPSD) refinery were made. These values as well as the Minimum Acute Toxicity Effluent (MATE) are also shown in Table 3.17. Table 3.18 compares generation rates with

Table 3.15 Percentages of Oil, Water, and Solids in DAF Float

Oil	12.5	16.9	14.4	5.9	2.4	6.1	11.25	10 to 22
Solids	*	*	*	*	*	1.2	2.5	3 to 3.6
Water	*	*	*	*	*	92.7	86.25	75 to 85
Reference	4	4	4	4	4	9	9	9
Refinery Identification Code	C4	B4	A2	A4	C2	A	B	C

*Rosenberg et al. do not list specific percentages of solids or water for the five samples it presents, but average values of 82 percent for water (range 30 percent to 99 percent) were obtained. An average content value of 5.5 percent for solids was found by subtraction.

Table 3.16 Calculation of Specific Gravity of DAF Float

<u>Component</u>	<u>Percent of Composition</u>	<u>Assumptions</u>	
		<u>Assumed Specific Gravity</u>	<u>Basis for Assumption</u>
Water	82	1.0000	This value ignores dissolved solids. Consequently, it is a minimum value.
Oil	12.5	.8871	This is the average specific gravity for crude oil. The true specific gravity for DAF float oil is probably lower, since the heavier oil would tend to sink.
Solids	5.5	2.65	This is the average specific gravity for quartz. This value was assumed in the absence of additional information because most of the solids are fine sands and silts which are commonly quartz.

<u>Calculations</u>			
<u>Component</u>	<u>Composition</u>	<u>Specific Gravity</u>	<u>Subtotal</u>
Water	.82	1.0000	.8200
Oil	.125	.8871	.1109
Solids	.055	2.65	<u>.1458</u>
			1.077

Table 3.17 Concentrations, Generation Rates, and Minimum Toxicity Levels of 28 Elements Found in DAF Scum

Constituent	Concentration in DAF Float (mg/kg) ¹	Total Annual Quantity (kg/yr) ²	Annual Quantity at a typical 32,000 cu.m./day (200,000 BPSD) Refinery (mg/year)	Minimum Acute Toxicity Effluents (MATES) ³					
				Health			Ecology		
				Air (mg/m ³)	Water (mg/L)	Land (mg/g)	Air (mg/m ³)	Water (mg/L)	Land (mg/g)
Aluminum	13*	800	9,490	5.2	80.	.16	--	1.	.002
Arsenic	2.0	120	1,460	.002	.25	.0005	--	.05	.0001
Barium	31	1,900	22,630	.5	5.	.01	--	2.5	.005
Beryllium	.003	.2	1.8	.002	.03	.00006	--	.055	.00011
Boron	2*	120	1,460	3.1	47.	.093	--	25.	.05
Cadmium	.005	.3	3.6	.01	.05	.0001	--	.0001	.000002
Calcium	246*	15,200	179,580	--	--	--	--	--	--
Chlorine	7*	430	5,110	--	--	--	--	--	--
Chromium	140	8,700	102,200	.001	.25	.0005	--	.25	.0005
Cobalt	2.0	120	1,460	.05	.75	.0015	--	.25	.0005
Copper	7.0	430	5,110	.2	5.	.01	--	.05	.0001
Fluorine	15*	930	10,950	--	--	--	--	--	--
Gallium	2*	120	1,460	4.95	74.	.15	--	--	--
Iron	29*	1,800	21,170	--	--	--	--	--	--
Lead	7.5	460	5,470	.15	.25	.0005	--	.05	.0001
Magnesium	340*	21,000	248,200	6.	90.	.18	--	87.	.174
Manganese	2*	120	1,460	5.	.25	.0005	--	.1	.0002
Mercury	.27	17	197	.05	.01	.00002	.01	.25	.0005
Molybdenum	.05	3	36	5.	75.	.15	--	7.	.014
Nickel	.025	2	18	.015	.225	.00045	--	.01	.00002
Phosphorus	18*	1,100	13,140	1.	15.	.03	--	.0005	.000002
Potassium	76*	4,700	55,480	2.	30.	--	--	23.	--
Selenium	2.0	120	1,460	.2	.05	.0001	--	.025	.00005
Silver	.25	15	182	.01	.25	.0005	--	.005	.00001
Strontium	45*	2,800	32,850	3.06	46.	.092	--	--	--
Sulfur	3370.	208,000	2,460,100	--	--	--	--	--	--
Vanadium	.05	3	36	.5	2.5	.005	.001	.15	.0003
Zinc	85.	5,200	62,050	4.	25.	.05	--	.1	.0002

1) Values taken from Rosenberg, et al., except for those marked with an asterisk, which were calculated from Tarnay and Krishnan, using a specific gravity for DAF skimmings of 1.077.

2) Calculated from the concentration based on a dry weight generation rate of 3.64 metric tons/year/1000 BPSD and a total capacity of 17,000,000 BPSD (1 April 1979).

3) Source: Cleland and Kingsbury, 1977.

MATEs for these elements. Daily generation rates were calculated by dividing annual production at a typical refinery (Table 3.17) by 365 days per year. The amount of land needed daily to meet MATEs were calculated by dividing the daily generation rate by the appropriate MATE. This calculation assumes all these elements will be disposed on land, either by landfilling, landspreading, or lagooning. The data indicate that lead, chromium, selenium, zinc, and phosphorous would appear to be the most troublesome metals. A typical refinery could need up to 20 metric tons (about 10 cubic yards) of soil per day, or 7,300 metric tons (about 2 acre feet) per year, to dispose of its DAF scum while meeting MATE levels. Although these calculations are inexact and tend to be liberal, the numbers are high enough to warrant added concern about safe disposal of DAF float.

The presence of solvents and organic chemicals is also of interest in assessing the hazardousness of trace materials in DAF skimmings. While many compounds have been identified in this waste stream, few have been measured precisely. Table 3.19 lists 27 chemicals that have been identified in DAF influents and some of their physical and chemical properties. It is not known which compounds are in DAF float. Their concentrations are also unknown. However, insoluble, and some slightly soluble chemicals with a low specific gravity (less than 1.077) probably do rise in the system and mix with the float. Chemicals having a higher specific gravity (e.g., tetraethyl lead) or aqueous solubility (e.g., pyridine) may also be present in the scum layer if they are dissolved in the scum oil. Some of these chemicals are highly volatile and ignitable. Hydrogen sulfide, hydrogen cyanide, benzene, cyclohexane, hexene, methanethiol, and methyl-2-butene all have high vapor pressures and low flash points. In sufficient concentrations, they appear to present a significant potential for explosion.

Table 3.20 measures the hazardousness of these 27 chemicals. Some are highly toxic (e.g., tetraethyl lead, hydrogen cyanide, and cresol) and some tend to become magnified in the food chain (e.g., anthracene and biphenyl). Many of these compounds pose a threat to health and environment even in miniscule amounts (e.g., hydrogen cyanide, cresol, phenol, ammonia, tetraethyl lead, and naphthalene). It is impossible

Table 3.18 Comparison of Daily Generation Rates for 28 Elements in DAF Float with Their MATE Values

<u>Constituent</u>	<u>Daily generation rate at a typical 200,000 BPSD refinery in mg/day</u>	<u>Amount of soil needed daily to meet MATEs for land in kg</u>	
		<u>Health</u>	<u>Ecology</u>
Aluminum	26.	.2	13.
Arsenic	4.	8.	40.
Barium	62.	6.	12.
Beryllium	.005	.08	.04
Boron	4.	.04	.08
Cadmium	.01	.1	5.
Calcium	492.	—	—
Chlorine	14.	—	—
Chromium	280.	560.	560.
Cobalt	4.	3.	8.
Copper	14.	1.	140.
Fluorine	30.	—	—
Gallium	4.	.03	—
Iron	58.	—	—
Lead	15.	30.	150.
Magnesium	680.	4.	4.
Manganese	4.	8.	20.
Mercury	.5	25.	1.
Molybdenum	.1	.7	7.
Nickel	.05	.1	2.
Phosphorus	36.	1.	18,000.
Potassium	152.	—	—
Selenium	4.	40.	80.
Silver	.5	1.	50.
Strontium	90.	1.	—
Sulfur	6,740.	—	—
Vanadium	.1	.02	.3
Zinc	170.	3.	850.
Totals	8,842.3 mg/day	692.3 kg/ day	19,942.4 kg/day

Table 3.19 The Hazards of 27 Chemicals Found in DAF Influent

CHEMICAL Influents	CALCULATED BIOACCUM- ULATION FACTOR ¹	N F P A INDICES			MINIMUM ACUTE TOXICITY EFFLUENTS ⁴ (RATES)					
		Based on Human Health			Based on Ecological Effects					
		HEALTH ³	FLAMMA- BILITY ³	REAC- TIVITY ³	Air (mg/m ³)	Water (mg/l)	Land (mg/s)	Air (mg/m ³)	Water (mg/l)	Land (mg/s)
Methyl-2-Butene	—	—	—	—	—	—	—	—	—	—
1-Hexene	100	—	—	—	—	—	—	—	—	—
Cyclohexene	47	1	3	0	—	—	—	—	—	—
Isopropyl benzene (cumene)	120	0	2	0	—	—	—	—	—	—
Styrene	56	2	3	0	435	6,500	13	—	1	.002
Biphenyl	346	—	—	—	1	15	.03	—	—	—
Toluene	32	2	3	0	375	5,600	11	—	1	.002
Ethylbenzene	64	2	3	0	435	6,500	13	—	1	.002
Decalin	—	—	—	—	—	—	—	—	—	—
Naphthalene	139	2	2	0	50	750	1.5	—	.1	.00002
Anthracene	2,447	—	—	—	56	840	1.68	—	—	—
Tetraethyl Lead	—	3	2	3	0.1	1.5	.003	—	4.1	.00002
<u>Partly Soluble</u>										
Ethanthiol	5	—	—	—	1	15	.03	—	—	—
Methanthiol	3	—	—	—	1	15	.03	—	—	—
Benzene	16	2	3	0	3	45	.09	—	1	.002
Hexanoic Acid (Caproic Acid)	8	—	—	—	—	—	—	—	—	—
Cresol	5	3	2	0	22	.005	.00001	—	.5	.001
Benzoic Acid	15	—	—	—	140	2,100	4.2	—	—	—
Hydrogen Sulfide	7	3	4	0	15,000	23	—	—	.01	—
<u>Soluble</u>										
Hydrogen Cyanide	—	4	4	2	11	.5	.001	34	.025	.000005
Ammonia	.04	3	1	0	18	2.5	.005	.35	.05	.00001
Formaldehyde	0.5	2	2	0	1.6	24	.048	.5	1	.002
Pyridine	—	2	3	0	150	225	.45	—	10	.020
Hydrochloric Acid	0.5	3	0	0	—	—	—	—	—	—
Acetic Acid	—	2	2	1	25	380	.76	—	1	.002
Phenol	2.5	3	2	0	19	.005	.00001	—	.5	.001
Formic Acid	—	3	2	0	9	140	.28	—	—	—

1) Calculated from the formula bioaccumulation factor = 10^a where $a = 3.41 - 0.508 \log$ (aqueous solubility in μ moles per liter). (Chiu et al., 1977)

2) Source: Gloland and Kingsbury, 1977

3) National Fire Protection Association Indices, 1969. (See next page.)

4) Source: HFFA, 1969

Table 3.20 National Fire Protection Association Indices for Hazards of 27 Chemicals Found in DAF Influent

<u>HEALTH</u>	<u>FLAMMABILITY</u>	<u>REACTIVITY</u>
4 - Materials which on very short exposure could cause death or major residual injury even though prompt medical treatment were given	4 - Materials which will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or which are readily dispersed in air and which will burn readily.	4 - Materials which in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures.
3 - Materials which on short exposure could cause serious temporary or residual injury even though prompt medical treatment were given.	3 - Liquids and solids that can be ignited under almost all ambient temperature conditions.	3 - Materials which in themselves are capable of detonation or explosive reaction but require a strong initiating source or which must be heated under confinement before initiation or which react explosively with water.
2 - Materials which on intense or continued exposure could cause temporary incapacitation or possible residual injury unless prompt medical treatment is given	2 - Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur.	2 - Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. Also materials which may react violently with water or which may form potentially explosive mixtures with water.
1 - Materials which on exposure would cause irritation but only minor residual injury even if no treatment is given.	1 - Materials that must be preheated before ignition can occur.	1 - Materials which in themselves are normally stable, but which can become unstable at elevated temperatures and pressures which may react with water with some release of energy but not violently.
0 - Materials which on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material.	0 - Materials that will not burn.	0 - Materials which in themselves are normally stable, even under fire exposure conditions, and which are not reactive with water.

to determine how much of a hazard these compounds present without data on their levels in DAF skimmings. Research in this area would be quite beneficial.

One trace substance that merits special attention in assessing the hazardousness of DAF float is benzo(a)pyrene. This compound is closely associated with oil and is a known carcinogen. It is insoluble in water but soluble in oil and has been measured in DAF scum at an average level of .002 mg/kg (Rosenberg et al., 1976). Based on the float generation rate and industry capacity assumptions mentioned previously, 124,000 mg benzo(a)pyrene will be produced in the United States this year. A typical 200,000 BPSD refinery could generate as much as 1,460 mg per year, or about 4 mg per day. Because MATEs based on human health for benzo(a)pyrene are so low (.020 mg/m³ for air, .300 mg/l for water, and 6 µg/g for land) special care is needed to ensure that the public's health will not be endangered at DAF float disposal sites.

Based on these considerations, DAF float has significant potential for causing damage to man and the environment because of the toxicity, volatility, and ignitability of the waste stream, and because it is generated in relatively large quantities.

3.6.5.3 Current DAF Waste Treatment Storage and Disposal Practices

Petroleum refineries currently use a variety of methods to treat, store, and dispose of DAF skimmings. Table 3.21 outlines the treatment and disposal strategies of eight refineries. These refineries are typical of the industry in that most use some type of treatment to dewater the scum before disposal and most use a land-based disposal technique.

(a) Treatment alternatives

DAF float is approximately 82 percent water, and dewatering results in a significant reduction in waste volume. Refineries use four methods to dewater DAF wastes: gravitational separation; filtration; heat treatment; and chemical treatment.

Table 3.21 Treatment/Disposal Strategies for DAF Float at Eight Petroleum Refineries
(Rosenberg et al., 1976)

Refinery Code	Source of Influent to DAF System	Processes Applied to DAF Float Before Disposal	Disposal Method	Comments
A	• Two-stage API separator	• Centrifuging • Oil recovery	• Unspecified off-site method	• Float is mixed with DAF sludge and wastes from slop oil recovery system before being centrifuged
A-2	• API separator	• Centrifuging • Vacuum filtering or Incineration	• Filtered material is landspread • Incinerated residues are landfilled on-site	• Float is mixed with API separator sludge and waste biosludge before centrifuging and with tank bottoms afterwards
A-3	• API separator	• Centrifuging	• Centrifuge tops are returned to the API separator; centrifuge bottoms are landfilled on-site	• Float is mixed with API separator sludge before centrifuging
A-4	• API separator	• Vacuum filtering	• Landfilled off-site	• Float is mixed with wastes from emulsion-breaking treatment of slop oils and with waste biosludge before filtering
B-4	• API separator	• None	• Unspecified on-site method	
C-1	• API separator and bio-oxidation system	• Dewatered in a cone-shaped tank	• Landfilled off-site	• Mixed with thickened API separator sludge and waste bio-oxidation sludge before dewatering
C-2	• API separator	• None	• Lagooned	
C-4	• API separator and bio-treatment system	• None	• Landfilled off-site	

Gravitational separation is based on differences in the specific gravities of the three components of scum: water, oil, and solids. The simplest method of physical separation is to let the scum stand, allowing water and solids to settle out. The remaining float is then decanted. Up to 15 percent by volume of the waste stream can be eliminated in this manner, most of it as water (American Petroleum Institute, 1969). In some cases, the three components are tightly bound together and settling is not very efficient. Several refineries are experimenting with centrifuging their DAF float. Industrial centrifuges provide a fast, efficient, but costly method for dewatering this waste. This physical separation technique is limited to small volumes of scum and has not always proved successful where oil and solids are bound together. Furthermore, erosion from gritty solids may cause significant maintenance problems.

Scum filtration is usually done with a precoat filter. Processing with these filters is done in three stages. A slurry of diatomaceous earth and recirculated water is pumped through the filter unit until a thin protective precoating layer of the earth is deposited on the filter elements. Then wastewater is fed into the filter with a small ratio of the slurry in a continuous operation. The filter is considered fully operable when effluent water is sufficiently clear to be sent to the next treatment process or discharged into sewers. Slurry is added continuously to the feed to maintain the porosity of the filter cake on the filter elements. When the pressure differential increases, indicating that the filter cake is plugged, the wastewater feed is cut off and the filter system is back-washed to a sump. This removes the spent filter cake. The complete cycle is restarted. As oil/water emulsions pass through interstices of the filter cake and precoat material, globules break up and stabilizing solids are removed. The resulting effluent is then more amenable to gravitational separation.

Precoat filters usually require less space than other solid/liquid separation equipment and can filter out even some clay-sized solids. They are also capable of adjusting to variations in the conditions of a wastestream. Although operating costs are usually high, and the diatomite slurry makes an additional solids disposal problem, many petroleum

refineries use precoat filters to treat DAF scum before routing the oils back to the process area.

Heating DAF scum to break up oil/water emulsions is a simple and economical technique which is nearly always advantageous. Heat markedly reduces the viscosity of the oil phase, melts interfacial waxy films, and occasionally reduces the efficiency of emulsifying agents. Heat is frequently used in conjunction with centrifuging, filtering, and chemical treating. The cost-to-benefit ratio can be reduced dramatically if waste heat can be used for treating DAF scum, or if waste heat from scum treatment can be used elsewhere in the refinery.

An extreme form of heat treatment is distillation. In this process, oils are removed from the scum in a much purer form than in other treatment processes. However, distillation is very energy intensive and costly. No refineries use distillation to treat scum on a full-time basis.

The primary purpose of chemical treatment of DAF scum is to break oil/water emulsions. Certain chemicals balance or reverse interfacial surface tension on each side of an interfacial film, neutralize stabilizing electrical charges or precipitate emulsifying agents, thus enabling oil and water to separate. Reactive cations such as H^+ , Al^{+++} , and Fe^{+++} will break oil/water emulsions.

While nearly all refineries use chemicals to aid in the DAF process itself, some also use them on the resulting sludges and skimmings in order to extract more usable oil. It is frequently difficult to predict how efficient a given chemical will be in treating DAF scum because of the chemical and physical variability of the waste stream.

Selection of a treatment scenario for a refinery's DAF float depends to a great extent on how much oil can be recovered from the waste. Most refineries use gravitational separation to treat their DAF scum when they are attempting to recover oil or reduce the waste quantity. Chemical treatment is used primarily during, and not after, the air flotation process. When heat treating is used it is usually in conjunction with another form of treatment. More elaborate schemes, such as the combination of heating with filtering and/or centrifuging,

are common only where oil recovery on a large scale is a goal. Otherwise, if any treatment is used at all, it is a simpler and less costly treatment such as gravitational settling.

(b) Storage

Petroleum refineries have not generally been concerned about the storage of DAF float. Most commonly, the scum is collected in open troughs until hauled away for disposal. This procedure permits volatile components to contaminate the air surrounding the DAF unit and the collection troughs. The industry's lack of concern may be due to lack of any data on air contamination from DAF operations. At this time, it is unknown whether DAF scum storage represents a serious problem or not.

(c) Disposal Alternatives

Land disposal is the most frequent means of disposing of DAF wastes. Landfilling is now used at a majority of U.S. refineries. Land treatment and lagooning are less common. However, land treatment is on the rise and landfilling and lagooning of DAF scum are declining. Oil recovery is also increasing as the price of crude oil escalates. Most refineries already have in-plant schemes for oil recovery from process wastes although DAF wastes are not always included. Incineration is used primarily where oily wastes are not recoverable and where other methods are not cost-effective for reasons such as the cost of suitable land for landspreading.

Table 3.22 gives estimates of the current and projected use of these five waste management methods.

1. Landfilling and lagooning

Landfilling and lagooning are, theoretically, the simplest methods for disposal of DAF float. They are also the most commonly used. However, lagooning frequently leads to air and ground water contamination, and cases exist where a lagoon's berms fail, resulting in a massive release of wastes to soils and surface waters. There is pressure on industry from environmental groups to phase out this disposal method.

Table 3.22 Current and Projected Percent Use of Several Methods
For Managing DAF Scum

<u>Method</u>	<u>Current Use^{1,2}</u>	<u>Projected Use^{2,3}</u>	<u>Rationale for Projected Use</u>
Lagooning	20%	0%	Lagooning will be phased out as a disposal method because it does not adequately protect the environment. It may still be used for temporary storage, however.
Landfilling	70%	50%	Landfilling will continue to be popular because the technology is so well established. However, the shift to land treatment will cause a decline in landfill use.
Land treatment	20%	50%	The use of land treatment will increase dramatically as more research is done on solving the problems of protecting the environment.
Incineration	10%	10%	The high cost of land in some areas will continue to make incineration of non-recoverable oils cost effective despite rising fuel costs.
Oil Recovery	20% ⁴	80%	Attempting to recover oils from DAF scum will increase as the price of crude oil increases. Some DAF waste streams, however, will probably not be recoverable.

1) Based on Table 3.21.

2) The estimates sum to more than 100 percent because some refineries use more than one method.

3) Based on current trends in technological development, the economy, and environmental protection.

4) The value of oil recovery from any refinery waste stream is much higher---probably over 75 percent. Refer to Table 3.13 for estimates of the percent of use of disposal methods for all refinery wastes.

Landfills tend to be somewhat safer than lagoons. However, since oil does not degrade very rapidly under the anaerobic conditions found in fills, they are, in a sense, permanent storage facilities. There are three basic types of landfills: open dumps, sanitary landfills, and secure landfills. Open dumps are pits where wastes are dumped and left uncovered until the pit is filled. Like lagoons, open dumps are being phased out of use.

Sanitary landfills are similar in design to open dumps but their operation is quite a bit different. In a sanitary landfill, wastes are covered at frequent intervals, usually daily or after each disposal operation. This method of landfilling is rapidly becoming the most common because it frequently provides adequate protection for the environment, and is always less expensive than a secure landfill.

In 1976, a well managed sanitary landfill for oil wastes (at least 3.5 percent oil by weight) cost about \$5.39 per wet ton of wastes disposed, or about \$28.23 per dry ton. By comparison a secure landfill costs about \$16.54 per wet ton or about \$86.61 per dry ton (Tarnay and Krishnan, 1978).

Secure landfills are more expensive because advantageous geohydrologic conditions and leachate containment structures such as liners must provide extra protection from leachate migration. Favorable geohydrologic conditions require thick, impermeable earth materials under a site, and very deep water tables. Not all liners are chemically compatible with oily wastes such as DAF float. Only oil-resistant PVC, polyethylene, polypropylene, soil cement, soil bentonite, and compacted clay liners are acceptable from a chemical resistance point of view (Stewart, 1978). Besides liners, containment structures include cement structures and metal drums (Ghassemi and Quinlivan, 1975). However, acceptability may change with the issuance of Final EPA regulations under RCRA.

2. Land Treatment

Land treatment is becoming increasingly important as a method for disposing of oily wastes. The strategy behind this technique is to

leave the waste on or near the land's surface where it can degrade. Degradation is mainly by oxidation, solution, and emulsification. Most of the degradation results from oxidation. However, evaporation plays a major role in decreasing the volume of wastes disposed on the surface. Oxidation, including photo-oxidation, auto-oxidation, and especially bio-oxidation accounts for most of the degradation occurring at land treatment facilities for oily wastes.

Bio-oxidation agents are known to include species from 28 genera of bacteria, 30 genera of filamentous fungi, and 12 genera of yeasts (Zobell, 1973). The rate at which oils are degraded depends primarily on these factors:

- availability of free oxygen
- temperature
- concentration and dispersion of the oil
- organic content of the soil
- abundance of bio-oxidizing organisms
- availability of nutrients, such as nitrogen and phosphorous.

The overall rate of decomposition is usually in the range of 5 to 60 pounds of oil per cubic foot of soil per month. Besides carbon dioxide and water, the principal products of the breakdown of oil by micro-organisms includes various hydroperoxides, alcohols, phenols, carbonyls, aldehydes, ketones and esters. These products probably do not accumulate in sufficient concentrations to be injurious to the environment (Zobell, 1973).

Selection of a site that will not release contaminants to groundwater or surface water, and control of air emissions, are probably the two most basic problems associated with landspreading. Equations have been derived to calculate the maximum areal migration of pollutants from landspreading sites (Ministry of Interior, Federal Republic of Germany, 1970). Cold weather is also a problem although some oil degradation goes on even under Arctic conditions (Loynachan, 1978). Some hydrocarbons appear to be fairly persistent, such as paraffin waxes and the

high molecular weight, polyaromatic material typically found in catalytically-cracked, slurry oil. However, even these are eventually consumed (Zobell, 1973). The problem that receives the most attention from researchers, however, concerns the buildup of heavy metals in the soil, and their transmission to other environmental media, especially vegetation, where they can enter the food chain.

In 1977, Parr et al. listed the most important factors affecting metal uptake and accumulation in plants:

- Soil pH: Toxic metals are more available to plants below pH 6.5
- Organic matter: Organic matter can chelate and complex heavy metals so they are less available to plants
- Soil phosphorus: Phosphorus interacts with certain metal cations to reduce their availability to plants
- Cation exchange capacity (CEC): Important in binding of metal cations; soils with a high CEC are safer for disposal of sludges
- Moisture, temperature, and aeration: These can affect plant growth and therefore the uptake of metals
- Plant species and varieties: Vegetable crops are more sensitive to heavy metals than grasses
- Organs of the plant: Grain and fruit accumulate lower amounts of heavy metals than leafy tissues
- Plant age and seasonal effects: Older leaves of plants will contain higher amounts of metals
- Time: With time, metals may revert to unavailable forms in soil
- Amount and type of metals: Zinc, copper, nickel and other metals differ in their relative toxicities to plants and in their reactivity in soils.

Under certain conditions, high enough concentrations of heavy metals can accumulate in plants to be toxic to animals using the plants as a food source. Research results are often conflicting however. One

study done on an API separator sludge landspreading site in southeastern Texas, showed significant increases in sodium, zinc, and lead concentrations in both soil and vegetation (Phung et al., 1977). The data from this study are summarized in Table 3.23. However, a second study found the main problem arising from applications of large amounts of spent motor oil to soil was immobilization of nutrients, primarily nitrogen. Furthermore, this second study seemed to show no problem from plant uptake of metals (Gliddens, 1976). The differences may be simply due to differences in chemical constituents between API separator sludge and waste oil.

Land treatment of oils continues to increase despite the potential for environmental problems, because of its relatively low cost. In 1972, one land treatment operation in California cost less than \$11 per dry ton, making it comparable with landfilling (Gliddens, 1976).

Land treatment has definite advantages over landfilling, but there are still unanswered questions regarding its environmental safety. Careful operation and monitoring is needed to ensure that these sites do not become a major source of contamination of soils.

3. Incineration

In areas where the price of land suitable for disposal of oily wastes is too high to be cost-effective, DAF float can be destroyed by burning and incineration. Successful burning requires that the waste have a high enough heat content to sustain combustion. No special equipment is used to control either combustion or air contamination. Consequently, burning waste oil without removing contaminants can result in significant emissions to air of lead and other heavy metals, and volatile organic chemicals. DAF scum must be extensively dewatered to sustain combustion, therefore open burning is not an important method of disposal for this waste stream.

Incineration, on the other hand, is a common disposal method for DAF float. Equipment is specially designed to control both combustion and air emissions, and fuel can be added to sustain combustion. DAF scum must usually be dewatered and filtered to a certain extent before

Table 3.23 Summary of the Data From a Study of the Effects of Land Treatment API Separator Sludges (Phung, Ross, Landreth study)

Background information on the site:

Area of Site	8.2 ha (20 ac)
Waste Type	API oil/water separator sludges
Waste Volume	Periodic disposal, 29,600 m ³ /yr (185,000 bbl/yr)
Application Rate	1.27 x 10 ³ m ³ /ha (3.22 x 10 ³ bbl/ac)
Fertilization/Liming	None
Soil Characteristics	Clay, poorly-drained, alkaline
Depth of Soil/Waste Mixture	15 to 30 cm (6 to 12 in)
Site Age	5 Years
Vegetative Types	Weeds and shrubs along the disposal area perimeter

Chemical Characteristics of the Surface Soils from Control and Oil-Treated Plots on the Site:

	<u>Control</u>	<u>Treated</u>	<u>Change</u>
pH	7.41	7.40	-0.01
EC, mmhos/cm	2.21	3.91	+1.70
Oil, %	—	2.06	+2.06
TKN, %	0.080	0.134	+0.054
Org. C, %	2.10	5.10	+3.00
--- ppm ---			
P	17.5	17.5	0
Na	185	375	+190
B	0.2	0.22	+0.02
Mn	65	71.6	+6.6
Ni	4.8	5.3	+0.5
Zn	53.5	71.5	+18.0
Se	0.01	0.028	+0.018
Mo	0.6	0.55	-0.05
Cd	0.06	0.06	0
Pb	212	242	+30

Table 3.23 Summary of the Data From a Study of the Effects of Land Treatment API Separator Sludges (Continued)

Analysis of Vegetation Sampled from the Control and Treated Plots at the Site:

Element	Nutgrass Leaves			Cocklebur Seeds		
	Control	Treated	Change	Control	Treated	Change
	%					
N	1.44	1.42	-0.02	3.05	1.07	-1.98
P	0.17	0.11	-0.06	0.29	0.16	-0.13
	ppm					
Na	2,062	6,187	+4,125	1,000	6,870	+5,870
B	7	15	+8	28	14	+14
Mn	63.6	48.7	-14.9	18.8	19.1	+0.3
Ni	1.9	6.3	+4.4	3.6	3.1	-0.5
Zn	93.8	131.9	+38.1	43.8	53.1	+9.3
Se	0.23	0.23	0	0.04	0.04	0
No	7.1	9.5	+2.4	4.2	8.7	+4.5
Cd	0.41	0.41	0	0.15	0.15	0
Pb	61.5	90.5	+29.0	11.2	23.2	+12.0

API separator sludge will have more oil and solids and less water than DAF scum. The sludge averages 22.6% oil, 24.4% solids, and 53% water (before dewatering). Scum averages 12.5% oil, 5.5% solids, and 82% water (NFPA, 1969).

it can be incinerated because the water and solids in the waste are not combustible. If there is a substantial total volume of waste (above 50 gallons per hour), then removal of water by either chemical or mechanical separation is usually advisable because the oily layer probably will sustain combustion by itself (Mann, et al., 1970). However, if the oily waste is miscible and in small quantity, then it is not economical to separate the water prior to incineration.

DAF scum that contains emulsions may require chemical treatment prior to incineration. Emulsions pose special problems for incineration systems because they contain inconsistent mixtures of oil and water resulting in erratic combustion. This requires greater use of auxiliary fuel. There is no rule-of-thumb concerning the selection of direct incineration of an emulsion versus prior breaking of the emulsion because costs of auxiliary fuel vary too widely throughout the country. Each case must be evaluated separately.

Combustible liquid mixtures normally have calorific values above 8,000 BTUs/lb (Mann, et al., 1970). Grease and scum will have a heating value about 16,700 BTUs/lb (EPA, 1974a), but they represent only a small portion of the DAF waste stream. Auxiliary fuel is usually needed. Most organic waste materials require temperatures between 650°C and 980°C (1200°F and 1800°F) for complete combustion (Mann, et al., 1970).

Incinerator design for a partially combustible liquid waste oil may take a variety of forms, depending on concentration of the organic material in the waste, viscosity, specific gravity, and a number of other factors. Most incinerators used for oily wastes are cylindrical and refractory-lined. They may be either vertical or horizontal.

Three types of incinerators have been used for DAF float: Rotary kiln; multiple hearth; and fluidized bed. However, studies suggest that fluidized bed incineration is the optimum choice for refinery wastes (Tarnay and Krishan, 1978).

A fluidized bed is essentially a vessel containing inert granular particles, such as sand. Blower-driven air enters at the bottom of the bed and rises vertically, agitating the particle mass and causing it to behave like a dense liquid. Wastes are injected into the bed by pumping,

by air pressure, or by gravity, where rapid and relatively uniform mixing of wastes and bed material occurs. Wastes must usually be predried in order for adequate combustion to take place.

In the combustion process, heat transfer occurs between bed materials and the injected waste materials. Typical bed temperatures are in the range of 760° to 870°C (1400° to 1600°F). Due to the high heat capacity of the bed material, the heat content of the fluidized bed is approximately $142,000 \text{ kg-cal/m}^3$ ($16,000 \text{ BTUs/ft}^3$), about three orders of magnitude greater than the heat capacity of flue gases in typical incinerators operating in the same temperature range (Tarnay and Krishnam, 1978). Heat from the combustion process is transferred back to the bed material. Solid materials remain in the bed until they have become small and light enough to be carried off with the flue gas as a particulate. As with most other incineration techniques, fluidized bed combustion generates both particulates and gases which require air pollution controls prior to release. Wet scrubbers are effective in reducing particulate emissions. The method used to control gaseous pollutants depends on the particular combustion products. Normally, no odors and little nitrogen oxide is produced from fluidized bed combustion, due to relatively low gas temperatures and low excess air requirements.

The cost of incinerating the majority of a typical refinery's oily wastes using a fluidized bed is about \$29.77 per dry metric ton or about \$5.50 per wet metric ton in 1976 dollars (Tarnay and Krishnan, 1978). By comparison, the cost of incinerating a similar amount of waste using a multiple hearth would be about \$25 per dry metric ton (EPA, 1974 b). These costs are comparable to disposal in a sanitary landfill.

Incineration does have disadvantages. The process has a high capital cost as well as high annual operation and maintenance costs. Stricter air pollution regulations may require extremely expensive and complicated air pollution control devices at some future date, thus reducing the cost-effectiveness of the process. Finally, as much oil as possible is now extracted from all refinery waste streams. As a result, the thermal value of the various sludges has decreased to

such a point that combustion is no longer self-sustaining or is only marginally so. Continued operation of incinerators thus requires additional thermal energy. Therefore, incineration should not be considered a panacea for the disposal of DAF float, especially in light of the high demand for an uncertain supply of oil in this country.

4. Resource Recovery

As the price of oil increases, resource recovery becomes more attractive. Resource recovery involves three different strategies for managing oil in refinery waste streams: direct reuse, product reclamation, and oil rerefining. Because the oil in DAF float comes from so many different processes and is so variable, product reclamation is not applicable. Reuse and rerefining are applicable, however.

The extent to which oils can be reused is determined, in part, by their composition and condition. Thus, reuse potential must be evaluated on a case-by-case basis. DAF waste oils may be useful as form release oils for concrete pouring operations and as raw materials for asphalt production. They have also been used successfully in several areas to control dust and weeds and to provide considerable surface consolidation to unpaved roads. However, road oiling can result in substantial environmental contamination, since 70 percent to 90 percent of untreated waste oil applied is transported to the atmosphere on dust particles or to surface water via runoff (Fennelly et al., 1977). This reuse may constitute disposal under RCRA Section 3007 regulations.

In some cases, rerefining waste oil is more cost effective than finding an environmentally safe use. Waste oil very low in solids can be returned directly to the slop oil recovery system in the refinery. Otherwise, it must be pretreated. The American Petroleum Institute has outlined nine basic processes for handling recovered oils from oil-water separators, slop emulsions, and other refinery sources (API Manual on Disposal of Refinery Wastes: Liquid Wastes). The cost and suitability of each process for recovering DAF oils would vary widely between refineries and must be evaluated on an individual basis. Nevertheless, rerefining has proved to be technically and economically successful both in the petroleum refining industry and in other industries.

A western Pennsylvania steel mill refines an average of 50,000 gallons of used hydraulic oil a year. The oil is collected and settled in a large storage tank. Then it is processed in a package rerefining unit that filters the oil and vacuum distills the filtrate. This process produces a distillate and a reusable hydraulic oil. The cost of the operation is 14¢ per gallon, for a savings of 16¢ per gallon or \$8,000 per year (Mann et al., 1970).

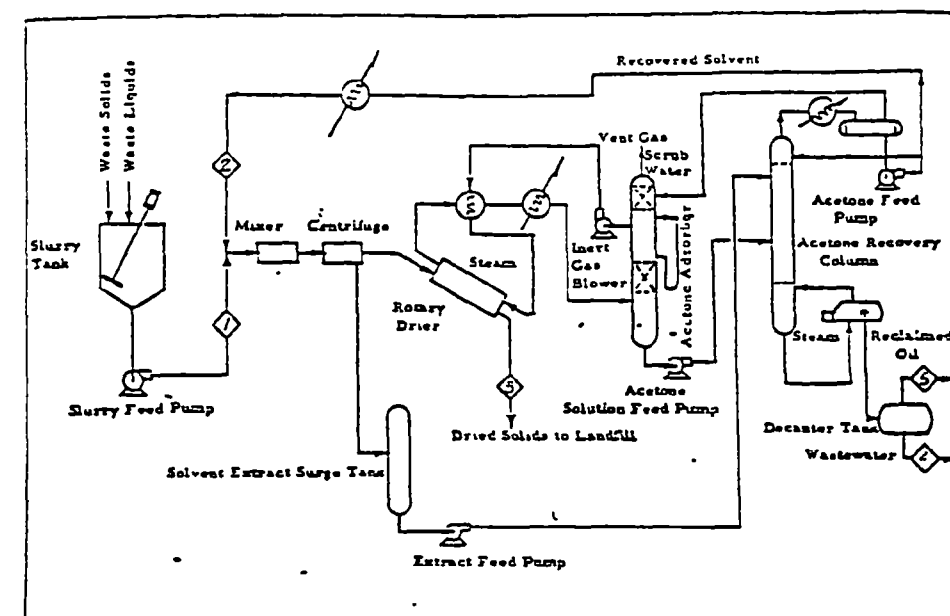
Jacobs Engineering Co. (JEC) has designed an oil recovery system that can be used to process all oily wastes from a typical refinery. Figure 3.15 is a process flow diagram of this system. This approach is notable because it considers all refinery wastestreams and not just ones with very high oil contents. JEC estimates treatment costs with this system to be \$6.90 per wet metric ton or \$36.13 per dry metric ton, making it only slightly more costly than either incineration or land disposal (Tarnay and Krishnan, 1978). These costs are based on a value of recovered oil of \$8 per barrel. As the price of virgin crude rises on the world market, so too will the price of recovered oil. Consequently the unit cost of recovering oil will decrease somewhat, making the re-refining of oily wastes in the industry more attractive.

The trend to more recovery of oil is most apparent with regards to waste oils. In Massachusetts in 1975, 23 percent of the waste oils generated in the state was reclaimed; 13 percent was used for dust control; and 4 percent was used in making asphalt. Almost 52 percent was used as fuel, either in industrial burners or in incinerators. Only 4 percent was landfilled and most of that was spilled oil contained on absorbing media (Fennelly et al., 1977).

In summary, the basic technology for recovering oil from wastes presently exists. However, the cost-to-benefit ratio is not always favorable. As the price of crude oil continues to increase, this situation will change, making oil recovery more economical.

3.6.5.4 Methods Suggested by Related Technology

Two recent innovations in landfill design for other kinds of industrial wastes may be applicable to oily wastes. The first involves



Sample Point	(1)	(2)	(3)	(4)	(5)
Sample Description	Waste Slurry Feed	Acetone Solvent ⁽¹⁾	Dried Solids	Wastewater	Reclaimed Oil
Components -					
Acetone					
kg/hr		7,647	0.1		
lbs/hr		(16,823)	(0.2)		
Oils					
kg/hr	807		14		793
lbs/hr	(1,773)		(31)		(1,745)
Water					
kg/hr	1,608		16	1,584	
lbs/hr	(3,520)		(35)	(3,485)	
Solids					
kg/hr	568		568		
lbs/hr	(1,250)		(1,250)		
TOTAL:					
kg/hr	2,975	7,647	598.1	1,584	793
lbs/hr	(6,543)	(16,823)	(1,316)	(3,485)	(1,745)

(1) - Rate Varies with Slurry Composition.

Figure 3.15 Process Flow Diagram of a General Oil Recovery System for Refining Wastes (Tarnay and Kirshnan, 1978)

2. DAF Operations

- Are volatile components emitted in harmful quantities during the operation of the DAF unit or during storage of the scum?
- If there are harmful air emissions, what can be done to reduce them?

3. Oily-waste Landfills

- Is the concept of using an "absorption barrier" in landfills that receive oily wastes worth pursuing?
- If it is, what is the best absorptive media in terms of capacity, long-term stability, and cost-effectiveness?

4. Rerefinability

- Are all DAF scum oils technically and economically rerefinable?
- What unusable wastes will be produced from rerefining? And how can these wastes be safely disposed of?
- Is the phase separation system developed by Jacobs Engineering Co. practical?

Because the composition and generation rate of DAF float is so variable, environmentally-safe, cost-effective, treatment/storage/disposal processes for each refinery must be developed on an individual basis. This is especially true for the treatment and storage options. Furthermore, greater emphasis should be placed on ensuring that the operation of DAF units and the temporary storage of DAF float does not contribute to air contamination.

Unlike treatment and storage procedures, disposal methods can be evaluated in more general terms because they are not so dependent on the composition of the waste. Table 3.24 lists the primary advantages and disadvantages of the disposal methods now used for DAF scum. Table 3.25 rates the potential for air, land, and water contamination from each method. Table 3.26 gives estimates of the costs of the methods. Based on these tables, sanitary landfilling appears to be a

use of gravel "drainage blankets" between layers of sludge in conjunction with a leachate collection/treatment system to manage waste from the pulp and paper industry (Ledbetter, 1976). The second relies on a "neutralization barrier" of limestone particles to stabilize sludges from the electroplating industry that contain heavy metals (Crumpler, 1977). In place of the gravel and limestone used in these designs, perhaps some oil-absorbent medium could be used. Straw, perlite, chalk, diatomaceous earth, talc, polyurethane foam, pine bark, sawdust, peat, composted refuse (Vaux, et al., 1971), silt, and paper processing sludge (Jones, 1975), are all useful for absorbing oil. Use of an oil absorption barrier in a sanitary landfill might provide increased environmental safety at only a moderate increase in cost. However, none of these media have been used for this purpose in a landfill, and their long-term effectiveness is unknown.

3.6.6 Recommendations

Although quite a bit of information concerning treatment, storage, and disposal of DAF float has been presented, there are gaps in the data. JRB has defined four areas of inquiry: the waste stream, DAF operations, oily waste landfills, and rerefinability. Within each area, we have also developed a set of questions to help direct future research activities. The areas of inquiry and research questions are as follows:

1. Waste stream

- What are the physical and chemical characteristics (and variability) of the oils in DAF float?
- What are the concentrations (and variabilities) of the trace substances listed in Tables 3.18 and 3.19 in the oil, water, and solid fractions?
- What are the physical characteristics (e.g., density, degree of emulsification, volatility, ignitability) of the waste?

simple, cheap method of disposal that has a relatively high potential for polluting the environment. Secure landfilling is a bit more complex and much safer environmentally, but it is very expensive. Incineration can be pollution-free if residues are managed properly, and comparable to sanitary landfilling in cost. Reuse can be the most cost-effective, method also yielding the most pollution. Rerefining is safe, but slightly more expensive, and not applicable in all cases.

Any of these techniques can be suitable for disposing of DAF float if implemented correctly. However, rerefining provides both safe disposal and an environmentally-optimum method. Where practical, JRB recommends that refineries recycle DAF skimmings and all other oily wastes as well.

Table 3.24 Summary of Environmental Effects of Disposal Methods for DAF Float

Method	Advantages	Disadvantages
Sanitary landfilling and lagooning	<ul style="list-style-type: none"> • Technology is well established • Operation is simple • Existing sites are very available throughout the country 	<ul style="list-style-type: none"> • Potential for environmental contamination is high • May become a long-term liability • Not suitable for all hazardous wastes • Public opposition may be high
Secure landfilling	<ul style="list-style-type: none"> • Technology is fairly well established • Potential for environmental contamination is low • Suitable for most hazardous wastes 	<ul style="list-style-type: none"> • Successful implementation of the method can be difficult • Existing sites are relatively scarce • Finding suitable sites can be very difficult • Site volumes are generally limited • Perpetual care is needed because of the hazardous nature of the wastes • Public opposition may be high
Landspreading	<ul style="list-style-type: none"> • Technology is fairly well established • Operation is fairly simple • Site may be able to be returned to another use 	<ul style="list-style-type: none"> • Finding suitable sites may be difficult • Not suitable for all hazardous wastes • Site volumes limited by waste decomposition rates • Potential for environmental contamination can be high • Public opposition may be high
Incineration	<ul style="list-style-type: none"> • Technology is well established • Operation is relatively simple • Existing sites are fairly available throughout the country • Decreased total volume of wastes for final disposal • Suitable for many hazardous wastes 	<ul style="list-style-type: none"> • Potential for environmental contamination is low with adequate controls • May require supplemental fuels • Public opposition may be high • Residues must be disposed • Potential for mechanical failure can be relatively high
Resource recovery	<ul style="list-style-type: none"> • Technology is fairly well established • Potential for environmental contamination is lower because there is less waste • Public opposition would be low • Could help to reduce somewhat the U.S.'s dependence on imported oil 	<ul style="list-style-type: none"> • Successful operation may be complex • Not suitable for many hazardous wastes • Residuals still must be disposed of • Recovered oil may cause problems in some refinery processes

Table 3.25 Summary of Potential Emission Levels from Disposal Methods for DAF Float

Method	Potential For Release To		
	Air	Land	Water
Sanitary landfilling and lagooning	<u>Low</u> (landfilling) to <u>High</u> (lagooning)--depends on the thickness and permeability of the cover material used (for landfills), on the quality of waste management; and on the volatility of the wastes	<u>Moderate</u> --some release of contaminants is likely depending on soil permeability	<u>Moderate</u> --(same as for land)
Secure landfilling	<u>Low</u> --depends on the speed and success of waste-cell construction	<u>Low</u> --assuming that the liner or geologic control remains intact and that water is kept out of the site	<u>Low</u> --(same as for land)
Land treatment	<u>High</u> --direct release of contaminants to the air; volatile components may reach high concentrations	<u>High</u> --direct release of contaminants to the soil	<u>Moderate</u> --depends on the site's geologic and hydrologic conditions; could be very low at well selected, well managed sites
Incineration	<u>Low</u> --assumes proper residence and temperature for the incinerator. Adequate measures taken for controlling air pollution	<u>Low</u> --assumes adequate disposal method used for solid residues	<u>Low</u> --assumes adequate treatment and disposal of scrubber waste-waters
Resource recovery	<u>Low</u> --assumes adequate controls used during reuse of recovery	<u>Very high</u> --if used as a dust control measure. <u>Low</u> --if rerefined	<u>Low</u> --with rerefining

Table 3.26 Summary of Costs of Disposal Methods for DAF Float

Cost per metric ton in
second quarter 1979 dollars

<u>Method</u>	<u>Wet basis</u>	<u>Dry basis</u>	<u>References</u>
Sanitary landfilling	6.60 45.42	34.54 ₂ 237.84 ₂	Tarnay and Krishnan, 1978 Rosenberg et al., 1976
Secure landfilling	20.24 77.05	105.98 ₂ 403.48 ₂	Tarnay and Krishnan Rosenberg et al.
Landspreading	9.98 19.90	52.28 ₃ 104.20 ₂	Bratby, 1977 Rosenberg et al.
Incineration	6.73 ⁴	36.43 ⁴	Tarnay and Krishnan
Resource recovery	8.44	44.21	Tarnay and Krishnan

1. All costs were derived from 1976 dollars, multiplying by 1.2237 (except as noted).
2. Calculated for DAF float only; the other costs in this table assume that most refinery wastes would use the same disposal system.
.. These values were inflated from 1973 dollars to 1979 dollars, multiplying by 1.5463.
3. Average of six values first converted from \$/ton to \$/metric ton and then inflated from 1972 dollars to 1979 dollars, multiplying by 1.6379.
4. These costs do not include the cost of waste disposal from incineration and air pollution control.

3.7 WASTEWATER TREATMENT SLUDGE FROM THE ELECTROPLATING INDUSTRY

In 1976, there were a total of 2,254 electroplating and metal finishing industry job shops in the United States. An EPA study indicated that 89 percent of the job shops are small and medium-size plants with 1 to 50 employees (EPA, 1976a).

3.7.1 Manufacturing Process and Waste Stream Characterization

Most electroplating or metal finishing operations involve a series of unit operations that includes prefinishing, finishing and postfinishing. There are a total of 12 electroplating and finishing processes, with most of the operations being electroplating. An average of four different metals or alloys are deposited per job shop (EPA, 1976a).

Prefinishing operations prepare the piece for plating by removing all foreign matter, such as oil, grease, dirt and oxide, that could retard or prevent the plate from adhering to the workpiece surface. This operation includes deburring, degreasing, acid pickling, and alkaline cleaning. Finishing operations include application of one or more electroplates, such as copper, chromium, nickel, zinc, or anodizing, and electroless plating. Postfinishing operations include bright-dipping, passivating, chromating, phosphating, buffing and polishing.

The services offered by this industry, listed under SIC 3471, vary from a single operation to multiple-step processing. A simple electroplating process generally includes sequential operations of cleaning-rinsing-plating-rinsing-drying. Very complex operations require a number of cleaning steps with additional steps of acid dipping, striking, activation, multiple rinses and deposition of more than one metal. Figure 3.16 is a flow chart for a typical electroplating facility (EPA, 1978a). Cleaning prepares the piece for plating by removing all foreign matter. Abrading, pickling, and other preliminary treatment is often necessary, followed by rinsing to remove pretreatment solutions. Rinsing enhances surface adhesion and prevents contamination of plating

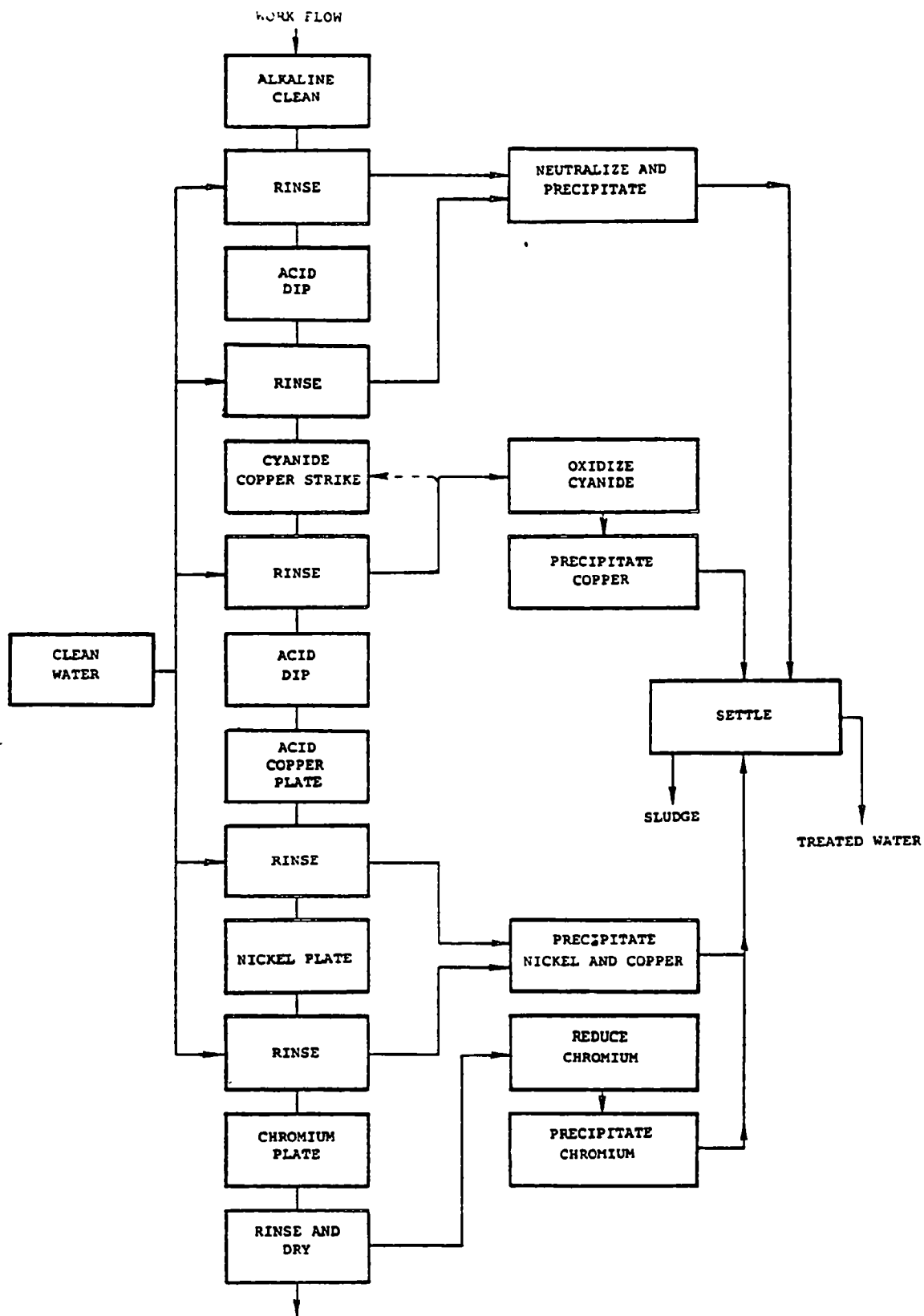


Figure 316 Process Flow For a Typical Electroplating Facility

solutions. At the end of the plating process, all workpieces are rinsed before being allowed to dry, to avoid spotting.

The primary source of pollutants in the electroplating industry is the process solution drag out from workpieces as they are moved from tank to tank in plating operations. Drag out appears in rinse waters, spent process solutions, and in spills and leaks from the process tanks. Rinse waters, representing 90 percent of water usage in electroplating processes, become polluted with drag out from various process tanks and are discharged (EPA, 1978a),

Toxic substances accumulating in the rinse water, or used in the plating solutions, often find their way into plant wastewaters through accidental spillage or tank leaks, intentional tank dumpings, drag out from one tank to another, periodic cleaning and replacing of filters and vapor sprays or mist collection systems.

Closer supervision of the electroplating process will reduce accidental spillage and leaks, toxic vapors, and losses from the cleaning of filters. Drag out is a more difficult and continuous problem resulting from the transfer of racks or barrels from one solution to another and is the major source of pollution. Intermediate rinsing solutions become contaminated with solutions from previous tanks, necessitating periodic dumpings. However, the volume of plating and the type of process used are important elements in determining the amount of pollution.

The estimated quantities of potentially hazardous water pollution control sludge generated from the electroplating and metal finishing industry for 1975, and projected for 1977 and 1983, are given in Table 3.27 (EPA, 1976 b). The 56,399 metric tons (dry weight) represents nearly three times the sludge quantity in 1975. Only an estimated 35 percent of the total electroplating and metal finishing plants produced water pollution control sludge in 1975. Regulations which have taken effect since 1975 require wastewater treatment, resulting in production of more of these sludges.

Table 3.27 Production of Water Pollution Control Sludge From the Electroplating and Metal Finishing Industry (Job Shops)

<u>Year</u>	<u>Sludge (Dry Weight)</u>	
	<u>Metric Ton (ton) Per Year</u>	
1975	19,740	(21,764)
Projected 1977	56,399	(62,182)
Projected 1983	73,882	(81,458)

Water pollution control sludges are the single largest waste streams destined for land disposal in the electroplating and metal finishing industry. The sludge contains solids levels ranging from less than 5 to more than 20 percent, depending on water pollution control technology and degree of sludge dewatering employed. The liquid portion includes rinse waters from each plating step and process solutions such as alkaline cleaners, acid dips and pickles, and conversion coating solutions, and may contain significant concentrations of cyanides. Solids in the sludge are precipitated metal hydroxides. Metal hydroxides found in this wastewater sludge, and their comparative values, are shown in Table 3.28.

Table 3.28 Metal Hydroxide Wastes in Water Pollution Control Sludges From the Electroplating Industry (1975)

<u>Metal Hydroxide</u>	<u>Percent*</u>
Iron	12.36
Copper	8.88
Zinc	12.72
Nickel	17.90
Aluminum	10.65
Chromium	33.37
Cadmium	1.73
Tin	0.14
Lead	1.98
Manganese	0.03

*Calculated from the total quantity of hazardous metal hydroxide wastes generated in the water pollution control sludges from the electroplating and metal finishing industry (job shops); metric tons; dry weight; 1975 (EPA, 1976 b). It does not reflect waste production from any one plant.

Although destruction of cyanides through chlorination is practiced in the industry, certain cyanide complexes require longer reaction times and large amounts of oxidizing chemicals to insure removal from

wastewater streams. Thus, it is likely that significant concentrations of cyanides are disposed with the wastewater treatment sludge. Simple compounds such as sodium or zinc cyanide are more easily broken down by chlorination than silver, gold, nickel and cobalt salts. Iron cyanides are not amenable to treatment by chlorination, but they are not as toxic as most cyanides (National Commission on Water Quality, 1975).

There is no indication of changes in the unit operations and technology of the electroplating and metal finishing industry, and no sudden changes are expected in the foreseeable future. Therefore, characteristics of the water pollution control sludge are not expected to change to any significant degree in the near future. Indiscriminate mixing of spent process solutions from pre- and postplating operations can make waste streams extremely variable, however, and this might overload and upset wastewater treatment system performance and efficiency.

The quantity of sludge generated in an electroplating and metal finishing plant is not uniform for any given process because drag out and spillage vary from plant to plant. Wastewater and sludge volumes depend on the total production of the electroplating and metal finishing industries.

There is no by-product other than sludge generated from the wastewater treatment plant in the electroplating and metal finishing industry.

Water pollution control sludge in the electroplating and metal finishing industry is suspected to be reactive and volatile because it contains various heavy metal hydroxides and may contain cyanide compounds. An EPA report indicates that chromium metal ions, which are present in many electroplating sludges, are hazardous to man in various valence states. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates also have corrosive effects on the intestinal tract and can cause inflammation of the kidneys (EPA, 1974a). Chromium (VI) is a known carcinogen.

Specific data on toxic effects of sludge waste from the electroplating and metal finishing industry which is destined for land disposal are very sparse, and little is known about possible synergistic effects.

The most widely accepted basis for defining many of these materials as potentially hazardous is the relatively low acceptable levels of the various metals in drinking water. Criteria for public water supplies issued by the U.S. Environmental Protection Agency are shown in Table 3.29. Water containing any of these metals in concentrations equal to, or more than, that listed is considered hazardous to health. On this basis, all known wastes from electroplating and metal finishing operations have the potential to contaminate ground water to hazardous levels.

Bioconcentration is the selective concentration, or storing, of a specific chemical species by an organism. Studies show that several substances in wastes from the plating industry can be retained and stored by organisms at harmful levels. These include cadmium, lead, and mercury (EPA, 1977c).

Mutagenic or teratogenic materials are not widespread in electroplating industry wastes. Other than chromium (VI), a few other suspected carcinogens may be present, although trichloroethylene is the only suspected carcinogenic agent in common use in this industry. Mutagens cause changes within the genes. The literature indicates that nitrates are probably the only suspected mutagens which may be present in the wastes of these industries. A teratogenic effect is one creating abnormalities during gestation. According to the National Academy of Sciences, teratogenic effects are usually seen only at doses well above likely exposure levels for environmental chemicals such as solvents, and some compounds of mercury, lead, cadmium, and other metals (NAS, 1975).

Table 3.30 summarizes treatment, storage, and disposal technology which is, or may be, applicable to the water pollution control sludge waste stream from the electroplating and metal finishing industry. The current practice is solids concentration through the use of lagoon and holding tank settling to produce a 1 to 5 percent solids sludge for disposal in a landfill. Approximately 60 to 70 percent of the plants use off-site disposal for their sludge (EPA, 1976b). Although a few plants may use advanced treatment techniques such as chemical fixation, solidification, etc., common practice is to utilize the simplest, least expensive disposal techniques acceptable to pertinent regulatory

Table 3.29 Criteria for Public Water Supplies

Waste Constituents	Permissible Concentrations, ppm
Arsenic	0.05
Beryllium	0.2
Cadmium	0.01
Chromium (hexavalent)	0.05
Copper	1.0
Cyanide	0.01
Gold	0.4
Iron (filterable)	0.3
Lead	0.05
Manganese (filterable)	0.05
Mercury	0.004
Nickel	0.8
Oil and Grease	7
Palladium	7
Phosphates	545
Selenium	10.01
Silver	0.05
Sulfates	250
Tin	1.2
Zinc	5.0

Table 3.30 Summary of Treatment, Storage, and Disposal Technology for Water Pollution Control Sludge From the Electroplating and Metal Finishing Industry

<u>Practices</u>	<u>Current or Broad Average</u>	<u>Best Available Technology</u>	<u>Suggested By Related Technology</u>
Treatment	Concentration to 1-5 percent solids through the use of lagoon, holding tank or clarifier settling	Sludge is concentrated to >20 percent solids through the use of centrifugation or filtration	Chemical fixation/solidification
Storage	Holding lagoon	Steel drums	Encapsulation
Disposal	Lagoon or landfill	Approved landfill	Secured landfill or reclamation

agencies. This generalization applies to both the industry and to waste disposal contractors. Discussions of levels of treatment, and storage and disposal technology applicable to the water pollution control sludge are included in the following sections.

3.7.2 Treatment Alternatives

3.7.2.1 Current Practice

The usual practice employed to separate treated wastewater is to concentrate solids through the use of simple settling using lagoons, holding tanks or clarifiers to create a 1 to 5 percent solids sludge for disposal. Table 3.31 shows the treatment methods used by the 30 job shops in a survey reported in a 1976 EPA study. Thirteen of the 50 plants (26 percent) used holding tanks to separate the sludge from the treated wastewater.

Table 3.31 Treatment Methods Used by Fifty Job Shops to Separate Solids From Treated Wastewater (EPA, 1976b)

Treatment Method	No. of Plants	Percent
Lagoon	8	16
Holding Tanks	13	26
Tank and Clarifier	4	8
Clarifier and Dewatering	2	4
Direct Dewatering	10	20
Unknown	13	26
Total Plants	50*	

*The number of shops reporting disposal was 50; more than one treatment is used in some shops.

Lagoons may be natural water bodies or man-made water bodies constructed either by digging out a depression in the earth or by erecting dikes. Most lagoons used in waste disposal operations are man-made on specific selected sites. The lagoon may be unlined, or it may be lined

with clay or plastic sheets overlaid with about 1 foot of gravel. Lagoons are used for clarification of both chemical plant process waters and wastewaters, and can concentrate solids to 1 to 5 percent. Settling or thickening lagoons are used when conventional units are overloaded or, sometimes, as substitutes for conventional processes.

As the basins fill, they are cleaned and the sludges removed and discarded, or the sludges are left to dry in the basin and new basins are constructed. If the liquid portion of the waste can contaminate groundwater, the lagoon bottom must be sealed to prevent leakage.

Instead of settling wastewater in a lagoon over a period of months or years, some plants dewater their slurries to sludge immediately. This treatment is used when: land is not available or is too expensive for lagooning; states prohibit lagooning of these wastes; or lagoons may overflow, leak or break. In many instances, dewatering is the only treatment available. The degree of dewatering depends on the local situation, particularly on the distance between the plant and disposal site.

The least complex treatment method is a holding tank in which solids may be concentrated to about 1 to 2 percent. A thickener or clarifier may be used to treat overflow from the tank to increase density of slurries. This operation can increase the solids content to about 2 to 3 percent. These thickening slurries may be sent directly to a lagoon or landfill, or may be further treated by filtration or centrifugation. Slurries may also bypass tank settling and/or thickening and be processed by direct dewatering.

3.7.2.2 Best Available Technology

The best treatment technology for electroplating water pollution control sludge involves concentration of solids and dewatering to levels of 20 percent or more. The dewatering operation utilizes filtration or centrifugation to produce a high solids, lower volume sludge cake for ultimate disposal. Rotary vacuum filters can concentrate sludge containing 4 to 8 percent solids to 20 to 25 percent solids (EPA, 1976^b). Because the effluent concentration of solids is usually less than 4 percent, a

thickener tank is often employed between the clarifier and the filter. The filtrate often contains excessive suspended solids and is recirculated to the clarifier.

Centrifuges can also thicken sludges to 20 to 25 percent consistency, and have the advantage of using less floor space. The effluent contains suspended solids in excess of 20 mg/l and needs to be recirculated to the clarifier.

The same solids content can also be attained with pressure filters. This filtrate contains less than 3 mg/l of suspended solids so return to the clarifier is not needed. Semicontinuous tank filters may further increase solids content to as high as 35 percent. Plate and frame presses can produce filter cake of 40 to 50 percent solids, while automated tank type pressure filters will produce the highest solids content waste of about 60 percent (EPA, 1976 b).

An estimated 24 percent of the plants employ centrifugation and filtration to dewater their sludge prior to land disposal (EPA, 1976). The choice of dewatering technique is highly dependent on economics, available space, or environmental limitations imposed on the ultimate disposal site.

An EPA study estimated capital investment costs in centrifuge system and operating costs for waste handling and disposal at three model electroplating and metal finishing plants of different sizes (EPA, 1976). These costs are shown in Table 3.32. Model plant operations were based on 250 working days per year, and costs are in December 1973 dollars. The centrifuge systems were designed to dewater the sludge to 20 percent solids. Capital and operating costs for filter units which thicken sludge to the above range of consistency would be comparable to those for centrifuges.

Table 3.32 Estimated Centrifuge System Capital and Operating Costs For Three Different Size Electroplating and Metal Finishing Model Plants

<u>Model Plant Size</u>	<u>Amount of WPC Sludge 20% Solids Metric Ton/Year</u>	<u>Installed Centrifuge System Cost</u>	<u>Cost of Handling and Disposal of Wastes*/Metric Ton</u>
Small (16-man)	76.25	\$ 7,150	\$129.57
Medium (38-man)	176.00	19,500	122.22
Large (87-man)	353.00	48,700	115.96

*This represents the total cost for collecting, hauling, handling and landfill disposal for the wastes.

3.7.2.3 Methods Suggested by Related Technology

Chemical fixation utilizes a physical chemical matrix structure to tie up hazardous liquids and solids for disposal. Sludge may be solidified by addition of chemical fixing agents which insolubilize the metal hydroxides, and thus prevent or retard leaching of the waste in the environment. Approximately 2 percent of all plating sludges are treated on-site by the chemical fixation and solidification treatment techniques (EPA, 1976b).

Chemical fixation/solidification is a process that involves mixing cementing agents such as Portland cement, lime-pozzolin cements, lime-based mortars, certain mixed organic polymers or inorganic compounds to produce a friable, solid-like material which may be acceptable for landfill. After mixing the cementing agent with the semi-solid lagoon sludge, the mixture is pumped out on land for solidification. It is then disposed as landfill. A number of firms offer chemical fixation/solidification commercially. Some processors have portable equipment for on-site treatment at a client's plant (Fields and Lindary, 1974). Units are also sold for permanent installation at sites requiring continuing processing of wastes.

Costs for fixation and solidification of industrial wastes vary widely, depending on such factors as the process used, type of waste, transportation costs, equipment renting, and landfilling costs.

A typical price range given by several waste processors for treating an industrial waste is from \$8.00 to \$20.00 per metric ton of waste (Crumpler, 1977).

The advantages for using this method for plating wastes are:

- commercial availability and applicability to both large and small sludge generators
- low cost of fixation
- decreased leachate production
- stabilization of wastes so that metal ions do not migrate
- ease of disposal
- reduced disposal cost, since fixed solidified material may be acceptable for general landfill.

3.7.3 Storage Alternatives

3.7.3.1 Current Practice

The most prevalent storage practice in the electroplating and metal finishing industry is lagoon storage. The wastes stored in the lagoons include both liquids and sludges, including water pollution control sludge. The lagoons are usually located on company owned lands. It is estimated that more than 30 percent of the plants store waste sludge in lagoons on a short-term basis (EPA, 1976b). This technique provides a simple and economic approach to on-site waste disposal, where applicable. However, there are significant drawbacks.

- The lagoons must provide protection from both surface and groundwater contamination. In almost all areas this means a lined pond. Liners include clay, plastic, concrete and epoxy, all relatively expensive.
- Lagoons are prone to be "flushed out" with massive rainfall. It is difficult and expensive to provide flood protection.
- Except in very dry climates, lagoons that do not normally discharge will overflow after rainfall.

3.7.3.2 Best Available Technology

Containerization of water pollution control sludge in steel drums prior to disposal is considered the best storage technique for the electroplating and metal finishing industry. Both plastic lined and unlined drums and barrels are used. A 1976 EPA study estimated less than 4 percent of the plants in this industry employ this storage method.

Steel drums provide some long-term containment and are the most convenient storage and transportation mode for relatively small quantities of potentially hazardous wastes. Drum burial procedure usually entails filling the drum with the waste, sealing the drum, transporting drums to the disposal site and, finally, land storage or land burial. The obvious problem with this method is eventual decay of the steel drums. Unless disposed of in an approved or secured landfill, future release of drum contents to the environment is likely.

3.7.3.3 Methods Suggested by Related Technology

Encapsulation and cementation of potentially hazardous waste are special disposal safeguards currently employed for only the most hazardous wastes, such as nerve gas, biological warfare agents, radioactive wastes, etc. If permanent storage is required, these techniques could be used to transform waste pollution control sludge for ultimate disposal. At present, there is no indication that these techniques are employed for the water pollution control sludge in the industry. EPA found that one waste disposal contractor actually uses concrete encapsulation for disposal of small quantities of plating wastes so that the waste is isolated from the environment. It is assumed that less than 1 percent of the total quantity of the plating waste is disposed utilizing this technology (EPA, 1976b). A detailed discussion of encapsulation and cementation techniques is presented in Section 3.2.3.3. The cost of encapsulation is estimated to be approximately \$40 to \$85 per ton of dry waste (Buck, et al., 1974). This cost is based on 1973 dollars.

3.7.4 Disposal Alternatives

3.7.4.1 Current Practice

The usual disposal practice for water pollution control sludge after solids concentration treatment is simple land disposal, including surface and deep burial, open dumps, lagoon and municipal landfills. EPA estimates that 59 percent of the plants employed this simple land disposal method both on-site and off-site. Sixty-six percent of the plants employ off-site disposal (EPA, 1976).

This disposal technique is considered inadequate for health and environmental protection, because of potential contamination of groundwater or surface water supplies. The waste sludge is mainly an aqueous slurry of metal hydroxides, and when exposed to an acid environment, metals re-enter solution. The metal ions can then migrate to groundwater, by way of rain water percolating through the land disposal site.

A summary of contractor hauling, treatment, and disposal charges for electroplating and metal finishing sludges for a simple or municipal landfill is presented in Table 3.33.

3.7.4.2 Best Available Technology

The best available disposal technology for water pollution control sludge is an approved sanitary landfill. An EPA study reported that about 4 percent of the plants employed this method for off-site disposal (EPA, 1976b). These landfills meet the criteria under Section 4004 of RCRA as well as Section 3004 criteria as given in the Federal Register of Thursday, September 13, 1979, while Section 3004 criteria were under development as of August, 1980.

Disposal of water pollution control sludges in an approved sanitary landfill is considered adequate for short-term disposal. Long-term protection cannot be assured since surface run-off and rain water can percolate through the disposal area, leading to leachate formation (EPA, 1976b).

Estimated costs for contractor disposal at an approved landfill is shown in Table 3.33.

3.7.4.3 Methods Suggested by Related Technology

The disposal technologies considered environmentally adequate for water pollution control sludge include use of secured landfill and materials reclamation. A secured landfill employs basic site selection and leachate control procedures described for an approval landfill, with additional safeguards discussed in the previous section. Estimated cost for disposal in a secured landfill by a contractor is shown in Table 3.33.

Sludges and liquids from electroplating and metal finishing wastes contain valuable metals and other materials which, theoretically, may be recovered by chemical treatment. By reclaiming the dissolved plating metals in the wastewater during the plating operations, sludge formation would be circumvented altogether. At present, no viable techniques for the reclamation of these materials from sludges have been demonstrated on a commercial scale. However, many techniques for metals recovery are currently practiced and techniques for concentrating aqueous liquids, such as reverse osmosis and evaporation, have been demonstrated successfully (EPA, 1976b). Other recovery methods are being tested on bench-scale but have not yet reached commercial scale. These are electrodialysis, freezing, carbon adsorption, ion-flotation techniques, and liquid-liquid extraction (Crumpler, 1977). Other such operations include chemical precipitation and crystallization from solution.

Table 3.33 Summary of Estimated Contractor Hauling, Treatment, and Disposal Charges for Electroplating and Metal Finishing Waste Destined for Land Disposal (EPA, 1976b)

Treatment Technology	Hauling Charge (a)		Contractor Charge For Combined Hauling, Treatment and Disposal (b)		Contractor Charge for Treatment and Disposal (c)		Total Contractor Charge to the Electroplater	
	¢ per liter	¢ per gal	¢ per liter	¢ per gal	¢ per liter	¢ per gal	¢ per liter	¢ per gal
Simple or municipal landfill	1.32	5.0	3.6	13.6	-	-	3.6	13.6
Approved landfill	1.32	5.0	5.0	19.0	-	-	5.0	19.0
Secured landfill	1.32	5.0	-	-	6.9	26.0	8.2	31.0

- (a) This is the charge made by the contractor for collecting and hauling the waste to the disposal site.
- (b) This represents the charge made by the contractor to the electroplater for combined hauling, treatment (if any), and disposal in a landfill. The charge includes landfill fees.
- (c) This is the charge for treatment and disposal of the waste after delivery to the disposal site.

The practicability of reclamation schemes is determined by such factors as recovery costs versus virgin materials costs, energy requirements, the availability of energy, and the cost of environmental protection (EPA, 1976 b).

3.7.5 Recommended Treatment and Disposal Techniques

The most appropriate treatment and disposal methods for the water pollution control sludge in the electroplating and metal finishing industry would be chemical fixation and solidification treatment followed by disposal in an approved landfill.

The advantages of chemical fixation are:

- Wastes may be stabilized so that metal ions are not readily available to the environment.
- Costs of fixation are reasonable (\$8 to \$20 per metric ton of waste).
- The process is commercially available and applicable to both large and small plants.

The advantages of approved landfill are:

- Hazardous heavy metal sludge may be disposed of in a controlled and environmentally safe fashion.
- Selection of landfill sites and disposal technology for environmental suitability still leaves a great number of available landfill sites.
- Disposal costs for transporting sludge to treatment site and landfilling site are at levels close to those for general purpose sites and much lower than for secured landfill.

The disadvantage of the above treatment and disposal techniques is that no resource recovery is practiced. However, it appears that resource recovery may become a viable option in the future. Long-term storage of these sludges may be a feasible alternative to allow subsequent resource recovery of a large volume of wastes.

3.7.6 Environmental Impact

Table 3.34 shows a comparison of emissions of alkali cyanides in wastewater treatment sludge with associated MATE values. The basis for the values is the properties of cyanide which create problems for treatment and disposal. These include a generally low vapor pressure and high solubility in water, and release of hydrogen cyanide from contact with acid.

Table 3.35 compares emissions of chromium from wastewater treatment sludge with its associated MATE values. Properties of chromium include low vapor pressure and low solubility.

These tables are used to show very rough estimates of releases. Although disposal of this waste in steel drums may not appear to provide long-term protection, it was determined to be the best method in practice at this time.

A means of comparing disposal methods for metallic constituents in plating sludge with criteria offered by the State of Illinois is offered in Table 3.36. The Illinois criteria describing methods of disposal for Alternatives I, II and III follows. Assuming a high degree of leachability of the sludge components, the characteristics of an acceptable disposal site may be determined from this comparison.

It appears that an Alternative II disposal site would probably have to be used to dispose of plating sludge in the State of Illinois. Actual laboratory testing of sludge samples, including leachability, would be necessary to verify this.

Table 3.34 Cyanides In Wastewater Treatment Sludge

Estimated Emissions

		Current Practice	Best Available	Transfer of Technology
		Landfill	Sludge dewatering, disposal in steel drums in approved landfill.	Sludge dewatering, encapsulation, disposal in secure landfill.
Media	MATE VALUES			
Air, mg/m ³	Health 5.0	<5.0	<5.0	<5.0
	Ecology _			
Water, mg/l	Health 0.5	>0.5	<0.5	<0.025
	Ecology 0.025			
Land, ug/g	Health 1.0	>1.0	<0.025	<0.05
	Ecology 0.05			

Table 3.35 Chromium In Wastewater Treatment Sludge

Estimated Emissions

		Current Practice	Best Available	Transfer of Technology
		Landfill	Sludge de-watering, disposal in steel drums in approved landfill.	Sludge dewatering encapsulation, disposal in secure landfill.
Media	MATE VALUES			
Air, mg/m ³	Health 0.001	Low	<0.001	<0.001
	Ecology -			
Water, mg/l	Health 0.25	>0.25	<0.25	<0.25
	Ecology 0.25			
Land, ug/g	Health 0.5	>0.5	<0.5	<0.5
	Ecology 0.5			

Table 3.36 Comparison of Plating Sludge Metallic Constituents With State of Illinois Criteria

	Concentration in Dry Sludge mg/kg	Criteria for Alternative I	Criteria for Alternative II	Criteria for Alternative III
Iron	6,180			
Copper	4,440	500	2,000	6,000
Zinc	6,360	250	750	2,250
Nickel	8,950	200	600	1,800
Aluminum	5,325			
Chromium	16,685	500	2,000	6,000
Cadmium	865	150	450	1,350
Tin	700			
Lead	990	275	825	2,475
Manganese	15			

Assumptions: (1) 5% solids in sludge.

- (2) Constituent concentrations in plating sludges calculated from information in the discussion of chemical composition of sludge.
- (3) Illinois criteria stipulates that allowable concentrations may double if waste contains greater than 2.5 percent excess lime alkalinity and quadruple if 5 percent.

The following offers additional explanation of Table 3.36 and was taken from Illinois Pollution Control Board Rules and Regulations, Chapter 9 Special Waste Handling Regulations, Supplemental Permit System, and was promulgated on March 15, 1979. (Illinois, 1979):

"Waste components are examined to determine the major contaminants, their environmental pollution potential, and the suitability of the proposed disposal method and site. Waste containing higher leachable heavy metals (as determined by Agency leach test procedures) or significant toxic chemicals concentrations are required to utilize more conservative disposal methods and sites with better geology to minimize potential environmental harm.

Criteria applied to wastes containing significant leachable heavy metals (up to those values in Alternative I) allows for co-disposal with municipal waste, above grade, at a site with at least ten feet of underlying soils with a permeability of 1×10^{-7} cm/sec or less. Wastes containing leachable heavy metals up to those values in Alternative II, may be co-disposed with municipal waste below grade in a site with ten feet of underlying soils with a permeability of 1×10^{-7} cm/sec or less. Wastes with leachable heavy metals up to those in Alternative III may be disposed of in a trench accepting only like materials in a site with at least ten feet on bottom and sides of 5×10^{-8} cm/sec or better soil. Wastes with leachable heavy metals greater than those in Table III must be disposed of in a trench accepting only like materials in a site with at least ten feet on bottom and sides of 1×10^{-8} cm/sec or better soil.

Since no specific criteria relating toxicity to disposal method of organic wastes has been devised, best engineering judgment is applied to all supplemental permit applications. The more toxic the waste, the better the geology, and disposal method required, e.g., a chlorinated organic such as hexachlorocyclopentadiene in any significant concentrations would be required to be containerized, utilize best available geology, and be disposed of in a trench containing only compatible or similar materials. A less toxic and less persistent organic in concentrations which presented no bulk handling problem could be permitted to be disposed of along with municipal waste at a special waste sanitary landfill having underlying soils with the permeability of 1×10^{-7} cm/sec."

3.8 WASTEWATER TREATMENT SLUDGES FROM WOVEN FABRIC DYEING AND FINISHING IN THE TEXTILE INDUSTRY

3.8.1 Manufacturing Process and Waste Stream Characterization

Of the 5366 textile plants in the United States (SIC 2261, 2262) EPA has identified 651 as plants that perform woven fabric dyeing and finishing operations. The typical product is a polyester-cotton blend fabric, although some plants only process 100 percent cotton fabric or only process 100 percent synthetic fabric. The total estimated annual production was about 1,801,000 kkg/year, based on the 1972 Census of Manufacturers (EPA, 1976c). An estimated 56 percent of plants performing woven fabric dyeing and finishing operations have wastewater treatment systems (EPA, 1976c and EPA, 1977d). Therefore, sludges are generated only in facilities having their own wastewater treatment systems. The total estimated quantities of wastewater treatment sludges from woven fabric dyeing and finishing operations in 1977 were 13,661 metric tons (dry weight). This amount is expected to increase to 48,481 metric tons (dry weight) by 1983 (EPA, 1976c).

A typical woven fabric dyeing and finishing process in textile plants includes the following operations:

- singe
- desize
- scour
- mercerize
- bleach and wash
- dye and/or print
- applied finish
- mechanical finish.

A mass balance flow diagram of the typical woven fabric dyeing and finishing process is shown in Figure 3.17. The waste streams generated from the dyeing and finishing process are listed in Table 3.37.

Table 3.37 Waste Streams Generated by Typical Woven Fabric Dyeing and Finishing Plant (EPA, 1976;c)

<u>Waste</u>	<u>Source</u>	<u>Quantity (kg of waste/ kkg of product)</u>
Cloth	Singe and desize	0.2
Cloth	Mercerize	0.1
Cloth	Bleach and wash	0.2
Cloth	Mechanical finish	6
Flock	Mechanical finish	4
Dye containers	Dye and/or print	0.5
Chemical containers	Dye and/or print, applied finish	0.8
Fiber	Wastewater treatment screening	0.8 (dry) 2.8 (wet)
Wasted sludge	Wastewater treatment	20 (dry) 2,300 (wet)
Retained sludge*	Wastewater treatment	67 (dry) 7,300 kg (wet)

*The retained sludge quantity is an accumulation over the life of the pond.

Note: The typical plant produces 5,600 metric tons of product per year.

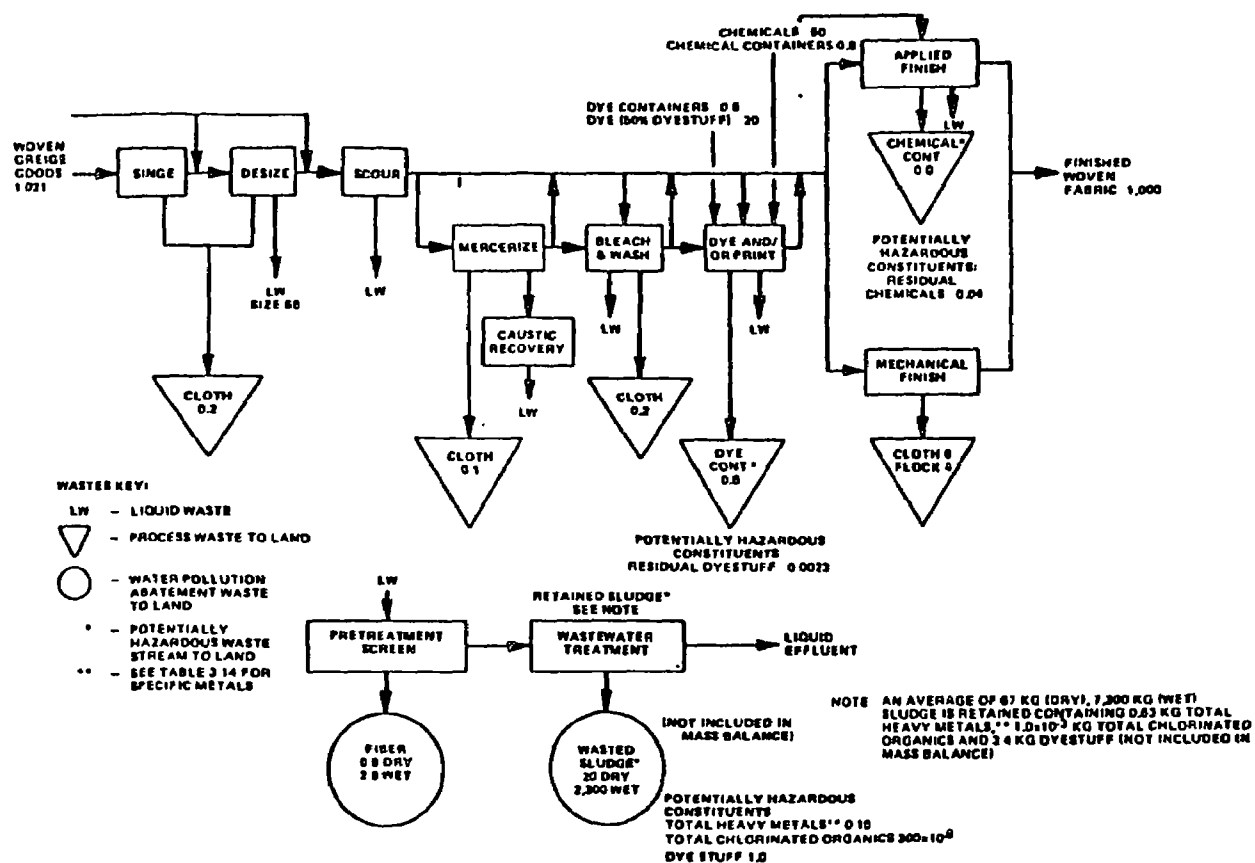


Figure 3.17 Typical Woven Fabric Dyeing and Finishing Process (EPA, 1976c)

Sludges in the wastewater system contain hazardous constituents such as the heavy metals chromium, copper, and zinc and chlorinated organics, and dyestuffs which are considered potentially hazardous.

No by-products are generated from the process. All wastes from woven fabric dyeing and finishing operations are routed to the wastewater treatment system where sludges are produced.

Wastewater treatment sludge has solid concentrations ranging from less than 1 percent to more than 20 percent, depending on the wastewater pollution control technology and degree of sludge dewatering techniques employed (EPA, 1976c). The sludge wastes include some of the many chemicals used in dyeing and finishing operations, such as acids, alkalies, bleaches, adhesives and polymers, cross-linking agents, conditioners, catalysts, detergents, dye carriers, chemical finishes (including flame retardants) and solvents. Solvents commonly used in the operations include acetone, methanol, naphtha, trichloroethane, dioxane, butyl carbitol, and butyl cellosolve. Dye carriers are organic compounds that also appear in the sludge. They include biphenyl, orthophenylphenol, butyl benzoate, methyl salicylate, trichlorobenzene, perchloroethylene, and other chlorinated aromatics (EPA, 1976c). The sludge contains an estimated 75 percent (by weight) of non-hazardous materials such as common salt and sodium sulfate. The hazardous chemical composition of the sludge is shown in Table 3.35. Iron accounted for 52 percent by weight of the total heavy metal content, and zinc accounted for 25 percent of the total heavy metal content according to these measurements. Additional analysis for total chlorinated organics showed 98.8 percent by weight of the total content (15.2 ppm) was found in the solid phase of the sludge, with the remainder in the liquid phase (EPA, 1976c).

Because products in the woven fabric dyeing and finishing operations are ultimately used for apparel, furnishings, and other consumer products, waste projections are closely related to population growth. This is about 3 percent per year (EPA, 1976c). Little or no change is anticipated in the near future in wastewater treatment technology or dyeing and finishing operations for woven fabrics. Therefore, the broad characteristics of the waste stream are not expected to change to any significant

Table 3.38 Woven Fabric Dyeing and Finishing Sludge Chemical Composition

	<u>mg/kg of dry sludge*</u>	<u>mg/kg of wet sludge*</u>
Arsenic	1	0.01
Barium	39	0.56
Cadmium	4.4	0.07
Chromium	1,196	20.43
Cobalt	26	0.26
Copper	652	8.46
Iron	4,910	77.23
Lead	36	0.57
Manganese	128	1.90
Mercury	0.35	0.004
Molybdenum	17	0.2
Nickel	32	0.51
Zinc	2,370	39.92
 Total Heavy Metals	 9,412	
 Aluminum	 4,640	 72.74
Magnesium	2,820	29.59
Potassium	3,580	38.44
Sodium	51,300	525
Strontium	16	0.23
 Total Chlorinated Organic	 15.2	
 Suspended Solids	 0.88	
 Total Solids	 1.26	

*Average of 20 measurements from five points

degree in the near future. However, sludge constituents may vary due to process starting, process shut down, or changing products. When textiles are dyed, a sufficient amount of dyestuff is used to make the shade. Various other chemicals may be used to help deposit the dye, or to develop the color. Dye loading varies widely, depending on the weight of fabrics being treated and the depth of color desired. The range of chemicals employed in dyeing varies widely from plant to plant and process to process, and depends substantially upon the dictates of the marketplace.

Wastewater treatment sludge from woven fabric dyeing and finishing operations is the most complex waste stream generated from the textile industry. It includes such hazardous components as heavy metals, residuals and absorbed dyestuffs, organic solvents and chlorinated organics. Because it contains toxic compounds (heavy metals, chlorinated organics), and ignitable compounds (flammable hydrocarbon solvents), this waste stream is considered potentially hazardous. Although believed to be present, it is not known to what degree flammable hydrocarbon solvents may be contained in the sludge, since this analysis was not shown in the literature.

Cadmium, lead and mercury bioaccumulate in the environment because very low levels of these pollutants can be retained or stored by organisms until harmful quantities are accumulated (EPA, 1977c). Carcinogens, mutagens or teratogens are not widespread in textile industry wastes. However, a few suspected carcinogens may be present depending on use of solvents, dye carriers and finishing agents such as trichlorobenzene, polyvinyl chloride, perchloroethylene and others. A teratogenic effect is one creating abnormalities during gestation. According to the National Academy of Sciences, teratogenic effects are generally seen only at doses well above likely exposure levels from disposed solvents and compounds of mercury, lead, cadmium, and other metals used in textiles manufacturing (EPA, 1977c).

Table 3.39 Drinking Water Limit for Metals and Chlorinated Organics

<u>Parameter</u>	<u>Limit (ppm)</u>
Arsenic	0.05
Barium	1.00
Cadmium	0.01
Chromium	0.05
Copper	1.00
Iron	0.30
Lead	0.05
Manganese	0.05
Magnesium	60.00
Zinc	5.00
Total Chlorinated Organics	0.70

U. S. Public Health Service, Drinking Water Standards, 1962.

3.8.2 Treatment Alternatives

Treatment, storage and disposal methods usable for wastewater treatment sludge from woven fabric dyeing and finishing operations in the textile industry are summarized in Table 3.40. The most prevalent method currently used for the wastewater treatment sludge are lagoon disposal or storage, open dumping, landfill, and landspreading. Most of the sludges are stored (disposed) in unlined lagoons. Land disposal (open dumping, landfill, landspreading), both on and off-site are commonly practiced by the majority of plants. Advanced technology such as use of special landfilling techniques, chemical fixation, incineration, etc., is seldom employed by the industry or off-site waste disposal contractors. Discussions of treatment, storage, and disposal technology which are, or may be, applicable to wastewater treatment sludge are discussed in the following sections.

3.8.2.1 Current Practices

For wastewater pollution control sludges, universal practice in the textile industries would be lagoon or pond settling. This technique produces a sludge with a solids content from 1 to 10 percent. Some of the ponds are used for aeration or activated sludge treatment. The excess sludge is periodically removed and disposed. About 208 plants or 32 percent of those having their own treatment facilities are not using pond settling (EPA, 1976c). Because some 46 percent of the treatment ponds are unlined thus permitting percolation to groundwater, this treatment practice is considered to be environmentally inadequate (EPA, 1976c). Discussion of lagoon or pond settling was presented earlier in Section 3.7.3.1.

3.8.2.2 Best Available Technology

The best treatment technology for wastewater treatment sludge is solids concentration and dewatering to at least 20 percent solids by means of centrifugation and filtration. Presently, the sludge from woven fabric dyeing and finishing is not treated by these techniques. Further

Table 3. 40 Summary of Treatment, Storage, and Disposal Technology for Wastewater Treatment Sludge from Woven Fabric Dyeing and Finishing Operations

Practices	Current or Broad Average	Best Available	Technology Suggested by Related Technology
Treatment	Sludge concentrated to 1-5 percent solids through the use of lagoon or pond settling	Sludge concentrated to 20 percent solids through use of centrifugation or filtration	Incineration
Storage	Unlined lagoons	Lined lagoons	Encapsulation
Disposal	Land disposal (open dump, landfill, land-spreading, or lagoon)	Approved land-fill	Secured landfill

discussions of centrifugation and filtration treatments are presented in Section 3.7.2.2.

3.8.2.3 Methods Suggested by Related Technology

Incineration is another potential treatment alternative applicable to wastewater treatment sludge. The two areas of concern related to sludge incineration are incinerator air emissions, and contaminated ash containing dye and chemical carrier residue and leachable heavy metals (EPA, 1976c). The air emissions probably do not differ greatly from those from incineration of municipal trash or activated sludge, since dyes and chemicals usually constitute a minor portion of the wastes. Therefore air pollution abatement facilities of normal capabilities will be required. The major concern is the incineration end-product, ash, which contains a significant quantity of heavy metal contaminants and is considered a potentially hazardous material. Disposal of the ash in an approved or secured landfill is environmentally adequate (EPA, 1976c). At present, most of the textile plants do not incinerate wastewater treatment sludges because of high costs of environmentally adequate incineration equipment and the high cost of fuel. Detailed discussions of the incineration process are presented in Section 3.2.2.2 and 3.2.2.3. It is estimated that on-site incineration of wastewater treatment sludge from textile industries will cost approximately \$100 to \$300 per metric ton of dye solids, in 1975 dollars, based on charges cited by a contractor (EPA, 1976c).

3.8.3 Storage Alternatives

3.8.3.1 Current Practices

Wastewater treatment sludges from woven fabric dyeing and finishing operations are currently stored or retained in wastewater treatment systems, either in disposal ponds or in the bottom of ponds or lagoons used for aeration and activated sludge treatment. The sludge will eventually reach the capacity of the pond or lagoon and other storage will become

necessary. These storage ponds are usually unlined, which may result in percolation to groundwater supplies (EPA, 1976c). Therefore, present storage technology is considered not environmentally adequate.

3.8.3.2 Best Available Technology

As mentioned previously, storage ponds in the woven fabric dyeing and finishing operations are usually unlined. Lining the ponds would be the best method of preventing leachate from reaching groundwater. This technology is widely used in this and other industries. Lining materials employed can be plastic sheeting, clay or concrete. The disadvantages of this method include possible chemical attack or the inadvertent cracking of pond liner, and costs of lining ponds will be high. Table 3.41 gives estimates of installed costs for various types of pond liners (EPA, 1976c).

A typical pond size used in the woven fabric dyeing and finishing operations is 0.38 hectare (0.9 acres). Estimated costs for cleaning and preparing the typical pond prior to installation of liners are:

	<u>Pond Size</u>
	0.38 ha. (0.9 acre)
Cleaning of existing pond (\$10 per m ³ of removed sludge)	\$18,750
Earthwork on existing pond (\$1 per m ³ of earth moving)	\$ 1,250
	<hr/>
Total Cost	\$20,000

The estimated costs are based on 1975 dollars (EPA, 1976c)

3.8.3.3 Methods Suggested by Related Technology

Encapsulation is used primarily for those hazardous wastes not amenable to other pretreatment methods. Candidate wastes include sludges containing toxic compounds, and arsenic waste compounds. Encapsulation of a waste usually involves packaging and containment of a specific quantity of a hazardous waste to prevent leaching. This is

Table 3.41 Estimated Installed Costs for Various Types of Pond Liners
(EPA, 1976c)

<u>Liner Material</u>	<u>Installed Cost \$/square meter*</u>
Thin Clay liner (2 inch)	2.50
Sprayed asphalt	2.50
20 millimeter PVC	3.70
30 millimeter Hypalon	7.40
Concrete	10.00
Thick Clay liner (2 feet)	10.00

*Estimated costs are based on 1975 dollars.

achieved by forming a watertight jacket around the waste. Materials used to form this capsule include concrete, polyethylene or polyurethane polymers, asphalt and tars. Prior to actual covering, the wastes are usually agglomerated with a binder. Materials that have been used as binders include cement, asphalt, polybutadiene, and other polymers (Wiles and Lubowitz, 1976). Further discussion of the encapsulation technique is presented in Section 3.2.3.3.

This encapsulation technique could be applied for storage of wastewater treatment sludge generated by the woven fabric dyeing and finishing operations. Presently there is no indication that this technique is practiced by the textile industries. Encapsulating a waste could cost an estimated \$40 to \$85 per ton of dry waste (Buck and Lobowitz, 1974). The estimated cost is based on 1973 dollars.

3.8.4 Disposal Alternatives

3.8.4.1 Current Practices

A 1976 EPA study estimates that approximately 68 percent of woven fabric dyeing and finishing operations discharge their wastes into a municipal system without any treatment. Only 208 plants (32 percent) have their own wastewater treatment facilities and retain sludge in unlined aeration ponds (EPA, 1976c). Of the 208 plants with treatment systems, eighty-six (41 percent) disposed of sludge. Current disposal practices used for the wastewater treatment sludge are lagoon disposal, open dumping, landfill and landspreading. Most wastewater treatment sludges are disposed or retained in unlined disposal lagoons. Open dumping of sludge, both on and off-site is practiced by some plants. Most landfilled sludge is mixed with municipal refuse and other organic materials. A few plants dispose their sludge on-site by landspreading on fields around the treatment facilities. One plant disposes the sludge off-site by allowing an employee to haul the sludge to his farm for use as fertilizer (EPA, 1976c).

Current disposal technologies employed by the industry are considered to be environmentally inadequate, because sludge retention in unlined lagoons could result in percolation to groundwater supplies, and land disposal of sludge by landfilling or landspreading in uncontrolled facilities can lead to leachate and surface water run-off problems.

The textile industry has claimed that the wastewater treatment sludge is comparable to common municipal sludge. Apparently, heavy metals in the sludge from the textile mills (Table 3.38) are higher than the heavy metals in selected municipal mills (Table 3.42). Heavy metal uptake by plants grown on the land used for sludge disposal and incorporation into the food chain is likely. Surface water run-off problems also may occur during heavy rain.

3.8.4.2 Best Available Technology

The best available disposal technology for wastewater treatment sludge from woven fabric dyeing and finishing operations would be an approved landfill. Presently, this disposal technique has not been employed in the textile industries. An EPA study indicated that approved landfill liners may deteriorate and may not provide adequate protection for long-term disposal (EPA, 1976c). In addition, there are very few approved landfills near most textile industry plants. Further discussions of approved landfill and its cost can be found in Section 3.7.4.2.

3.8.4.3 Methods Suggested by Related Technology

At present, secured landfill is generally the best available land-filling technique suggested by related industries. This technology is considered adequate to prevent environmental damage to air, ground and surface waters on a long-term basis. Detailed discussions of secured landfill, including costs, were previously described in Section 3.2.4.2.

3.8.5 Recommended Treatment and Disposal Techniques

The most acceptable treatment and disposal methods for wastewater treatment sludge from woven fabric dyeing and finishing operations in the textile industry would be disposal of the dewatered sludge (20 percent solids) in approved landfills. This technique provides environmentally adequate disposal of this sludge and the technology is widely used and demonstrated in this and other industries. Landfill liners may deteriorate and will not provide adequate long-term disposal, so secured landfill may be the next best available alternative for ultimate disposal of this waste.

3.8.6 Environmental Impact

Table 3.43 shows estimated emissions of chlorinated organics in wastewater treatment sludge. MATE values were not available. Further investigation, such as actual chlorinated organic measurements, would be necessary to determine emissions more accurately.

Table 3.44 compares metallic composition of wastewater treatment sludge from woven fabric dyeing and finishing with State of Illinois criteria. A narrative from the Illinois criteria which describes methods for disposal for Alternatives I, II and III is given in Section 3.7.6. From this comparison, assuming a high degree of leachability, the characteristics of an acceptable disposal site may be determined.

From this analysis, it appears that Alternative III must be chosen due to the high concentration of zinc in the sludge. Therefore Alternative III disposal methods would probably have to be used for disposal of this sludge in the State of Illinois.

Table 3.42 Summary of Major and Minor Elements in Sludge (Dean et al, 1974)
(mg/kg dried sludge)†

<u>Element</u>	<u>Primary Sludge</u>	<u>Activated Sludge</u>	<u>Digested Sludge</u>
Aluminum	5.1	10.0	17.9
Antimony	n.a.*	n.a.	0.9
Arsenic	1.2	1.2	n.a.
Barium	2.2	1.2	1.4
Beryllium	0.0025	0.0035	0.0025
Boron	0.10	0.70	0.046
Cadmium	0.19	0.35	0.26
Calcium	n.a.	13.0	33.5
Chromium	2.0	4.3	2.3
Cobalt	0.22	0.002	n.a.
Copper	2.0	1.1	1.6
Gallium	0.06	0.05	0.05
Iron	16.1	40.5	30.6
Lead	1.0	1.5	1.9
Magnesium	10.6	7.0	7.5
Manganese	0.78	0.31	0.98
Mercury	0.005	0.02	n.a.
Molybdenum	0.36	0.20	0.25
Nickel	0.52	0.38	0.38
Phosphorus	3.8	19.9	12.8
Potassium	n.a.	4.2	2.8
Silicon	n.a.	40.0	162
Silver	0.24	0.15	0.20
Sodium	4.0	4.4	6.2
Strontium	0.13	0.16	0.26
Sulfur	n.a.	10.1	12.3
Tin	0.95	0.50	0.60
Titanium	14.8	11.8	14.2
Vanadium	2.1	0.7	5.2
Zinc	6.9	3.3	4.0
Zirconium	1.7	10.0	2.0

*n.a. not available
After Salotto et al, 1971

†Multiply by 1,000 to get mg/kg

Table 3.43 Chlorinated Organics in Wastewater Treatment Sludge

Estimated Emissions

		Current Practice	Best Available	Transfer of Technology
		Discharge to unlined lagoon	Sludge dewater- ing, disposal in approved landfill	Encapsulation, disposal in secure landfill
Media	MATE VALUES			
Air, mg/m ³	Health N.G.	High	Medium	Low
	Ecology N.G.			
Water, mg/l	Health N.G.	High	Medium	Low
	Ecology N.G.			
Land, ug/g	Health N.G.	High	High	Low
	Ecology N.G.			

Table 3.44 Comparison of Wastewater Treatment Sludge with State of Illinois Criteria

	mg/kg of dry sludge	Illinois Criteria, mg/l		
		<u>Alt. I</u>	<u>Alt. II</u>	<u>Alt. III</u>
Arsenic	1	25	75	225
Barium	39	--	--	--
Cadmium	4.4	150**	450**	1,350**
Chromium (total)	1,196	Cr+675 Cr+3500	225 2,000**	675 6,000**
Cobalt	26	--	--	--
Copper	652	500**	2,000**	6,000**
Iron	4,910	--	--	--
Lead	36	275**	825**	2,475**
Manganese	128	--	--	--
Mercury	0.35	25	75	225**
Molybdenum	17	--	--	--
Nickel	32	200**	600**	1,800**
Zinc	2,370	250**	750**	2,250**
 Total Heavy Metals	 9,370			
 Aluminum	 4,640			
Magnesium	2,820			
Potassium	3,580			
Sodium	51,300			
Strontium	16			
 Total Chlorinated Organic	 15.2			
 Suspended Solids	 0.88			
 Total Solids	 1.26			

*Average of 20 measurements from five plants

**Illinois criteria stipulates that allowable concentrations may double if waste contains greater than 2.5 percent excess lime alkalinity and quadruple if greater than 5 percent.

3.9 SOLVENT-THINNED TRADE SALES PAINT PROCESS LIQUID WASTES

The paint industry (SIC 28511 and SIC 28513) comprises small businesses which are typically located in larger urban areas. An estimated 65,000 people were employed in these businesses in 1972, including 37,000 production workers. Simple technology and the relatively low capital investment required to begin production operations have allowed many small firms to thrive in the paint industry. More than half of the approximately 1,544 manufacturing plants (who account for less than 5 percent of total industry sales) employ less than 20 people. Approximately 41 percent employ fewer than 10 workers. The four largest firms, Sherwin Williams, DuPont, PPG Industries and SCM-Glidden, accounted for 30 percent of total industry sales in 1974 (Sludge Magazine, 1979). Approximately 3.6 million kkg (4 million tons) of paint and coatings were produced in the United States in 1972 (EPA, 1976c).

Significant industry trends include a decrease in total number of plants and an increase in average plant size. Small plants with less than 10 employees lack the necessary capital to make changes in compliance with safety requirements, including those under OSHA, and with air and water pollution abatement regulations. The number of these plants is therefore decreasing.

Larger plants have coped with these changes by making capital improvements or changing their production process to produce water-thinned paints, thus trading off the safety and pollution problems associated with solvents for the wastewater discharges associated with water-thinned paints. Certain specialized uses for solvent-thinned paints will, however, remain until satisfactory replacements are found. For example, paints used in marine environments are nearly always solvent-thinned.

Although many paint plants produce both solvent-thinned and water-thinned paints, approximately 44 percent of the industry does not discharge any wastewater, probably indicating exclusive solvent-thinned paint, lacquer, industrial finish, putty and miscellaneous paint product production. However, 75 percent of the 1,374 plants identified in the

EPA Water Effluent Guidelines Development Document for paint manufacturing produce some water based paint (Sludge Magazine, 1979).

3.9.1 Manufacturing Process and Wastewater Characterization

Batch processes involving sizing and mixing are utilized to produce various solvent-thinned paint formulations. A general process flow diagram is shown in Figure 3.18.

Although the process itself is simple, a wide variety of products are produced for very specific end uses. This necessitates utilization of up to 1,500 to 5,000 different raw materials, depending on size of manufacturing operation, to produce a relatively complete line of paints. Paint formulations are also varied to enhance certain desirable properties. In Table 3.45, formulation changes for various paints are shown. High gloss paints are very washable, but have low hiding properties; flat paints, however, have better hiding power but low washability. Minor ingredients such as antissettling agents, fungicides and leveling agents are omitted because they vary depending on end use and never comprise more than 1 percent by weight of product (Sludge Magazine, 1979).

There are no identifiable by-products normally associated with the solvent-thinned paint manufacturing process.

Waste streams and 1974 quantities are shown in Table 3.36. Process liquid wastes include cleanings, spoiled batches and spills and total 92,300 kky/yr (101,400 ton/yr). Approximately 15 percent, or 14,265 kkg/yr (15,734 tons/yr) of this waste stream are solvents. Approximately 0.7 percent, or 636 kkg/yr (700 tons/yr) are toxic chemical compounds in the waste stream (EPA, 1976c).

Solvents are used for cleaning of process equipment prior to shut-down and before a substantial change in color of paint or type of raw materials used. Often solvents with higher boiling points than those used in the paint being processed are used for cleaning, due to lower cost and reduced evaporation losses. If the solvent used for cleaning is identical to the solvent used in the paint, then reuse of cleaning solvent in subsequent paint batches may be facilitated. Volume of

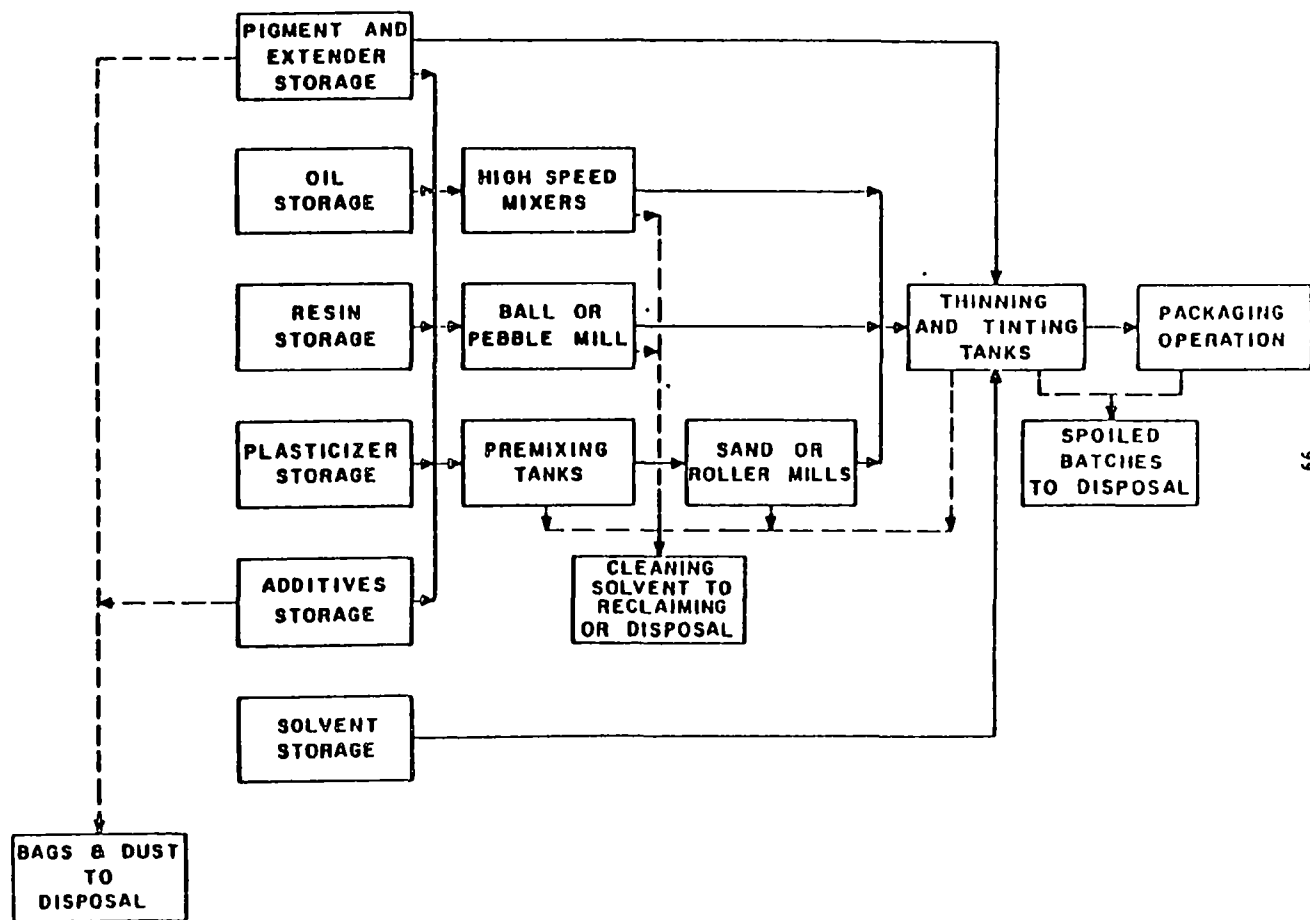


Figure 3.18 Solvent-thinned Paint Manufacturing Flow Diagram (EPA, 1976c)

Table 3.45 Typical Formulation Changes to Achieve a Variety of Coatings (Percentage by Weight)*

Typical Alkyd Finishes

	<u>High Gloss</u>	<u>Semi-gloss</u>	<u>Flat</u>
Titanium dioxide	30.0	25.0	20.0
Extenders	--	10.0	25.0
Alkyd solids	40.0	30.0	19.0
Solvents	28.0	33.5	35.0
Driers	2.0	1.5	1.0
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>

Typical Floor Finishes

	<u>Clear</u>	<u>Oak Stain</u>	<u>Brown Enamel</u>
Yellow iron oxide		5.0	.
Brown iron oxide			20.0
Extenders		5.0	
Resin solids	50.0	28.0	40.0
Solvents	47.5	60.0	38.0
Driers	2.5	2.0	2.0
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>

* EPA, 1976 C

Table 3.46 Paint and Coatings Manufacture Summary of Total Wastes in 1974
 kkg/yr (tons/yr) (Wet weight) (EPA, 1976) C

<u>Waste Stream</u>	<u>Total Waste</u>	<u>Potentially Hazardous Waste Stream</u>	<u>Hazardous Solvents In Waste</u>	<u>Toxic Compounds In Waste</u>
Cleanings	82,000(90,000) ¹	82,000(90,000) ¹	13,600(15,000)	590(650)
Raw Material Packaging	302,000(333,000)	2,000(2,200)	---	128(140)
Air Pollution Collection	1,600(1,700)	1,600(1,700)	---	80(88)
Spoiled Batches	4,900(5,400) ²	4,900(5,400) ²	580(640)	41(45)
Spills	<u>5,400(6,000)³</u>	<u>5,400(6,000)³</u>	<u>85(94)</u>	<u>5(5)</u>
TOTAL	395,900(436,100) ²	95,900(105,300) ⁴	14,265(15,734)	844(928)

¹ Includes about 25 percent water.

² Includes about 5 percent water.

³ Includes about 6 percent water.

⁴ Includes about 22 percent water.

equipment cleaning wastes requiring disposal depends more on frequency of shutdown, frequency of color and raw material changes and the extent to which recovery for reuse in the product or for reuse in subsequent equipment washings is practiced, rather than on plant production. A typical 3,800,000 liter (1,000,000 gal) per year plant which produces both water- and solvent-based products would normally use about 9 kkg (10 tons) of waste cleaning solvent per year (EPA, 1976c).

According to a 1974 survey, finished products which cannot be sold, or recycled to the process, due to quality control restrictions, comprise a waste stream amounting to 0.2 percent of total production (EPA, 1976c).

Spills are normally collected and recycled to the process when quality control requirements permit. If any portion of a spill cannot be recycled, it is normally collected using absorbent materials and disposed.

Warehouse stocks, unsold within their expected shelf lives, are reclaimed for reuse in the process when economically feasible. The effort required to open small containers and return the contents to the production process probably exceeds the economic gains to be realized.

The quantity of spoiled batches, spills and stored product wastes depends more on plant housekeeping and the types of products manufactured than on production quantity. A lower volume of product wastes is generated from paints which contain significant amounts of toxic metals such as cadmium and chromium because the value of the metals justifies the effort to reclaim smaller quantities.

Variability of waste streams is high due to the variety of raw materials used in the industry, the batch operation of both process and equipment cleanings, and the unpredictability of spoiled batches and spills.

Waste streams include components of the paint product, solvents, still bottoms and sludges from solvent reclaiming, and absorbent used for spill cleanup. A typical paint formulation is given in Figure 3.19.

More detail may be derived from lists of materials used in various paint formulations tailored to a specific end use. Tables 3.47 through 3.51 show these materials. These tables refer to use in 1972, in the entire paint industry. Therefore, the figures give only relative usage data for the solvent-thinned trade sales portion of the industry.

Although process liquid wastes are normally considered ignitable and volatile, these waste streams are difficult to assess accurately because of the variety of components and their toxicities, as evaluated in the Sax toxicity rating (Sax, 1975). Toxicity of raw materials used in paint plants is shown in Table 3.52. As previously mentioned, the presence of valuable constituents in paint products, such as heavy metals and organic solvents, encourages reuse of waste streams in the process, and recovery of solvents.

A further difficulty with handling actual waste stream is the wide variety of products. Solvent-thinned paint, water-thinned paint, and varnishes made by many plants, and many of the other waste streams are usually disposed together.

<u>MATERIAL</u>	<u>Composition</u>	
	<u>Weight Percent</u>	<u>Volume Percent</u>
Pigment:		
Titanium Dioxide	29	9
Solvent:		
Mineral Spirits	15	22
Resin:		
Long oil, tall oil alkyd (70% NVM)	52	65
Additives:		
Suspension and flow agent	<1	<1
6% Cobalt naphthenate	<1	<1
4% Calcium naphthenate	<1	<1
6% Zirconium drier catalyst	<1	2
Antiskinning agent	<u><1</u>	<u><1</u>
	100	100

Figure 3.19 Typical Solvent-thinned Paint Formulation (EPA, 1976) C

Table 3.47 Estimated Pigment Usage by Paint Industry, 1972^a

	Usage	
	Million lbs/yr	Thousand kkg/yr
<u>LEAD</u>		
*Basic lead carbonate	0.91	0.41
*Basic white lead silicate	2.44	1.10
*Red lead	5.94	2.70
*Other lead pigments	4.70	2.13
<u>WHITES</u>		
*Antimony oxide	0.52	0.24
Lithopone	4.78	2.17
Titanium dioxide, pure	592.69	268.84
Titanium dioxide, extended (usually 50% TiO ₂)	26.26	11.91
*Zinc oxide, leaded ²	0.70	0.32
Zinc oxide (pure)	22.22	10.08
Other white pigments	0.71	0.32
<u>BLACKS</u>		
Carbon black	6.08	2.76
Lamp black	2.03	1.00
Other black pigments (except black iron oxide)	1.57	0.77
<u>YELLOW AND ORANGES - INORGANIC</u>		
*C.P. cadmium oranges and reds	0.07	0.04
*Cadmium lithopone	0.04	0.02
*Chrome yellow	29.06	14.35
*Molybdate orange	5.02	2.48
*Strontium chromate	0.64	0.32
*Zinc chromate	7.33	3.62
Other inorganic yellow and orange pigments	9.17	4.53
Organic yellows and oranges	1.67	0.83
<u>BLUES AND VIOLETS</u>		
Iron blue (Milorí-Chinese-Prussian)	0.55	0.27
Ultramarine blue	0.49	0.24
Other inorganic blues and violets	0.10	0.05
*Phthalocyanine blue	1.14	0.56
Other organic blues and violets	0.13	0.07

* Indicates hazardous materials.

^a Based on National Paint and Coatings Association Raw Materials Usage Survey (EPA, 1976 c).

Table 3.47 Estimated Pigment Usage by Paint Industry, 1972^a (continued)

	Usage	
	Million lbs/yr	Thousand kkg/yr
<u>GREENS</u>		
*Chrome green	0.90	0.44
*Chromium oxide and hydrated chromium oxide	2.31	1.14
*Phthalocyanine green	1.09	0.54
Pigment green B	0.02	0.01
<u>REDS AND MAROONS - INORGANIC</u> (except iron oxide)	3.68	1.82
<u>REDS AND MAROONS - ORGANIC</u>		
B.O.N. maroon	0.37	0.17
Chlorinated para reds	0.21	0.10
Lithol red and rubine	0.15	0.07
Other organic reds and maroons	3.98	1.80
<u>FLUSHED COLORS</u>	2.48	1.12
<u>AQUEOUS DISPERSIONS</u>		
Hansa yellow	0.84	0.38
Iron oxides	12.51	5.67
*Phthalocyanine blue	0.41	0.18
*Phthalocyanine green	0.49	0.22
Toluidine red	0.11	0.05
Other aqueous dispersions	5.38	2.44
Other pigment dispersions	5.85	2.65
<u>METALLIC</u>		
Aluminum pastes	10.70	4.85
Aluminum powder	0.33	0.15
Bronze powders	0.21	0.09
*Copper powders	0.16	0.07
Other metallic flakes	0.80	0.36
<u>IRON OXIDES</u>		
Synthetic iron oxides (reds)	12.91	5.86
Synthetic iron oxides (yellows)	17.46	7.92
Synthetic iron oxides (other)	4.95	2.25
Natural iron oxides	6.05	2.74
Ochres, siennas, and umbers	3.41	1.55
<u>EXTENDERS</u>		
Calcium carbonate - precipitated	75.78	34.37
Calcium carbonate - natural	185.18	84.00
Magnesium silicate (talcs)	137.11	62.19
Barytes - natural	50.02	22.69
Diatomaceous earths	31.11	14.11

Table 3.47 Estimated Pigment Usage by Paint Industry, 1972^a (concluded)

	Usage	
	<u>Million lbs/yr</u>	<u>Thousand kkg/yr</u>
<u>EXTENDERS</u> (continued)		
Koalin (calcined and other clays)	160.17	72.65
Mica, dry and water-ground	20.14	9.14
Silicas, ground	154.56	70.11
Other extender pigments	75.66	34.32
<u>MISCELLANEOUS</u>		
*Cuprous oxide	3.35	1.52
Fluorescent pigments	0.15	0.07
Zinc dust	28.59	13.00
Other miscellaneous pigments	4.78	2.17

Table 3.48 Estimated Resin Usage by Paint Industry, 1972^a

	Usage	
	Million lbs/yr (Dry weight) ^c	Thousand kkg/yr
<u>RESINS FOR SOLVENT-THINNED</u>		
<u>VEHICLES^{b*}</u>		
Acrylic, lacquer type	8.41	3.82
Acrylic, thermo-setting type	43.36	19.67
Alkyds	211.41	95.89
Epoxy resins	68.84	31.22
Epoxy ester resins	7.27	3.30
Hydrocarbon resins	19.10	8.66
Maleic resins	7.27	3.30
Phenolic resins, pure	9.84	4.46
Polyurethane resins	12.99	5.89
Silicone resins	2.85	1.29
Urea and melamine formaldehyde resins	16.50	7.48
Vinyl (formal and butyral) acetal resins	4.22	1.91
Vinyl acetate solution-type copolymers	9.65	4.38
Other solvent-phase resins	14.85	6.74

^a Based on National Paint and Coatings Association Raw Materials Usage Survey (EPA, 1976 c).

^b Substantial amounts of cellulose nitrate, cellulose acetate, cellulose butyrate, and ethyl cellulose are used as resins in coatings, particularly lacquers. However, production data on these products are withheld to protect the interests of a very limited number of producers.

^c Most of these resins are normally sold in solution, so it can be assumed that they are usually accompanied by an equal weight of solvent.

* These materials are not considered hazardous by the industry.

Table 3.49 Estimated Drying Oil Usage By Paint Industry, 1972^a

<u>OILS*</u>	Usage	
	<u>Million lbs/yr</u>	<u>Thousand kkg/yr</u>
Castor oil, raw	3.50	1.59
Castor oil, dehydrated	8.08	3.67
Tung oil	15.21	6.90
Coconut oil	6.24	2.83
Linseed oil	88.63	40.20
Safflower oil	15.32	6.95
Soybean oil	62.16	28.20
Fish oil	1.17	0.53
Other oils	22.22	10.08
<u>FATTY ACIDS*</u>		
Coconut	0.62	0.28
Linseed	6.06	2.75
Soybean	4.55	2.06
Tall oil	46.87	21.26
Other fatty acids	8.36	3.79

^a Based on National Paint and Coatings Association Raw Materials Usage Survey (EPA, 1976 c).

* These are generally not considered hazardous materials.

Table 3.50 Estimated Solvent Usage by Paint Industry, 1972^a

	Usage	
	<u>Million gal/yr</u>	<u>Million liters/yr</u>
<u>ALIPHATIC HYDROCARBONS</u>		
*Mineral spirits, regular and low odor	63.74	241.26
*Mineral spirits, odorless	12.28	46.48
*Kerosene	1.66	6.28
*Mineral spirits, heavy	5.17	19.57
*Other aliphatic hydrocarbons	30.69	116.16
<u>AROMATIC AND NAPHTHENIC HYDROCARBONS</u>		
*Benzene	0.96	3.63
*Toluene	52.73	199.55
*Xylene	66.92	253.29
*Naphtha, high flash	13.90	52.61
*Other aromatic hydrocarbons	29.57	111.92
<u>TERPENIC HYDROCARBONS</u>		
(Pine Oil and turpentine)	0.98	3.71
<u>KETONES</u>		
*Acetone	134.70	509.84
*Methyl ethyl ketone (MEK)	114.78	547.99
*Methyl isobutyl ketone (MIBK)	57.75	218.58
*Other ketones	10.29	38.94
<u>ESTERS</u>		
*Ethyl acetate	6.01	22.75
*Isopropyl acetate	5.81	22.14
*Normal butyl acetate	65.36	247.39
*Other esters	43.12	163.21

^a Based on National Paint and Coatings Association Raw Materials Usage Survey (EPA, 1976c).

* Indicates hazardous material by DOT.

Table 3.51 Estimated Miscellaneous Materials Usage, 1972^a

	Usage	
	<u>Million lbs/yr</u>	<u>Thousand kkg/yr</u>
<u>ANTI-SKINNING AGENTS</u>	4.90	2.23
<u>METALLIC SOAPS</u>		
Aluminum stearate	0.32	0.15
*Zinc Stearate	1.52	0.69
Calcium Stearate	0.23	0.10
Other metallic soaps	0.28	0.12
<u>BODYING AGENTS, SOLVENT SYSTEMS</u> (other than above)	4.91	2.23
<u>DISPERSING AND MIXING AIDS</u>	25.51	11.57
<u>DRIERS</u>		
Calcium soaps	1.90	0.86
*Cobalt soaps	3.97	1.80
*Lead soaps	5.40	2.45
Manganese soaps	1.53	0.69
*Zirconium soaps	1.73	0.78
Other driers	1.55	0.70
<u>FUNGICIDES, GERMICIDES, AND</u> <u>MILDEWCIDES</u>		
*Phenols, halogenated phenols, and their salts	0.41	0.19
*Phenyl mercuric acetate	0.88	0.40
*Phenyl mercuric oleate	0.19	0.09
Others	3.19	1.45

^a Based on National Paint and Coatings Association Raw Materials Usage Survey (EPA, 1976^c).

* Indicates potentially hazardous materials.

Table 3.52 Toxicity of Raw Materials Used in Surveyed Paint Plants

	Sax Toxicity			
	<u>A_L</u>	<u>A_S</u>	<u>C_L</u>	<u>C_S</u>
Antimony Trioxide	3	3	2	3
Antimony Trisulfide	3	3	2	3
Asbestos	2	0	3	3
Barium Carbonate	1	3	1	2
Barium Lithol		No reference		
Barium Metaborate		No reference		
Cadmium Selenide	3	3	Var.	3
Chlorinated Paraffin		No reference		
Chlorinated Rubber		No reference		
Chrome Oxide	3	4	3	3
Cobalt Naphthenate	1	1	4	4
Copper Naphthenate	1	2	1	1
Cuprous Oxide	1	2	1	1
Lead Carbonate	0	3	0	3
Lead Chromate	3	3	3	3
Lead Molybdate	0	3	0	3
Lead Monoxide (Lithage)	0	3	0	3
Lead Naphthenate	0	3	0	3
Lead Phosphate	0	3	0	3
Lead Silicochromate		No reference		
Lead Sulfate	0	3	0	3
Lead Tetroxide		No reference		
Mercury Drier		No reference		
Pentachlorophenol	3	3	2	2
PMA		Primary irritant		
PMO		No reference		
Copper Phthalocyanine		No reference		
Phenyl Mercuric Succinate		No reference		
Strontium Chromate	3	4	3	3
Tributyl Tin Fluoride		No reference		
Zinc Chromate	3	4	3	3
Zinc Naphthenate		Variable, generally low		
Zinc Peroxide		Variable, generally low		
Zinc Phosphate		No reference		
Zinc Resinate		No reference		
Zinc Stearate		Variable		

A_L = Acute LocalA_S = Acute SystemicC_L = Chronic LocalC_S = Chronic Systemic

Table 3.52 Toxicity of Raw Materials Used in Surveyed Paint Plants
(concluded)

	Sax Toxicity			
	<u>A_L</u>	<u>A_S</u>	<u>C_L</u>	<u>C_S</u>
Acetone	2	2	1	1
N-Butyl Acetate	1	2	1	1
Ethanol	1	2	1	1
Diacetone Alcohol	1	2	1	1
Ethyl Acetate	1	2	1	4
Heptane	1	1	1	4
Hexane	1	2	4	1
Isopropanol	1	2	1	4
MEK	2	3	4	4
MIBK	1	3	1	2
Methanol	1	2	4	4
Mineral Spirits	1	2	1	2
Toluene	2	2	1	1
VM&P Naphtha	2	2	1	1
Xylene	1	2	1	2

3.9.2 Treatment Alternatives

3.9.2.1 Current Practice

Current practice is to dispose a large portion of liquid process wastes on land. As of 1974, approximately 35 percent of plants recover at least some solvents. Almost all plants disposed at least some wastes off-site (EPA, 1976c). Based on the small number of secured landfills in existence, disposal must be in either open dumps or sanitary landfills. Although solvents are becoming more expensive with decreased availability, it appears that a great number of small plants in the industry have not solved the logistics of recovering solvents themselves or finding an off-site solvent recovery contractor. Problems encountered by paint producers include the capital investment necessary for installing an on-site solvent recovery unit and/or incinerator, locating off-site solvent recovery contractors, storing and handling small batches of wastes to minimize workplace hazards, and optimizing the value of wastes by keeping pure solvents and spoiled product batches in separate containers for each product. Wastes in small quantities must be accumulated to make hauling to the recovery site economical. For small plants, accumulation of a full truck load of wastes may take days, not accounting for high volume spills and spoiled batches that may occur at infrequent intervals.

Waste product collected on cleanup absorbents and still bottoms, residue and waste scrubbing solution from on-site solvent recovery units and incinerators are normally land disposed.

Cost of disposal has been estimated at \$9 to \$20 per metric ton based on the necessity of hauling wastes to a site and disposing of it. One major paint plant is paying as much as \$87 per metric ton for flammable liquid disposal. Variability in costs stems from disposal method utilized and hauling distance. Cost information by disposal method was not found in the literature. Another estimate can be obtained by assuming \$8 per cubic meter (\$7 per cubic yard) for handling and storage at the plant site and an additional \$8 per cubic meter (\$7 per cubic yard) for disposal. Hauling costs are estimated at \$0.20/ton-mile, which leads to hauling costs of \$20 for a 16,000 meter (100 mile) trip, which is

likely to occur for some plants. On this basis, disposal costs could easily reach \$40 per metric ton (\$36 per ton).

3.9.2.2 Best Available Technology

Although many plants incinerate their process liquid wastes, it appears that a better use of a valuable resource is solvent recovery. Many plants use contract haulers which recover solvents for resale or "launder" them for reuse in the same plant. A few plants have recently installed package solvent recovery units (see Section 4.0).

Additionally, spoiled product and spills should be reused in the process where feasible. Residues from solvent recovery are normally landfilled. Other process liquid wastes such as spills collected on absorbents and spoiled product and spills that are not reusable in the process are also landfilled.

Incineration of solvent recovery residue is complicated by fine particulates which could make air quality compliance difficult. Volume reduction achieved by incineration of paint residues may not justify use of incineration in many cases. The presence of metals in the residue may restrict use of incineration unless metals are removed (Rollins Environmental Services, personal communication, 1979). So landfilling is recommended for solvent recovery residues and other process wastes, volume is reduced considerably by solvent recovery, thus reducing disposal costs.

Costs of solvent recovery depend on the use of off-site contractors versus purchase of on-site solvent recovery equipment. Purchase of equipment is becoming more attractive to the paint industry, because small, low cost package units are being produced and can be afforded by more paint plants.

Although an average cost has not been obtained for solvent recovery equipment, off-site contractors normally pay for used solvents and pick them up at the plant site. It is assumed that

purchase of solvent recovery equipment is more attractive financially than continuing to use off-site contractors.

Use of solvent recovery techniques is probably now feasible for some, but not all, plants without process change.

Recovery and reuse of solvents, and process changes to permit recycling of a wider variety of spoiled batches, spills, and stored products, are practices receiving increased attention in the paint industry and may be currently achievable by some plants. Theoretically, wastes from the industry should be reduced to residues from solvent recovery operations and absorbed spills should be disposed with absorbent spill control materials.

Problems in implementing this technology include a reluctance by industry (particularly small plants) to change solvent-thinned paint processes. One reason is the increase in use of water-thinned paints resulting in decreased usage of solvent-thinned paints, thus diverting plant funds to emphasize water-thinned paint production. Recent research has resulted in some new paint products which contain as much as 60 percent less solvent and can be cleaned up with water. Although the future looks bright for these and other reduced-solvent paints, their performance has not been completely proven and much more research is necessary to develop a replacement for solvent-thinned paints (National Paint and Coatings Association, personal communication, 1979).

Not all spills and spoiled batches are recoverable by a given plant. Quality control specifications required by the customer, particularly color, limit quantities and types of paints which can be rebled in the process. In addition, paint components such as polymers, silicones and wetting agents must be compatible for successful recycling. Ease of recycling is complicated by the increasing number of paint products produced at a facility and decreasing product quantity required in a given production run. Recycling in a plant of this type requires much storage space and strict adherence to separation of waste product types during storage. Most plants, particularly smaller plants, do not have proper storage space to meet safety and environmental requirements and do not have the personnel to give this matter their full attention.

For successful implementation of best available technology, plant operators must become aware of the disposal alternatives for paints and solvents and be able to apply the best alternatives to a particular plant. An industry trade group, the National Paint and Coatings Association (NPCA), has recently taken steps to make information on recycling and solvent recovery that complies with current and upcoming regulations, and waste management in a small plant, topics for discussion at their 1979 annual conference (NPCA, personal communication, 1979). Cost estimates and engineering aspects of this technology will vary tremendously. Most of the technology consists of changes in operation to allow recovery of valuable raw materials and product. Therefore, the relatively small investment necessary may be offset to a large extent by the value of recovered materials.

3.9.3 Environmental Impact

Table 3.53 gives estimated emissions from process liquid wastes. More research is needed to provide better estimates. The environmental impact of best treatment, storage and disposal technologies includes possible air emissions from solvent recovery, and emissions to water and soils from disposal of residues.

The impact of solvent recovery techniques is much less, because small quantities of waste are disposed.

The environmental impact of other methods of disposal used in the industry also should be considered. Some plants, particularly in the Northeast, collect solvent washings in drums. The drums are stored, allowed to settle, and used as supplemental fuel as needed. The environmental impact could be as low as that for incineration, depending on the combustion conditions. Assuming that compliance with

Table 3.53 Process Liquid Wastes from Solvent-Thinned Trade Sales Paint Manufacture

Media	MATE Values *	Current Practice	Best Available	Transfer of Technology
		Landfill	Recovery with land disposal or incineration of residue	More complete recovery with land disposal or incineration of residue
Air, ³ mg/m	Health	High	Medium	Low
	Ecology			
Water, mg/l	Health	High	Medium	Low
	Ecology			
Land, µg/g	Health	High	Medium	Low
	Ecology			

*Many solvents are possible; see Table 3.54.

air quality regulations is the determining factor in successful use of this method, the tradeoff in environmental impact is for on-site combustion versus recovery.

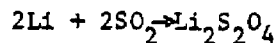
Some work has been done on recovery of wastewater treatment sludges from water-thinned paint production used in asphalt paving materials and in cement production for its fuel value in cement kilns (NPCA, personal communication, 1979).

3.10 SCRAP CELLS FROM Li-SO₂ BATTERY PRODUCTION

Lithium metal SO₂ batteries are dry cell batteries which are expanding their market position because they have higher performance standards than Ni-Cd or other dry cells, along with much longer shelf life and a broader operating temperature range (-40° to 160°C).

3.10.1 Manufacturing Process and Waste Stream Characterization

The production process involves several proprietary operations which have not been disclosed to date. The general reaction for these batteries is:



Storage densities of 95 watt-hrs/lb are attainable for these high-performance batteries at 2-3 volts. This compares to about 20 watt-hrs/lb for conventional 1.5 volt carbon-zinc dry cells (EPA, 1975 and Brunner and Keller, 1972). The amount produced is not known.

The production of Lithium-organic electrolyte -SO₂ batteries results in a waste stream of spent battery cells resulting from quality control requirements of the production facility. This waste stream is expected to contain about 1-3 percent, by weight, of the production of a battery plant (Hegner, 1970).

Components of this scrap cell waste stream include the active ingredients of Lithium and SO₂, organic solvents and other materials. The expected composition of the waste stream is presented in Table 3.56. This table shows the contents of the Li-SO₂ battery both under normal conditions and in a potentially hazardous form which might result from reaction in a landfill situation. The table identifies the specific toxic materials which must be recognized in proposing and evaluating waste management options. Although disposal may be preceded by storage or treatment, all waste management options for this waste stream ultimately lead to land disposal. Examination of the characteristics of land disposal sites as they relate to containment of hazardous components of waste is useful in identifying specific disposal characteristics

TABLE 3.54. Contents of Li-SO₂ Battery (Ref. Slimak, M. et al. 1977b)

Casing: Variable, depending on battery size and geometry.

Contents: Normal Conditions (charged cell)

<u>Component</u>	<u>Percent Of Weight</u>
Lithium metal	8
Lithium bromide	4
Sulfur dioxide	46
Carbon	20
Teflon	5
Acetonitrile	16
Polypropylene	2

Hazardous Condition (Resulting from Land Proposal)

<u>Component</u>	<u>Percent of Weight</u>
Lithium	8
Bromine	3
Sulfur dioxide	46
Cyanide	10
Methyl compounds	6

which are expected to be effective and treatment alternatives which could contribute to waste management improvements through modification of waste form or reduction of migration potential. Emissions from land disposal sites can occur either to air or to the landfill leachate and runoff.

Atmospheric emissions from this waste stream may result from releases of gaseous components or gaseous reaction products of the battery wastes. Several potential releases by the gaseous route are presented in summary fashion in Table 3.55. These air releases are identified as potential, since their actual occurrence is dependent upon specific reactions occurring in the case of H_2 and CH_4/CH_3OH or adequate temperatures being achieved in the case of SO_2 .

The release to the atmosphere of gas components identified in Table 3.57 from this waste are likely to occur because of the low molecular weight and small size of the molecules and lack of retention capability of many landfill covers.

Liquid releases from landfill sites are more complex because certain contaminants are retained when moving through the ground. This phenomenon is due to filtration and/or exchange processes. Factors influencing this retention process include soil properties, water pH, water composition and water flow patterns.

Soil characteristics of a landfill can vary from clays to silts, loams, sands or other soil types. Changes in soil types mean that soil ion-exchange and groundwater/leachate flow characteristics also change. The extent of the variations which are possible can be seen from the soil characteristics presented in Figure 3.20 (Ferguson, 1976). It shows the variation that can occur with critical ion-exchange capacity and permeability.

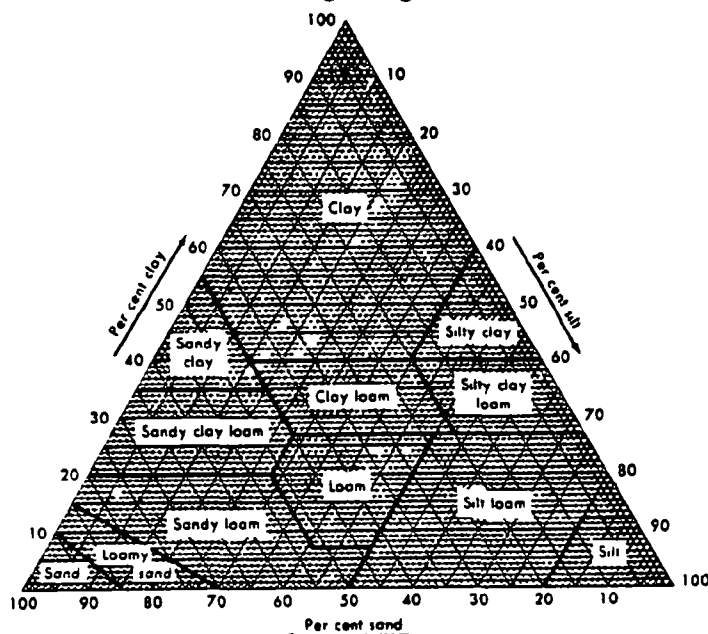
Another aspect of soil retention characteristics is selectivity for certain waste components, such as selective removal of Sr^{+2} over K^+ when both are present. In general, soils are negatively charged and therefore act as cation exchangers. Anions (negatively charged particles)

Table 3.55 Potential Air Releases from Li-SO₂ Battery Disposal

<u>Release</u>	<u>Mechanism</u>	<u>Amount</u>	<u>Comment</u>
H ₂	Reaction product of H ₂ O and Li	0.14g metallic Lithium	Fast reaction
SO ₂	Existing component of waste	Not Available	Vapor pressure higher than H ₂ O by a factor of 10-100, while its density is over twice that of air
CH ₄ , CH ₃ OH	Reaction products of organic components	Not Available	Speed of reaction depends on land-fill conditions

Ion Exchange Capacity

5-100 meg/100g



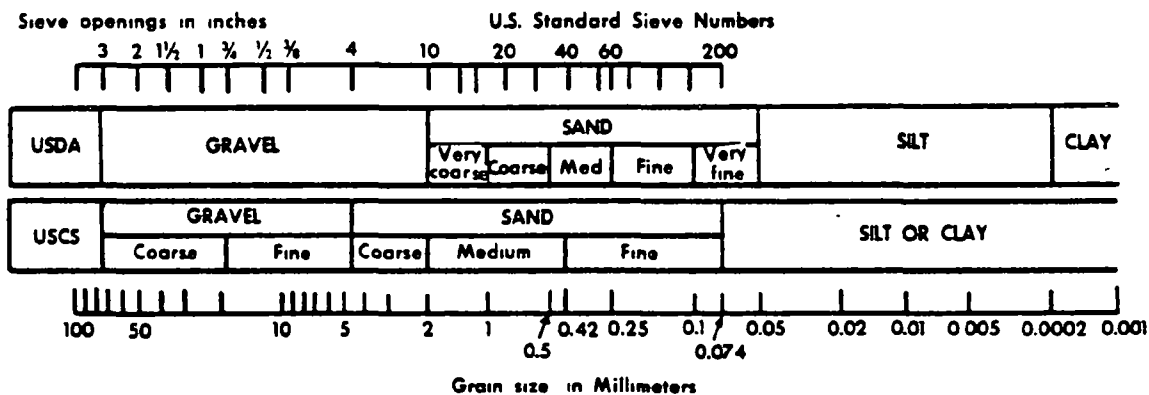
Sand—2.0 to 0.05 mm diameter
Silt—0.05 to 0.002 mm diameter
Clay—smaller than 0.002 mm diameter

Ion Exchange Capacity
5 meg/100g

Organic Matter
Has ion Exchange Capacity 200 meg/100g

Ion Exchange Capacity
10-20 meg/100g

COMPARISON OF PARTICLE SIZE SCALES



Excellent

Permeability

Practically Impervious

FIGURE 3.20 Comparison of Soil Characteristics. (Ferguson, 1976)

and organic materials are largely unaffected by the ion-exchange process. For cations (positively charged particles), the general order of preference is trivalent ions before divalent ions before singly charged ions. More specifically, the general ranking of selectivity is $\text{Li}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{CK}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{Mg}^{++} < \text{Ca}^{++} < \text{Sr}^{++} < \text{Ba}^{++}$ (Ferguson, 1976.)

Examination of the waste material to determine its expected attenuation by soils suggests that the acetonitrile and the methyl compounds and cyanide resulting from its degradation will not be retained by the various soils. Bromide ions and the sulfite or sulfate ions also will be unaffected by soil properties. Lithium will be adsorbed but the extent will depend upon specific competing cations.

Several components of the Li-SO₂ battery waste stream are hazardous because of potential detrimental human health effects resulting from exposure. The relative hazards from disposal of this waste stream can be developed by comparing mobility and toxicity characteristics of the components. Table 3.56 provides this comparison, based on available information regarding element toxicity and mobility. Several conclusions can be drawn from the information presented in this table:

- The toxic hazard is chiefly determined by sulfur and hydrocarbons in the waste.
- Cyanide is a moderate toxic hazard in the waste stream coupled with the high mobility.
- Lithium presents the least toxic hazard of the waste constituents examined.

Another hazardous aspect of these waste materials is that they can produce combustible gases. With Li-SO₂ battery wastes the sources for combustible gases are Lithium metal, which can react with water to produce hydrogen, and the organic electrolyte and its combustion products. These potential combustion products add inflammability to the hazards from these battery wastes.

Analysis suggests that any processing performed on battery wastes be designed to reduce the hazards and problems associated with SO₂, organic (acetonitrile) materials and metallic lithium. The processes should modify the sulfur compounds to a less hazardous and/or mobile

Table 3.56 Comparison of Hazardous Nature of Li-SO₂ Cell Components

<u>COMPONENT</u>	<u>MASS</u>	<u>TOXIC THRESHOLD</u>	<u>NO. OF DOSES</u>	<u>MOBILITY</u>	<u>COMMENT</u>
<u>Molecules</u>	max g/100g waste				
SO ₂	46	13 mg/M ³²	.28	High	
CH ₄	6.4	-	-	High	Flammable
CH ₃ OH	12.8	260 mg/H ³²	20.3	High	
H ₂	1.1	-	-	High	Flammable
<u>Ions</u>					
SO ₃ ⁻	57	210 mg/l ^c	3.68	High	
CN ⁻	10	0.2 mg/l ^b	.02	High	
Li ⁺	8	5.mg/l ^b	.63	Moderate	
CH ₃ ⁻	6	-	-	High	
Br ⁻	3	-	-	High	

a from Proposed Guidelines and Regulations and Proposal on Identification and Listing, Federal Register, Dec 18, 1979, Part IV

b from ECOM-76-1752-1

c derived from 250 mg/l limit for SO₄⁼ based on assumption of SO₃⁻ oxidization to SO₄⁼

form. The organic materials should be modified to destroy both the methyl group and the cyanide. Lithium should be converted to a less environmentally reactive form. In addition, any waste processing should not cause degradation of waste components into compatible or toxic compounds.

3.10.2 Treatment

Treatment of this waste stream consists of processes which in some way modify or fractionate the waste. A summary of these methods has been listed previously by EPA (EPA, 1974c). Those with a potential application to scrap cell wastes are the incineration processes, physical treatment and chemical treatment included as Appendix C. Of these waste treatment processes, incineration appears the most effective, because it destroys cyanide and organic compounds. Other treatment options involve separation rather than destruction and so appear less desirable. Of the various incinerator types, the simpler controlled air type appears to be the most practical for Li-SO₂ battery scrap cells because of few moving parts and reduced off-gas handling problems. There does not appear to be a need for the complexity associated with fluidized beds, rotary kilns or moving grates. Use of an incinerator, regardless of its design, requires a pretreatment step to rupture the battery container mechanically in a completely dry atmosphere to preclude the possibility of battery explosion. An off-gas handling system will also be required for removal of particulates and SO₂ from the combustion gases. Lithium is not expected to volatilize, but entrained lithium compounds could be removed by liquid scrubbers or mechanical air cleaning devices. Lithium recovery from the air cleaning waste might be carried out depending on concentration in the waste and the total volume of waste.

3.10.3 Storage Alternatives

Storage of waste material may represent a hazard potential. If the battery were to be ruptured, water from the ground, rain or even the air could react with metallic lithium to form hydrogen (H₂), which represents

an explosion and fire hazard. In addition, if high temperature were encountered during storage, volatile components such as SO_2 and organic degradation products could rupture cell containers. This could lead in turn to lithium reaction with atmospheric moisture to produce hydrogen.

Specific methods of waste storage are not as well established as those for treatment or disposal because of limited use. Specific storage options which might be utilized for scrap cells are package or bulk storage.

In package storage, scrap cells would be placed in drums (55 or 30 gallon) or bags and the containers accumulated at a storage area. It is possible to add material such as cement to the scrap battery cells to form a more integral package but it adds to the cost of storage and increases costs of any reclamation efforts. Bulk storage is possible utilizing either above or below-grade storage areas. This is a lower cost storage method, but any hazardous constituents in the waste are more subject to release.

Besides providing the mechanism for potentially hazardous reactions, storage increases the costs of total waste management since storage costs must be added to the costs of ultimate disposal. Storage can be considered a necessary short term option because of economics of scale for treatment or because of delays in disposal capacity. It may be more cost effective to store waste material and wait for the industry to grow so that larger processing plants with lower unit cost can be built. In such cases storage is a waste management alternative which becomes necessary rather than a primary objective. It is expected that battery cell storage, if used, will be an interim measure until means for recovery of all components are developed or until more cost-effective disposal methods meeting existing standards are found.

Storage of these scrap cells must be accomplished without exposure to moisture. It would be difficult to store scrap cells for long periods of time without risking fires or explosions. Storage in inert media, such as an oil bath, should be considered to reduce risk.

3.10.4 Disposal Alternatives

Eventually, whether treated or untreated and whether stored or not components from the battery waste stream must be disposed. Six disposal options applicable to waste material have been identified by EPA solid waste programs for disposal of hazardous wastes (Marynowski, 1972). Of these, one is a storage option discussed in the previous section. Four others are potentially applicable to spent Li-SO₂ battery cells. These options are landfill disposal, deep well disposal, subsurface injection, land burial.

Landfill disposal is a well-controlled and sanitary method for disposal of wastes upon land. Common landfill disposal methods are:

- mixing with soil
- shallow burial
- combinations of these.

The design and operation of these landfills must integrate the physicochemical characteristics of both site and hazardous waste.

Deep-well disposal is a system of disposing of raw or treated, filtered hazardous waste by pumping it into deep wells where it is contained in the pores of permeable subsurface rock separated from other groundwater supplies by impermeable layers of rock or clay. The depth of injection varies with local hydrology. Subsurface injection has been extensively used in disposal of oil field brines. There are between 10,000 and 50,000 brine injection wells in the United States. The number of industrial waste injection wells in the United States numbers more than 100. Injection wells can be used by virtually any type of industry that is located in a proper geologic environment and that has a waste product amenable to this method. Some industries presently using this method are chemical and pharmaceutical plants, refineries, steel and metal industries, paper mills, and coke plants.

Land burial disposal is a method adaptable to those hazardous materials that require permanent disposal. Disposal is accomplished by either near-surface or deep burial. In near-surface burial, the material is deposited directly into the ground or is deposited in stainless steel tanks or concrete lined pits beneath the ground. In land burial, the waste is transported to a selected site where it is

prepared for final burial. At the present time, near-surface burial of both radioactive and chemical wastes is being conducted at several AEC and commercially operated burial sites. Pilot plant studies have been conducted for deep burial in salt formations and hard bedrock. Land burial is a possible choice for hazardous materials that require complete containment and permanent disposal. This includes radioactive wastes as well as highly toxic chemical wastes. At the present time, only near-surface burial is used for the disposal of most wastes.

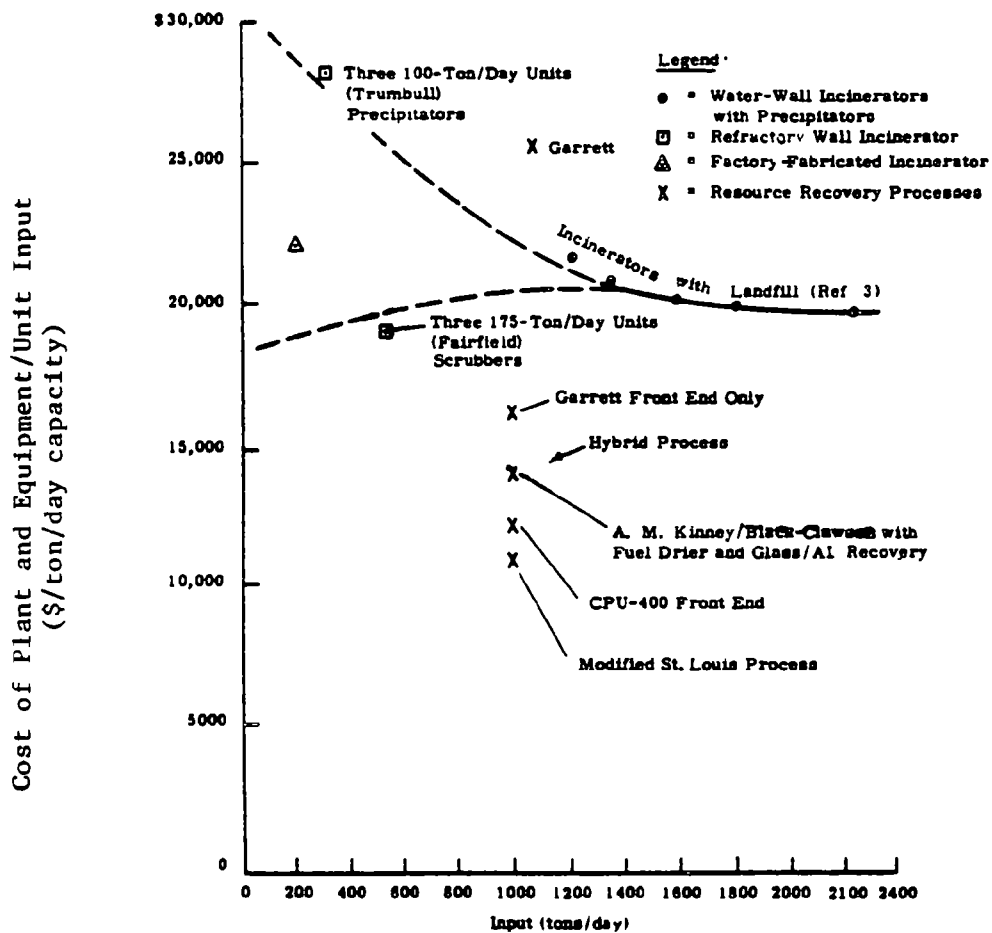
Ocean dumping utilizes the ocean as an ultimate disposal sink for all types of waste materials, including hazardous wastes. There are three basic techniques for ocean disposal of hazardous wastes. One is bulk disposal for liquid or slurry-type wastes. Another is to strip obsolete or surplus World War II cargo ships, load the ships with obsolete munitions, and tow them out to sea, scuttling them at some designated spot. The third technique is the sinking at sea of containerized hazardous toxic wastes. The broad classes of hazardous wastes dumped at sea include:

- industrial wastes
- obsolete, surplus, and nonserviceable conventional explosive ordinance
- chemical warfare wastes
- miscellaneous hazardous wastes.

The technical viability of a specific alternative depends on the degree of waste treatment, and local geology and hydrology. Deep-well disposal is feasible only if the waste has been processed to slurries or solutions and an acceptable injection site is available. The other waste disposal options -- landfill with its many alternatives, land burial, ocean dumping and engineered storage -- are all feasible regardless of pretreatment. Their usage depends upon the availability of specific sites and the economics of each disposal method.

The cost of waste management depends on the nature of treatment operations, transportation requirements and the disposal costs. These cost elements are reviewed in the following paragraphs.

The cost of waste incineration includes both capital and operating costs, which vary depending on specific incineration technology and facility size. Figure 3.21, derived from a study conducted by General



Note: 1972 Dollars

Figure 3.21 Capital Costs for Waste Incinerators

Electric shows capital cost variation according to incinerator type and capacity (General Electric Co., 1975). The figure also illustrates cost changes for variations in off-gas treatment technologies.

Operating cost for municipal incinerators are reported to average \$5/ton. The combination of these costs, when a twenty-year life is assumed, results in unit processing costs of \$10-20/ton of material.

Disposal of solid waste including treated or untreated battery wastes can be accomplished in a variety of ways. Cost estimates for the various disposal methods collected from a variety of sources are presented in Table 3.57.

From the data in Table 3.54 it appears that the most reasonable waste management options involve landfill disposal with or without waste incineration. The reasons for these conclusions are:

- Treatment alternatives other than incineration are less well developed and offer no potential for reducing the toxicity of the waste.
- Disposal alternatives other than landfill are very expensive and do not appear necessary.

It is assumed that decisions on where to locate waste management activities are made by waste producers on an individual economic basis. Specific analyses are not done in this section, but could be performed comparing on-site treatment and disposal costs with off-site transportation, treatment and disposal costs. Costs are expected to vary with the volume of waste and the distance between waste generator and disposal site. An example of the results which might come from such analysis is presented in Figure 3.22 which is taken from EPA's Hazardous Waste Analysis (EPA, 1974 b).

Landfill disposal with and without incineration can be compared using a cost-benefit technique which presents in clearer fashion the cost of reducing the waste stream hazard using incineration. If only the liquid leachate hazards are considered, it can be seen from Table 3.56 that there are a potential 4.33 threshold doses in 100 grams, or 39316 per ton of battery cell waste. Incineration will destroy the cyanide but probably not SO_2 . The latter will be captured in a

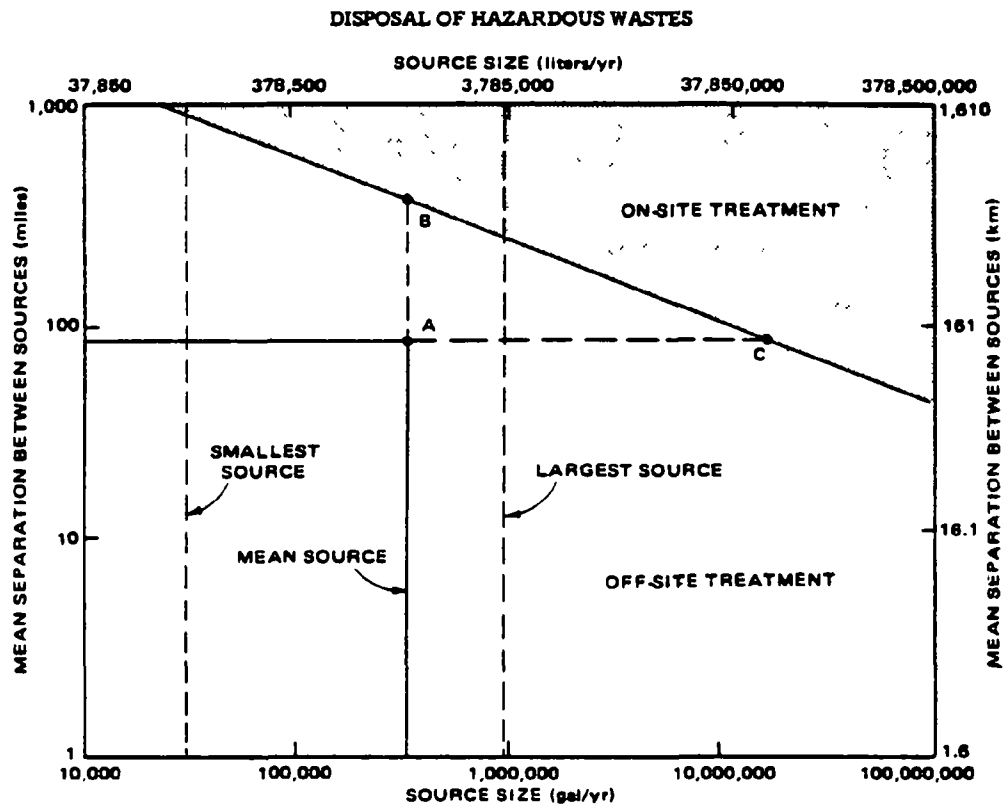


Figure 3.22 Example of the Results of Specific Siting Analysis

Table 3.57 Cost Estimates for Various Disposal Methods

DISPOSAL COST SUMMARY			
	Cost (\$/ton)	Reference	Remark
Landfill	1.50 - 2.00 8	Macbeth and Hickman, 1974 Schneider and Platt, 1974	
Deep Well	25-50	Macbeth and Hickman	For liquid or slurry waste form
Land burial (engineered structure & con- tainers)	35 4000-8000	EPA, 1974 b Macbeth and Hickman, 1974	Surface management deep geologic management
Ocean Dumping			

Note: Costs scaled to 1979 using Chemical Engineering Plant Cost Index.

in a scrubber and disposed in a landfill. Assuming negligible change in total waste mass upon incineration, Table 3.58 presents a cost-benefit comparison for the two procedures. The table shows significant cost increases for a small potential dose reduction. It should be noted that leachate rate or transportation costs were not considered in the analysis, but these will probably not change the net result. It shows incineration to be the best available technology but possibly not the best practicable technology based on cost.

3.10.5 Environmental Evaluation

At present, disposal of Li-SO₂ scrap cells is in landfills. Estimated emissions to air, water and land from this disposal method are given in Table 3.59. Air emissions are based on the reaction between lithium metal and water to produce hydrogen. Water emissions are based on the formation and release of cyanide in the disposal environment.

3.10.6 Best Available Technology

The best available technology for disposal of the Li-SO₂ scrap cell waste stream is incineration of its disassembled components. Fluegas scrubbing and land disposal of incineration residue are required.

The most environmentally sound technology would be recovery and reuse of disassembled parts. Based on practices in other industries, it appears that this technology is feasible although much research would be needed to determine the best methods for safely disassembling the sealed cells.

Table 3.58 Cost-Benefit Comparison of Landfill With and Without Prior Incineration
 Basis: 1 Ton Cell Waste, 1979 Costs

<u>ALTERNATIVE</u>	<u>COST (\$)</u>	<u>POTENTIAL DOSES</u>	<u>REMARKS</u>
Landfill	5	39316	\$5.00/ton for Landfill
Incineration & Landfill	20	393134	\$15.00/ton for incineration
	15	182	

Incremental Cost-Benefit Ratio \$.08/Potential Dose

Baseline Cost-Benefit Ratio \$.00013/Potential Dose

Table 3.59 Li-SO₂ Scrap Cell Treatment and Disposal

Estimated Emissions

		Current Practice	Best Available	Transfer of Technology
		Landfill	Disassembly, incineration with fluegas scrubbing and land disposal of residue	Disassembly, recovery of components for reuse
Media	MATE VALUES			
Air, mg/m ³	Health N.G. Ecology N.G.	High	Medium	Low
Water, mg/l	Health N.G. Ecology N.G.	High	Medium	Low
Land, ug/g	Health N.G. Ecology N.G.	High	Medium	Low

3.11 SUMMARY OF WASTE STREAM STUDIES

These ten waste streams coupled with the explosives wastes addressed in Chapter 5 and solvent studies in Chapter 4 form the basis for evaluation of regulatory options and identification of future research needs.

3.11.1 Manufacturing Processes and Waste Characterizations

An understanding of the manufacturing processes producing the waste streams studied enabled a better characterization of waste streams based on estimated variability of the process due to start-up and shut-down, production of off-specification items, process changes necessary for different products, necessary equipment cleanup, and housekeeping practices. Recommendations of process changes to reduce quantities and hazardous properties of wastes produced could result from further studies of manufacturing processes.

Key references for characterization of the waste streams were the Assessment of Hazardous Waste Practices series of reports from the EPA Office of Solid Waste. Apparently further efforts to characterize waste streams by EPA or industry have not been made.

An important item for future research is the characterization of at least the most significant IRV wastes. Chemical constituents would be important, although key properties of entire waste streams such as vapor pressure at 40°C, flash point, solubility, reactivity, and toxicity may reveal much about how the waste stream would act in a given treatment, storage, or disposal environment.

3.11.2 Treatment, Storage and Disposal Options

Incineration, the treatment most often recommended as best available, will have a financial impact on industry. Normally, industry invests in equipment that can be used 24 hours a day, seven days a week and has a payback on the investment of 12 to 18 months. Anticipated regulations may force industry out of this pattern and into handling wastes with little or no intrinsic value as if they had great value due to the consequences of mishandling. Some ideas for decreasing the financial impact of incineration include recovery of heat and recovery of valuable products of incineration such as HCl.

Plants that do not have IRV waste streams that require use of an incinerator for 24 hours a day, seven days a week will probably incinerate other wastes to get as close as possible to continual use. Plants that do not have large volume IRV wastes are probably better off contracting out the incineration of their wastes. Equipment manufacturers are beginning to offer much smaller waste incinerators which would allow more flexibility in the choice of off-site versus on-site incineration.

Equipment malfunctions and maintenance shut down and air emissions are other potential problems. According to one waste disposer contacted (see Section 6.9) incineration of IRV wastes is still more an art than a science. However the same disposer reported that by carefully choosing which wastes to incinerate and careful blending of wastes with fuel, use of supplemental fuel has been limited to incinerator start-up and malfunctions and air emissions have been minimized.

Little specific information on storage of IRV wastes was found. No storage of IRV wastes was found except for storage in steel drums for ease of handling. Anticipated regulations may encourage more bulk storage, which will require further investigation to determine if steel drum storage will remain an acceptable and cost effective storage method and if more acceptable and cost effective storage methods exist.

Disposal of IRV wastes is generally clearly defined in the waste stream discussions. Apparently a wide discrepancy exists between current disposal methods and those anticipated in the hazardous waste regulations. Further investigation is needed to determine if adequate disposal areas will be available to meet the demand.

Costs for implementing treatment, storage and disposal techniques were in many cases available only on a dollars per quantity of waste basis. More detailed cost information would require further investigation, and may not be available. Also, cost/benefit analyses such as that given in Section 3.10 would allow a more quantitative comparison between disposal options.

3.11.3 Achievement of Most Environmentally Sound Practices

For many waste streams, recovery of valuable constituents or chemical treatment to convert waste to a salable product comprised the most environmentally sound practice. Many of the processes mentioned require further investigation or adaptation to insure broad applicability for each waste stream.

3.11.4 Environmental Impact of Treatment, Storage and Disposal

Very little quantitative information was available to estimate emissions, except for the properties of known chemical constituents of the wastes and its form (solid, liquid, sludge, tar) for disposal.

The comparison of estimated emissions with Minimum Acute Toxicity Effluents (MATE's) (Cleland & Kingsbury, 1977) provided a good first step in attempting to characterize emissions from a waste disposal environment. However, comparisons with MATE's has its drawbacks, such as:

- lack of consideration of the disposal environment
- lack of consideration for waste form
- many substances¹ in waste streams studied were not covered in MATE's
- only pure substances are covered in MATE's
- worst cases were assumed by choosing the most critical components of wastes for comparison
- MATE's considers concentration only and does not consider mass of wastes disposed or emitted, thus rate of release and dilution are critical factors.

Further investigation is necessary to more accurately determine estimated emissions and to determine if a more meaningful means of comparison exists.

4.0 SOLVENT USE AND RECOVERY IN INDUSTRY

Solvents are used extensively by various industries as part of product manufacture, purification or application. Associated with the wide range of solvent uses are varying degrees of solvent recovery. In some instances solvent recovery and reuse is greater than 99 percent, while in other cases no solvent recovery is practiced.

In many continuous operations where a solvent is used as part of the manufacturing or purification process solvent recovery and recycling is a common practice. In the petroleum refining industry, solvents such as sulfolane or tetraethylene glycol are used for the recovery of aliphatic compounds from a mixture of aliphatic-aromatic material (EPA, 1976b). Similarly, in the metal extraction industry solvents such as organic phosphates, amines or ketones are used for recovery and purification of metals such as uranium, thorium, copper, zirconium, cobalt and rare earths (Schweitzer, 1979). The explosive manufacturing industry utilizes solvents such as alcohol and ether in their production processes, and these are recovered and recycled to the process for reasons of economics (Shreve, 1967). The textile industry utilizes solvents such as trichlorobenzene, perchloroethylene and other chlorinated aromatics as dye penetrant aids. These solvents are not currently recovered but are drummed for disposal (EPA, 1976a). Because of solvent losses that can occur due to water solubility or vaporization, secondary solvent recovery from these streams may also be practiced. In batch operations where throughput is generally lower, solvent recovery is frequently practiced. In the paint manufacturing industry solvents are a part of the product and spills, reject paint batches and equipment cleaning represent the only sources of solvent that might be recovered. Surveys of the paint industry suggest that about 25 percent of the paint plants perform solvent recovery on site (EPA, 1976b). The ink and dye industry utilizes solvents in a manner similar to the paint industry with solvent recovery being the exception rather than the rule. Metal degreasing operations in almost all metal handling industries utilize solvents as wash or leach solutions to remove mill oils and other residue from various metallic items. The solvent accumulates residues of both a soluble and insoluble nature.

Such solvents may be disposed or recovered depending on local regulations and economies of scale of the operations (EPA, 1976a).

Some of the major solvents which are utilized by the various industries are identified in Table 4.1. This table shows the formula of the solvent as well as its boiling point and solubility in water. These parameters are important indicators of the solvent's transport potential by air or water. Several of these solvents are included in Appendix A which shows vapor pressure, toxicity and NIOSH standards for selected substances.

Specific amounts of solvents used by the industries are unknown but some partial data presented in Table 4.2 illustrate that the uses are large.

It can be seen from this brief review that many solvents are used in many industries with varying degrees and techniques for recovery. The next section of this report addresses the solvent recovery techniques that are practiced in various industries.

4.1 SOLVENT RECOVERY METHODS

The recovery of solvent from waste and effluent streams involves the use of separation technology to either remove the solvent from the contaminants or remove contaminants from the solvents. The applicability of certain technologies depends upon the nature of the separation required. In examining solvent recovery methods it is useful to characterize the separation as being liquid-liquid, gas mixture or liquid-solid (Schweitzer, 1979).

Figure 4.1 is adapted from Drew (1975) and is a generalized flow diagram which shows the feed types and the operations which may be performed as appropriate in solvent recovery. It also serves to identify the various recovery methods which will be discussed in this section. Operations on the diagram which are addressed are identified with an asterisk (*).

Liquid-liquid separations can involve distillation, solvent extraction, adsorption or decanting.

Table 4.1 Typical Solvents and Selected Properties

<u>Solvent</u>	<u>Formula</u>	<u>B.P.°C</u>	<u>Solubility in H₂O</u>
Trichloroethylene	ClHCCCl_2	87	slightly
1,1,1 Trichloroethane	H_3CCCl_3	74	insoluble
Perchloroethylene	Cl_3CCCl_3	186	insoluble
Methyl Chloride	H_3Cl	-24.2	400 ml gas/100 ml H ₂ O
Trichlorotrifluoroethane	Cl_3CCF_3	45.8	insoluble
Benzene	C_6H_6	80	slightly
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	110	insoluble
Xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	138-144	insoluble
Cyclohexane	C_6H_{12}	81	insoluble
Orthophenylphenol	$\text{C}_{12}\text{H}_9\text{OH}$	286	insoluble
Mineral Spirits			
Acetone	CH_3COCH_3	56.2	infinity
Methylethylketone	$\text{C}_2\text{H}_5\text{COCH}_3$	79.6	very soluble
Methyl isobutyl ketone	$\text{CH}_3-\text{CO}-\text{C}_3\text{H}_9$	115.8	1.91 g/100 g
n-Butyl Acetate	$\text{CH}_3\text{COOC}_4\text{H}_9$	125	1 g/100 g
Methyl ether	CH_3OCH_3	-23.6	3700 ml gas/100 ml H ₂ O
Methanol	CH_3OH	65	infinity
Dioxane	$\text{C}_4\text{H}_8\text{O}_2$	101-105	infinity

Table 4.2 Solvent Consumption by Selected Industries

<u>Industry</u>	<u>Solvent Group</u>	<u>Usage 10⁶ liters/year</u> <u>(10⁶ gallons/year)</u>
Paints (EPA, 1976 c)	Aliphatic hydrocarbons	428 (113)
	Aromatic hydrocarbons	621 (164)
	Ketones	1,313 (347)
	Esters	454 (120)
Solvent Metal Cleaning (EPA, 1977 c)	Halogenated	416 (110)
	Aliphatic hydrocarbons	227 (60)
	Aromatic hydrocarbons	45 (12)
	Ketones	15 (4)
Electronic Components (EPA, 1977 e)	Halogenated	0.8 (0.2)
	Non-Halogenated	1.1 (0.3)

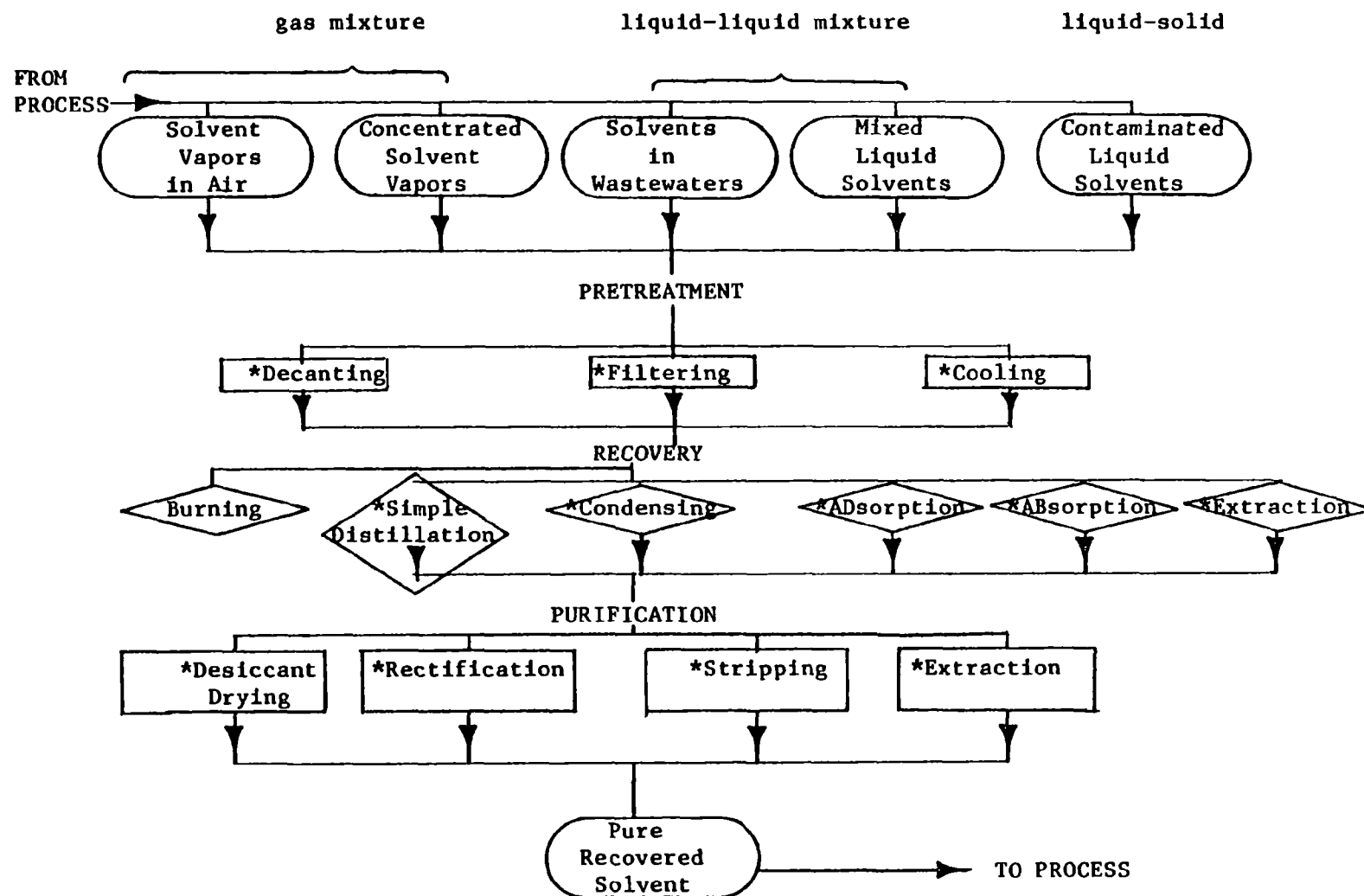


Figure 4.1 Generalized Flow Diagram for Solvent Recovery

*Operations addressed
in discussion

For distillation there are several alternatives which are considered here. The alternatives involve different methods of supplying the necessary heat to the solvent solution which is to be evaporated. These methods are:

1. Direct Injection of Steam. Steam is injected directly into the liquid to be evaporated. Solvent vapors pass from the evaporator into a condenser where liquid solvent is collected. This method is only suitable for those solvents which have low boiling points, are not miscible with water, and can be readily separated from water. Because of these limitations, this type of still is not commonly used and is normally confined to small specialized operations.
2. Coil Still. The vessel containing the material to be distilled contains a coiled tube through which steam or hot fluid is passed to heat the contents. Electric heating coils are also used. Heat transfer is fast and efficient, providing no fouling occurs on the heat transfer surface. This type of equipment is not suitable for reprocessing solvents which have a high solids content (roughly 5 percent or more) or contain resinous materials which could polymerize on the coils and require expensive hand cleaning. Evaporated solvent passes to a non-contact water-cooled condenser where liquid solvent is collected.

Stills of this type are widely used for reprocessing solvents such as chlorinated hydrocarbons used in dry cleaning operations. They range from 28 to 950 liters (8 to 250 gal.) per hour capacity.

3. Scraped Surface or Wiped-Film Evaporator. In this device, the distillation tank is surrounded by a heating jacket and the interior of the cylindrical heated surface is continuously wiped by blades attached to a central rotating shaft. This is best suited for use with solvents containing sludge or solids and insures a clean heat transfer surface by its use of mechanical energy from the agitator.

In addition to utilizing one of the three types of heat addition systems, a distillation or fractionating column will be required if sepa-

ration of volatilized components is necessary. Such a column may utilize either internal plates or packing to enhance separation.

Solvent extraction involves the use of a second solvent to recover either the desired solvent material or the undesired contaminants.

The separation technique involves two immiscible liquid phases. It is an indirect separation technique because two components are not separated directly. A foreign substance, the second solvent, is introduced to provide a second phase. This is in contrast to direct separation techniques, e.g., distillation, where heat is used to provide a vapor phase, or melt crystallization, where cooling is used to provide a solid phase.

A separation can be performed by solvent extraction whenever the ratio of one component to another is different in the two liquid phases. This is the same as performing a separation by distillation whenever the relative volatility is greater or less than 1.0. The simplest separation in extraction is when an immiscible solvent can be used to remove one component from a binary mixture. For this application, an example is solvent extraction of solvent from wastewater. This is similar to a stripping or an absorption step in distillation where mass is transferred between phases.

Solvent extraction is useful as a separation technique when the material being recovered shows an adequate selectivity or preference for the second solvent. Efficiencies are attained by staging the contact operations in the same manner as in multicomponent distillation.

Adsorption involves the retention of the material of interest (in this case the original solvent) on a solid phase material (the adsorbent). Activated carbon is the most commonly used adsorbent, particularly for organic molecules, which most solvents are. The adsorbent is regenerated using hot gases to reverse the adsorption process. This results in a vapor phase solvent mixture, more concentrated than the original feed. This stream will generally have to be treated further before solvent recovery is complete.

Decantation is the operation where two liquid phases are separated on the basis of density differences. The separation may be strictly gravitational or it may be aided by centrifugal effects or wetting agents. It will produce a solvent stream which may require further purification if soluble contaminants are present that restrict subsequent uses.

Gas mixture separation includes adsorption, absorption and condensation.

Gas phase adsorption is similar to liquid phase adsorption in that material (the solvent) is collected on the exterior surface of an adsorbent. Again it is usually activated carbon which can be regenerated by purging the equipment with hot gases or steam.

Gas absorption involves the transfer of solvent molecules from the gas phase into a second solvent phase. The transfer process must be reversible in order to recover the primary solvent from the secondary solvent. The operation takes place in mass transfer equipment similar to distillation and solvent extraction.

Condensation can be used to recover solvent from a vapor phase. For this to be effective as a separation technique for vapor recovery the gas phase composition and dew points of non-solvent components must be such that relatively pure solvent can be condensed.

Liquid/solid separations are useful for material such as used degreasing solvents which contain solids. The technical alternatives involve variations on filtering. There are three major variations: cake filtration, depth filtration and surface filtration.

Cake filtration occurs when a liquid containing solid particles is forced through a porous filter medium which is open enough to allow the passage of the liquid, but tight enough to retain the solid particles. As more and more liquid is forced through the medium, the solids form a thicker and thicker filter cake. The main characteristic of cake filtration is that the cake which is formed must be porous enough to permit continued fluid flow through it as filtration progresses.

In depth filtration, the liquid containing solid particles is forced through a bed of porous material. The solid particles are trapped within the relatively coarse interstices of the bed, allowing relatively clear liquid to pass through. Sand filtration and cartridge filtration exemplify depth filtration. As solid particles continue to accumulate within the filter bed, there comes a time when either fluid flow is restricted below acceptable limits, or solid particles are forced through the bed into the filtrate. At this time the bed must be regenerated, or the cartridge replaced.

Surface filtration is essentially a straining mechanism where the solid particles are stopped by a matrix of controlled pore size. This case differs from cake filtration in that the flow rate decreases because of plugging of the matrix pores. The matrix becomes plugged before any significant cake thickness is attained.

From this review of solvent recovery technologies it is obvious that there are a large number of techniques available but that specific process selection must hinge on the nature of the spent solvent, its contaminants and the purity required in the recovered material.

For example, selection of distillation or adsorption/desorption methods for solvent recovery would depend on solvent properties, such as whether single or mixed solvents are to be recovered, and the boiling points of the solvents.

Treatment at the recovery facility visited as part of this study was primarily simple decanting. Waste oils and solvents were decanted and blended to rough equivalents of Number 2 and Number 4 fuel oils and sold to nearby industries. Oily wastewaters are treated and discharged to the sanitary sewer. Some distillation of waste solvents is performed in a pot still, but fractionation has not been attempted. Sludges from decanting and distillation are removed to one of two company owned secure landfills. (Visit of February 21, 1980 and Easterbrook, 1979)

4.2 SOLVENT RECOVERY SYSTEM PERFORMANCE

The effectiveness of a solvent recovery system will vary with the technology of the system (distillation versus adsorption), with the design of the system (simple vaporization-condensation versus vaporization-rectification-condensation) and the method of operation. Generalization of system performance is not possible, but systems not capable of greater than about 25 percent recovery are not practical. Some examples of existing operations which illustrate this point are:

- contract solvent recovery operations average 75 percent solvent recovery rate (EPA, 1976c).

- vinyl monomers and mineral oil are recovered in plant at 99+ percent efficiency (Environmental Science and Technology, 1970).
- practical activated carbon removal efficiencies are 80 - 95 percent even though 98 percent is possible (Schweitzer, 1979).

4.3 STORAGE OF FEED SOLVENT, WASTE RESIDUES AND RECYCLE SOLVENT

The storage of material is necessary when there is a mismatch between material generation rate and material consumption. Solvent recovery, like any other process, has the potential for this mismatch.

When solvent recovery is an integral part of the plant process, in line tankage is used sparingly except for the recycle solvent storage. Design of the tanks is done in accordance with American Petroleum Institute (API) and National Fire Protection Association (NFPA) standards. Vapor emissions rate is predominantly a function of storage temperature, and cooling costs have been provided at plants where it has been deemed necessary. The storage tanks may also have a vapor recovery system (adsorption or condensation) if the material is valuable enough to justify the capital expenditures (Newton, 1978).

When solvent recovery is not an integral part of a production plant containers such as 55 gallon drums are generally used for storage. These serve as a common package readily handled by both solvent producer and solvent receiver (EPA, 1976 c; Randall et al, 1976).

The practice of using 55 gallon drums may become less viable when RCRA is implemented because of the increased sampling requirements. For liquids, bulk or tank storage may become more viable, because fewer samples will require analysis, thus a cost savings is realized. The 55 gallon drum will probably remain in common usage for solid and heavy slurry wastes. Use of floating roof tanks for bulk storage may be feasible, although the seal between the floating roof and tank wall is critical and its integrity must be maintained. Storage of extremely volatile substances in floating roof tanks may not be feasible due to possible atmospheric emissions.

Floating roof tanks are especially applicable for temporary storage of volatile wastes due to frequent liquid level changes. Evaporation losses are reduced by limiting the space above the surface of the liquid. Floating roof tanks are constructed with or without fixed roofs above the floating roof. The fixed roof design (expansion roof) would be more amenable to collecting volatile emissions from the tank and routing them through a carbon adsorption bed for removal of hydrocarbons. In the past, floating roof tanks have been used to store very large quantities of bulk volatile liquids. For example, Peters and Timmerhause (1968) listed a "small" expansion roof tank capacity of 1,500,000 ℓ (400,000 gal.). As previously mentioned, storage temperature is just as important as tank design for limiting volatile emissions. Storage tanks may be insulated or installed entirely or partially underground to keep temperatures as low as possible. Refrigeration costs are expected to be prohibitively high, except under special circumstances.

Volatilization of wastes can be reduced by designing tanks so that their intake pipes are submerged during most of the tank filling operations. This limits volatilization by not allowing free falling and splashing of liquids as tanks are filled.

For fire protection all tanks storing combustible wastes must be grounded.

A solvent recovery facility was visited as part of this study. The plant itself used to be an old specialty chemical production facility that was purchased and is still being refurbished in stages according to need. Its location is such that it is near many industries that use and dispose of solvents and other chemical wastes. As of May 1979, the plant was receiving about 50,000 gallons of liquids per day. In addition to waste solvents and oils, the plant receives and treats acids, industrial wastewaters and organic wastes. Prior to receiving a waste, the plant requires specific information from the generator on waste constituents. Samples are then taken and analyzed before the waste is transported from the generator. Then wastes are run through a laboratory-scale process to help determine ease of treatment/recovery and to set

fees for handling the waste. These fees range from 11 cents to 3 dollars per gallon, and are very waste-specific.

Once laboratory analysis is complete, the site operator hauls the waste to the recovery facility and additional testing is performed before the waste is pumped from the truck to verify that the waste in the truck matches the lab analysis.

Finally, oily wastes and solvents are pumped into storage tanks prior to treatment or recovery. Various tanks are used to store wastes by NFPA standard levels of reactivity, ignitability and corrosivity. Tanks are well insulated and are above ground. The tanks are closed. Empty tanks as well as tank trucks are cleaned frequently. Sludges are sent to one of two company owned landfills. Liquids are treated in the plant and discharged to the sanitary sewer. (Visit of February 21, 1980 and Easterbrook, 1979)

4.4 WASTE TREATMENT ALTERNATIVES

The major treatment option for nonrecoverable waste solvents, solvent sludge and solvent vapors is incineration. Incineration oxidizes the solvent material to CO_2 , H_2O and oxides of metallic contaminants (ash). Selection of the most appropriate incineration configuration depends upon the heating value, solids content and composition of the waste. In addition, requirements for the incineration of material besides spent solvent can weigh heavily on selection of incinerator equipment. The major equipment choices are multicell, rotary kiln, fluidized bed and vortex incinerators (Witt, 1972; Bowerman, 1970; Dunn, 1975). A brief discussion of each of these is presented in the following paragraphs.

It is generally considered that two types, namely the multi-chamber, multicell units and the rotaries, are the most flexible. The "inline" units have a distinct advantage of allowing the products of combustion from one cell to be used to bring succeeding cells up to temperature, as well as allowing considerable flexibility for the arrangement of firing equipment and ash removal on either side of the plant.

Rotary-kiln-type furnaces have been used with success in Europe and the U.S., and are now firing mixed residues that include up to 30 percent plastics in the feed material. The furnace consists of a refractory-lined cylinder slightly inclined to the horizontal at an angle usually variable between 2 - 5° and rotating at slow speed (4 - 5 rpm). By varying both the speed of rotation and the inclination of the furnace, the flow of material through the cylinder and the retention time for combustion can be controlled. When liquids are being fired as well as mixed solids then these are usually counter-fired at the opposite end of the furnace from the solid waste feed. Afterburning facilities can be incorporated in a separate chamber, and the equipment generally lends itself to flexible plant layout.

Rotary kiln incinerators offer the advantage of a gentle and continuous mixing of the incoming wastes, but capital and maintenance costs are high. These derive from the rigidity of the cylinder and close tolerances for the roller path drive as well as the high-temperature seals between fixed and moving parts. Another major disadvantage is that the cascading action of the burning waste, as the kiln rotates, gives all the fine ash in the charge ample opportunity to become entrained in the exhaust gases. The linings suffer both from abrasion and from contact with distillation products that can penetrate the surface before burning, thus making it necessary to install dense refractory material of higher grade than normally required in stationary furnaces.

Rotaries can, in some circumstances, be extremely suitable for sludge burning. There are also examples to be found of rotaries installed in combination with separate liquids furnaces, providing a higher degree of flexibility in the overall design of a multi-purpose destruction unit.

The fluidized bed incinerator is simple and compact, using sand or some other solid noncombustible material for the bed medium. Limitations are that bed temperature must be less than the fusing temperature of the bed material and the gas flowrate must be less than the terminal velocity of the sand. Advantages can be claimed for this type of unit. The enriched oxygen of the bed coupled with mixing of the sand and waste aids combustion rate, prevents carbon monoxide emissions and minimizes

hydrocarbon emissions; the low uniform temperature within the bed limits the formation of nitrogen oxides. Addition of limestone to the bed material means that the emission of HCl and sulfur oxides can be reduced.

To date, the principal field of fluidized-bed incinerator application has been in the refinery and paper industries where, despite high installed costs, the economics, with waste-heat recovery, are acceptable. In other fields, such as burning of municipal sludge, operating costs have proved to be very high in comparison with other designs and, in consequence, their use is presently restricted. However, most development work is at present being undertaken in order to apply the theories to refuse-burning boiler plants, and there is no doubt that in the course of this work, acceptable solutions will be found to some of the existing problems. As a method, the fluidized bed process cannot be considered, at this time, to have a high degree of flexibility in handling a wide range of wastes, and power consumption will of necessity remain inherently high.

The vortex incinerator is a cylindrical refractory-lined vessel that utilizes several tangentially firing modified oil burners. The gas flow pattern moves spirally upward. Secondary air is also introduced to further promote combustion and control the vortex. Such an incinerator is ideal for solvents with a low solids content and a high heating value. Increases in solids contents introduce operational problems with equipment erosion and ash removal rates.

Depending on the nature of the incinerator feed and the gas-solid dynamics within the incinerator, varying degrees of off gas treatment will be required. Incinerators with high gas flow rates require significant particulate removal equipment while feed material with phosphorus, halogens and sulfur will require acid gas removal.

In Denmark, all the municipalities have banded together to construct and operate a central waste oil and chemical treatment and disposal facility called Kommunekemi A/S. The operation, which began in 1971, is now operated by a private firm under contract to the national government. The treatment and disposal process for waste solvents includes distillation or decanting followed by incineration of residues in a rotary kiln incinerator. Residue from waste oil recovery is incinerated while

water removed in the recovery process is sprayed into a post-incineration chamber. No information was given in literature on disposal of incinerator residues. Examples of fees charged for wastes are given in Table 4.3. (Henriksen, 1974)

4.5 WASTE DISPOSAL ALTERNATIVES

The disposal of solid solvent processing wastes, whether they be sludges from recovery, loaded absorbents or incinerated ash, will involve either landfilling or land treatment. These two disposal alternatives are examined briefly in the following paragraphs.

4.5.1 Landfill

Landfilling is presently the most widely used method for disposing of a wide range of industrial waste products. The environmental adequacy of this method is contingent not only upon the types and characteristics of generated wastes, but also upon methods of operation and on specific site geologic and climatologic conditions. Landfilling operations range from open dumping of waste and debris to controlled disposal in secure landfills. The range of variation may be realized by considering three levels of control, which are secure landfill, sanitary landfill and land burial. Secure and sanitary landfill are described in Sections 3.2 and 3.7. Secure landfill represents excellently engineered burial techniques coupled with excellent site geohydrology. Sanitary landfill represents excellently engineered burial with less favorable site geohydrology.

Land burial sites have inadequate protection of water quality, where wastes would enter directly into ground or surface waters and are acceptable only for inert wastes which are non-water soluble and non-decomposing.

In general, the environmental adequacy of landfill site of any type is affected by the following operational and management practices:

- (1) The extent of segregation of wastes to prevent mixing of incompatible compounds, such as solids containing heavy metals with acids, or solutions with other wastes which together produce explosions, heat, or noxious gases.

Table 4.3 Charges Levied for Treatment and Disposal of Wastes Oils
and Chemicals in Denmark (Henriksen, 1974)

Type of Discard	Rate Per Ton*
Oil wastes (under 5% water)	\$0
Oil wastes (5%-10% water)	\$ 3.75
Oil wastes (20%-50% water)	\$ 7.50
Oil wastes (over 50% water)	\$10.50
Halogen-containing organic solvents	\$37.50
Other organic solvents in tankers	\$22.50
Other organic solvents in drums	\$30.00

*Rates based on approximate Danish kroner-U.S. dollar exchange

- (2) The extent to which liquid or semi-liquid wastes are blended with soil or refuse materials to suitably absorb their moisture content and reduce their fluid mobility within the landfill (co-disposal).
- (3) The extent to which acids or caustic sludges are neutralized to minimize their reactivity.
- (4) Selection of sites in which the active fill area is large enough to allow efficient truck discharging operations, as well as to assure that blended wastes may be spread, compacted, and covered daily with approximately six inches of cover soil.
- (5) The routing of ground and surface waters around the landfill site and sloping of cover soil to avoid on-site runoff and erosion.

4.5.2 Land Treatment

The second major waste treatment alternative for solvent wastes is land treatment.

Land treatment is a relatively inexpensive method of disposal of industrial wastes, and is being used by a growing number of waste handlers. The success of land treatment in the warm southwestern states has prompted many U.S. industries in colder climates to experiment with this method of disposal. Species of bacteria, yeast and fungi attack and break down a multitude of organic compounds. The rate of organic breakdown is a complex relationship between organic content of waste material, soil water content, microbial population and soil pH.

The operation of a land treatment facility involves the application of biodegradable material to the land so that it can be broken down by the microbes. Application rate and material composition must be controlled in order to maximize organic breakdown rate.

4.5.3 Emissions From Disposal

A recent study performed for the EPA Office of Air Quality Planning and Standards estimated emissions from disposal of wastes from the synthetic organic chemicals manufacturing industry (SOCMI) (Cudahy and

Standifer, 1979). These secondary emissions account for 2 to 5% of the total volatile organic compound (VOC) emissions from the SOCFI in 1978. Estimated emissions from waste disposal for 34 of the most significant organic chemicals, including many high production volume and high volatility chemicals are shown in Table 4.4. The product chemicals shown are less than 10% of the industry in number, but account for more than 70% of the total industry production.

The estimates given were primarily based on the physical and chemical properties of the major waste components and estimates of waste compositions and quantities disposed of. Significant sources of emissions include aqueous waste handling, storage, pretreatment and final treatment. Additional emissions result from landfilling, surface impoundment, and incineration of liquid and solid wastes. Handling, storage and treatment of aqueous wastes account for 50 to 90% of secondary emissions.

Additional analysis was performed to relate emissions from wastewater treatment systems, landfills and surface impoundments. A theoretical sensitivity analysis performed for hexachlorobenzene, p-dichlorobenzene, benzene, acetone and acetic acid suggests that for low water solubility, low vapor pressure chemicals, most of the secondary VOC emissions will be from wastewater treatment. It was also suggested that for low water solubility and high vapor pressure chemicals such as benzene, an increase in secondary VOC emissions from landfill would occur when compared with wastewater emissions. Secondary VOC emissions may be higher from landfills than from wastewater when liquid chemicals with higher vapor pressures and water stability, such as acetone and acetic acid, are used for comparison. No conclusions were drawn for surface impoundments, except that secondary VOC emissions from surface impoundments are potentially significant when compared with landfill emissions.

Table 4.5 shows a summary of control methods for VOC emissions from secondary sources. Waste source controls result in reduction or elimination of emissions by changing waste generating processes. Resource recovery is performed between the generating process and terminal treatment to recover organics for recycle, for sale as byproducts or for

Table 4.4 SOCM I Secondary Emission Sources and Estimated Emissions (Cudahy and Standifer, 1979)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Mg) ^a	Rate (Mg/yr)
Acetaldehyde	Ethylene oxidation	450	Aqueous	Biotreatment or deep-well	b	b
			Liquid	Incineration or deep-well	b	b
Acetone/phenol	Cumene	900	Aqueous	Biotreatment	1.6	1300
Acetic anhydride	Acetic acid pyrolysis	680	Aqueous	Biotreatment	b	b
			Solid	Landfill or incineration	b	b
Acrylic acid and esters	Propylene oxidation	410	Aqueous	Biotreatment	0.05	
			Liquid	Incineration	0.001	
			Solid	Incineration		
Total					0.051 ^c	40 ^c
Acrylonitrile	Propylene oxidation	815	Aqueous	Holding pond, deep-well	5.34	
			Liquid	Incineration	0.36	
Total					5.71	4650
Adipic acid	Nitric acid oxidation	855	Aqueous	Holding pond, deep-well	Neg.	Neg.

^a kg of emission per Mg of product produced^b Information not available.^c Does not include emissions resulting from H₂SO₄ recovery

Table 4.4 SOCM I Secondary Emission Sources and Estimated Emissions (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Mg) ^a	Rate (Mg/yr)
Alkylbenzene	Olefins	250	Aqueous	Deep-well injection	0.033	3.0
			Solid	Landfill		
	Chlorination		Aqueous	Biotreatment	0.253	45.0
			Liquid	Incineration		
			Solid	Landfill		
Total						48
Butadiene	n-Butane dehydro- genation	260	Aqueous	Biotreatment	0.150	40
			Solid	Incineration		
	Oxidative dehydro- genation	265	Aqueous	Biotreatment	0.240	64
			Solid	Incineration		
	By-product of ethy- lene manufacture	975	Aqueous	Biotreatment	0.150	146
			Solid	Incineration		
Total						250
Caprolactam	Cyclohexanone	400	Aqueous	Biotreatment		
			Liquid	Incineration		

Table 4.4 SOCM Secondary Emission Sources and Estimated Emissions (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Mg) ^a	Rate (Mg/yr)
Chlorobenzenes	Benzene chlorina- tion	220	Aqueous	Bioreatment	0.28	62
			Solid	Landfill	Neg.	Neg.
Total						62
Chloromethanes	Methane chlorina- tion	930	Aqueous	Disposal	0.13	120
			Liquid	Incineration		
Cumene	Phosphoric acid catalyst	968	Aqueous	Biological treatment	0.008	8
			Solid	Landfill	b	b
	Aluminum chloride catalyst	289	Aqueous	Biological treatment	0.23	67
Total						75
Cyclohexanol/ cyclohexanone	Cyclohexane	1,012	Aqueous	Biological treatment	0.0911	92
			Liquid	Incineration		
	Phenol hydrogenation	178	Aqueous	Biological treatment	Neg.	Neg.
			Liquid	Not indicated	Neg.	—
Total						92

Table 4.4 SOCOMI Secondary Emission Sources and Estimated Emissions (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Mg) ^a	Rate (Mg/yr)
Ethanolamines	Ethylene oxide and ammonia	165	Aqueous	Biotreatment	b	b
Ethylene	Ethane/propane feed	6,100	Liquid	Landfill, incineration, sales	b	b
			Aqueous	Phase separation and bio-treatment	0.02	122
	Naphtha feed	3,000	Solid	Landfill	Neg	b
			Aqueous	Phase separation and bio-treatment	0.04	122
	Gas oil feed	3,000	Solid	Landfill	Neg	b
			Aqueous	Phase separation and bio-treatment	0.07	214
Total			Solid	Landfill	Neg.	458
Ethylbenzene/ styrene	Benzene alkylation dehydrogenation	3,200	Aqueous		0.079	253
			Liquid } Solid }	Incineration	0.009	29
					0.088	282
Total						

Table 4.4 SOCM Secondary Emission Sources and Estimated Emissions (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Mg) ^a	Rate (Mg/yr)
Ethylene dichloride/vinyl chloride	Direct chlorination	4,900	Aqueous	Biotreatment	0.027	130
			Liquid and/or solid	Incineration	0.095	470
					—	—
Total					0.122	600
Ethylene glycol	Ethylene oxide hydration	1,960	Aqueous	Biotreatment	0.772	1513
			Liquid	Incineration of landfill	Neg.	<u>b</u>
						1513
Ethylene oxide	Ethylene oxidation (air)	1,460	Liquid	Incineration	0.0116	17
			Solid	Landfill	Neg.	—
	Ethylene oxidation (oxygen)	729	Liquid	Incineration	0.013	10
			Solid	Landfill	Neg.	—
						27

Table 4.4 SOEMI Secondary Emission Sources and Estimated Emissions (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Hg) ^a	Rate (Hg/yr)
Formaldehyde	Metallic silver catalyst	2,250	Aqueous	Biotreatment	0.01	23
	Metal oxide catalyst	750	Aqueous	Diotreatment	0.05	38
Total						61
Glycol ethers	Reaction of alcohols with ethylene and/or propylene oxide	281	Aqueous	Biotreatment	0.0019	0.5
			Liquid	Not specified	0.025	7.0
Total						7.5
Maleic anhydride	Benzene oxidation	135	Aqueous	Handling and biotreatment } Incineration Catalyst reclamation	0.05	6.8
			Liquid		Neg.	Neg.
			Solid			
Total						6.8
Methanol	Low pressure	335	Aqueous	Biotreatment	0.00044	
			Liquid	Incineration	0.00006	
Total						1.7

Table 4.4 SOCM I Secondary Emission Sources and Estimated Emissions (Continued)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Hg) ^a	Rate (Hg/yr)
Methyl methacrylate	Acetone cyanohydrin	398	Aqueous	Biological treatment	b	b
			Liquid	Sulfuric acid recovery	b	b
			Solid	Incineration or landfill	b	b
Nitrobenzene	Benzene nitration	434	Aqueous	Sulfuric acid recovery	0.33	143
				Wastewater treatment		
Perchloroethylene/ trichloroethylene	Oxychlorination	300	Aqueous	Biotreatment	b	b
		135	Liquid and/or solid	Incineration	b	b
Propylene oxide	Chlorohydrination	500	Aqueous	Biotreatment	2.6	2100
	i-Butane peroxida- tion ^d	280	Aqueous	Biotreatment		
			Liquid	Incineration		
	Ethylbenzene per- oxidation	130	Aqueous	Biotreatment		
			Liquid	Incineration		
			Solid	Landfill		
Total					2.6	2100

^d t-Butanol produced as co-product.

Table 4.4 SOCM I Secondary Emission Sources and Estimated Emissions (Concluded)

Product	Primary Process	Estimated 1978 Production (Gg/yr)	Type of Waste	Secondary Emission Source	Estimated Secondary Emissions	
					Ratio (kg/Hg) ^a	Rate (Hg/yr)
Terephthalic acid (crude)	Air oxidation	1,989	Aqueous	Biotreatment	0.004	8
			Liquid	Incineration	0.006	<u>12</u>
Total						20
1,1,1-Trichloro- ethane	Vinyl chloride	310	Aqueous	Biotreatment	0.001	0.62
			Liquid/ solid	Incineration	<0.001	
	Ethane	18	Aqueous	Biotreatment	0.001	0.04
			Liquid/ solid	Incineration	<0.001	
Total						<u>0.66</u>

Table 4.5 Applicable Control Methods (Cudahy and Standifer, 1979)

Secondary Emission Source Operation	Waste Source Control								Resource Recovery						Alternative Terminal Treatment				Add-On Controls				
	Alternative Waste Source Processes	Alternative Raw Materials	Improved Separations	Internal Recycle	Leak Elimination	Reduced Water/Steam Use	Prevent Water/Organic Contact	Improved Process Control	Steam Stripping	Conventional Distillation	Adsorption	Extraction	Emulsion Breaking	Membrane Separations	Incineration	Deep-Well Disposal	Landfill	Advanced Biological Treatment	Covers	Carbon Adsorption	Thermal Destruction	Stabilization	Refrigerated Condenser
Physical separation																							
Distillation/steam stripping	X	X	X	X		X	X	X					X							X	X		X
Liquid/liquid phase separation	X	X	X	X	X	X	X	X	X										X	X	X		X
Solid/liquid separation	X	X	X	X	X	X	X	X	X						X	X	X		X	X	X		X
Chemical treatment																							
Neutralization	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X		
Precipitation/coagulation	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X			X	X	X		X
Chemical oxidation	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X		X
Thermal destruction																							
Incineration	X	X	X	X	X			X		X	X	X	X	X		X		X					
Biological treatment																							
Activated sludge reaction	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X		X	X	X		
Clarification	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X		X	X	X		
Thickening/dewatering	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X		X	X	X		
Terminal storage																							
Landfill	X	X	X	X	X			X	X	X	X	X	X	X	X	X		X				X	
Surface impoundment	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X
Deep-well disposal	X	X	X	X	X	X	X	X										X					
Discharge to natural waters	X	X	X	X	X	X	X	X										X					
Open dumping	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X			

burning to recover heat. Alternative terminal treatment methods offer choices that may apply where resource recovery and waste source control do not. Add-on controls are used to lower emissions from waste treatment and disposal operations.

Reduction of VOC emissions by using additional controls at waste treatment and disposal facilities is shown in Table 4.6. Although many have not experienced wide use, they offer significant reductions in emissions.

4.6 CONCLUSION

Industrial activities in the area of solvent recovery are many and diverse. The diversity arises because of difference in solvents used, methods of use, scale of operation and regulations.

The evolution of waste disposal regulations such as RCRA will have an effect on solvent use practices primarily through the economic mechanism. Specific practices which are expected to evolve from more restrictive waste disposal regulations and higher costs are:

- review of solvent selection and use methods in order to render the material more recoverable - i.e., less discharges and emissions
- review of housekeeping practices to assure that they do not result in excessive losses or degrade recoverability through unnecessary contamination
- review of disposal practices to examine land treatment of biodegradable solvent wastes and the secure landfilling of non-biodegradable material.

These reviews and the subsequent evolution of practices will be more readily accomplished by the smaller companies if they are made aware of the options available to them for solvent handling and recovery. To reduce capital requirement for plant modification, equipment or service leasing arrangements may be encouraged.

Table 4.6 Secondary VOC Emission Reductions by Various Control Techniques or Methods* (Cudahy and Standifer, 1979)

Control Option	Reduction Range (%)
Organically contaminated wastewater	
Source control	10—90
Resource recovery	10—90
Immiscible organic cover	50—90
Floating plastic spheres	70—90
Floating plastic cover	>99
Collection/carbon adsorption	>99
Collection/thermal destruction	>99
Organic liquid and solid	
Landfill	
Soil cover	75—99+
Plastic cover	>99
Surface impoundment	
Immiscible organic cover	50—90
Floating plastic spheres	70—90
Floating plastic cover	>99

*Based on the limited data available plus engineering experience and judgement.

5.0 WASTES FROM EXPLOSIVES MANUFACTURE

5.1 INDUSTRY OVERVIEW

Current regulations governing air, water, and land emissions from commercial and military explosives manufacturing may not address all hazards associated with explosives manufacture. Effluent limitations and guidelines for the Best Practicable Control Technology Currently Available (BPCTCA) set by the Environmental Protection Agency in 1976 provide the only standard available for wastewater for subcategories: A. Manufacture of Explosives; B. Manufacture of Propellants; and D. Manufacture of Initiating Compounds. Guidelines for subcategory C. Load, Assemble and Pack Plants have not yet been published (EPA, 1976d). These guidelines fail, however, to cover various constituents known to be characteristic of explosive wastewater streams, such as extreme pH, sulfates, color, and toxic metals. In addition, air and land emissions resulting from the manufacturing process and treatment method will also require standards that have not yet been promulgated. Toxic metals, cyclotrimethylene trinitramine (RDX), trinitrotoluene (TNT) and other explosives in the form of particulates, and oxides of nitrogen (NO_x) have been observed following destruction of explosives munitions (U.S. Army, 1978). Open burning, one of the oldest and universally utilized disposal methods for pyrotechnics and detonators, emits large quantities of NO_x and particulates. Characterization of these air and potential land emissions is necessary to determine the magnitude of environmental pollution that occurs.

In light of the potentially hazardous nature of explosives, and because of their ignitability, reactivity and volatility, air, land, and water criteria must be established which reflect these significant concerns. The following chapter describes the military and commercial explosives industries, the waste streams they generate and current and alternative methods of handling them.

The explosives industry manufactures over 120 different chemicals and formulations which can be considered useful. Approximately 45 are

used by the industry in mining, quarrying, ditching, in oil and gas wells, in road building and for sporting ammunition. Forty-five have military applications in weapons, rockets, missiles, and space vehicles and 15 are useful for both military and commercial uses. The distribution of commercial uses is shown in Table 5.1. Explosives are characterized by their rate of transformation (burning rate), ease of initiation (sensitivity) and the maximum explosive energy available for useful work. They are usually classified in two groups: low or deflagrating explosives, exhibiting low burning rates and used primarily as propellants; and high or detonating explosives, exhibiting great shattering strength due to production of high velocity detonating waves. High explosives are further sub-classified into primary and secondary explosives. The primary or initiating group of explosives, such as lead azide, are sensitive to heat, impact or friction. They undergo decomposition when subjected to these, and develop detonation waves in extremely short time periods. Secondary or non-initiating explosives require detonators (fuse caps) and/or boosters for detonation. Boosters, more sensitive secondary explosives, are typically TNT, RDX, or TNT and pentaerythritol tetranitrate (TNT-PETN). They are usually required for less sensitive secondary explosives, such as the 94/6 (94 percent to 6 percent ratio) prilled ammonium nitrate and oil mixture and the "slurry blasting agents," comprised of ammonium nitrate, coarse TNT and water.

Explosives are manufactured by both the commercial and governmental sectors. SIC 2892 refers to plants owned by both sectors, but operated by private firms including government-owned, commercially operated (GOCO) plants. Government-owned and operated operations (GOGO) are not included in SIC 2892. Figure 5.1 summarizes the geographical distribution of these facilities within the United States. Both sectors manufacture high explosives and initiating compounds and perform loading operations. They utilize similar, and sometimes identical, production processes, but differ in plant size, major projects, end uses, and production rates. The commercial sector primarily provides ammonium nitrate based explosives, dynamites and nitroglycerin (NG); the military makes TNT, cyclo-tetramethylene tetranitramine (HMX), RDX, NG and the NG-containing components of military propellants.

Table 5.1 Percentage Distribution of Commercial Explosives Use (EPA, 1975a)

Year	Coal mining	Quarrying and non-metal Mining	Railroad and other Construction	Metal mining	Seismographic exploration	Other purposes
1963	34.7	22.0	21.0	17.4	4.2	0.7
1964	33.0	21.7	19.9	19.1	5.5	0.8
1965	31.6	19.7	21.8	18.9	7.4	0.6
1966	31.4	20.1	22.2	17.9	7.7	0.7
1967	34.7	21.5	21.7	17.2	4.5	0.4
1968	35.1	20.4	21.1	20.7	2.1	0.5
1969	36.8	19.7	20.0	21.1	1.8	0.6
1970	40.2	19.0	18.7	20.0	1.1	1.0
1971	42.0	19.2	18.7	17.9	0.7	1.5
1972	45.4	18.5	17.5	16.1	0.7	1.8

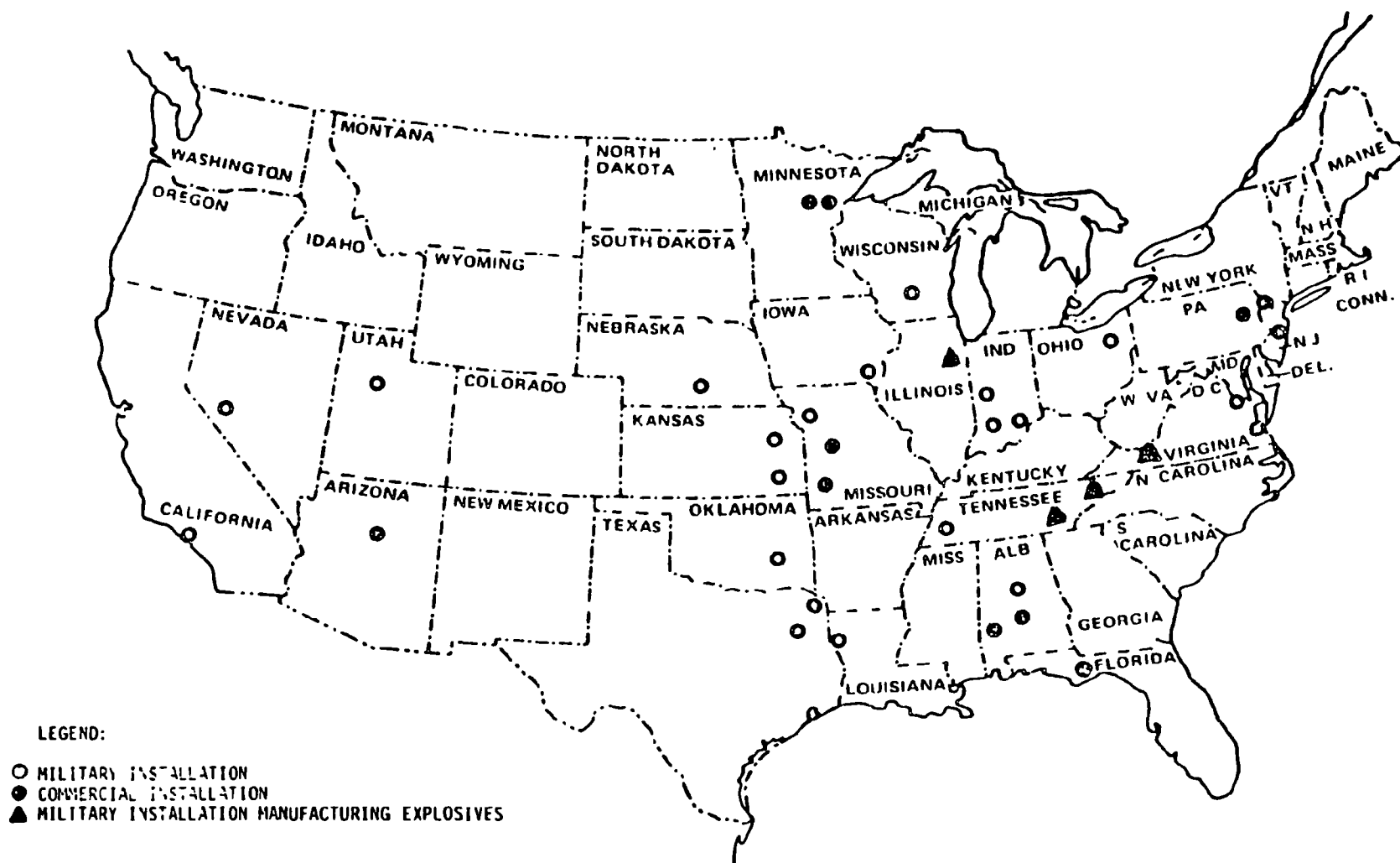


Figure 5.1 Major Explosives and Propellant Facilities In the U.S. (Booz-Allen Applied Research, Inc., 1973)
(EPA, 1977 b)

In developing guidelines for wastewater effluents and atmospheric emissions, EPA has divided the explosive industry by production process and explosives type, into four subcategories:

- A. Manufacture of Explosives, such as dynamite, NG, RDX, HMX, TNT, and nitroguanidine (NGu).
- B. Manufacture of Propellants, such as rolled powder, high-energy ball power, and nitrocellulose (NC). Propellants can be single-, double-, or triple-based.
- C. Load, Assemble and Pack (LAP) Operations, which include plants blending and marketing a final product and those filling shells and blasting caps; plants manufacturing ammonium nitrate and fuel oil (ANFO), nitrocarbonitrate (NCN), slurries, water gels and shells are examples.
- D. Manufacture of Initiating Compounds, including such highly-sensitive explosives used for detonation as PETN, lead styphnate, tetryle, mercury fulminate, lead azide, nitromannite (HMN) and isosorbide dinitrate.

Solid wastes from explosives manufacture are chiefly wastewater treatment sludges and waste product. Little information was available on wastewater treatment sludges, particularly for commercial explosives. Waste product is typically released in the production process where quality control standards allow.

5.2 MANUFACTURE OF COMMERCIAL EXPLOSIVES

Commercial explosives are nitrogen-based organic compounds which decompose rapidly and spontaneously under the influence of thermal or mechanical shock, releasing large quantities of heat and gas. They are categorized according to their behavior as high or low explosives (see Table 5.2.). Primary high explosives function by the application of fire on slight impact. They are used in small quantities in primers, detonators and percussion caps, are dangerous to handle, and are typically mercury or lead compounds (mercury fulminate, lead azide, styphnate, or diazodinitrophenol). Secondary high explosives are relatively insensitive

to mechanical shock and flame, but explode with great violence when set off by explosive shock from detonation. Decomposition then proceeds rapidly by chemical reaction progressing through the mass of secondary explosive. Low explosives only burn and therefore differ in their rate of decomposition. The reaction proceeds in layers parallel to the surface, rather than throughout the body of the explosive, and is therefore slower in action with less shattering force.

Table 5.2 Examples of High and Low Explosives

<u>Primary High Explosives</u>	<u>Secondary High Explosives</u>	<u>Low Explosives</u>
blasting caps	dynamites	ammonium nitrate (prilled or grained)
detonation cords	NG	AFNO
electric matches	PETN	black powder
lead azide		NCN
mercury fulminate		smokless powder
safety fuses		water gels & slurries
 <u>Low Explosive Sensitizers</u>		
amine nitrate		
dinitrotoluene (DNT)		
TNT		

The final explosive product may contain a variety of absorbents, coating agents, fuels, oxidizers and other materials. Both high and low explosives involve either single organic compounds or mixtures of these and inorganic salts.

The explosive NG, produced by nitration of glycerin with nitric and sulfuric acid, and NC are both extremely sensitive to impact. For that reason, they are usually manufactured into dynamites for safe handling. Dynamites, which contain a mixture of ingredients depending on their specifications for use, are usually comprised of wood flour, ammonium or sodium nitrate (to absorb the NG), oxidizers and ethylene glycol (see Table 5.3).

Table 5.3 Common Ingredients of Dynamites

NG	sawdust and wood flour
ammonium nitrate	coal
sodium nitrate	cornmeal and starch
sodium chloride	trace inorganic salts
sulfur	grain and seed hulls and flours.
phenolic resin beads	

PETN, produced by nitration of pentaerythritol with concentrated nitric acid, is one of the most shattering and sensitive high explosives. For this reason, if used as a booster explosive, it must be desensitized by the addition of TNT or wax. PETN lends itself to the manufacture of detonating cord. Ammonium-based explosives, which consist of prilled or grained 99.5 percent nitrate mixed with a carbon fuel, have replaced others for the surface mining, quarrying and construction industry.

Premixed ammonium nitrate (94 percent) and carbon fuel (6 percent), frequently containing powdered aluminum, stabilizers, and inhibitors, form ANFO. This is blended to customer-specification and transported by truck in bulk, bags, or cylinders to mine fields. NCN is used primarily for seismic exploration and is similar in composition to ANFO, containing mineral oil, sodium nitrate, DNT or TNT, plus some proprietary ingredients.

Water gels and slurries are basically a mixture of oxidizer, fuel, and sensitizer in an aqueous media, thickened with gum and gelled with a cross-linking agent. They exhibit an infinite number of formulations.

Smokeless powder is used as a propellant in ammunition and as an addition, in small quantities, to water gels and slurries and some dynamites. It is manufactured by nitrating cotton or specially prepared wood pulp with concentrated nitric acid, purified, and colloided with nitrated cellulose. This last step transforms the product into a uniform mass with a reduced surface, for greater rapidity of explosion.

The commercial explosives industry has three divisions:

- Complex facilities manufacturing a variety of intermediates and products such as ammonium nitrate, nitric acid, NG, dynamites, water gels, ANFO.

- Small plants usually near mining fields, blending explosives for nearby use (ANFO, water gels) with intermediates received in bulk, and formulating compounds to customer specification.
- Specialty product plants manufacturing selected ingredients such as lead azide, blasting caps, and electric matches.

Generally, large volumes of water are used for cooling and processing effluents. These are typically high in biological oxygen demand (BOD), oil and grease, ammonium- and nitrate-nitrogen, and solids, and have pH extreme. Their hazardous nature is further increased by the frequent appearance of trace quantities of dissolved and particulate explosives products.

5.2.1 Ammonia-Nitric Acid Production Processes and Waste Stream Characterization

Most of the major explosives manufacturers produce their own ingredients for formulation and selected intermediates. On-site production of ammonia, ammonium nitrate and nitric acid is common to the industry. Raw materials include natural gas, air and steam, which are catalytically reformed to produce nitrogen, hydrogen, CO and CO₂. The impurities are scrubbed and removed, and the reaction proceeds catalytically to produce ammonia, which is stored as a gas or aqueous solution. The ammonia is then oxidized to produce nitric acid (HNO₃). Cooling water is required at each step and is discharged with any other leakage or clean-up water as waste. The waste stream itself is highly acidic and contains appreciable quantities of nitrate- and ammonia-nitrogen. Current treatment practices rely solely on pH adjustment. Nitric acid can also be concentrated by the continuous distillation of weak nitric acid in the presence of sulfuric acid.

Process effluents from the absorber tail gas, can contain appreciable quantities of NO_x. These are probably due to an insufficient air supply, leaks, or temperatures exceeding design capabilities in the absorption tower. Wastewater effluents are characterized by low pH, high ammonia- or nitrate-nitrogen (NH₃-N₂, NO₃-N₂), and high sulfate levels. Treatment practices involve acid neutralization and calcium sulfate sludge removal.

Spent acids from NG, PETN, or TNT manufacture, are also processed to recover nitric acid. However, they may exhibit high levels of dissolved solids, high sulfate, and quantities of nitrogen salts. This would contribute to variability in NO_x emission from nitric acid production.

5.2.2 Nitroglycerin Production Process and Waste Stream Characterization

Nitroglycerin is a highly unstable explosive very sensitive to shock. The safest method of production involves the controlled nitration of very pure glycerin required for safety and stability with concentrated sulfuric and nitric acids. (See Figure 5.2.) The product, which contains about 0.5 percent water, is stored in lead-lined tanks. The Biazzi process, a continuous nitration process, is already being used by the military and is rapidly being adopted by the commercial industrial sector. This process is shown in Figure 5.3.

The waste effluents associated with nitration are similar in both processes. They are NO_x and nitric acid fumes of unknown quantity. These are vented through the absorber to the atmosphere. Wastewaters from building and equipment clean-up contains trace amounts of pollutants. However, the dilution effect from various wastewater streams precludes characterization of each stream separately. Spent acid effluents are identical to other spent nitration acids. After nitration, the product is neutralized, washed and separated. The latter produces a 3 percent sodium carbonate residual requiring disposal. Washing produces "sour water," which proceeds to a catch tank for further treatment.

5.2.3 Dynamite Production Process and Waste Stream Characterization

It was the extremely high sensitivity of NG to shock that originally led to the formulation of dynamites. Major ingredients are NG and ammonium nitrate. Table 5.4 shows the typical composition for dynamite. Ammonium nitrate is first mixed with minor ingredients (wood pulp, sawdust, flour, starch) and a small amount of antacid (CaCO_3 or ZnO) to form a "dope" to which nitroglycerin is added. The "dope" is oxygen-balanced for maximum strength and minimum fumes. Varying amounts of NG are used. For example, a 40 percent straight dynamite contains 40 percent NG, 44 percent

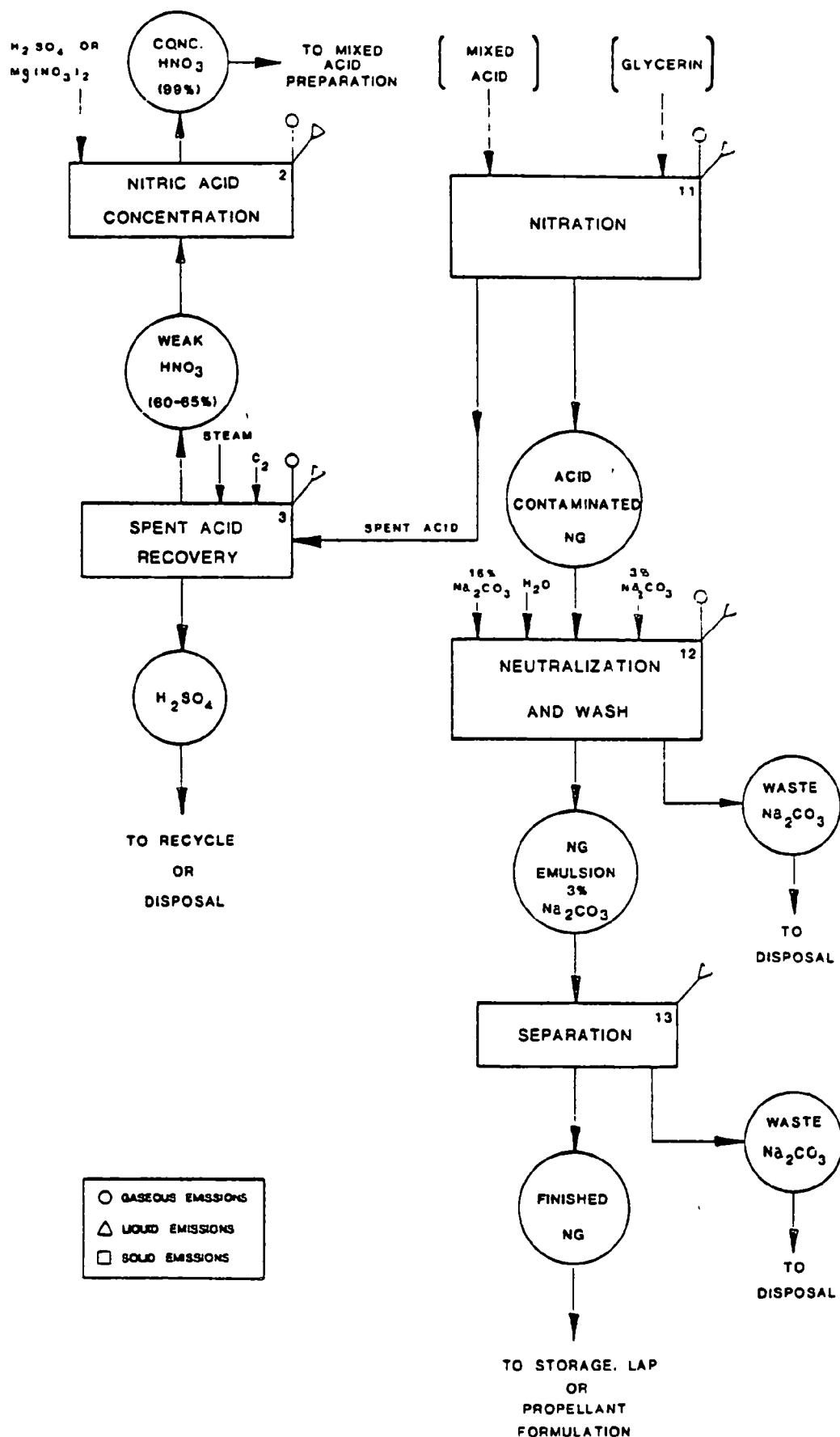


Figure 5.2 Flow Chart for Nitroglycerin Production (EPA, 1977b)

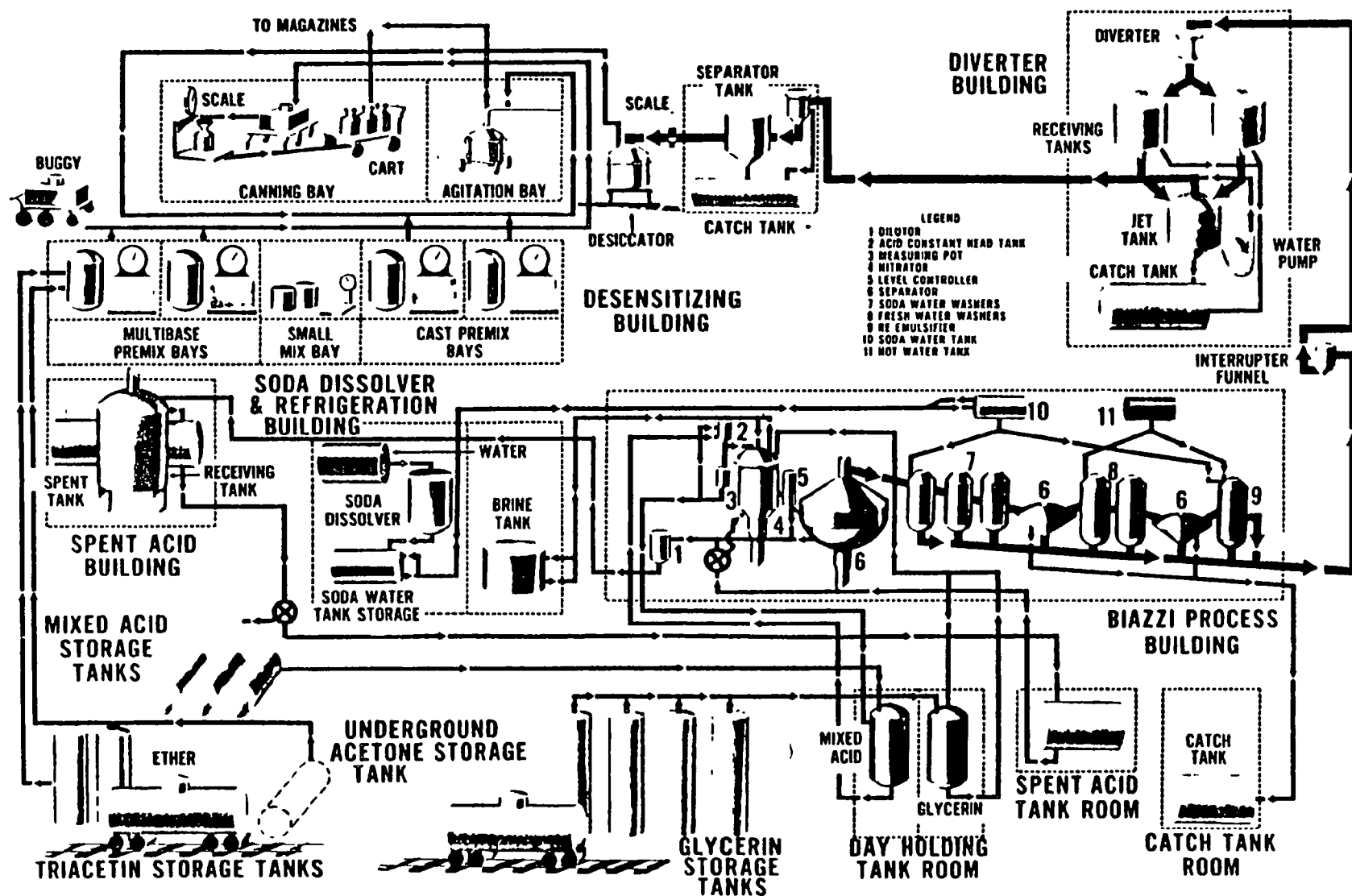


Figure 5.3 Biazzi Nitroglycerin Process (Courtesy, U.S. Naval Ordnance Station, Indian Head)
(EPA, 1976 d)

sodium nitrate, 14 percent carbonaceous material, 1 percent antacid and 1 percent moisture. A 40 percent ammonia dynamite contains 15 percent NG, 32 percent ammonium nitrate, 38 percent sodium nitrate, 4 percent sulfate, 9 percent carbonaceous material, 1 percent antacid and 1 percent moisture. Straight dynamites usually contain 20-60 percent NG. NG may also be gelatinized with 7-8 percent collodion cotton to make blasting gelatin. Gelatin dynamites are mixtures of gelatin and "dope" ranging from 20-90 percent grades (gelatin:dope). These have the greatest shattering action.

Liquid nitroglycerin for the formulation of dynamite is handled in small lots in rubber pails. The products are packaged by automatic machinery into waxed cardboard or plastic tubes and then boxed in sawdust for transportation.

5.2.4 Smokeless Powder Production Process and Waste Stream Characterization

Smokeless powder is colloided NC containing approximately 1 percent diphenylamine to improve storage life, plus a small amount of plasticizer such as dibutyl phthalate. (See Figure 5.4.) Cotton, or specially prepared wood pulp is nitrated with concentrated nitric acid, purified, and the nitrated cellulose is disintegrated. The product is colloided by mixing with alcohol, ether diphenylamine and other agents to transform it into a dense uniform mass with a reduced surface area for greater rapidity of explosion. NC is obtained from an outside supplier.

Scrap powder is stored as a water slurry to reduce the potential hazard. Overflow from this storage contributes to the waste stream as does the filter backwash in its last step of preparation. These are both discharged to the wastewater production stream, and would be removed in sludges from wastewater treatment. However, wastewater is generally not treated.

5.2.5 ANFO Production Processes and Waste Stream Characterization

The major ingredients of ANFO explosives are ammonium nitrate, ferrophosphate, calcium silicate, fuel oil, aluminum, coal and mineral oils. The only source of wastewater arises from clean-up of spills and

Table 5.4 Typical Composition of Dynamite (EPA, 1975a)

Component	Percent, Wt.
Ammonium nitrate	50-55
Nitroglycerin	15-18
Sodium nitrate	0-17
Trace ingredients	10-35

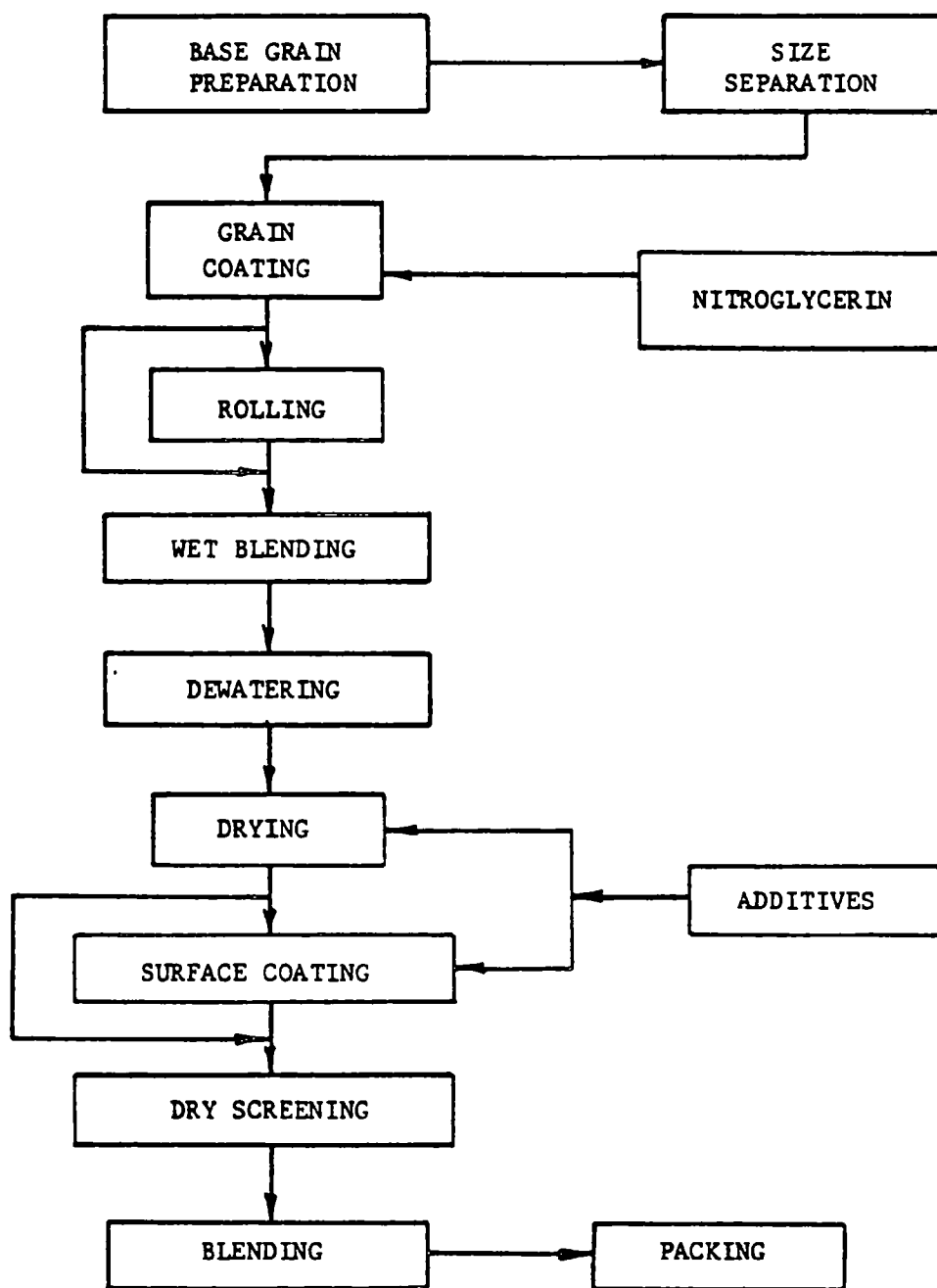


Figure 5.4 Smokeless Powder Process Flow Chart (EPA, 1975 a)

and equipment. NCN is similar in constituents to ANFO, but it may also contain sodium nitrate, proprietary ingredients, and DNT or TNT (which is usually purchased from a supplier). The wastewater stream is restricted to clean-up of spills and equipment and may or may not be hazardous depending on the presence of DNT or TNT in the stream. Wastewater is generally not treated; therefore, sludges are not produced.

5.2.6 PETN Production Process and Waste Stream Characterization

Production of PETN involves the nitration of pentaerythritol by 94 percent nitric acid (see Figure 5.5). Waste effluents from nitration are similar to the nitric acid recovery process. Stabilization produces a final product which is 40 percent water. The effluents are combined with those from washing, filtering, and still bottoms to form the wastewater stream. The slurry is hot-dried before being used in explosives formulation. Although air and water emissions data were not found in literature, it is likely that the wastewater effluent is contaminated with traces of basic salts from the stabilization step, nitrates from the basic salts reacting with nitric acid, and acetone. Solid wastes are mainly still bottoms from steam distillation in the acetone recovery process.

5.2.7 NC Production Process and Waste Stream Characterization

NC is characterized by its degree of nitration. Uncolloided dry cellulose nitrate is a violent and sensitive explosive. Treatment with special plasticizers produces a colloidal form which is less sensitive and more prone to burning than detonation. Production involves pre-purification of cotton linters or specially prepared wood pulp, nitration by nitric/sulfuric acid in special reaction pots, centrifugation of the crude NC, and dumping in a "drowning tub" to stop the reaction. Any NO_x from the reactor and centrifuge goes to the absorber where it is oxidized to produce weak nitric acid. This is subsequently concentrated.

Air emissions of NO_x from the first absorber vent, and NO_x and SO_x from the systems' second absorber result. The concentrator and reactor pots would also emit NO_x and SO_x . Wastewaters from clean-up are characterized by low pH, high levels of suspended solids, and high nitrate-nitrogen. (See Figure 5.6.)

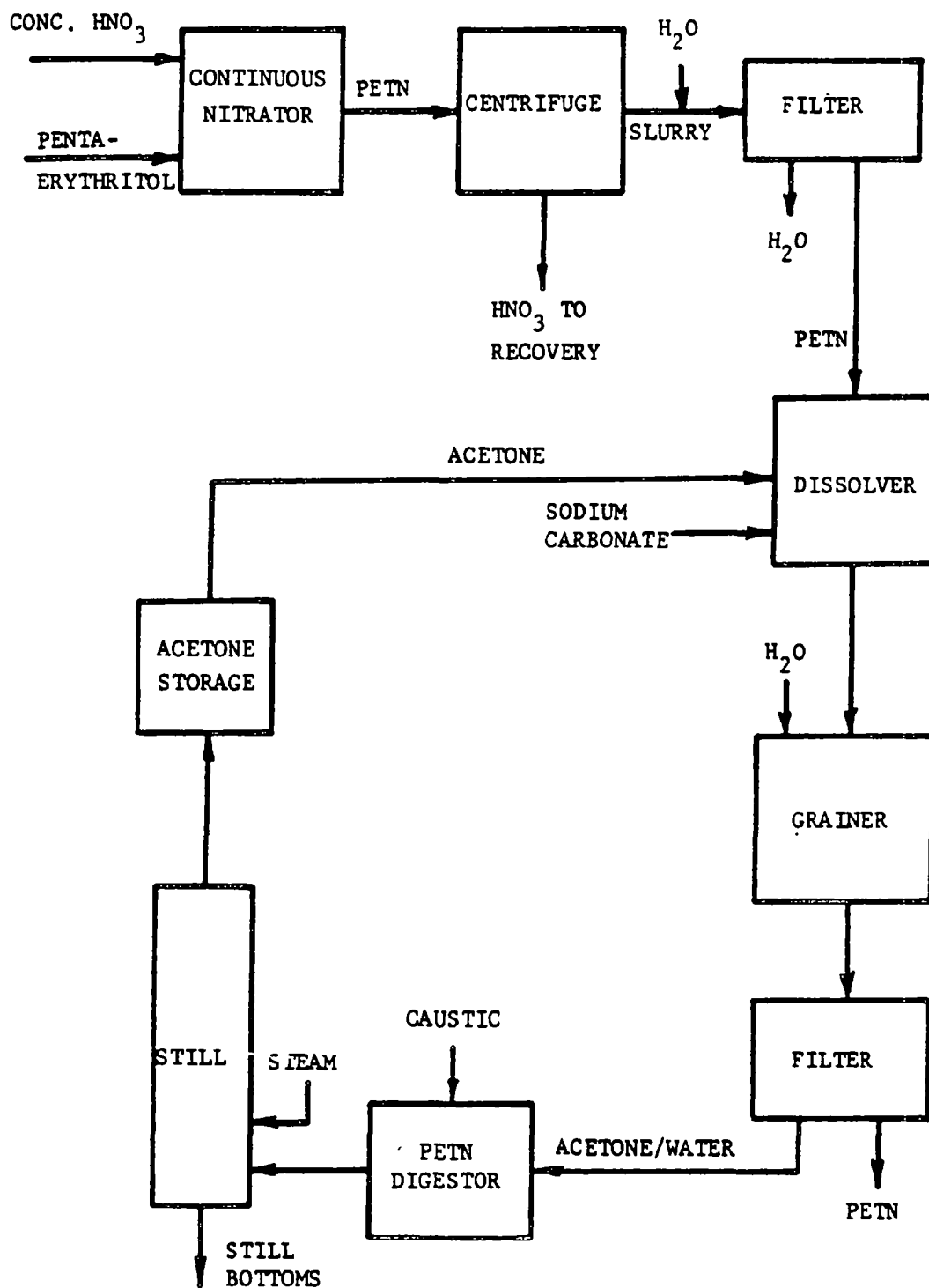


Figure 5.5 PETN Production and Acetone Recovery (EPA, 1975 a)

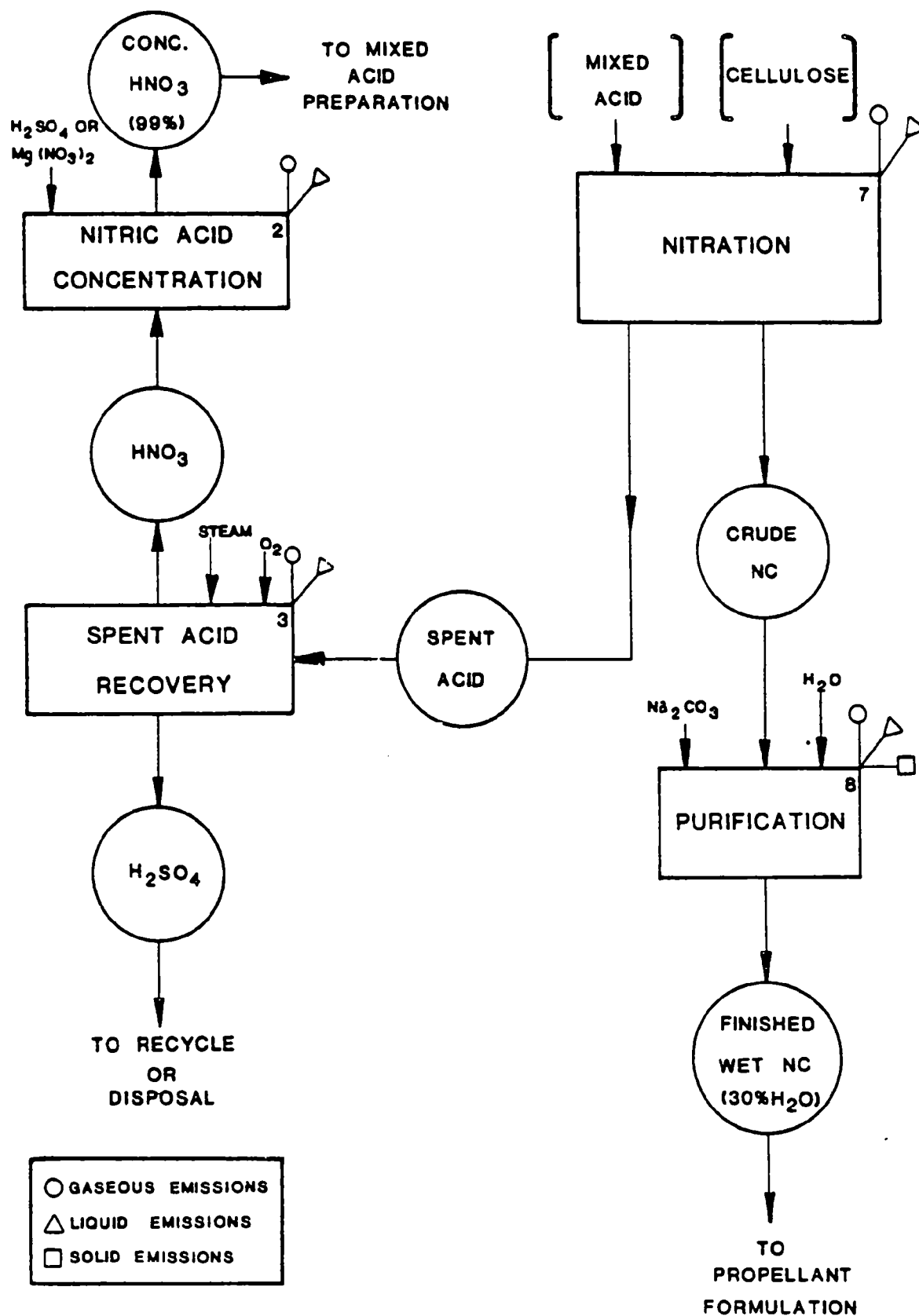


Figure 3.6 Flow Chart for NC Production (EPA, 1977b)

Purification of NC is vitally important to production. Residual spent acids trapped by the cellular structure during nitration will render the explosive unstable during storage. A number of distinct steps are involved. The NC water slurry undergoes acid hydrolysis to remove unstable sulfate esters and nitrates, and is beaten and reduced to a desirable degree of fineness. It is poached with sodium carbonate solution, blended with NC fines from settling pits for various grades, and finally centrifuged. The finished wet NC contains 30 percent water.

All of these processes require huge amounts of water which must eventually undergo treatment and disposal. Washwaters from acid hydrolysis and acidic wash water drains into settling pits. There, NC fines are removed. Pit overflow is neutralized by calcium carbonate as a lime slurry in the acid neutralization facility and then transferred to settling lagoons or discharged directly. Sludge from the lagoon is buried on-site on land adjacent to the plant.

5.3 MANUFACTURE OF MILITARY EXPLOSIVES

The military explosives industry as a whole is involved in two operations:

- Manufacturing and production of explosives, propellants, or intermediates, such as TNT, NG, NC, nitric acid.
- Loading, assembling, and packing of explosive or propellant products into munitions. This usually involves blending various ingredients.

Three major categories of products are included: acids, which are intermediate products, and explosives and propellants, which are final products.

About 17 "Army Ammunition Plants" (AAP), located mostly in the east and the south, have a role in one or both of these two activities. Seven are involved only in manufacturing; eight in loading, assembling and packing (LAP) activities; and two in both. (See Figure 5.7.) The

	Activity		Product Capabilities																	Dry assembly	Ingredients Used in Formulations																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																											
	HFRE	LAP	Acids							Explosives					Propellants						A ₁	Al	CuCl ₂	DNT	HMX	HC	HO	RDX	H ₂ O ₂	Ammonium Picrate	Polyurethane	RDX	Solvents	TBT	Vac	NaNO ₂																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																												
			Acetic Anhydride	Glacial Acetic acid	Succinic acid	Nitric acid	Malic acid	Citric acid	Sulfuric acid	Oleum	DNT	TNT	HC	Tetryl	RDX	HMX	RDX	Primers	EC																		Single Base	Multi-Base	Solventless	Composites																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								
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Figure 5.7 The Military Explosives and Propellants Industry (EPA, 1976d)

Army also supplies other government defense agencies with high explosives and propellant products. All explosives, with the exception of NG used by the Air Force, are manufactured by the Army. They also load, assemble and pack munitions for these agencies. Two Navy facilities produce casting powder and NG, but obtain loaded explosives from the AAP network. The Navy also loads and assembles solid rocket motors with propellants obtained from AAP or manufactured in-house. It is also the Navy's responsibility to load most of the bombs for the other defense agencies.

There are four major steps in munitions manufacture:

- manufacture or purchase of ingredients such as NC, NG, TNT, or HMX
- combination of ingredients into blends, grains, or formulations such as composition B
- loading of warheads, bombs and rocket motors with blends or formulations
- final assembly and packing of complete munitions.

Explosives and propellants manufacture uses operations similar to those in other chemical production operations. However, they are housed in plants occupying a much greater area for safety consideration. They are generally isolated geographically.

Four materials account for most of the tonnage produced. They are TNT, NC, RDX and NG. These are rarely used alone, but are used for blending and in formulations. The manufacture of nitration acids, particularly nitric acid and sulfuric acid, is also significant.

Wastewater streams associated with these manufacturing processes are also similar to those from a chemical manufacturing operation. They result from acid drippings, solvent spills, stack scrubber drainings and floor washdown. Waste streams unique to military explosives manufacture will be discussed in following sections. In general, acid manufacture produces small volume wastes that originate from leakage and drainage from air pollution abatement scrubbers. Their composition includes

the following:

- acid waters which are neutralized with lime or soda ash
- azeotroping agents such as n-propylacetate
- heavy metals from equipment corrosion
- nitro bodies from acid recovery.

The worst problems and the greatest quantity of waste originate from the basic explosives manufacturing process. These consist of acid matters, chemical washes, spills and washdowns. Red water, a wastewater stream unique to the military, is the major by-product from TNT manufacture. It is a brick red solution composed of sodium nitrate (NaNO_3), sodium sulfate (Na_2SO_4), sodium sulfite (Na_2SO_3), sodium nitrite, sulfonated or sellited nitro-compounds, and complex unidentified dye-bodies in varying proportions. Other streams from manufacture include pink water which is dissolved TNT in water (≈ 100 ppm) from equipment washdown and work area clean-up, and is found wherever TNT is made or handled; suspended explosive particles in the form of dust and chips; and sometimes solvents such as acetone, benzene and dimethyl aniline. Efforts are currently being made to eliminate these waste streams by installing effluent treatment units, replacing outdated process equipment, automating production lines, recycling and use of newly developed, more environmentally sound processes. Major wastewater problems from the military explosives industry are shown in Figure 5.8.

5.3.1 TNT Production Process and Waste Stream Characterization

TNT, one of the most important military explosives, is produced by treatment of liquid toluene with mixed nitric and sulfuric acids. The undesirable isomers are removed by treatment with a sodium sulfate solution. Residual DNT, used for the manufacture of propellants, is removed by conversion to a soluble salt and subsequent extraction.

Two process variations exist: the conventional stepwise batch process, shown in Figure 5.9, and the new Canadian Industries Limited (CIL) continuous process, shown in Figure 5.10. Both include the nitration of toluene by a mixture of oleum, nitric and fuming sulfuric acid,

Wastes	Manufacture of Chemicals									Loading			
	Trinitrotoluene & DNT	Tetryl	Primer materials	RDX/HMX	Nitrocellulose	Nitroglycerin	NC-based propellants	Ball powder	Black powder	Acid manufacture	Filling of warheads	Mfg. of extruded rocket grains	Mfg. of cast rocket grains
Acid waters, nitrate & sulfate salts, etc.	+	+		+	+	+				+			
Red Water	+												
Pink Water	+										+		
Other dissolved explosives and/or dust and chips	+	+	+	+	+	+	+	+	+		+	+	+
Organic solvents and resins		+		+			+	+					+
Chromium and other metals from corrosion										+	+		
Perchlorate and other oxidizers													+

Figure 5.8 Major Wastewater Problems in the Military Explosives Industry (EPA, 1976d)

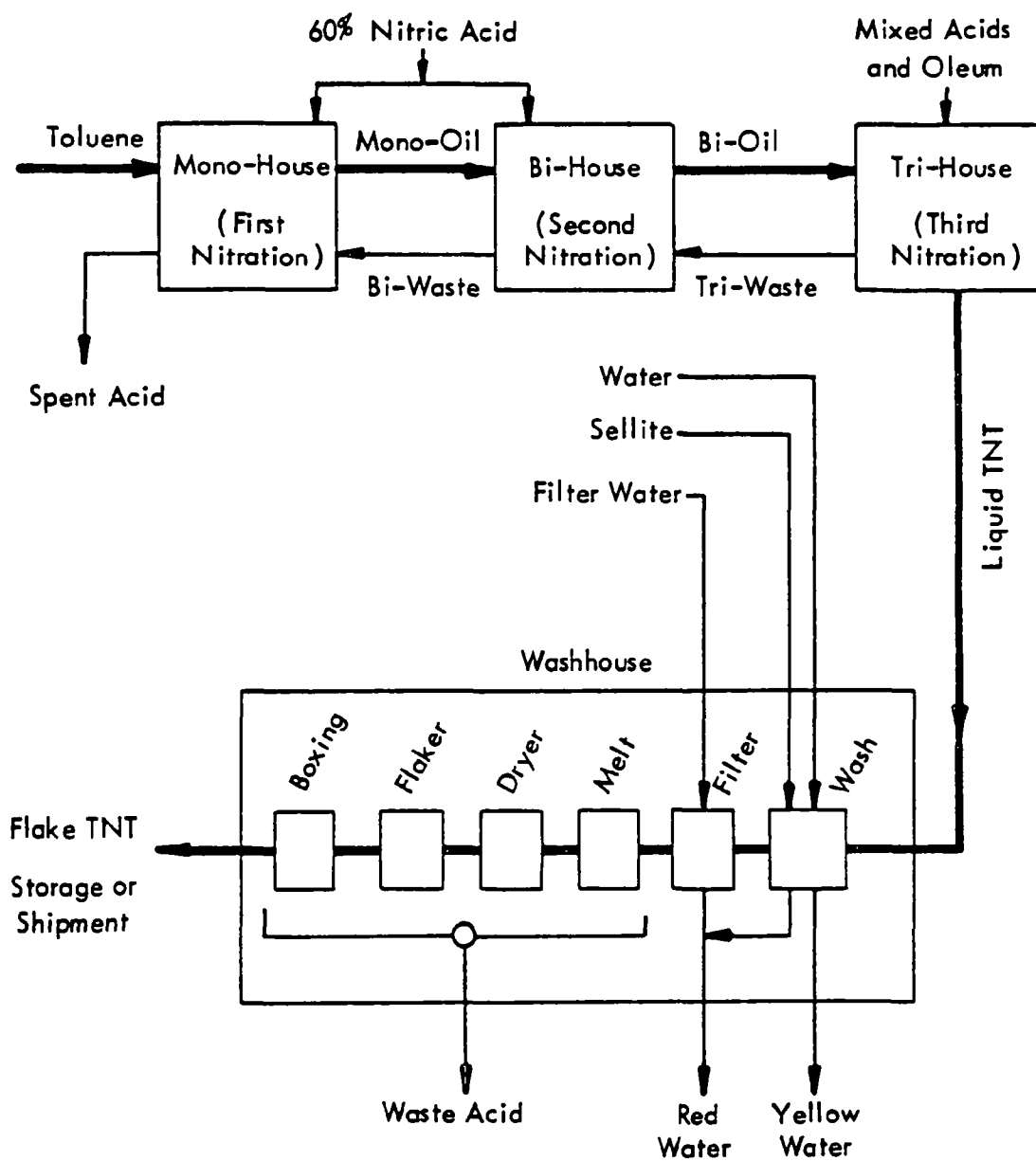


Figure 5.9 Batch Process for TNT Manufacture (EPA, 1976 d)

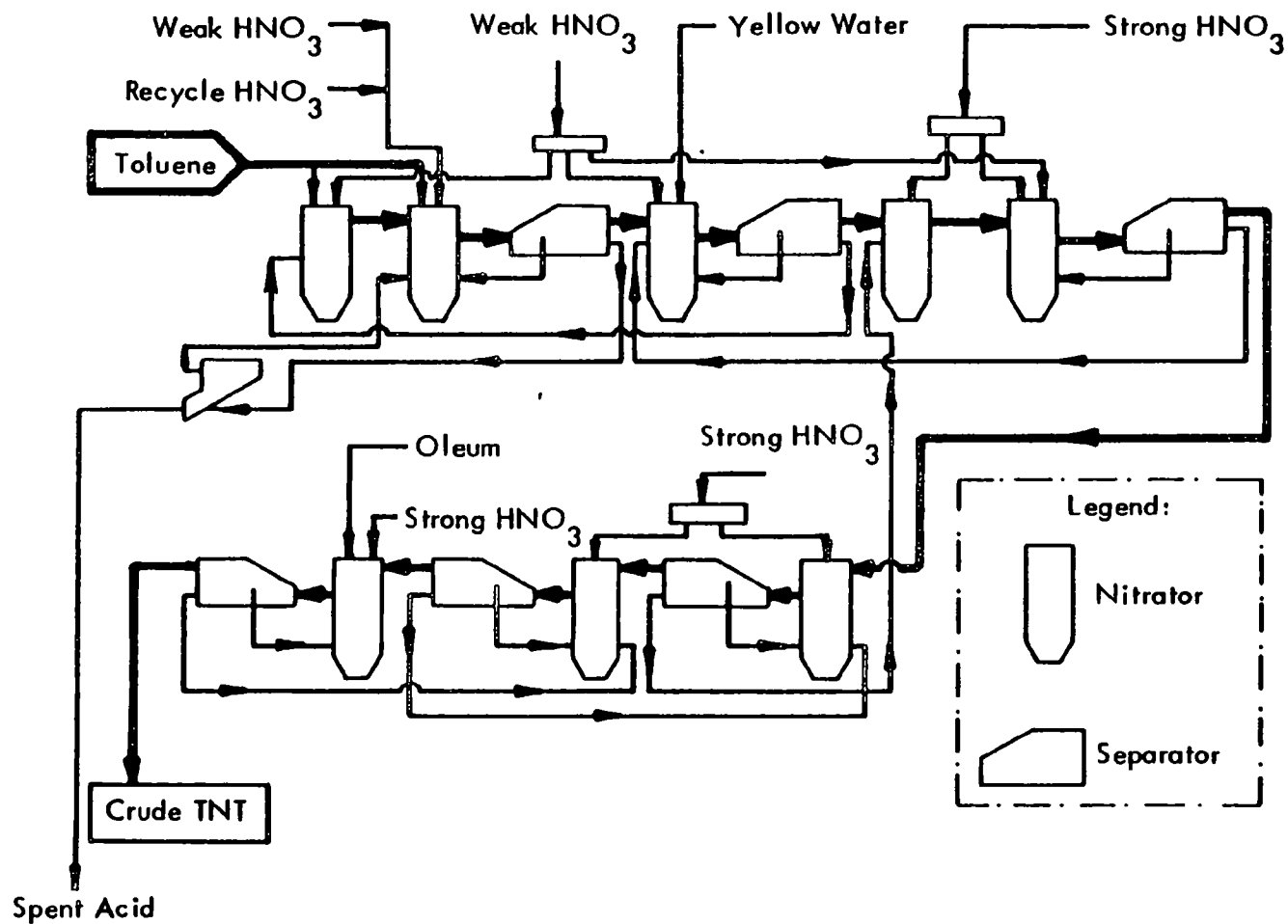


Figure 5.10 CIL Continuous Process for TNT Manufacture (EPA, 1976 d)

followed by purification and finishing of the product. Gaseous emissions from nitration are released from the nitrators and separators and are composed of CO, CO₂, NO, NO₂, N₂O and trinitromethane (TNM), a violent explosive. TNM is currently vented to the atmosphere. Before discharge, the effluent is passed through a fume recovery system to recover the NO_x as nitric acid. Traces of TNM have also been found in this acid and fume recovery system. The final effluent vented to the atmosphere contains quantities of unabsorbed NO_x and some TNM. Spent filter media is an occasional solid waste from the batch process.

Yellow water, which is a dilute solution of crude TNT in water plus acids, results from the first crystallization and water wash in the CIL nitration step. It is recycled to the second nitrator for consumption within the process. The spent acid waste stream is not discharged. Nitric acid is recovered from the waste and reused. Any residue water is sold for commercial use. Waste acids resulting from spillage and floor drainage are neutralized with lime or soda ash and then discharged to a chemical waste sewer for further treatment. Wastewater from the nitration step is carried through the acid recovery system and then discharged.

Following nitration, TNT undergoes purification with a number of water washes, neutralization with soda ash, and treatment with a 16 percent aqueous sodium sulfate (sellite) solution to remove the contaminating isomers.

The waste streams generated in TNT manufacture, in order of decreasing strength, are red water, pink water and yellow water. In terms of production amounts, approximately 0.34 kg/kg TNT waste is produced consisting of 0.26 kg process water, 0.06 kg organics (nitro-toluenes and nitrotoluenesulfonic acid salts), and 0.02 kg dissolved inorganics (NaNO_x and Na₂SO_x). The red water consists of extraction waters and the sellitic solution. It is concentrated to 35 to 40 percent and sold to the paper industry as a source of sulfite liquor, or water is removed by evaporation and the waste is incinerated. Red water contains approximately 77.6 percent water, 17.3 percent organics, 5.2 percent NaNO_x, and approximately 2.9 percent Na₂SO_x. Approximations are due to conflicting analytical methods.

Incineration produces atmospheric emissions containing NO_x and SO_2 and solid waste as ash, primarily sodium sulfate, which is approximately 90 percent soluble. When this ash is landfilled or stockpiled, the current practice, the ash is susceptible to leaching by rain water and could cause contamination of both surface and ground water.

TNT manufacture, and LAP operations, also generate pink water which, like red water, is of variable composition. Pink water may contain isomers of DNT, TNT, and usually has high nitrobody content. Sources include: nitration fumes, scrubber discharge, red water concentrate distillates, finishing operation hoods, scrubber and washdown effluents, and possible spent acid recovery washes.

Treatment practices involve removing the solids with a sump, and treating the effluent by carbon adsorption or evaporation/leaching. Risk of explosion has been reported for adsorbing high concentrations of TNT on carbon. Ultimate disposal of the sump sludge is by open burning.

Yellow water, which is excess water from the first washing that has not been returned to the nitration process, is combined with other waste process water for final treatment.

Finishing is the final step in TNT production. The TNT crystals resulting from purification are slurried with water, melted, re-evaporated, solidified, flaked and packaged. Waste streams generated include waste acid and wash waters. The acid stream from the finishing process results from spillage, floor drainage and washings in the work area. Treatment of the effluent consists of neutralization with lime or soda ash and subsequent discharge to a chemical sewer for further treatment. The average waste stream contains NO_x , SO_x , high COD, and α -TNT. Additional minor wastes produced by the finishing step include waters associated with sellite manufacture, from gaseous effluent scrubbing, spills of soda ash and sellite solution, and floor washdowns.

5.3.2 DNT Production Process and Waste Stream Characterization

DNT is an explosive by-product of TNT manufacture which can be produced on-site at the TNT plant. The crude discharge undergoes

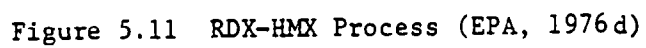
"sweating." This is a controlled step-wise temperature change to produce pure DNT crystals in a contaminated liquor. The liquor is subsequently drained off. The liquor undergoes further sweating, combined with the pure DNT, screened, and packaged in drums for storage. All impurities from the process are fed back into the TNT manufacturing process. Uncontaminated cooling water is the only aqueous effluent.

5.3.3 RDX-HMX Production Process and Waste Stream Characterization

RDX (cyclonite) is the third most important military explosive and has replaced tetryl as a base charge in military detonators. It is about 50 percent more powerful than low-density granular TNT, and more stable than PETN and tetryl. It is never handled in a pure and dry state because of its sensitivity. RDX is usually incorporated into formulations such as Composition B, which is RDX crystals with TNT and/or wax, and desensitized with beeswax or polyisobutylene. It is used for press-loading into shells, slurried with TNT for casting, or mixed with a special oil to make plastic explosives for commercial demolition work. It is always shipped water or solvent wet.

Manufacture is started with the nitration of hexamine, a relatively non-toxic compound purchased from the civilian sector. (See Figure 5.11.) The hexamine is nitrated using a nitric acid - ammonium nitrate mixture in the presence of acetic anhydride and acetic acid. Acid vapors from the reactor vessel, aging tank and simmer tank are vented to a scrubber, recovered and recycled back into the reaction. HMX is produced as a by-product of the reaction.

If a 110 percent yield were assumed, 0.32 pounds of hexamine would produce 1 pound of RDX (Tucker, 1972), 0.2023 pounds hexamine would produce 1 pound HMX, with 35 to 40 percent of the hexamine tied up in unwanted by-products.



The atmospheric emissions from the scrubber vents contain NO_x , acetic acid, traces of formic acid and methyl nitrate. Stripped sludge from the acetic acid is treated with sodium hydroxide, converting the ammonium nitrate in the sludge to sodium nitrate and ammonia. Residual acetic acid is also converted to ammonia, formates, amines and sodium nitrate. The ammonia is either vented to the air in small amounts as a vapor or discharged as a condensate with traces of impurities in the effluent wastewater. Methylamine and demethylamine and any sludge residue, largely sodium nitrate, are used as fertilizer.

Cooling water, pump seal water and condensate washdown which are relatively uncontaminated, are discharged to catch basins and then to sewers ultimately destined for surface waters. Catch basin residues are currently disposed of by open burning. The wastewater discharge from the actual RDX/HMX process is typically recycled for recovery of substantial amounts of product, by-product, or spent reactants.

Refinement, the final step in the manufacturing process, produces fugitive emissions which are vented to the atmosphere from the organic solvent distillation step. Wastewaters associated with this step arise from recrystallization and dewatering.

5.3.4 Tetryl Production Process and Waste Stream Characterization

Tetryl (2, 4, 6-trinitrophenylmethylnitramine) is used as a booster explosive or as the explosive ignited by a detonation charge. This in turn detonates the bursting charge. Its extreme sensitivity and toxicity hazards of handling the dry product (like RDX) has eliminated any current production, even though Joliet AAP is equipped to handle the manufacture.

Like the preceding explosives, tetryl is produced by the nitration of an aromatic feed-stock in mixed nitric and sulfuric acid. (See Figure 5.12.) The product is then washed and recrystallized. Specifically, demethylaniline (DMA) is sulfonated with 93 percent sulfuric

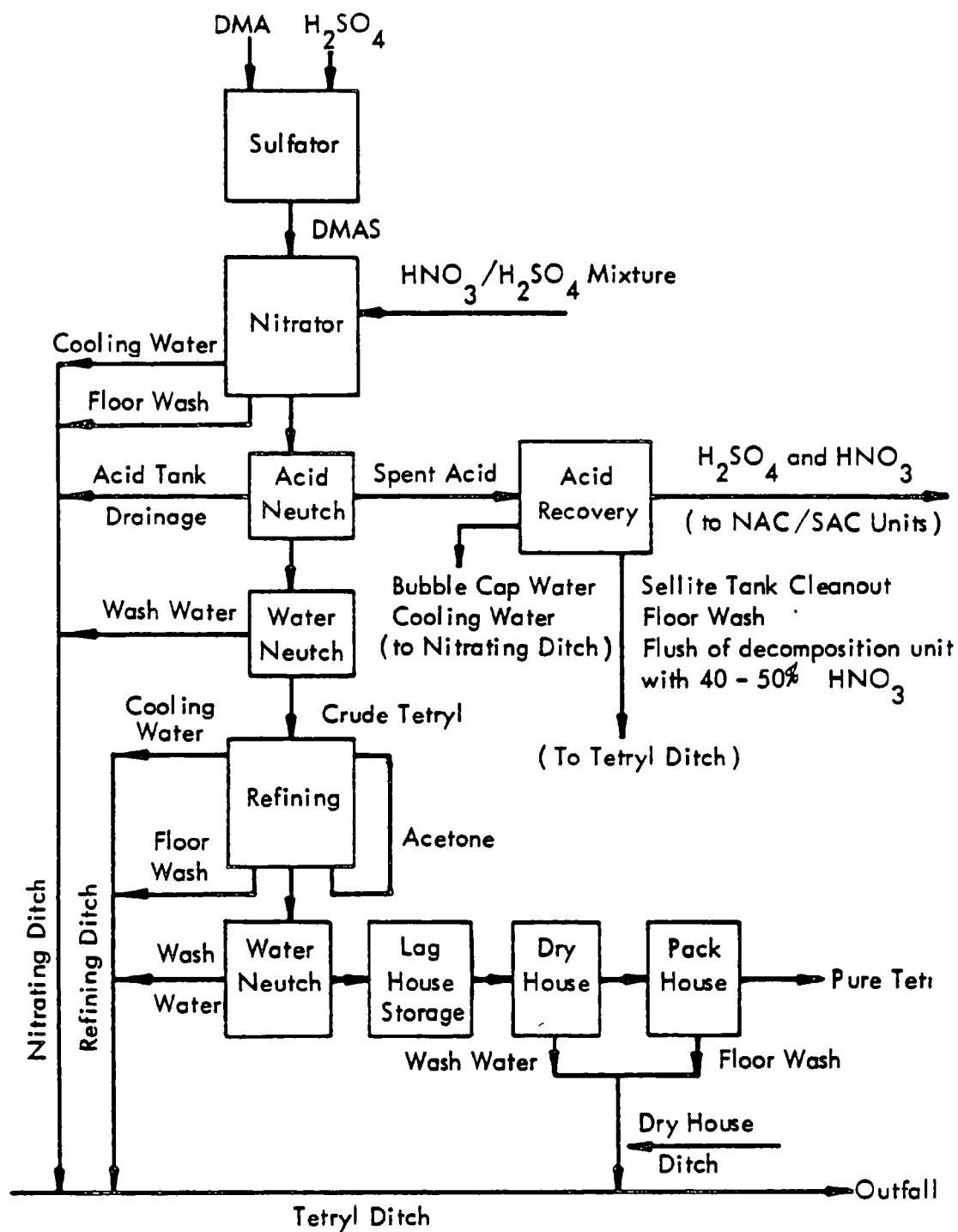


Figure 5.12 Tetryl Manufacturing Process at Joliet AAP (EPA, 1976d)

acid forming dimethylaniline sulfate (DMAS). DMAS is subsequently nitrated with sulfuric and nitric acid, washed, dissolved in acetone, evaporated and purified. The major waste stream is composed of nitric and sulfuric acids. These acids are recovered and sent to the concentrating facilities.

Wastes originate from tetryl purification, chemical spills, tank clean-up, cooling water and the sellite solutions used for floor washdown and equipment clean-up.

5.3.5 NC Production Process and Waste Stream Characterization

NC constitutes the second largest volume of explosive product manufactured by U.S. Army Ammunition Plants. Manufacturing involves treating cotton linter or wood pulp cellulose with mixed nitric and sulfuric acid. (See Figure 5.13.) The resulting slurry is acid-boiled, washed and recovered, and re-slurried. It is then beaten with sodium carbonate, slurried and poached, and allowed to settle. The water is then drained off.

In the near future, NC manufacture will be converted from the batch process to a continuous process in which almost all water will be recycled and the acid neutralization plant eliminated. Minor wastewater streams will result only from typical washdown procedures, spills and leaks and the sweepings from the dehydration press. NC is used as the fundamental ingredient in gun and rocket propellants. (See commercial explosives sections for greater detail.) Solid wastes will result from process clean-up and wastewater treatment.

5.3.6 NG Production Process and Waste Stream Characterization

NG is an explosive plasticizer used as the military's primary ingredient in double- and triple-based propellants and for casting plastisol double-base rocket motors. The continuous Biazzi Process

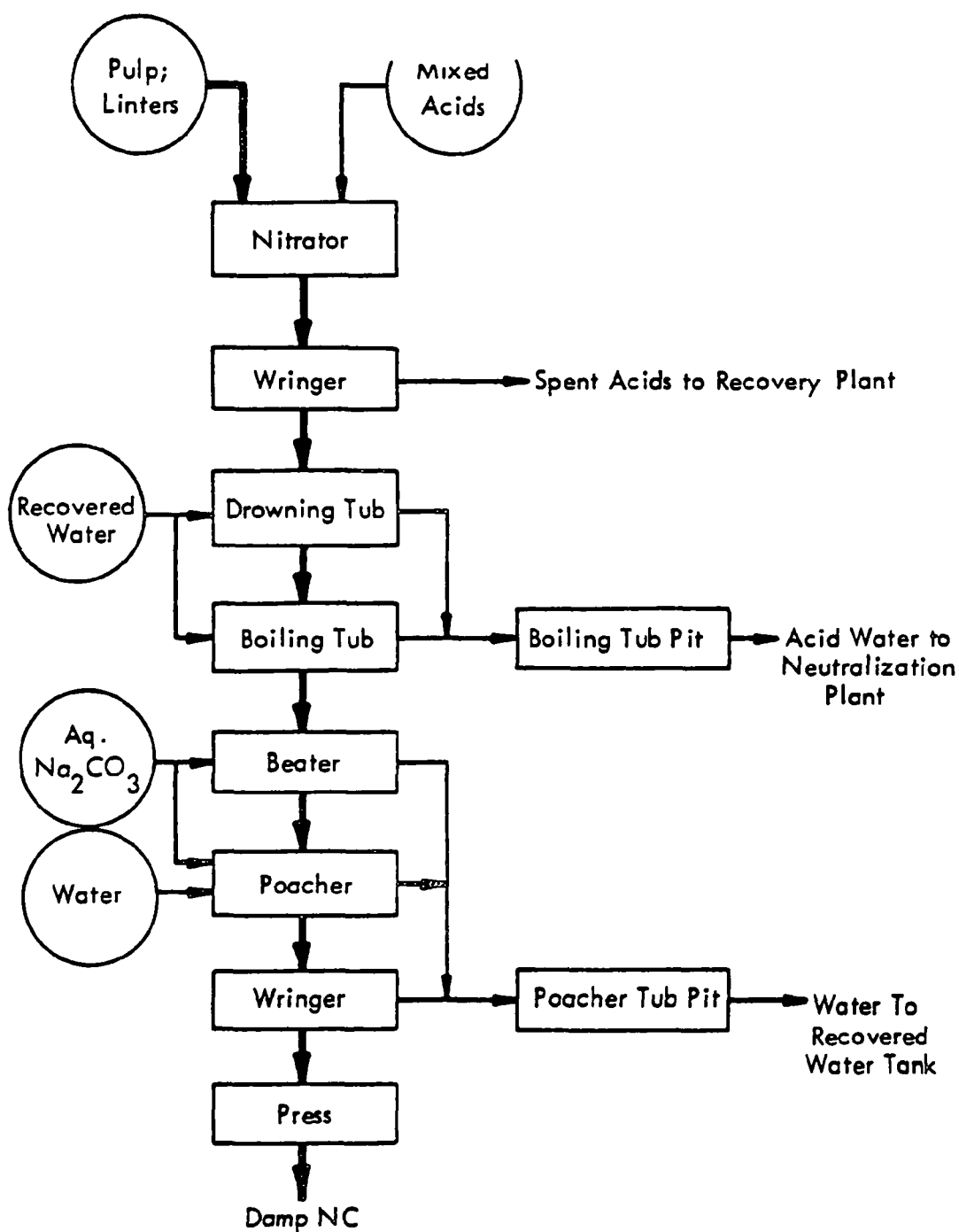


Figure 5.13 Batch Nitrocellulose Manufacture (EPA, 1976 d)

shown in Figure 5.3 is used. NG is manufactured when it is used. This avoids the shipment of extremely hazardous product.

Wastewater from the process contains NG, transfer waters and uncontaminated cooling waters.

5.3.7 NC-Based Propellant Production Process and Waste Stream Characterization

The majority of NC and NG manufactured by the AAP is incorporated into single, double, or multi-based propellants for shells and rocket motors. A rocket is an energy conversion device in which propellant chemical reactions occur generating heat and gases. The gases expand through a nozzle, producing thrust to propel the rocket system.

Two types of propellants exist, solid and liquid. Both require an oxidizer and a fuel. Hybrid propellants, a combination of both solid and liquid types, are also used. The solid becomes the propellant fuel and the liquid, the oxidizer. Manufacturing involves colloidizing the ingredients and then molding them like a plastic.

Single-based propellants are NC-containing compounds with minor amounts of plasticizer, stabilizers and burning-rate catalysts. Double-based propellants consist of NC swollen by a nitrate plasticizer (nitrate ester), usually NC, forming a rubbery, gelled structure with visoelectric properties. The NC densitizes the shock-sensitive NG so it can be used. Stabilizers and catalysts are also part of the formulation. Multi-base propellants are combinations of several nitrate materials, such as NC, NG, NGu, triethylene glycol, dinitrate and stabilizers.

Military NC is also cast into smokeless powders for shells and casting powders for missiles. Manufacture of these powders utilizes a solvent extrusion process. In this process, the NC fibers are masticated with solvents to form a dough, blended with other ingredients and extruded into strands. These are then cut, dried, and washed.

Ball powder propellant formed with spheres, is also manufactured

in small quantities at the APP's. Cooling water used in ball powder manufacture is entirely recycled, but process water, containing benzene, ethyl acetate, NC, NG, sodium sulfate and collagen is usually discarded.

Pyrotechnics and primer mixes, which consist of various initiator materials such as lead azide, lead styphnate, tetracene, and others, are produced in very small quantities on a bench scale.

5.3.8 LAP Operations Waste Stream Characterization

The remaining major waste streams associated with the military explosives industry are those arising from compounding of explosives and propellants. These streams typically contain dust and chips, dissolved explosives to about 100 ppm, solvents, organic materials, and ammonium nitrate or perchlorate.

A small waste stream is generated from LAP Operations, the final operation in the military explosive manufacturing process. Table 5.5 lists wastewaters associated with LAP Operations. These operations generally include:

- melt-pour loading of high explosive warheads
- extruded, NC-base rocket motor grains
- cast-in-place rocket motor grains
- pressed explosive and pyrotechnic charges.

In melt-pour loading, ordinance items are filled with molten TNT or other high explosives and allowed to solidify. Pink water is produced in the catch basin. The basin also contains dissolved TNT and other explosive ingredients. These are periodically removed and burned. Exhaust fans with wet scrubbers catch dust produced by the flaked explosive and are vented to the atmosphere. Scrubber drainings are added to the catch basins.

Extruded, NC-base, rocket motor grains are formed when double-based (NC/NG) propellants are extruded, dried, and cured. Their exteriors are painted and they are boxed and shipped for further assembly.

Cast-in-place rocket motor grains consist of high-energy plastic sol-cast grains used in ICBM's and polymerization-cured grains cast

Table 5.5 Waste Waters Generated in LAP Operations (EPA, 1977b)

AAP ^a	Activities	Raw Materials	Flow m ³ /day	Pollutants	Discharge Load kg/day	Comments
CAAP	Load 8-inch shells	TNT	75.7 ^b	57 mg/l TNT	~4.3(TNT)	Disposal in evaporation ponds
	Load 500-, 750-, and 1,000-pound bombs	Tritonal (80% TNT and 20% flaked Al)				
	Laundry		54.8	2.7 mg/l TNT	~0.13(TNT)	Disposal in dry streams
	Overall		131		4.4(TNT)	
IAAP	Shell loading		341 (94.6)	Pink water 1 mg/l TNT ^d 145 mg/l RDX ^c 20 mg/l RDX ^d	0.34(TNT) ^d 49.4(RDX) ^c 6.8(RDX) ^d	Wastes subjected to diatomaceous earth filtration followed by adsorption on granular carbon columns
	Laundry		30.3	10 mg/l TNT	0.31(TNT) ^c	Discharged to surface streams
	Mold booster charges from bulk explosives		0.814	Tetryl		
	Overall		371		0.64(TNT) ^c 49.4(RDX) ^c 6.8(RDX) ^d	
InAAP	Fabricate cloth bags and paper tubes and load propellants into these containers for shipment	N.A.	N.A.	N.A.	N.A.	
JAAP	Loading of medium caliber ammunition and ammunition components	Composition-B being loaded into 105 mm shells at a rate of 200,000 shells per month	23.5	TNT 145 mg/l RDX ^c 20 mg/l RDX ^d	3.4(RDX) ^c 0.45(RDX) ^d	Filtered through diatomaceous earth and then through two granulated charcoal
KAAP	Load explosives, primarily formulations of TNT and RDX, into ordnance items	TNT, RDX	N.A.	TNT, RDX	N.A.	Currently waste-waters are disposed of by trucking them to evaporative ponds
	Detonators for 105 mm howitzer shells	Lead azide, lead styphnate, RDX	N.A.	N.A.		NaNO ₂ , acetic acid, and NaOH used to deactivate the lead azide

Table 5.5 Waste Waters Generated in LAP Operations (Continued)

AAP	Activities	Raw Materials	Flow m ³ /day	Pollutants	Discharge Load kg/day	Comments
LSAAP	Melt-pour (Area O)	Composition-B	N.A.	Pink water NO ₃ , TOC, color, TNT, pH	N.A.	Discharged to lagoon system
	Melt-pour (Area C)	Composition-B				
	Melt-pour (Area E)	TNT and Composi- tion-B	75.7 ^e	Pink water NO ₃ , TOC, color, TNT, pH	N.A.	Recycled
	Melt-pour (Area G)	Octyl, TNT, and Composition-B				
	Load Line (Area P)	Lead azide	N.A.	N.A.	N.A.	Batch destruction by use of ceric ammonium nitrate
	Load Line (Area Q)	Lead azide	N.A.	N.A.	N.A.	
	Black-powder load	Black powder	None except raw sewage and storm- water runoff	N.A.	N.A.	Spilled powder is dumped into surface waters
LHAAP	Mixing, processing	N.A.	N.A.	BOD, COD, Mn, Cr-, NO ₃ , PO ₄ , Fe, Cd, poly- sulfide polymers, aluminum pow- der, black powder, and ammonium per- chlorate	N.A.	Ammonium perchlor- ate goes to surface water. All solids go to evaporative ponds and are even- tually incinerated. Remaining wastes go to surface water
LAAP	Shell-loading	N.A.	522	80 mg/l TNT	41.7	Waste is trucked to leaching ponds on the plant grounds
MAAP	N.A.	N.A.	1,510	{.5 mg/l RDX 1.0 mg/l TNT	{0.90(RDX) 1.36(TNT)	Wastewaters are discharged to a drainage canal which flows to surface water
	Shell washout	N.A.	2.10	{145 mg/l RDX ² 40 mg/l TNT ²	{0.31(RDX) 0.239(TNT)	
	Overall	N.A.	1,510		1.22(RDX) 1.58(TNT)	
RaAAP	N.A.	N.A.	N.A.	N.A.	N.A.	

^a Acronyms used to identify Army Ammunition Plants (AAP):

CAAP	Cornhusker	LHAAP	Long Horn
IAAP	Iowa	LSAAP	Lone Star
IndAP	Indiana	MAAP	Milan
JAAP	Joliet	RaAAP	Ravenna
KAAP	Kansas	VAAP	Volunteer
LAAP	Louisiana		

¹ Primarily washdown waters

² Before treatment

³ After treatment

⁴ Includes raw sewage and storm-water runoff

N.A. = Data not available

Source: The American Defense Preparedness Assn., 1975

for vacuum bell shaped motors. No water is used for the plastisol cast grains. Polymerization-cured grains use water only for heating and cooling coils.

Pressed explosive and pyrotechnic charges are used for illuminating flares, black powder, and developmental explosive blends of dry granular ingredients to be loaded into shells. Water is not used in the process. Solid wastes are reused in the product.

5.3.9 Nitrating Acids Production Process and Waste Stream Characterization

Since most basic explosives are nitrated products, it is economical for each manufacturing plant to make its own acid. The waste streams are small and similar to those of the commercial explosives industry.

5.4 CURRENT TREATMENT FOR WASTE STREAMS FROM COMMERCIAL EXPLOSIVES

Waste streams associated with the commercial explosives industry consist of wastewater effluents, gaseous emissions, and solid waste such as sludge, ash and explosive items. Waste streams vary according to the production process and end products as described in the following sections. Because explosives manufacturing processes demand large volumes of water, wastewater effluents constitute most of the total waste output.

5.4.1 Commercial Waste Water From Explosives Production

Within the commercial explosives industry, wastewater results from the production process, equipment clean-up and cooling. Explosives production effluents result from the nitration and product finishing steps (the latter being the major factor). These product finishing operations include washing, refinement, and drying or dewatering. The constituents of most concern are extreme pH, BOD₅, suspended solids, oil and grease, nitrogen forms, residual explosives (NG), and high levels of dissolved solids, primarily sulfate (SO₄). Attempts to remove suspended solids using settling tanks and sumps have proven ineffective (EPA, 1975a).

Efforts to treat oily wastes associated with the manufacture or maintenance results in effluents with high levels of suspended solids. The type of facility producing the wastewater, however, is a major factor in the level of suspended solids output. Complex facilities discharge effluents with lower average levels of suspended solids than on-site plants. Complex facilities dilute suspended solids containing wastewater with cooling water, avoiding product and intermediate product loss to wastewater, and use dry clean-up procedures (sweeping and wiping of equipment instead of water washing) prior to final equipment wash-down. A complex facility might average a 30.7 mg/l suspended solids in its discharge, as opposed to the industry average of 93.4 mg/l. This represents a three-fold reduction of components in wastewater such as ANFO, or other explosives, leakage from pumps and motors, and chemical residuals appearing as oil, much as NG. Adherence to proven procedures such as these in other plants will help eliminate the need for more sophisticated technology to handle the problem. Suspended solids from this type of plant are primarily nitrogenous and organic.

Oil skimmers have been effective in the separation and removal of non-emulsified oils from wastewaters. (The collected oil is generally used for spraying on dirt roads to control dust.) However, poor design and maintenance of the separators at many plants has made these skimmers ineffective.

Neutralization has been employed to rectify pH extremes at complex facilities. On-site facilities exhibit near-neutral pH, and wastewater is discharged without neutralization. Process waters from acid production and recovery, nitration, and finishing operations for explosives such as NG or PETN, are highly acidic. Percolation of the first washwater from NG production through crushed limestone beds to neutralize the acid, has proved ineffective. Accompanying high sulfate concentrations encouraged formation of precipitates which subsequently coated the limestone and eliminated its neutralizing properties.

Other wastewater streams exhibiting extreme pH, such as acidic wastes from acid manufacture, alkaline wastes from acetone still bottoms, and sodium carbonate wash solution for NG (pH 9-10) are

diluted with other plant wastewaters and released without treatment. Alkalinity of the wastewater streams promotes a high level of dissolved solids such as nitrates and sulfates, and also allows increases in effluent NG, BOD, and oil content. The combination of alkaline and acidic waste streams in these plants, could help correct the extreme pH conditions and, with additional treatment, pollutant discharge would be dramatically reduced. Additional methods for effective pH control for acid wastes for commercial explosive operations have been well established (EPA, 1976d). Some of these include:

- passing acidic wastewaters not containing sulfates through limestone beds
- mixing acid wastes with lime or dolomitic lime slurries
- addition of concentrated caustic or soda ash to acidic wastewaters.

Dissolved NG, high nitrate, sulfate and dinitroglycemia (DNG) levels are present in waste water from NG manufacture in addition to extreme pH, BOD and suspended and dissolved solids. Since a decrease in temperature of the waste stream would precipitate dissolved NG, creating an explosive hazard, precautionary attempts are made to "catch" the precipitated NG by directing the wastewater flow through settling boxes. This has limited effectiveness. It has been possible to reduce effluent levels from several thousand mg/l of dissolved NG to 100-1000 mg/l, but these concentrations are still too high to eliminate the explosive hazard.

5.4.2 Treatment Alternatives For Commercial Explosives

Biological treatment has been studied as a potential solution to wastewater problems for commercial explosives manufacturers (EPA, 1976). Successful decomposition to nitric from a raw waste load of 400-500 mg/l of NG was reported following preliminary settling of the wastes and treatment by activated sludge. Quicklime has also successfully decomposed NG, forming calcium sulfate, sulfite and calcium salts of low molecular weight (EPA, 1976d). The effluent formed was alkaline, but the resultant sludge was stable and free of explosive properties.

The commercial explosives industry has apparently not investigated

means of treating its wastewater. However, increased interest in biological and chemical treatment of wastewaters to remove NG and DNG has been shown by the Army. For wastewaters containing approximately 1500 mg/ℓ NG and 850 mg/ℓ DNG, biological treatment has not proved effective. Physical/chemical treatment has been attempted with the addition of lime and calcium sulfate to the neutralizing wash to counteract sodium, carbonate and bicarbonate alkalinity. The NG was removed, but the sulfate level was increased to indescribable levels.

Other explosive wastes (such as smokeless powder) have been treated biologically through extended aeration with activated sludge, followed by lagooning. Preliminary results report BOD₅ removal greater than 95 percent. Ultimate disposal of the lagoon effluent is achieved by spray irrigation on a field.

Biological treatment of high ammonia- and nitrate-nitrogen levels in explosive wastewaters has been successful and effective. Treatment of dilute and concentrated ammonia wastewater and low level <60mg/ℓ nitrate-nitrogen wastewater effluents with activated sludge nitrification has also proved effective. High nitrate levels, however, which are common to explosives industry wastewaters, require combined biological nitrification-denitrification treatment for effective removal.

At the present, a nitrate abatement technology for the commercial explosives industry does not exist. Initial feasibility studies by the U.S. Army mention biodenitrification, ion-exchange and reverse-osmosis as promising treatment methods. Various nitrate treatment methods are shown in Table 5.6.

Table 5.6 Nitrate Treatment Methods (EPA, 1976)

Method	Removal Efficiency (%)	Approximate Cost, \$/mg
Biodenitrification	70-95	3.45-30
Algae harvesting	50-90	20-35
Ion exchange	80-99	170-300
Electrodialysis	30-50	100-250
Chemical reduction	33-90	-
Reverse osmosis	50-96	100-600
Distillation	90-98	400-1000
Land application	5-15	

Pilot scale studies on reverse osmosis of nitrate wastewaters showed effective nitrate recovery, depending on pH, and efficient sulfate removal. The sensitivity of the reverse osmosis membranes to temperature, pressure, bacteria, chemical change, hydrolysis and surface coating may limit potential application of this method. Reverse osmosis, with or without subsequent treatment methods, could eliminate the need for neutralization while allowing product recovery and reuse. Energy requirements, use of membranes tolerant to varying pH, and use of corrosion resistant materials, all need further investigation.

The recent availability of nitrate-selective ion exchange resins may permit removal of nitrates from wastewaters. A full scale continuous counter-current (chem-seps) ion exchange system is on-line for a plant manufacturing ammonium nitrate (EPA, 1976d). Reduced nitrate and ammonium nitrogen levels with effective ammonium nitrate recovery, has been reported. This method would be particularly appropriate for complex facilities utilizing ammonium nitrate as an intermediate in explosives manufacture.

Biological denitrification is rated by the Army as the most promising and efficient type of treatment at present. Pilot scale studies indicated excellent nitrate reduction (>90 percent for wastewaters containing methanol, provided pH and temperature are carefully controlled).

The commercial explosives industry does not attempt to remove sulfates from wastewaters although high levels are characteristic of explosive wastewater streams. Feasibility studies by the Army show that even though a proven treatment process does not exist, reverse osmosis, ion-exchange, evaporation and calcination methods show some promise. The reverse-osmosis option has been used for nitrate removal but suffers limitations of membrane specificity. Sulfate removal efficiencies of 99+ percent have been reported. To retain membrane integrity, pH must be controlled. Waste stream neutralization somewhat reduces membrane specificity requirement. Following sulfate removal, the resulting water effluent can be reused in the production process, and the brine reclaimed (EPA, 1975a). Using sulfate-specific resins, ion-exchange can produce reusable water. The resins can be regenerated with the sulfate by-product for reuse.

A method proposed to recover sulfuric acid utilizes a combination of reverse osmosis and evaporation. Reuse in the acid or explosives manufacturing process is possible. Calcination, the most promising method, precipitates the calcium in the acid stream to produce a sludge. High temperature calcination, which follows, recovers the lime and produces SO_2 . SO_2 must be catalytically converted to SO_3 for sulfuric acid production. The only disadvantage appears to be the high solubility of the calcium sulfate in the treatment system (EPA, 1975a). Economic feasibility of the process has not been proven.

Since treatment methods for nitrates and sulfates have not yet been proven technically and economically feasible, some commercial explosives plants are practicing disposal by spray irrigation on land. One complex facility manufacturing ANFO, dynamite, a variety of intermediates, and specialty products, treats its wastewaters by sedimentation and oil skimming. The resultant wastewater is then sprayed on a pasture used to graze cattle. This plant is located in an arid region. Another complex facility in the upper midwest pretreats the waste with activated sludge and lagooning before disposal by spray irrigation. The method is not as effective at this facility, however, since only half of the wastewater percolates into the soil. The remainder is runoff. A precautionary monitoring study should be instituted for effluent leachate should the effluent possess any potentially hazardous constituents. One on-site facility formulating water gels, collects its relatively small amount of waste in a tank car and sprays it into an abandoned mine overburden disposal site on their property. It appears reasonable that land disposal of explosives, wastewaters, provided there is some pretreatment, has some applicability. Soil and climate conditions must promote physical adsorption and microbial action and crop utilization of nitrates. Use of large amounts of land would be a limiting factor in more densely populated areas or for plants not owning a large tract of property. Ground water contamination might also be a possible deterrent to land application. On-site formulation of water gels in a process with wastewater streams that could cause groundwater contamination.

Evaporation in ponds has been used as a land disposal alternative. For example, a complex facility in an arid region ponds a small part of

its wastewater from ANFO blending equipment, clean-up, and NG neutralizer washes. Percolation and evaporation facilitates water loss. Care has been taken to prevent any overflow.

One northern midwest on-site facility discharges all of its wastewaters to a natural basin on its property. Water loss occurs by percolation and evaporation in the summer months. A third plant, manufacturing water gel explosives in the central southeast, utilizes evaporation ponds for its process waters. The pond has a projected life capacity of 13 years. All other process wastes and cooling waters are discharged directly to surface streams. Most explosives producers are located in remote areas on large tracts of land for safety considerations, so land availability for evaporative ponding does not appear to be a problem.

Propellant manufacturers usually have greater waste loads than those manufacturing explosives. The wastewaters show high levels of total suspended solids (TSS). This is especially true during NC manufacture, where nitrocellulose fines escape into the wastewater streams. Propellant wastewater effluent are also characterized by high BOD, COD and high total organic carbon (TOC) from the organics and solvents used in the processes. High nitrogen levels from nitric acid and organonitrates, and high sulfate levels from sulfuric acid, also prevail. There appears to be no significant treatment of these manufacturing wastewater effluents, and if any pollution abatement program is utilized, it usually consists of neutralization and sedimentation.

LAP operations generate a smaller, but more hazardous, volume of wastewater due to the presence of explosive particulates. Wastewater effluents associated with manufacture of initiating compounds, generate the highest waste load volume due to product specificity. Initiating compound demands are small and customer specific, and on a small scale. It is not economical for the industry to attempt recovery of spent materials, nor to have wastewater treatment facilities. The variability of the operations also causes sudden changes in waste effluents. High pollutant concentrations may be followed by periods of low pollutant concentration. Heavy metals are characteristic of these waste effluents. High levels of lead and mercury (lead azide, lead styphnate, and mercury fulminate) are often found in these waste streams. Therefore, such alternatives as spray irrigation for these wastes do not appear appropriate.

Gaseous emissions are usually composed of NO_x and oxides of sulfur (SO_x) and acid mists. They result from manufacturing and concentration and acid recovery operations during the nitration process. Air pollution abatement measures have not been taken by the industry, even though some absorption towers for gas scrubbing have been tested. Some of the emissions contain hazardous and explosive substances. TNT manufacturing emissions contain toluene and the explosive, TNM, which are vented to the atmosphere. TNM has also been found in the acid and fume recovery system, and also presents an explosive hazard.

Fugitive hydrocarbon emissions contribute to the gaseous effluent from explosives manufacture. These emissions result primarily from solvent recovery operations.

Finishing processes and propellant formulation also contribute organics to the gaseous waste stream. Controls have not been instituted or indicated for either type of emission.

Solid wastes generated during manufacturing are currently disposed in sanitary landfills by surface dumping. These waste streams include the sulfate residue from sellite incineration and sludge from settling lagoons. Long term pollution problems could arise with leaching, if these wastes contain heavy metals such as lead or mercury, or explosive fines (NC). Usually, wastes contaminated with explosive material, such as scrap, off-spec. items, contaminated packaging, dust and chips, are not reclaimable, and are disposed of by open burning. This method is unacceptable, even though commonly used, since uncontrolled emissions of NO_x and particulate matter result. There are alternative methods for disposal of solid wastes which appear safer than open burning. Technically and economically feasible methods of disposal have not yet been proven, even though several are under development.

5.5 CURRENT TREATMENT METHODS FOR THE MILITARY EXPLOSIVE INDUSTRY

Waste streams associated with the military explosives industry are similar to those produced by the commercial sector. The wastewater effluents, gaseous emissions and solid waste depend on the production process and end products. The following section describes the

significant waste effluents and their current and alternative treatment methods.

5.5.1 Current Treatment of TNT Wastes

Some waste streams unique to military explosives manufacturing preclude the generalized treatment methods discussed previously under Section 5.4. TNT manufacture and loading into munitions produces three major wastewater streams: red water, pink water, and acid wastes, including spent acids.

Red water results from the sellite purification of crude TNT. The sellite, a 16 percent concentrated sodium sulfate solution, removes 3-5 percent of the unwanted TNT isomers and a nitro group in the 3 to 5 position. The sellite residue is melted with the remaining rinse waters from this step. Typically, red water contains about 25 percent dissolved solids, approximately 17.3 percent organics, 2.3 percent sodium sulfite, 0.6 percent sodium sulfate, 3.5 percent sodium nitrite and about 1.7 percent sodium nitrate. Batch and continuous process red water differ in volume and composition. A neutralization wash with soda ash precedes the sellite wash in batch operations, but not in the continuous process. The continuous process, on the other hand, uses a water wash prior to the sellite wash step and produces "yellow water" by washing out the nitrating acids. This operation reduces wastewater volume by returning yellow water to the nitration process. It also reduces the discharge constituents found in the batch process wastewater. Excess yellow water is combined with the process waters and treated by neutralization or incineration. Efforts to reduce the wastewater volume by modifying the process, recycling transfer waters, returning yellow water to the process and then segregating waste streams with similar characteristics, have been initiated to facilitate treatment and disposal methods.

The current treatment method for red water first involves water evaporating in a rotary kiln to achieve 35-40 percent solids. The residue can then be sold to the paper industry or incinerated with subsequent land disposal of the ash. Both appear unsatisfactory as far as treatment and ultimate disposal are concerned. Both concentration and incineration are energy intensive methods of treatment. Although

the condensate liquor retains a pink color, which indicates the presence of nitrobenzenes, it is discharged directly without any further treatment. Finally, incineration produces significant quantities of ash, which must be land disposed. The potential for surface and groundwater contamination then arises. Joliet AAP stockpiles these residues on land; and about 200 million pounds have been stored to date. Since the ash is 90 percent soluble, runoff caused by rainwater poses a significant contamination problem. The paper industry is reducing their need for red water, so the total amount of ash resulting from incineration will rise, adding to an already existing ash disposal problem.

Inefficient incineration operation also leads to potential atmospheric pollution problems. Gaseous emissions of NO_x and SO_x have been detected from red water incineration at Radford AAP. These might be reduced by further treatment of the pink condensate or other modifications to the treatment process.

Volunteer AAP is pretreating its red water by pH adjustment, concentrating it by reverse osmosis and recovering the water for re-use. Desulfonation along with DNT recovery has been attempted by Radford AAP unsuccessfully.

A fluidized reduction system which chemically converts the red water ash to sodium carbonate and hydrogen sulfide has been shown to be technically feasible on a bench-scale level. In this process, red water incineration ash is ground for fluidization, incorporated into the fluidizing bed, and reacted with the reducing gas, water and carbon dioxide.

The most promising option for treatment of red water, is the Tampella process, which reduces the concentrated liquor and carbonates and hydrogen sulfide. These compounds can then be recycled to produce sellite.

5.5.2 Treatment Alternatives For TNT Wastes

Activated carbon and chemical destruction have been proposed as alternative treatment technologies for red water. Activated carbon is effective in removing DNT and TNT from red water, but somewhat inefficient for other constituents. They are hexanitrodibenzene, TNM, azobenzene

acid, trinitro benzoic acid, dinitrocresol, phenol and various nitro-toluene sulfuric acids. The chemical treatment alternative, uses chemical oxidents, chlorination, bromination, ozonation and uv-catalyzed ozonation for reduction and ultimate destruction of nitrocompounds (and red color) in the red water, with some success. No effort to prove this on a pilot scale has yet been undertaken.

5.5.3 Current Treatment Practices for Pink Water

Pink water wastes from TNT manufacturing and LAP plants arise from nitration fume scrubber discharges, red water concentration distillates, finishing and building hood scrubber and wash down effluents, and spent acid recovery wastes. LAP-pink water has been well characterized as containing α -TNT, RDX, HMX, wax and additives. However, pink water resulting from other operations has not been well characterized.

Both waste streams are usually combined for treatment. Carbon-adsorption has been used successfully for pink water treatment. Carbon-adsorption systems are currently in operation at Joliet and Iowa APP.

Raw pink water is high in solids and explosives, and is alkaline. Carbon treatment of the waste stream is a two-step process. The wastewater is routed to sumps to remove settleable solids, followed by a diatomaceous earth filter, which removes about 21.5 percent of gross suspended solids. Next, it is pumped through carbon columns to remove dissolved TNT and RDX contaminants. Single or multiple carbon beds may be connected, either in series for downflow system, in parallel for an upflow system, or a combination of the two. Uniform design criteria are lacking. The bulk of the removal occurs in the first of the carbon columns.

Each type of activated carbon has its own sorption capacity. When that limit is reached, the column integrity is broken and the carbon must either be replaced or regenerated. Since an economically and technically sound method for regeneration of the pink water carbon does not exist, the waste carbon is incinerated.

Disadvantages in using carbon treatment for pink water waste include:

- the costs of carbon use are very high
- potential for recovery and reuse of α -TNT is eliminated
- air pollution problems from carbon incineration

Thermal and solvent extraction regeneration of the carbon have been investigated. The temperature range in which thermal treatment can be safely performed is limited because of the explosion potential of the α -TNT within the carbon's cavities. Under favorable conditions it could explode, although no incidents were found in literature. It also emits NO_x and methane as components of the regeneration off-gas. After treatment, the regenerated carbon is reported to recover only about 60 percent of its original capacity.

Solvent extraction shows much more promise for carbon regeneration because of the following:

- regeneration occurs in a fixed bed
- TNT contaminated solvent can be reused in regeneration or as input to TNT manufacture
- a greater degree of carbon saturation can be achieved.

Studies using methanol, acetone, and toluene as a TNT stripper, show acetone as the best choice, although conflicting results were reported for acetone (22.3 percent removal versus 92 percent removal). However, regenerative capacity, is only partially adequate. Further investigation on these techniques is necessary. There is also need for a carbon or other sorbent with greater sorption capacity and increased specificity. Use of polymeric resins as an alternate sorbent or in combination with the carbon is a potential alternative, since it can be regenerated to a constant performance level many times. In addition to its regenerative advantage, resin use would reduce the amount of carbon undergoing incineration.

Evaporative treatment is also a current method of pink water disposal. Soil and climate conditions govern the quality of the method, since overflow could result in severe leaching problems and potential of surface or ground water contamination. Evaporative ponding does present an economically viable pink water treatment method.

5.5.4 Treatment Alternatives for Pink Water

Several alternatives for pink water treatment have been investigated. They include:

- solvent extraction
- reverse osmosis
- fly ash adsorption
- ion-exchange resins
- biological treatment

Treatment of wastewaters at Iowa AAP with solvent extraction or toluene by two stage countercurrent extraction has been shown to remove and recover up to 97 percent of the TNT contaminant. A proposed full scale system, however, does not look economically feasible. (Brown and Shapiro, 1979.)

The reverse osmosis process is effective in concentrating pink water, but early membrane failure has been a problem.

Adsorption capacity of fly ash is less than carbon and ultimate disposal of spent fly ash will remain a problem.

Investigated ion-exchange resins have shown good potential for multiple regeneration and reuse. However, carbon appears more effective in removal of color.

Biological treatment studies have shown successful biodegradation of α -TNT with the addition of large amounts of supplemental nutrients. However, color development increases the wastewater's resistance to this method. The toxicity of TNT in the environment represents a severe disadvantage of this method.

5.5.5 Current Treatment of NC Wastes

Spent nitrating acids from NC manufacture undergo separation or settling to remove NC fines. Neutral wastes from several other manufacturing operations are discharged to a different set of settling tubs because of the drastic difference in NC fines concentrations (<10 mg/l for neutral wastes, and =100-500 mg/l for the nitrating acid wastewater stream). Particle size precludes complete removal of fines. The NC fines which are insoluble and appear as suspended solids make the wastewaters potentially hazardous. No effective means of removal

have yet been found.

Other NC wastewaters are, for the most part, acidic to near-neutral, with moderate sulfate and nitrate concentrations and high COD. They are treated with lime to affect neutralization.

5.5.6 Treatment Alternatives for NC Wastes

Since the most hazardous constituent of NC wastewater effluents are the insoluble NC fines, centrifugation and coagulation technologies are effective in solids removal. Centrifugation also has the advantage of NC recovery. These, when coupled with water management plans already proposed, will provide almost complete recycling and reuse of waters with accompanying NC recovery.

5.5.7 Current Treatment of RDX/HMX Wastes

Wastewaters from the RDX/HMX manufacturing and LAP operations are contaminated with various explosives such as TNT, RDX, and HMX. Sources of these waste streams include: dewatering and decantation operations, floor and equipment clean-up, and contaminated waters from dust control scrubbers.

Current treatment methods are generally limited to catch basins or baffled sumps. Activated carbon treatment of LAP wastewaters is performed at Joliet AAP, while some inoperative ponding takes place at other LAP facilities. Holsten AAP discharges its untreated catch basin effluents, contaminated with RDX, HMX and TNT directly into industrial sewers. These sewers discharge into a surface stream, the Holsten River. Joliet AAP has shown some success in treating wastewaters containing TNT, RDX and HMX with activated carbon. However, analysis has shown preferential removal of TNT with less adequate efficiency for HMX and RDX.

5.5.8 Treatment Alternatives for RDX/HMX Wastes

The following methods are under consideration for RDX and HMX control:

- reverse osmosis
- activated carbon adsorption
- anaerobic biological degradation
- polymeric resin adsorption

Reverse osmosis and activated carbon adsorption have been discussed in previous sections. Anaerobic digestion is extremely sensitive to toxic wastes, but degrades non-toxic complex organic components very well. Provided HMX/RDX toxicity is low, anaerobic degradation might prove a successful treatment method. Polymeric resin adsorption has been promising when accompanied with hydrolysis and prior concentration of the RDX or HMX on the resin. At present, carbon adsorption appears to be more reliable for TNT and RDX control.

5.5.9 Current Treatment of NG Wastes

Wastewater streams from NG batch manufacture result from soda ash solution and water washes following the nitration step and from NG storage when dilute soda ash solution is decanted before NG use. The batch process, as opposed to the continuous Biazzi system, is only in operation at Badger AAP. The streams are similar in both the military and private sector.

Wastewater from NG manufacture shows variable pH, is high in nitrate, sulfate, NG, and DNG. The current limited treatment method consists of catch basins, with eventual discharge to evaporative ponds or waterway systems. Proposed alternate treatment methods have proved ineffective for both NG and DNG.

Radford AAP has proposed use of sodium sulfide treatment followed by treatment with activated sludge. Several disadvantages exist to this treatment method. They include toxic residual ion (sulfide) which exist in the process effluents, undesirable sulfide odors that arise during decomposition, and potential explosive hazards created by the exothermic reaction. Attempts to find alternative treatments may relieve this problem, and offer a potential means of NG and DNG recovery.

5.5.10 Current Treatment of Wastes From Propellants Manufacture

Solvent, solventless, and composite propellants are formulated into single, double and multi-base compositions in various ways with a variety of ingredients. Typical ingredients which might be reflected in the waste stream include NC, NG, NGu, ammonium perchlorate, HMX, powdered aluminum, stabilizers and catalysts.

Solvent propellant manufacture produces a relatively small volume of associated wastewaters, which are high in organic solvents and dissolved propellant constituents. Lack of treatment prior to discharge has led to increased efforts to reduce water use by recycling and to recover waste product. Investigation indicates two effective and reliable possibilities: activated carbon and biological treatment. Biological treatment has been used by a commercial producer and is proposed for two Army AAP's (Radford and Badger). However, the biotransformation of propellant wastes and the "toxic nature" of the final end-products have not been thoroughly explored.

Solventless propellant wastewater effluents, resulting from building clean-up and equipment washdown, are characteristically high in BOD, nitrate, suspended solids, NG, DNG, and lead. With the exception of lead removal, the wastes are discharged directly, without any prior treatment. Badger AAP is the exception. At this point, effluent volume is reduced by improved water management so that percolation/evaporation ponding can be utilized. Potential pollution problems for this method, including leaching and contamination of surface and ground waters, always arise with land use, but the method appears to be substantially effective.

An alternative pilot-scale biological treatment study is underway at Radford AAP, but inconclusive information on ultimate end products makes this method still questionable.

5.5.11 Treatment of Wastes From Miscellaneous LAP Activities

Wastewater effluent associated with load and pack operations characteristically contain TNT or HMX and RDX, or the explosive being loaded. They result from casting of propellants, processing of secondary ingredients of pressed explosives, and casting of plastic bonded

explosives, and include wastes from building and equipment clean-up procedures and air pollution treatment. Explosives are brought in from outside the plant, and treatment focuses on the operations for incorporating the explosives into munitions.

Dust abatement procedures are usually required by activities such as grinding of ammonium perchlorate and HMX, size reduction by hammermills, size control screening, and by evergoing operations. At Radford AAP, duct systems remove the dust, which is carried to a wet scrubber. The flow from the scrubber is discharged without treatment. A dry dust collection system, with subsequent incineration, has been proposed at Radford AAP, but has not been implemented. Venting of explosive dusts to wet scrubber systems is also used at a number of other LAP plants, including Longhorn AAP and Redstone Arsenal. Longhorn dumps its scrubber wastes into a sump, the contents of which undergo evaporative ponding. Clean-up water is discharged to surface ditches on-site. Redstone Arsenal ships its scrubber wastes to the scrap propellant burning grounds for disposal. Building and equipment wash-down effluents are discharged through sumps to creeks.

Wastewaters from LAP activities involving pressed propellants characteristically contain powdered aluminum, and ammonium picrate. Those from detonator LAP process usually contain lead azide and lead styphnate. LAP activities also produce wastewaters from building and equipment washdown and dust scrubber systems but information concerning its characteristics or treatability are lacking. Kansas AAP routes its water effluents to holding pits, treats them with caustic to attack the lead styphnate, and discharges the waters into a holding pond. In effect, little is known about wastewater streams from LAP activities or their treatment. Such efforts need to be undertaken.

5.5.12 Treatment of Acid Manufacturing Waste

Acids manufacturing waste streams are discussed in Section 5.2.1. Recycling reuse and treatment efforts are similar in nature to those in the commercial explosives industry.

5.5.13 Treatment Methods For Bulk Propellants, Explosives, Pyrotechnics (PEP)

A U.S. Department of Defense study recently reported an inventory of approximately 168,000 tons (about 35 weight-percent PEP) of surplus, obsolete, or unserviceable munitions awaiting disposal. About 56,300 tons are generated annually, over and above that being stockpiled. The report states that 48,350 tons are demilitarized (demil) each year, showing a net inventory increase of some 10,000 tons. Since approximately 35 percent of the weight of munitions is represented by PEP, these figures mean that about 17,000 tons of PEP accumulates in unwanted munitions each year.

Logistically speaking, the problem is severe. About 2.4 million square feet of covered storage space with an equivalent replacement value of \$127,000,000 is being tied up by the stockpile. Disposal of these unwanted munitions requires removal of the PEP's from the munitions treatment/disposal of the PEP's, and treatment/disposal of inert parts of disassembled munitions. Examples of bulk PEP include: TNT, Composition-B, RDX, HMX, NC and double-base and composite propellants. The majority of PEP inventory, taking into account the U.S. manufacturing capacity, contains the following:

<u>PEP</u>	<u>Percentage</u>
TNT	49
NC	29
RDX	10
all others	12

Until 1971, obsolete munitions were disposed of by deepwater ocean dumping. The Secretary of Defense, in response to increased environmental concern, subsequently imposed a ban on all ocean dumping.

The oldest, most universally used, disposal option for bulk PEP's, other than ocean dumping, is open burning. It is a relatively simple operation with minimal labor and fuel cost. Unwanted materials, scrap, wastepaper, surplus rocket motors, shells, and other materials are piled up in a remote, open field with starter fuel, and ignited. The operation is smokey, polluting (NO_x and particulates), and unsafe (chunks of burning propellants can be thrown into the air to fall back

and finish burning on the ground. Air emissions from this process are unknown at present. More specific uses of open burning include destruction of high explosive and propellant wastes, and incinerating primary explosives wastes.

When disposing of various forms of NC by open burning, fiberboard and metal drums with leakproof liners filled with NC are covered with water, transported to an approved burning ground, and placed on a non-combustible pad made of asbestos. The drums are drained of water, covered with fuel oil, and ignited by firing a device into the wastes. Considerable NO_x is produced. Gelatinized NC or plastisol NC (PNC) is disposed only by this method. Bulk PETN and TNT is also disposed by open burning.

Detonators and primers such as lead, 2,4-dinitroresorcinate or lead styphnate are placed on flammable substances such as straw in burning pits and detonated by applying heat from a fire by electrical ignition. Personnel and other explosives should be shielded behind a barricade for safety with overhead protection and at a distance. The practice is unsatisfactory because un-detonated components present a hazard to personnel during clean-up, in addition to uncontrolled emission of NO_x and toxic metal particulates into the air.

Though unsafe and environmentally damaging, open burning still remains an economically viable disposal alternative.

Incineration is also currently used for disposal. The Army incinerator (APE-1236/1276 "deactivation furnace pollution abatement system") is the only fully developed design in use, although other systems are being developed. It consists of a steel rotary furnace 30 feet long, and 4 feet in diameter, with spiral internal flights carrying debris through as the tube rotates. It has an oil or gas-fired burner, and a stack mounted over the feed end. Temperatures are characteristically 1200°F near the burner, $600\text{--}900^\circ\text{F}$ in the middle and $400\text{--}500^\circ\text{F}$ in the stack. Pollution abatement is achieved by a baghouse preceded by a cyclone and flame arrester to eliminate visible smoke emissions. An NO_x or gaseous emission abatement system has not yet been developed. Feed rates are approximately one item per second.

Other systems under development include a rotary kiln incinerator designed to burn bulk PEP. It is similar to the APE-1236 deact furnace, but lacks the internal flights and is lined with firebrick. Radford AAP has demonstrated its capabilities. It is essentially smokeless and discharges about 200 ppm NO_x, which is the only significant gaseous emission. A fluidized bed incinerator under development for bulk PEP is a commercial adaptation of the system used for military explosives. PEP, as a 25 weight percent slurry, is injected into the hot fluidized alumina. Smoke is not visible and NO_x emissions are low due to a NO_x decomposition catalyst. The batch box is an oil fueled trash incinerator adapted for use in handling small PEP items and PEP-contaminated dunnage. It is expected to produce little or no smoke. NO_x abatement measures have not been undertaken. The SITPA-II incinerator is similar to the APE deact furnace currently in use, but it has been adapted for the feeding of bulk PEP. The APE-2048 Contaminated Waste Processor, originally a flashing furnace, shows potential for handling bulk PEP mixed with contaminated combustibles. It is to be a smokeless incinerator with negligible NO_x emission.

Additional conventional, well-developed processes used either for destruction of PEP's and munitions, or for removal of PEP from munitions, and newly developed demilitarization processes are listed below.

Conventional, Well-Developed Processes

- Hot-water steamout (APE 1300)
- Steam washout (Army-Navy)
- Steam meltout (sweatout)
- High-pressure water washout
- Open burning
- Open detonation
- Deactivation Furnace Incineration (APE 1236)
- Contour drillout (Navy)

Newly-Developed Processes

- Fluid bed bulk PEP incineration (Picatinny)
- Rotary kiln (Radford) bulk PEP incinerator
- Wet air oxidation (Zimpro) (Navy)
- Microwave Meltout (Tooele)
- Batch box incineration (Navy)
- Contaminated Waste Processor (CWP)
- Magnesium reclamation (Crane)
- Colored flare reclamation (Crane)
- Photoflash reclamation (Crane)
- Flashing chamber (Hawthorne)
- Continuous flashing furnace (Hawthorne)

The waste streams associated with each of preceding operations are determined by the method of disposal and the particular PEP being demilitarized. Demilitarization processes utilizing open burning and incineration result in emissions of NO_x and particulate matter to the atmosphere. Open burning does not employ any emission control devices or systems. Incineration designs, on the other hand, employ cost-effective baghouses (in the case of APE 1276) for particulate removal. NO_x emissions are uncontrolled, at present, but control methods are under development.

Rotary and kiln and fluidized bed incinerators are designed for destruction of PEP already removed from the munition. Their control of air emissions is uncertain. Recent conversations with military installations reveals severe pollution problems resulting from incineration (AEO, Ft. Detrick, Maryland and Tooele Army Depot, Utah). Baghouse collection devices have shown the presence of TNT, RDX, HMX and toxic metals in the gaseous effluent as well as the solid waste residues. The extremely hazardous and potentially explosive nature of these contaminants presents a dangerous situation. Attempts to localize and correct this hazard have already been undertaken. Detonation of munitions in earth-covered pits has shown no harmful air emissions.

Wastewater effluents result from operations using hot water, steam, or high-pressure water for washout of PEP from munition housing

parts. These waste streams are characterized by suspended or dissolved explosives or propellants. Current treatment methods for wastewater effluents from specific PEP's have been discussed in previous sections.

Demilitarization processes for PEP removal which are non-contaminating to the air or water, do exist. These are: contour drillout, a standard technique; microwave meltout, the safety of which has not been demonstrated; and pyrotechnic processes developed at the Crane Naval Facility in Indiana (NWSC, Crane). The solid waste stream from these demilitarization activities consists of scrap metal and inert furnace ashes. For the most part, it is inert and harmless to the environment if the processes are carried to completion. Scrap metal is typically sold. No information is available on the ultimate disposal of the ashes.

5.5.14 Treatment Alternatives for Bulk PEP

Other means of reducing the waste inventory are being used, but are not really viable forms for ultimate disposal. For example, the Navy has sold bulk PEP's (propellant powder, TNT, Composition-B) to commercial blasters, explosives manufacturers, and fireworks companies. Table 5.7 shows the quantities of bulk PEP sold for commercial use between 1974 and 1977.

Table 5.7 Bulk PEP Sold to Commercial Users

<u>Year</u>	<u>Composition-B (pounds)</u>	<u>TNT (pounds)</u>
1974	1,533,343	1,812,673
1975	750,544	2,545,165
1976	2,311,914	1,420,651
1977	1,953,452	2,059,959

Of these amounts, about one quarter was virgin material, such as drilling dust, and the remainder was reclaimed from meltout and washout of munitions. Recovered PEP also has been reused by the military. Large quantities of TNT, for example, have been used to simulate shock waves

from nuclear bursts. The military also is studying the possibility of reclaiming PEP for reuse in new munitions, but this poses various technical problems, including the difficulty of meeting new munitions specifications, and the question of PEP impurities.

Successful conversion of unwanted PEP into a saleable or useable non-PEP derivative has been shown to be technically feasible. For example, red water sulfonated TNT has been converted to plastics intermediate. Tooele Army Depot has started plans to build a pilot plant converting white phosphorous from unsuitable munitions into saleable phosphoric acid. Pine Bluff Arsenal has demonstrated the saleability of white phosphorus already, without prior conversion. Iowa AAP has been successful in converting surplus lead azide electrolytically to metallic lead.

A final alternative showing promise is the burning of scrap PEP for energy recovery. Admixtures to fuel oil would reduce fuel requirements for incineration. Up to the present, this has been objectionable due to safety considerations.

5.5.15 Costs For Demil Facilities

A recent meeting of John Brown Associates, Inc. (Brown, 1979) with personnel from Hawthorne AAP, Western Demil Facility (WDF) has resulted in detailed technical and economic information concerning Hawthorne's demilitarization alternatives. They have proposed an environmentally sound installation designed to handle a large ammunition demil inventory. It will be energy-intensive, however, and will lack adequate control for NO_x. The facility, which stockpiles about 2/3 of the Navy's demil inventory, projects a 5-year workload. Little PEP recovery is planned.

Cost estimates range in the millions: \$37M for facilities, \$18M for equipment, and \$6M for startup. Total operating manpower is estimated at 88 for production, 8 for engineering, and 26 for maintenance at full-scale operation. The burdened hourly costs for one 8-hour shift/day are \$36, \$33 and \$27 respectively.

The following cost breakdown delineates where some of these costs are incurred.

<u>Cost Breakdown</u>	<u>Cost</u>	<u>Manpower</u>
Preparation Building		Not Available
6 cells		
control room with remote control consoles for each cell		
Smokeless Powder Accumulation Building		Not Available
(capacity 4700 lb/hr)		
vacuum collector		
storage		
Mechanical Removal Buildings		Not Available
press/puncture		
equipment bandsaw		
gauged hole saw		
major caliber defuzer		
large bandsaw		
Refining Building (Steam Meltout)	\$2.03M	2
(for TNT, Comp.-B, 2200 rounds/8-hr)		
melt kettle		
vacuum kettle		
flaking belt		
Bulk Incinerator Building	\$1.48M	3
(Radford rotary kiln - capacity 1100 lb \$PEP/hr)		
explosives grinders		
slurry holding tanks with agitator		
2 rotary kilns, ceramic lined, afterburners		
fuel oil		
Washout/Steamout Building (Hydraulic cleaning)		
hot water washout (tower #2)	\$2.28M	7*
melt kettle		
vacuum kettle		
flaking belt		
high pressure washout (tower #2)	\$1.27M	2
(TNT, Comp-B, ammonium picrate- capacity 2100/8-hr shift)		

*8-hour shift

<u>Cost Breakdown</u>	<u>Cost</u>	<u>Manpower</u>
Decontamination Buildings		
rotary deactivation furnaces (capacity 8000 lb/furnace/hr)	\$1.67M	6
2 APE 1236 type feed system 5-section retort cyclone separators APE 1276 baghouse filters		
large-item flashing chamber (capacity 6 items/8 hr shift)	\$1.27M	4
35' cylindrical room with tracked car-bottom system gas cooler using 121, 8" diameter steel pipes in two 20' sections 6 baghouses		
continuous flashing furnace (capacity 1100 rounds/8 hr shift)	\$1.68M	6
2 cells conveyor baghouse filter		
Water Treatment Building	\$1.29M	
conventional municipal type treatment with flotation/clarifier		
3 coal/sand filters		
backflash equipment		
3 carbon bolumms		
heat transfer system		
Boiler Plant	Not Available	
three 50,000 lb/hr boilers		
6 baghouse filters		

The following cost breakdown of the NOS Indian Head facility, Maryland, also resulted from the meetings of John Brown Associates (Brown and Shapiro, 1979) with facility officials. Indian Head, however, is ocnstructing a demil site which has no full-scale counterparts at other sites. The four components are:

- Zimpro wet air oxidation unit
- fluidized bed incinerator
- high-pressure water washout system
- wastewater treatment plant.

Because of this, actual costs are not specified, but rather are best technical estimates.

Wet air oxidation equipment	\$400K	
Total system including engineering and construction		\$4.3M
Fluid bed incinerator unit	Unknown	
Total system including engineering and construction		\$6.0M
High pressure washout unit	Unknown	
Total system including engineering and construction		\$~ 4M/estimate
Water treatment plant		~1.2million
Total Capital Cost		\$10+M

5.6 SUMMARY OF EXPLOSIVES INDUSTRY WASTE STUDY

Complying with the proposed EPA hazardous waste regulations of December 1978 would presently be impossible for most of the commercial and military explosives industries. Treatment of waste effluents---gaseous, aqueous, or solid---to minimize pollution problems is currently less than adequate, and is not practiced in most cases. Because of the hazardous nature of explosives, producers are usually located in remote, sparsely populated areas on a large tract of land. Therefore, cases of leachate contamination of surface or groundwater have not been found, though they are likely. The increase in NO_x , particulates, or other gaseous pollutants to the surrounding atmosphere under these circumstances, would also be minimal. In isolated locations, ultimate disposal of potentially hazardous solid waste can easily be handled by open burning or land burial on-site---far removed from any sensitive geographic/demographic areas. Isolated locations are not always the case, however, especially for military institutions such as Iowa AAP.

Use of large land areas for disposal does not present severe economic or institutional barriers to most explosives manufacturers. The cost of hazardous waste treatment and disposal would be comparatively lower for these manufacturers.

Current methods of wastewater treatment are rudimentary, if they exist at all. Therefore, compliance with new regulations would impose a severe technical and economic burden on most commercial and military explosives facilities. This burden might be alleviated if the industry adopted sound water and waste management practices, such as good housekeeping practices, improved clean-up of equipment and buildings, adoptions of environmentally sound and updated processes for the various manufacturing operations, elimination of obsolete equipment in favor of automated process, handling and packaging operations, and substitution of less hazardous fuel or intermediate products. All these measures would reduce waste volume at the source with an accompanying reduction in the quantity of potentially hazardous and toxic constituents. Reuse and recycling of water effluents could also be achieved to further reduce waste loads.

Adoption of primary treatment methods, in some cases, might be as simple as pH adjustment, neutralization, filtration, and centrifugation, with subsequent land application of the residue. Where geographically permissible, open burning of the residue using precautionary safety measures may be the best approach until better alternatives for treatment and disposal become available. For the military, improved water management programs, reclamation, and reuse of bulk PEP removed from obsolete munitions, sale to commercial buyers of reclaimed metal and munitions still in fair condition, or reuse by foreign governments or within the military for munitions, and other useful applications, is perhaps the most economical and technically feasible approach to reducing the large waste PEP inventory.

6.0 REGULATORY OPTIONS

The final task in this project involved the assessment of alternatives for regulation of ignitable, reactive and volatile wastes. The following questions are addressed below:

- Should disposal of IRV wastes be allowed in landfills?
- Should the wastes be treated prior to disposal to render them less hazardous?
- How can resource recovery be encouraged?
- Would dilution of wastes render them less hazardous or more easily disposed of?
- Can dilution serve as a means for complying with Interim Status Standards?
- Should long term waste storage be allowed?
- What are the impacts of regulation on small businesses?
- Is there a size of operation below which less restrictive regulations will not seriously impact the environment?
- For IRV wastes, should industries, waste streams, or pure substances be regulated?
- Should wastes be regulated on the basis of their volatility?

6.1 LANDFILL DISPOSAL OF IGNITABLE, VOLATILE AND REACTIVE WASTES

The proposed Hazardous Waste Guidelines and Listing Section 250.45 Standards for Treatment and Disposal (December 18, 1978) leaves the burden of proof for environmental safety to the site owner and operator before disposal of ignitable, volatile and reactive wastes can be allowed in a landfill, surface impoundment, basin or landfarm. From our investigations, it appears that landfill disposal was the best currently applied technology for only two of the waste streams studied—wastewater treatment sludges from electroplating and woven fabric dyeing and finishing—and for these wastes, dewatering, chemical fixation or encapsulation were recommended prior to final disposal. Because the

waste streams studied are representative of a broad range of IRV waste streams in industry, and because landfill disposal was determined to be suitable for only two of the thirteen waste streams, it may be that landfill disposal, in general, does not represent the best available technology for IRV wastes.

6.2 TREATMENT TECHNIQUES FOR IGNITABLE, REACTIVE AND VOLATILE WASTES

Treatment techniques for ignitable, reactive and volatile wastes include incineration or other thermal destruction, concentration of the ignitable, reactive and volatile constituents for reuse, or chemical conversion of the waste into a salable product. Some form of incineration was applicable to 11 of the 13 waste streams studied, and was determined to be best available technology for eight of those waste streams. Incineration may be used to reduce volume and to destroy the IRV constituents in the waste stream; the residue can generally be disposed of in a landfill. The disadvantages of incineration include the need for maintaining high temperatures and long retention times to insure thermal destruction of many IRV wastes, the high capital cost of equipment, the high operation and maintenance costs for maintaining that equipment, and, the cost of providing supplemental fuel.

Enforcement of regulations for incineration was considered feasible. Stack emissions should be monitored at regular intervals, but savings in monitoring costs may be reduced by measuring, at frequent intervals, primary and secondary combustion temperature and the feed rate. Stack emissions may be monitored at longer intervals. The necessary retention time may be designed into the incinerator. The State of Connecticut has reported successful monitoring of emissions from incineration of non-chlorinated solvents by using the above monitoring system (Section 6.9).

The high cost and energy requirements of incineration encourage the consideration of other methods for removing IRV properties from waste streams. Recovery of valuable constituents in waste streams was observed for two of the 13 waste streams studied (Chapter 3). Recovery and reuse was determined to be the most environmentally sound practice for several other waste streams. Special circumstances, such as the

type of process and product quality control requirements, make it difficult to recommend the application of recovery practices by an exemplary production facility to all facilities of an entire industry. An example would be the reuse of spills and spoiled batches in paint production, described in Chapter 3. Although the recovery of valuable constituents from waste streams is desirable, it is difficult to encourage from a regulatory standpoint. Some financial incentives already exist. Raw materials savings are to be realized, as are savings in disposal costs due to the decreased volume for disposal and the decreased hazard posed by the waste, which may allow the use of less expensive handling and disposal techniques. Therefore, it does not appear that special regulations for recovery of valuable constituents are necessary at this time.

Chemical treatment for conversion of the waste into a salable product was not practiced for any of the 13 waste streams studied. Several chemical treatment processes were recommended as most environmentally sound methods. More research and development are needed to permit general application of these processes to IRV wastes.

In general, it appears that treatment of IRV wastes is feasible, but expensive. Except for incineration, further research is necessary in many areas before treatment processes can be applied to an entire industry. However, isolated plants have been found in many industries which treat wastes for recovery and reuse of valuable constituents.

6.3 WASTE STORAGE

The December 18, 1978 Draft RCRA 3002 Regulations proposed a 90-day cutoff period for permanent versus temporary waste storage. The 90-day period appears to be reasonable, considering the following:

- Containment vessels would probably not be breached except with poor management practices.
- Some time allowance is necessary to accumulate a full load of wastes for off-site disposal.
- Some time allowance is necessary in case of equipment breakdown, strikes, etc.

Certain reactive materials, such as explosives, should be handled on a case-by-case basis with no storage allowed unless adequate safety precautions are taken. Contact with off-site waste disposal facilities revealed that many do not accept explosives. A general discussion on storage of ignitable and volatile wastes is given in Section 3.2 and in Chapter 5. The current practice at industrial plants is to store IRV wastes in 55 gallon steel drums. Detailed information on other techniques for storage of wastes was not available. Lagoon storage was practiced for only two of the 13 waste streams studied.

6.4 MIXING OF WASTES

Mixing of wastes may be performed by either the generator or disposer. Generator practices vary depending on whether treatment, storage or disposal of wastes is performed on the plant site or by an off-site waste disposal contractor. If on-site, wastes may be segregated by their ultimate destinations (incineration, landfill materials, recovery) for a large multiproduct manufacturer, while a smaller facility with only an on-site landfill may not segregate wastes at all.

Off-site disposers must be careful to accept only those wastes that can be effectively treated by their particular equipment or safely disposed at their land disposal facility. Therefore, segregation of wastes becomes more critical, consequently careful segregation by a generator can result in decreased charges by the disposer. Segregation of wastes by the generator should be encouraged also because of the greater potential for recovery of valuable constituents for reuse.

Numerous instances of waste mixing were found in telephone contacts with disposers. The most obvious instances were mixing of acids and bases for rough neutralization prior to further addition of chemicals. Savings in neutralization chemicals were significant. Careful mixing of wastes with fuel prior to incineration allowed savings in supplemental fuel by utilizing heat values of combined wastes. In this manner, high heat value wastes can be combined with those having little

or not heat value; the objective is generally to use supplemental fuel only for start-up.

Mixing of inert materials such as water with explosives prior to incineration is common. The result is increased protection to personnel operating incineration equipment and to the equipment itself by limiting the potential for severe explosions.

Mixing of inert materials with other IRV wastes prior to landfill has been reported, although it is not generally considered by the disposers themselves as a good practice. IRV properties may be reduced, but the mass disposed and potentially released remains the same. One disposer commented that even if the practice were acceptable, it would not be economically feasible due to the large quantities of inert materials needed to dilute many IRV wastes to acceptable levels. Allowing the dilution of IRV wastes as part of Interim Status Standards is, therefore, not recommended.

6.5 TREATMENT, STORAGE OR DISPOSAL OF WASTES OFF THE PLANT SITE

Although general improvement in off-site disposal practices has been made over the last several years, the off-site disposers performing best available technology for IRV wastes are not as common as they should be to ease the transition as regulations are implemented. The question is, therefore, whether there will be enough complying off-site disposers to handle the quantity of wastes generated by industry, and whether the complying waste disposal contractors will be strategically located so that transportation of IRV wastes over long distances can be avoided.

Conversely, industry may feel that disposal on their plant site gives them better control over wastes for which they are ultimately responsible. It is believed that, in general, large plants will tend to dispose on-site, while smaller plants with smaller technical staffs and less available capital will use contract disposers. Smaller waste volumes, particularly those generated by small plants, will necessitate storage until enough is accumulated to justify a waste pick-up by the disposer or delivery to the disposal site by the generator.

6.6 IMPACT OF REGULATIONS ON SMALL BUSINESSES

Based on the study of industries such as electroplating and paint manufacturing given in Chapter 3 which are composed of many small businesses, it would be difficult to set a cutoff point for size of operation which would allow less restrictive regulation of small businesses. Although it is recognized that the impact of the regulations will probably be greatest for smaller businesses, their wastes are no less hazardous than those of large operations.

Paint industry wastes are good candidates for reuse. Spills and spoiled batches are already reworked into the process where possible, and solvents are frequently recovered for reuse. Some solvents, spills and spoiled batches are more easily recovered than others, however, and residues remain from recovery processes which require disposal. In the paint industry, much progress is being made toward reducing waste volumes by more efficient usage of materials, improving housekeeping practices and decreasing the quantities of hazardous materials such as pigments and solvents used in the process. Small businesses in other industries must become aware of the potential for reuse of wastes and the potential for reduction of wastes generated. For wastes which have uses, but not at the plant generated, a waste exchange between plants may become feasible. The regulatory aspects of this practice are not known.

6.7 DEVELOPING REGULATIONS FOR HAZARDOUS WASTES

The alternatives for regulations of hazardous wastes include:

- developing regulations for classes of hazardous wastes
- basing regulatory decisions on the hazards posed by pure chemicals or on the hazards posed by a waste stream
- developing regulations for waste streams on an industry-by-industry basis
- developing regulations on a plant-by-plant basis.

The above regulatory alternatives were briefly evaluated following the completed analyses of the thirteen specific waste streams, and in light of the technical alternatives assessed. Our conclusions follow.

Concerning the development of regulations on pure substances versus total waste stream composition, the waste streams studied were not pure substances but were mixtures of many compositions, some of which were hazardous. If pure substances were used as a basis for regulations, then a cut-off point would have to be determined (such as the one mg/l mentioned in the December 18, 1978 draft) below which the waste stream would not be considered hazardous. When waste streams were considered as a basis for regulatory process, differences which caused variations in waste streams became significant. These process differences may need to be carefully described in regulations based on waste streams. Therefore, it was found that both the application of a "pure substance rationale" and also the application of a "waste stream rationale" to our thirteen waste streams posed different problems and that neither was totally suitable.

It was also observed that both approaches did not fully consider other important aspects such as waste form (sludge, liquid, etc.) and the disposal environment.

When we consider the application of an industry-by-industry approach to the waste streams studied, it was found that identification and tracking of waste streams seemed easier. This was offset by problems posed by regulating facilities covered by many SIC codes and producing a mixed waste. In summary, regardless of the regulatory approaches used, it seemed important to consider the chemical composition, form, hazardous properties, and disposal environment of waste streams, and to consider variations in waste streams (both plant-by-plant and within a given plant). Our further analysis of regulatory approaches was hindered by the lack of statistically significant information on the composition of each waste stream and by a lack of information on spills, process changes, product changes, equipment changes, in-plant housekeeping and by the degree of waste stream mixing prior to disposal.

6.8 REGULATION OF VOLATILE WASTES

One of the initial tasks of this project was to develop a definition of volatility that would be useful in the remainder of the project and potentially useful for regulations. The definition of volatility proposed in the December 18, 1978 Draft was that substances having a vapor pressure greater than 78mm of mercury at 25°C would be considered volatile. The definition developed under this project considers volatile substances with vapor pressures greater than 78mm of mercury at 40°C, which represents a temperature likely to occur in a disposal site in the summer. Also considered volatile would be toxic substances with vapor pressures between 0.1mm Hg at 40°C and 78mm Hg at 40°C.

From studying the thirteen IRV waste streams it has become apparent that volatility is an important parameter to consider in regulations, particularly for toxic substances. Volatility covers a physical transport property of wastes not adequately addressed by the concepts of ignitability and reactivity. Appendix A describes incidents where physical harm resulted from inhaling toxic vapors of previously disposed substances.

The definition of volatility developed in this project needs verification on actual waste streams and development of a stronger basis for the cutoff points if eventual use in regulations is anticipated.

Our recommendations for regulation are summarized and presented in Chapter 2.

6.9 SUMMARY OF CONTACTS WITH STATE AGENCIES AND OFF-SITE WASTE DISPOSAL CONTRACTORS

Summaries of contacts with selected state agencies and off-site waste disposal contractors are given in Tables 6.1 and 6.2. It should be noted that these contacts represent better than average practices and regulations. Efforts were made to determine better than average waste disposal contractors through state contacts, the EPA Project Officer, and in-house knowledge of disposal contractors.

From these contacts it was learned that many states have either very recently passed regulations conforming to expected federal regulations, or are in the process of doing so. It was also learned that many of the better waste disposal contractors are either already complying with expected regulations or are making plans to do so. One waste disposal contractor commented that those who expect to modify their sites quickly as soon as regulations are out will make mistakes and could go out of business trying to comply. His operation, by gradually modifying and testing modifications, will need only minor modifications once regulations are implemented.

Table 6.1 Summary of Contacts with Selected State Agencies

	CALIFORNIA	ILLINOIS	NEW JERSEY	CONNECTICUT	MARYLAND
WASTE MANIFEST SYSTEM	X	X	X		X
PROHIBIT IRV WASTES IN LANDFILLS	Case by case basis	Case by case basis	X	Case by case basis	Case by case basis
SPECIAL CONTROL OF DISPOSAL OF WASTES WITH HIGH METALS CONTENT	Case by case basis	X	Case by case basis	X	Case by case basis
CHANGE IN REGULATION IN PROCESS	X			X	
COMMENT	Encourage reuse/recycling through waste exchange and information transfer		No secure landfills exist in state	Prohibit incineration of chlorinated organics	Provision for perpetual care of disposed facilities

Table 6.2 Summary of Telephone Contacts with Selected IRV
Waste Disposers

	Wescon, Inc. Twin Falls, Idaho	Waste Manage- ment, Inc. Eight Facili- ties, Based in Illinois	IT Corp. Martinez, Calif.	BKK Corp. Wilmington California	Rollins Env. Services Wilmington Delaware	Solvents Recovery, Inc., Linden New Jersey
Significant Characteristics	Water table 3300 ft deep Use abandoned missile silos and clay lined trenches	Located on natural clay deposits	Located in dry area, use solar evaporation	Located in dry area	Located in wet area	Operation set up to recover solvents
Incineration		X	X		X	X
Blending of fuels		X	X		X	X
Other treatment			X			
Storage			X		X	
Disposal Secure Landfill	X	X		X	X	
Encapsulation	X			X	X	
Deep Well Injection				X	X	
Land Farm			X		X	
Ground Water Monitoring		X	X	X	X	
Waste Location Records	X	X	X			
Solvent Recovery			X			X
Handle Reactive Wastes			X		X	
Determination of TSD Methods						
Lab Analysis	X	X	X	X	X	X
Waste Form		X	X	X	X	X
Exclusion of Explosives			X	X	X	X
Separation of In- compatible Wastes	X		X	X	X	
COMMENT	Excellent location	Adjusting operations to comply with antici- pated regu- lations	Excellent location allows use of solar evaporation	Bury con- tainers of IRV wastes in cells of absor- bent ma- terial	Incinerate still bottoms	Incinerate solvent re- covery residues, dispose incine- ration residue in off-site landfill

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APPENDIX A

WORKING DEFINITION OF VOLATILITY

WORKING DEFINITION OF VOLATILITY

Volatility is a chemical contact word used to describe the physical characteristics of a substance, as a result it has been used as a means of describing the potential hazard of a substance. Numerous damage incident reports exist which ascribe the volatility of a waste material as the cause of damage. Some of these are given in Table A.1.

Of the approximately 400 damage incidents in EPA's file of hazardous waste disposal damage reports, eight incidents were identified which were caused by air pollution from volatile substances (EPA, 1978). The remaining cases were related primarily to water pollution problems. Additional cases of incidents involving volatile waste disposal were also identified from a cumulative annual study of damages from hazardous wastes (Abbey, 1978).

One of the initial tasks of this project was to develop a working definition of volatility to correlate this property of wastes with damages that could result from improper disposal. This definition was developed and used to help determine whether or not waste streams should be considered volatile. Definitions for ignitability and reactivity, which had been included in draft regulations for RCRA Section 3001 (Federal Register, 1978), were used to determine whether waste streams fell into these categories. These three definitions are given in Table A-2.

The original intent of the definition development effort was solely to further the goals of this project. However, while the definition was being developed, the EPA Office of Solid Waste was also in the midst of considering definitions of volatility for the purpose of regulating volatile wastes. Because of this, some effort was expended to assist EPA by assessing how the developed definition could be used for regulating volatile wastes. The approach taken for developing this definition was considered for use in regulations and rejected by EPA. For the sake of completeness we have included some information gathered for regulatory efforts even though data gaps exist in some

Table A.1 Damage Incidents Involving Land Disposal of Volatile Wastes

<u>Injury</u>	<u>Cause</u>
Serious complaints of illness by 53 residents living in valley near Elkton, Maryland	Air pollution. Exposures to mixtures of solvents due to a nearby chemical plant that recovered solvents from discarded chemical materials (butyl alcohol; amyl alcohol, ethyl acetate, toluene, trichloroethylene, benzene, methyl ethyl ketone, acetone, carbon tetrachloride, chlorobenzenes, butanol, ethyl ether, o-, m-, and p-xylene.
100 homes in Niagara Falls, N.Y. abandoned with toxic fumes in basements, leaching of chemical waste in the backyards, and basements. Local residents were found to have health problems in areas such as liver function and success of pregnancy	Homes built on the old canal which had been used as industrial dump for 25 years. 82 different compounds, 11 of them suspected carcinogens, had been disposed there (aliphatics, aromatics and chlorinated compounds)
Brain abnormalities found in workers in Rocky Mountain Arsenal, CO	Inadvertant exposure to nerve gas (organophosphate)
Several homes abandoned with fumes and danger of fire in Conell Hts., PA	Paints and solvent dumped in sewer lines
17 workers sick in Louisville, KY	Spill of organic hydrocarbons into sewer
Compactor operator killed and compacter destroyed in Calumet, ILL	Explosion on compaction at landfill of illegally dumped solvents (ethyl acetate)
Bulldozer operator became nauseated	Fumes from benzene hexachloride manufacturing wastes uncovered during site preparation for a baseball field (lindane, BHC)
People suffered nose bleedings, nausea in Smithfield, RI	Landowner with unlicensed pit (PCB's; phenols, methyl chloride)
Persons suffered eye and throat irritation in Lake City, GA	Drums in landfill erupted sending fumes into air (cyanide and organic compounds)

Table A.1 (continued)

<u>Injury</u>	<u>Cause</u>
Loss of bulldozer in Genessee Co., MI	Bulldozer operator became dizzy and eyes irritated, left bulldozer and returned to find it in flames (Volatile substances)
Some workers in the building downwind became nauseated resulting from air pollution from the evaporation of volatile liquid wastes from pond surface in Contra Costa County, CA	Volatile wastes evaporated from the surface of a disposal pond. (crotyl chloride, amines, and C ₅ -C ₆ hydrocarbons)
Corrosive damage to homes in San Francisco Bay Area. Residents experienced noxious odors, eye and throat irritation	Fumes (organic vapors, acidic vapors etc.) from the surface of industrial liquid waste evaporation ponds (volatile industrial liquid)
Compacting bulldozer destroyed, fish killed. Contamination of air, and surface and groundwater down gradient from the landfill	Drums containing oily wastes and nickel exploded during compacttion (unidentified chemical wastes)
Alkyl lead intoxication at lead recovery facility in San Francisco, CA. 2 collectors on a bridge became ill from vapors escaping from trucks hauling organic lead wastes	Evaporation of organic lead vapors from disposal sites, recovery facilities, and from transporting vehicles.

Table A.2 Definitions of Volatility, Ignitability
and Reactivity Used in This Report

Developed Definition of Volatility

Volatile Substances are those with vapor pressures of 78 mm Hg and higher at 40°C and those with vapor pressures between 0.1 and 78 mm Hg at 40°C that have Sax toxicities of 2 or greater.

Substances that are not volatile are those with vapor pressures below 0.1 mm Hg at 40°C and those with vapor pressures between 0.1 and 78 mm Hg at 40°C that have Sax toxicities of less than 2.

Existing Definition of Ignitability

Ignitable substances are those with flash points of 60°C (140°F) or lower.

Existing Definition of Reactivity

Reactive substances are those which are normally unstable and readily undergo violent chemical change, or form toxic fumes or explode when exposed to moisture. Additionally, forbidden explosives as defined in 49CFR173.51, Class A explosive as defined in 49CFR173.53, and class B explosives as defined in 49CFR173.58 are included.

areas. This information is by no means conclusive and does not reflect current EPA thinking for regulating volatile wastes.

The developed definition was useful in determining whether waste streams were volatile. However, the major problem for regulating volatility using this definition, is the fact that a means of measuring volatility of an entire waste stream was needed. Vapor pressures and toxicities of waste streams are not widely available in literature. Therefore, a major data development effort would have been necessary to incorporate this definition in regulations.

A.1 RELATION OF STUDY TO THE APPROACH CHOSEN

The primary purpose of developing the working definition was to provide a relatively easy means for evaluating whether a waste stream was volatile by using existing information in the literature. The definition, in order to be useful to the study, had to incorporate the assessment of major waste stream constituents. This approach is illustrated by the list of substances, vapor pressures and toxicities in Table A.3 and also the application of information such as that in the table to the actual waste streams in Appendix B.

The purpose of this analysis was to evaluate the use of vapor pressure and toxicity as a means of using volatility to indicate the relative hazard of a substance. Vapor pressures are usually expressed in the literature for each chemical at 25°C temperature. One approach was to determine vapor pressure at 40°C, since it was believed that this temperature more nearly described the temperatures that may be encountered in land disposal facilities.

The developed definition was applied for specific pure substances. The substances were listed with 60th volatility indices and their toxicity ratings according to Sax.

Volatility for 40°C was calculated using the following formula which is the Clausius-Clapyron equation:

$$\log p = \frac{\Delta H}{2.303R} \frac{1}{T} + \text{constant}$$

Where $\frac{\Delta H}{2.303R}$ can be evaluated from the slope of the line and value of $\log p$ at a point on the line.

Table A.# illustrates the volatility at 25°C and 40°C for example chemical substances, also listed are their toxicity ratings according to Sax.

A.2 VOLATILITY OF PURE SUBSTANCES

A list of ignitable, volatile and reactive waste streams was assembled from the literature and is included as Appendix B. The definitions given in Table A.1 were used in determining whether waste streams belong in the list. Additionally, since most waste streams are made up of many components and some may be ignitable, volatile and reactive, while some may not, a waste's inclusion in the list was determined by considering known major constituents. Therefore, the definition developed for this study was applied to a number of pure substances to determine whether or not they would be considered volatile. A discussion of some of the findings follows.

There are many compounds that have vapor pressures above the 78 mm Hg level in the developed working definition. Among these is carbon tetrachloride, which at 40°C has a vapor pressure of 216 mm Hg and whose inhalation toxicity has a rating of 3 for both chronic and acute systemic effects. Acetonitrile, a major component of the waste stream generated in its production, also presents a hazard. At 40°C it has a vapor pressure of 140 mm Hg and an acute systemic inhalation toxicity rating of 3. Both of these compounds would be volatile according to the developed definition and the EPA proposed definition.

TABLE A.3 Comparison of Vapor Pressures and Toxicities of Selected Chemicals

Chemical	Vapor Pressure at 40°C mm Hg	Vapor Pressure at 25°C mm Hg	Toxic Hazard Rating by Inhalation				NIOSH* Standards
			Acute Local	Acute Systemic	Chronic Local	Chronic Systemic	
Ethyl ether, $C_4H_{10}O$	921.00	532.45	12	2	u	2	
Methylene Chloride, (Dichloromethane), CH_2Cl_2	784.28	425.07	12	3	u	1	75 ppm TWA 261 mg/m ³
Dioxane, $C_8H_{10}O_2$	79.68	40.08	2	3	u	3	1 ppm 3.6 mg/m ³
Acetone, C_3H_6O	421.00	228.80	2	2	11	1	
cis - 1,2 - Dichloroethylene, $C_2H_2Cl_2$	387.77	202.50	2	2	11	1	
Chloroform, $CHCl_3$	362.21	190.66	11	3	u	u	2 ppm 9.78 mg/m ³
Carbon tetrachloride, CCl_4	216.00	112.96	0	3	11	3	2 ppm 12.6 mg/m ³
Methyl ethyl ketone, C_4H_8O	185.36	95.82	1	2	11	u	
Ethyl acetate, $C_4H_8O_2$	178.50	87.66	11	2	11	1	
Benzene, C_6H_6	170.48	80.22	1	2	0	3	1 ppm 3.2 mg/m ³

*National Institute for Occupational Safety and Health

TABLE A.3 Comparison of Vapor Pressures and Toxicities of Selected Chemicals (continued)

Chemical	Vapor Pressure at 40°C mm Hg	Vapor Pressure at 25°C mm Hg	Toxic Hazard Rating by Inhalation				NIOSH Standards
			Acute Local	Acute Systemic	Chronic Local	Chronic Systemic	
Acetonitrile, C_2H_3N	170.18	87.78	11	3	12	1	< 4 ppm ³ 8.7 mg/m ³
Trichloroethylene, C_2HCl_3	141.04	71.98	11	3	11	1	
Ethyl Alcohol, C_2H_5OH	135.00	58.76	11	2	11	1	
1,2 - Dichloropropane, $C_3H_6Cl_2$	99.57	50.30	12	3	11	3	
1,4 - Dioxane, $C_4H_8O_2$	79.97	40.08	12	3	μ	3	1 ppm ³ 3.6 mg/m ³
Water, H_2O	55.32	23.76	0	0	0	0	
Toluene, C_7H_8	55.57	26.68	11	2	11	2	100 ppm ³ 375 mg/m ³
Tetrachloroethylene, C_2Cl_4	37.56	17.78 --	12	2	12	2	50 ppm ³ 339 mg/m ³
n-Octane, C_8H_{18}	31.00	13.77	0	2	11	μ	
Benzyl Chloride, C_6H_5Cl	24.28	11.20	1	2	0	2	5 mg/m ³
Ethyl benzene, C_8H_{10}	20.43	9.30	12	2	μ		

TABLE A.3 Comparison of Vapor Pressures and Toxicities of Selected Chemicals (continued)

Chemical	Vapor Pressure at 40°C mm Hg	Vapor Pressure at 25°C mm Hg	Toxic Hazard Rating by Inhalation				NIOSH Standards
			Acute Local	Acute Systemic	Chronic Local	Chronic Systemic	
Butanol, $C_4H_{10}O$	18.21	7.00	11	2	μ	1	
Styrene, C_8H_8	15.75	7.22	12	2	μ	2	
1,1,2,2 - Tetrachloroethane, $C_2H_2Cl_4$	14.04	6.29	3	3	μ	3	
Cyclohexanone, $C_6H_{10}O$	10.26	4.55	12	1	11	-	
Pentachloroethane, C_2HCl_5	10.10	4.44	12	3	μ	3	
1,4 - Dichlorobenzene, $C_6H_4Cl_2$	4.69	1.99	2	2	2	2	
Diacetone alcohol $C_6H_{12}O_2$	3.32	1.29	2	2	11	μ	
Phenol, C_6H_6O	1.00	0.40	3	3	12	2	5.2 ppm ₃ 20 mg/m ³ TWA
Nitrobenzene, $C_6H_5NO_2$	0.83	0.31	μ	3	μ	μ	

TABLE A.3 Comparison of Vapor Pressures and Toxicities of Selected Chemicals (continued)

Chemical	Vapor Pressure at 40°C mm Hg	Vapor Pressure at 25°C mm Hg	Toxic Hazard Rating by Inhalation				NIOSH Standards
			Acute Local	Acute Systemic	Chronic Local	Chronic Systemic	
1,2,4 - Trichlorobenzene, $C_6H_3Cl_3$	1.13	0.45	12	2	loss hair	2	
2,4,5 - Trichlorophenol, $C_6H_3Cl_3O$	0.14	0.05	μ	3	μ	μ	
1 - Chloronaphthalene, $C_{10}H_7Cl$	0.10	0.03	13	3	13	3	
γ - Hexachlorocyclohexane, $C_6H_6Cl_6$	< 0.14		A1, I1	2	A2	2	
Diethyl phthalate, $C_{12}H_{14}O_4$	0.012	0.003	2	2	μ	μ	
Mercury, metallic	0.007	0.002	13	3	12, A3	3	
PCB's	< 0.1		12	3	13	3	1 mg/m ³ IWA

0: not harmful, unless unusual conditions or overwhelming dosage

1: slightly harmful, effects readily reversible after exposure period

2: moderately harmful, irreversible and reversible effects not enough to cause death or permanent injury

3: highly toxic, can cause death and permanent injury

μ : unknown effects

I: Irritant

A: Allergen

A.2.1. Excluded Wastes

PCB's are an example of wastes known to have a significant inhalation toxicity (a rating of 3 for acute systemic and chronic local and systemic), but they are not volatile according to the definition. This class of compounds has a vapor pressure slightly below the 0.1 mm Hg level. Most organic compounds having 16 to 18 carbon atoms or more have vapor pressures below 0.1 mm Hg, and so would not be defined as volatile. The definition would exclude metallic mercury, an element known to be toxic. It has an inhalation toxicity index of 3 for both acute and chronic exposure. It also has a vapor pressure of 0.09 mm Hg at 40°C, which is below the minimum vapor pressure of compounds to be included by our definition. Despite this low vapor pressure it has significant toxic effects in its vapor phase and over time can saturate the air of a room with a high enough concentration of mercury vapors to have noticeable toxic effects.

A.2.2 Included Wastes

There are a large number of compounds that have vapor pressures between 78 mm Hg and 0.1 mm Hg. Examples include phenol and trichlorobenzene. Phenol, a constituent of the waste stream generated in the production of phenolic resins, has a vapor pressure of 1.57 mm Hg at 40°C and an inhalation toxicity rating of 3 for acute exposure and 2 for chronic exposure. Trichlorobenzene isomers are a major constituent of the waste stream generated by polyester manufacture. 1,2,3-trichlorobenzene has a vapor pressure of 1.0 at 40°C and an inhalation toxicity rating of 2 for both acute and chronic systemic effects. When present in sufficient concentrations in the waste stream, both of these compounds pose a potential hazard due to their vapors.

Heavy metals and organometallics are typically present in very small concentrations in waste streams, yet are hazardous due to their volatility and inhalation toxicity. Examples are tetraethyl lead and organo arsenic compounds. Tetraethyl lead is a constituent of the waste stream generated when it is produced. It has a vapor pressure

of 1 mm Hg at 38.4°C and an inhalation toxicity of 3 for chronic and acute exposure. Organo arsenic compounds are constituents of waste waters of pharmaceutical manufacturing. They have inhalation toxicities of 3 for both acute and chronic exposure. Both compounds, though they appear as minor constituents of waste streams and have fairly low vapor pressures, pose a hazard due to their inhalation toxicity.

Comparison of JRB's list of components of potentially hazardous waste streams (Appendix B) with the OSHA (1979) and NIOSH (1979) lists of Threshold Limit Values (TLV) guidelines for industrial exposure, we have found that with the exception of kerosene and crotyl chloride, which is not widely used, JRB's list of key components is contained within the OSHA and NIOSH lists. A more exhaustive search of waste streams may reveal more compounds not on the OSHA and NIOSH lists. However, our list of waste streams is aimed at waste disposal problems as opposed to exposure to hazards in the work place dealt with by the OSHA and NIOSH lists. Waste streams by their nature are mixtures of many components that do not behave in the same way as pure compounds and must be handled differently.

A.3 VOLATILITY IN LANDFILLS, IMPOUNDMENTS AND LAND TREATMENT FACILITIES

Volatility would apply to a waste regardless of its disposal in a landfill, an impoundment or a land treatment facility (land farm) operation. Volatility as defined previously describes a property of a substance at 40°C, which is more conservative than the 25°C at which vapor pressures are normally given.

In a landfill, the presence of soils of low permeability may allow the build-up of pressure from volatile substances. The compacted soil may develop fissures through which vapors can escape. Ambient temperatures at the surface may approach 40°C in summer months, while temperatures below the surface will be somewhat less and will decrease with depth to roughly the mean annual temperature for the landfill site. Exceptions are where decomposition and other reactions are taking place, which may increase temperatures to as much as 60°C.

Impoundments will contain combinations of substances such as liquids and sludges which would flow if unrestrained. Volatile components in impoundments then tend to be released to the atmosphere continuously from the surface unless impeded by a top layer of another substance of relatively low specific gravity. Pressure will not build to the degree that may occur in a landfill.

Land treatment is a waste management practice that includes the application of waste onto the soil and/or incorporation into the soil surface. The soil serves as a physical-chemical filter medium to immobilize inorganic waste constituents, and as a substance for bacterial degradation of organic waste constituents. Compaction of the soil is not necessary. Volatile substances in a land farm can be released to the atmosphere more easily than in a landfill, although pressures may temporarily build in the deeper portions of disturbed soils. Temperatures may approach 40°C at the surface, but would normally decrease below the level at which wastes are disposed.

A.4 VOLATILITY OF IMPURE SUBSTANCES

Very few waste streams are pure substances. Therefore, the volatility of impure substances also must be considered to make the definition useful for evaluating mixed wastes. Advantages and disadvantages of various approaches to the issue of concentration, particularly low concentrations of highly volatile substances in an impure waste stream, are presented below.

A.4.1 Concentration Cutoff Point of 1 Percent

Consideration was given to establishing a low limit below which concentrations of volatile substances in a waste stream could be disregarded. A 1 percent value has been suggested because this concentration could be easily determined by a waste generator or disposer. A waste stream containing 99 percent or more nonvolatile substances and 1 percent or less volatile substances would be considered nonvolatile. This approach has the advantage of simplicity since it would apply

under all conditions. The disadvantages are the possibility of allowing improper disposal of a highly volatile, highly toxic substance which remains hazardous at a concentration of less than 1 percent.

A.4.2 Sliding Scale of Volatility Weighted by Potential Hazard

Use of a sliding scale utilizing potential hazard for determination of volatility of impure substances was considered. Substances would be ranked according to volatility so that the more volatile a substance, the lower its acceptable concentration in a waste stream. Highly volatile substances at low concentrations would be weighted by their potential hazard, although computations would be difficult for a waste stream containing many volatile substances. A methodology would have to be developed for implementing this method, if chosen.

A.4.3 Application of NIOSH Environmental Standards to Waste Streams

One method suggested for determining a concentration at which volatile materials could be present in a waste stream without the entire waste being classified as volatile involved the use of NIOSH environmental standards (NIOSH, 1979). This concept would apply NIOSH environmental standards for a constituent directly to a waste stream. Thus, if the NIOSH standard for a substance is 3 ppm and the volatile constituent is present at a concentration below 3 ppm, the waste would not be classed as volatile. On the other hand, if the constituent were present at 4 ppm the entire waste stream would be considered volatile. The rationale for this method is that if the concentration of a volatile constituent does not exceed the environmental standard, even under the most favorable meteorological conditions, the environmental standard would not be exceeded.

Detailed studies of each constituent and a thorough analysis of its effects on human health covered by the OSHA regulations have been made in a series of documents issued by NIOSH called Criteria Documents. However, limiting waste stream concentrations to these standards would result in unnecessarily restrictive concentrations. Also, the list of

some 400 constituents does not necessarily cover all hazardous waste streams, nor does it cover the properties of the waste stream when it contains two or more constituents. EPA has proposed a formula for adding the contribution of two or more constituents that are toxic.

A.4.4 Utilization of Partial Pressures

Partial pressures of individual constituents of a given waste stream must be determined to apply this methodology to the developed definition of volatility. According to this definition the waste stream would be volatile if one or more of its constituents are volatile and the sum of the contributions to the total pressure exceeded the limits of the definition.

Additional work is necessary to determine the validity of this method for actual waste streams and techniques for measurement of partial pressures of waste stream constituents must be chosen. Utilization of partial pressures would achieve the goal of assigning lower allowable concentrations to constituents with higher volatilities, while remaining consistent with the developed definition.

A.5 SUMMARY

Many alternatives exist with which volatility can be applied to impure substances. The greatest problems with applying volatility to impure substances is that for many waste streams, the exact composition is not known.

Secondly, the synergistic effects of the impure substances are not known and without laboratory tests on each substance, the volatility is not known. None of the alternatives given is complete in itself, and more work is necessary to further develop them.

A.5.1 Chosen Alternatives

The approach used in this study for applying the definition of volatility to waste streams is to use the volatility of the pure

substance in the stream which is of the largest concentration. This provided the ability to identify volatile waste streams without actually performing the research necessary before alternatives could be put into practice. For example, while the concentration cutoff at 1 percent is the simplest approach, and would have been used in this study, insufficient information on composition of wastes was available to justify its use.

A.5.2 How the Definition May Be Used

Using the developed working definition of volatility for applications beyond this study may be feasible. Although not actually a part of this study it may provide some possible approaches for future regulatory activities. The approach for using the definition for this study involved identifying major constituents of wastes and determining whether the constituents were volatile and then extrapolating this information to the parent waste streams. While this approach was necessary for this study due to a lack of analytical data on waste stream compositions, the approach does not appear satisfactory for regulating volatile wastes. If a regulatory approach required the identification and use of individual waste stream constituents, then the approaches described in Section A.4 should be considered. If waste stream constituents are not required, then approaches such as using vapor pressures and toxicities of entire waste stream to determine volatility should be considered.

A.5.3 Measurement in Wastes

Further research and experimentation needs to be performed on the subject of volatility of hazardous waste streams. Volatility is a property of wastes that has caused damage to human health and the environment. Some of the other ideas proposed for measuring volatility have included use of such things as molecular weights of chemical constituents and solubility in water as well as vapor pressure. These ideas present problems similar to those experienced for the working definition in this report. Molecular weights of numerous chemicals

may have to be synthesized to determine how volatilization may occur in a disposal facility. Additionally, solubility in water is not likely to accurately describe volatilization from leachate or watery wastes.

Measurement of vapor pressures of entire waste streams is feasible, however and some laboratory experimentation has been performed at Utah State University to measure vapor pressures of mixed wastes. Toxicity of wastes will be determined as EPA extraction procedures are implemented. Therefore, we feel that coupling vapor pressures and toxicities of mixed wastes should not be abandoned as an approach for regulating volatility.

APPENDIX B

DATA BASE LIST OF IGNITABLE,
REACTIVE AND VOLATILE WASTE STREAMS

In the following list:

- Annual Production (waste generation) is given in metric tons per year.
- Toxicities are taken from Sax, Dangerous Properties of Industrial Materials, 4th edition. Blanks indicate the substance was not listed in Sax.
- Toxicities are given for major components of the waste stream.
- References cited in list are given at end of the Appendix. Numbers are those given in list of references. Page numbers are given where applicable.

INDUSTRY	WASTE STREAM	1	2	3	ANNUAL PRODUCTION OF HAZARDOUS WASTES (METRIC TONS)	TOX				MAJOR COMPONENT	4	MINOR COMPONENTS	5	FORM	CURRENT DISPOSAL	WASTE CHARACTERISTICS	COMMENTS	6
						AL	AS	CI	CS									
BATTERY MANUFACTURING	LEAD ACID PROCESS WASTES			X		0	3	0	3	PbSO ₄ , PbON, CaSO ₄	41, 43 2002	Pb ⁴	1	SLUDGE	LANDFILL	WASTEWATER EFFLUENT SLUDGE	TOX: Pb BOTH TWP ACID & BASE CAN BE REACTIVE	p. 9
	NICKEL-CADMIUM PROCESS WASTES			X		1	3	1	1	Ni, Cd, CdON, NiON	2, 5 5, 2			SLUDGE	LANDFILL	WASTEWATER EFFLUENT SLUDGE	TOX: Ni, Cd REACTIVE DUE TO HYDROXIDE	p. 94
	ZINC-SILVER OXIDE PROCESS WASTES			X		1	1	1	1	Ag, Cd, SiO ₂ , CaON	3, 5 2, 5				LANDFILL		TOX: Ag, Cd REACTIVE DUE TO HYDROXIDE	p. 94
	IRON-NICKLE OXIDE PROCESS WASTES			X		1	1	1	1	Fe, Ni, FeO, NiO					LANDFILL		TOX: Fe, Ni R: DUE TO CORROSIBILITY	p. 98
	NICKEL-ZINC PROCESS WASTES			X		1	1	1	1	Zn, ZnON, ZnO, Si					LANDFILL		TOX: Zn REACTIVE DUE TO HYDROXIDE	p. 98
	SILVER LEAD PROCESS WASTES			X		1	1	1	1	Pb, Ag, Ag					LANDFILL		TOX: Pb, Ag P: REACTIVE WITH WASTE AND ACID	p. 98
	Hg-Cd MERCURY CADMIUM PROCESS WASTES			X		1	1	1	1	Cd, Zn, Hg					LANDFILL		TOX: Cd, Zn R: DUE TO CORROSIBLE CHARACTERISTICS	p. 102
	CARBON-ZINC PROCESS WASTES			X		1	1	1	1	Hg, Zn, ZnCl ₂ , NaO ₂	11, 4 3, 6	Cd, Pb, Zn ALLOY	41		LANDFILL		TOX: Hg, Zn R: SLIGHTLY VOLATILE AT ORDINARY T.	p. 102
	ALKALINE MANGANESE DIOXIDE PROCESS WASTES			X		1	1	1	1	MnO ₂ , Zn	3, 3	Hg	41				TOX: Mn, Zn R: DUE TO ALKALINE MnO ₂	p. 102
	MERCURY PROCESS WASTES			X		1	1	1	1	HgO, Hg, Zn	2, 4 6						TOX: Hg, Zn R: SLIGHTLY VOLATILE @ ORDINARY T	
	MAGNESIUM CARBON PROCESS WASTES			X		1	1	1	1	HgO ₂ , HYDROXY CARBONATE	1.5, 1.1	Cv					TOX: Mn, Cv R: DUE TO HYDROXY CARBONATE	p. 109
	ZINC SILVER PROCESS WASTES			X		2	2	2	2	Hg, Zn, AgO							TOX: Hg, Zn R: SLIGHTLY VOLATILE AT ORDINARY T.	p. 109
	LEAD ACID RESERVE CELL PROCESS WASTES			X		1	1	1	1	Pb, Ni							TOX: Pb, Ni R: Pb REACTIVE WITH WATER AND ACID	p. 119
	ZINC SILVER CHLORIDE PROCESS WASTES			X		1	1	1	1								TOX: Zn, Ag	p. 109
	THERMAL CELL PROCESS WASTES			X											INCINERATE			p. 87
	NUCLEAR PROCESS WASTES			X		3	3	3	3	Pu							TOX: Pu HIGHLY TOXIC Pu: HIGHLY REACTIVE	p. 119
	LITHIUM PROCESS WASTES			X		2	2	2	2	Li							TOX: Li FINE PARTICLES IGNITABLE AT ROOM TEMPERATURE	p. 119
	Ca-Ag OXIDE BATTERY PROD. WASTE WATER TREATMENT SLUDGE			X		2	2	2	2	Ca(OH) ₂ , SILVER OXIDE	5, 2			SLUDGE		TOXIC	TOXICITY: Ca R: DUE TO Ca(OH) ₂	p. 98

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INDUSTRY	WASTE STREAM	I	R	V	ANNUAL PRODUCTION	TOX AL AS CL CB	MAJOR COMPONENT	Z	THINK (COMP) (H) (U) (V)	Z	FORM	CURRENT DISPOSAL	WASTE CHARACTERISTICS	COMMENTS	PG
EXPLOSIVES:	DNT PROCESS WASTE; SCRAP EXPLOSIVE			X		1 3 2 3	2,4 DINITROPHENOL (DNP)				SOLID	BURNING	WASTES OF LOW CONCENTRA- TIONS SENT TO SPACE TREATMENT	PRESSURE SENSITIVE HIGHLY TOXIC V: MODERATE	36,37,39
	DNT PROCESS WASTE; WASTE WATER SCRAP EXPLOSIVE	X	X	X		1 2 2 3 1 3 3 3	2,4 DNT 2,4 DNT	75	DNT	20	LIQUID SOLID	BURNING		RESISTANT TO BIOLOGICAL DEGRADATION; PRESSURE SENSITIVE; V, I: MODERATE	37,39
	TETRYL PROCESS WASTE; WASTE WATER SCRAP EXPLOSIVE	X	X		1500 gal/mk	2 2 2 2	TETRYL TETRYL				LIQUID SOLID	LAND (SEDI- MENTATION POND)	SURFACE & SUBSURFACE WATERS AHEAD LEACHED TETRYL INTO SOIL (ESTI- MATED AT 33,000lb)	MORE SENSITIVE TO SHOCK & FRICTION THAN TNT; I: SPON- TANEOUS CHEMICAL REACTION EXPLODES AT 187°C	35,37 39
	TNT PROCESS WASTE; SCRAP EXPLOSIVE RED H ₂ O	X	X			2 3 2 3 - - - - - - - -	TNT NITROBODIES, TNT PARTICLES, ASYMMETRIC ISOMERS		SALTS OF SULFATES SALTS OF NITRATES	05kg TNT PROD	SOLID LIQUID	OPEN BURNING INCINERATION OR NEUTRAL- IZED WITH SOA ASH AND SELLUTE	SCRAP & SETTLED SLUDGES INCINERATED OR NEUTRAL- IZED WITH SOA ASH AND SELLUTE	SOMETIMES PINK H ₂ O - CON- TAINS TNT & NITRO BODIES OF LESS CONCENTRATION PRESSURE SENSITIVE; EMITS TOXIC SMOKE WHEN HEATED; V: UNDER SEVERE SHOCK	16,37,39 37 16,39
	WASTE WATER (VULCAN WATERS) SPENT ACIDS			X	370kg/kg TNT	1 3 3 3 1 3 3 3	RDX/RDX RDX/RDX				LIQUID LIQUID				
	EXPLOSIVE CONTAMINATED INERT WASTE SPENT ACTIVATED CARBON	X	X			2 3 2 3 - - - -	TNT TNT PARTICLES				SOLID SOLID	FLASHING THERMAL TREATMENT OR OPEN BURNING			30,39
	NITROGLYCERIN PROCESS WASTE: SCRAP EXPLOSIVE WASTE WATER	X	X	X		2 3 2 2 2 3 2 2	NO PARTICLES NO PARTICLES		ETHYLENE GLYCOL - DEGRADATE	05kg kg BC	SOLID LIQUID	BURNING	REUSED & RE- SOLD (CHEMI- CAL DETOIL- IFICATION TO LAGOON LIQ.)	PRESSURE SENSITIVE, AT FLASH POINT, EXPLODES, TOXIC FUMES EMITTED OR DE- COMPOSITION; I: SPONTANEOUS CHEMICAL REACTION; V: EXPLODES WITH SHOCK	16,35,37,39
	OIL AND GREASE	X				2 3 2 2 - - - -	RESIDUAL NITRO & DINITROGLYCERIN								
	RDX/RDX PROCESS WASTE; NON-SPEC SCRAP EXPLOSIVES	X		X	169 tons/day		RDX/RDX				SOLID	BURNED			16,35,39
	SPENT ACIDS			X		4 2 0 2 3 4 0 2	NITRIL NITRATE ACETIC ACID	10 601	NITROETHANE, NITRIL ACETATE PRETILFORMATE PROYLACETATE RNO ₃	2-31	LIQUID	BIOLOGICAL DEGRADATION	HIGH CONCENTRATION OF VAR- IOUS SLUDGES RECYCLED BACK INTO PROCESS TO ELIMINATE RDX/RDX & TNT		
	LAP OPERATION/PROCESS WASTE: PINK H ₂ O	X				2 3 2 3	TNT				LIQUID LIQUID SOLID	C-ADSORPTION EVAPORATION BURNING		TOTAL PRODUCTION OF COM B, B-4, CYCLOTOLS AND OCTOLS- 1970 WAS CITED AT 211, 927,000/6 PRESSURE SENSITIVE	16,35,37,39
	FLOOR SWEEPINGS, EXPLOSIVE SCRAP, PINK WATER	X					RDX NITROBODIES	912	WAX PLASTICIZERS	91	SOLID LIQUID	C-ADSORPTION LAGOON	SLUDGES W/EXPLOSIVES		
MILITARY EXPLOSIVES:	COMPOSITION C PROCESS WASTE: EXPLOSIVE SCRAP	X					RDX/RDX	APPLY 911				BURNING			
	CYCLOTOL 70/30 PROCESS WASTE: SCRAP	X					RDX	70	SPEC PLASTICIZER TNT	91 30		BURNING BURNING			16,35 16,35
	OCTOL 70/30 PROCESS WASTE: SCRAP	X					RDX	70				BURNING			16,35
	OCTOL 75/25 PROCESS WASTE: SCRAP	X					RDX	75				BURNING			16,35
	COMPOSITION B PROCESS WASTE: SCRAP	X		X	05K OF PRODUCTION		RDX	612	TNT WAX	30 08		BURNING BURNING BURNING			16,35 16,35 16,35

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INDUSTRY	WASTE STREAM	I	II	V	ANNUAL PRODUCTION OF HAZARDOUS WASTES (METRIC TONS)	TONS				MAJOR CONSTITUENT	I	MINOR CONSTITUENTS	II	FORM	CURRENT DISPOSAL	WASTE CHARACTERISTICS	COMMENTS	R1
						AL	AS	CL	CS									
INORGANIC CHEMICALS	CHLORO-ALKALI PROCESS WASTES			X	275	2	2	1	1	CHLORINATED HYDROCARBONS, Hg SLUDGES		Pb SALTS, Hg		SLUDGE	INCINERATION	BRINE MUDS & SALTS	VOLATILE HYDROCARBONS	#17 (3-2)
	SODIUM PROCESS WASTES		X		600					SODIUM/CALCIUM FILTER CAKE		FILTER CAKE MATERIAL		SOLID	LANDFILL		Hg: REACTIVE	(3-1)
	TITANIUM OXIDE PROCESS WASTES		X		35	3	4	3	3	CrOH		HEAVY METAL HYDROXIDES		SLUDGE	LANDFILL		HYDROXIDE: REACTIVE	(3-8)
	CHROMIUM COLORES/ORGANIC PIGMENT PROCESS WASTES		X		280.5	3	8	3	3	Cr(OH) ₃ , PbCrO ₄	19.6 58.8	Zn(OH) ₂ , Pb(OH) ₂ , Fe ₂ (SO ₄) ₃	9.8, 5.9, 5.9	SOLID	LANDFILL/LAGOON		HYDROXIDE: REACTIVE	(3-11)
	HYDROFLUORIC ACID PROCESS WASTES		X	X	1925	3	3	1	3	CaF		HF		SLUDGE	LANDFILL		REACTIVE DUE TO HF	(3-15)
	BORIC ACID PROCESS WASTES		X		100	3	3	2	3	FERRIC ARSENATE		ARSENIC	1-10	SOLID	LANDFILL		R1 DUE TO ACIDIC WASTES	(3-18)
	ALUMINUM FLUORIDE PROCESS WASTES		X		3300	3	3	1	3	CaF		CaSO ₄ , SiO ₂		LIQUID	LAGOON/LANDFILL		REACTIVE DUE TO F	(3-2)
	SODIUM SILICATE FLOURIDE PROCESS WASTES		X			3	3	1	3	CaF					LAGOON		REACTIVE DUE TO F	(3-21)
	CHROMATE PROCESS WASTES		X			3	4	3	3	Cr(OH) ₃ , Cr	6.9, 1.4 1000/yr	IRON OXIDES, SULFIDES		LIQUID	LAGOON/LANDFILL		REACTIVE DUE TO HYDROXIDE	(3-25)
	NICKEL SULFATE PROCESS WASTES		X		275	1	3	1	3	NICH	63.6	NI					REACTIVE DUE TO HYDROXIDE	(3-25)
	PHOSPHORUS PROCESS WASTES		X	X		3	3	1	3	CaF		CALCIUM HYPOPHOSPHITE		SLUDGE	LAGOON/LANDFILL		REACTIVE DUE TO F	(3-25)
	PHOSPHORUS PENTA SULFIDE PROCESS WASTES	X	II		131	3	3	3	3	PHOSPHATE SULFIDE, As ₂ S ₃	6.7 2.5	ARSENIC		LIQUID	ENCAPSULATION		R1: PHOSPHORUS PENTASULFIDE SPONTANEOUSLY HEATED & MAY IGNITE WITH MOISTURE	(3-28)
	PHOSPHORUS TRICHLORIDE PROCESS WASTES		X			3	3	2	4	PCl ₃ , AsCl ₃					CONTAINERS/LANDFILL		SLIGHTLY REACTIVE WITH WATER	
	ALKALI & AMMONIUM FLUORIDES PROCESS WASTES		X			3	3	1	3	AMMONIUM FLUORIDES				LIQUID	LAGOON		REACTIVE DUE TO F	191
	Al, Be, Co FLUORIDES PROCESS WASTES		X			3	3	1	3	AlF ₃ , BeF ₂ , CoF ₂		HCl, HF, BeSO ₄		SLUDGE	LANDFILL		REACTIVE DUE TO F	200
	Sn FLUORIDE PROCESS WASTES		X			3	3	1	3	CaF ₂ , CaCl ₂					LANDFILL		REACTIVE DUE TO F	234
	AsCl ₃ PROCESS WASTES		X	X		3	3	2	3	AsCl ₃				LIQUID	LANDFILL		AsCl ₃ : EXTREMELY TOXIC FUMES IN AIR	235
	Be PROCESS WASTES		X			3	3	3	3	Be					LANDFILL		Be: REACTS TO ACIDS & BASES	235
	CAUSTIC CHLORINE PROCESS WASTES		X			2	0	0	0	ASBESTOS, Pb, CHLORINATED HC				SLUDGES	LANDFILL/LAGOON		TOX: ASBESTOS, Pb R1: DUE TO CAUSTIC WASTE	237
	H ₂ CELLS PROCESS WASTES			X		3	0	0	0	H ₂ , H ₂ SO ₄		H ₂ SO ₄		SLUDGES	LANDFILL		VOLATILE AT ORDINARY TEMP	238

INDUSTRY	WASTE STREAM	1	2	3	ANNUAL PRODUCTION OF HAZARDOUS WASTES (METRIC TONS)	TOX				MAJOR COMPONENT	8	MINOR COMPONENTS	9	FORM	CURRENT DISPOSAL	WASTE CHARACTERISTICS	COMMENTS	REF
						AL	AS	CL	CH									
INORGANIC CHEMICALS CONT	H ₂ SO ₄		X				2	2	3	H ₂ (OH) ₂								
	ANTIMONY OXIDE FILTER CAKE		X		270	3	3	3	3	Sb, As				SOLID	LAGOON/LANDFILL		TOXIC WASTE STREAM R: DUE TO HYDROXIDE	242
	PHOSPHATE SLICEL		X	X		2	2	2	2	H ₃ PO ₄	3, .1			SLUDGE	LANDFILL		TOXIC WASTE STREAM	3-3'
	CHLORIDE PRODUCTION WASTEWATER TREATMENT SLUDGE		X		220,000					Cr	6			SLUDGE			H ₃ PO ₄ - VOLATILE AND REACTIVE TOXIC WASTE STREAM C: REACTS WITH DILUTE ACIDS	3-4'
	HgCl ₂ - HgCl ₂		X											LIQUID/SLUDGE	LAGOON/LANDFILL		HIGHLY TOXIC, LD ₅₀ 37mg/kg	
LEATHER TANNING & FINISHING	COUPLE CHROME TANNERY		X		1950	3	2	3	3	Cr	82	LEAD, ZINC	9, 9	SOLID	LANDFILL		Cr: REACTS WITH DILUTE ACIDS	823
	VEGETABLE TANNERY		X		9550					H ₂ S		ACIDS, TANNING AGENTS		SLUDGE	LANDFILL		R & D: DUE TO ACIDS	61
	(NOTE: 1 OF COMPONENTS IS 2 OF HAZARDOUS PROPERTIES)																	
	SHEEPSKIN TANNERY		X		3940	3	2	3	3	Cr	80	COPPER, LEAD, ZINC	10, 6, 4	SLUDGE	LANDFILL		Cr: REACTS WITH DILUTE ACIDS	84
	SPLIT TANNERY		X		29100	3	2	3	3	Cr	89	LEAD	11	SOLID	LANDFILL		Cr: REACTS WITH DILUTE ACIDS	94
	LEATHER FINISHERS		X		61	3	2	3	3	Cr	90	LEAD, ZINC	3, 3	SOLID	LANDFILL		Cr: REACTS WITH DILUTE ACIDS	98
	BEANHOUSE/TANNHOUSE		X		21500	3	2	3	3	Cr	93	Pb	5	SLUDGE			Cr: REACTS WITH DILUTE ACIDS	
	WASTEWATER TREATMENT SLUDGE FROM DYEING OPERATIONS		X			3	2	3	3	Cr							TOXIC WASTE Cr: REACTS WITH DILUTE ACIDS	
MACHINE MANUFACTURING	METAL CASTING		X			0	3	0	2	Pb, Bi, Zn, Fe, K, Na		FLOX, OIL, SOLVENT PLASTICS		SOLID	LANDFILL		TOX: Pb, Bi VOLATILE DUE TO OIL AND SOLVENTS	48
	METAL FORGING		X	V	161,000 bkg					HEAVY METALS		OILS, ACIDS		SOLID	LANDFILL		R & V DUP TO APPROX	113
	ELECTROPLATING/ETCHING		X		3,700 bkg					SOLVENTS	43	HEAVY METALS, ACIDS/ALKALIES, OIL	2, 3, 2	LIQUID	LANDFILL		V: DUE TO SOLVENTS	15, 114
	HEAT TREATING		X	X	8,300 bkg					OIL	87	ACID/ALKALI, Cu	6, 2, 5	LIQUID	LANDFILL		OIL: KNOWN CARCINOGEN V & R: OIL AND ACIDS	15, 115
	CALVARIZING		X	X						Zn, SOLVENT DEGREASERS		ALKALIES/ACIDS		LIQUID	LANDFILL		TOX: Zn	128
	MACHINING		X		70,000 bkg					SOLVENTS	40	METALS, OIL	6, 2, 5	LIQUID	LANDFILL		VOLATILE DUE TO SOLVENTS	3, 130
	PLATE/STRUCTURAL FABRICATION		X							HEAVY METALS		SOLVENTS		LIQUID	LANDFILL		VOLATILE SOLVENTS	138
	STAMPING/BLANKING & FORMING		X							HEAVY METALS		OIL		LIQUID	LANDFILL		VOLATILE OIL	119

		A. TOTAL PROCESSED TONS OF HAZARDOUS WASTE															COMMENTS		
		(METRIC TONS)																	
MACHINERY MANUFACTURING COM'Y	COATING			9,000 kg				SOLVENTS	77	HEAVY METALS (Cd, Cr, Cu, Zn, Fe, Pb)	11	LIQUID	LANDFILL						
	PLASTIC MOLDING							PLASTICS		SOLVENTS		SLUDGE	LANDFILL				144		
	ASSEMBLY							HEAVY METALS		OIL, SOLVENTS		LIQUID	LANDFILL				147		
	STAMPING PLANT WASTES							OIL, HYDRAULIC FLUID	10	COOLANTS, CLEANING FLUID		LIQUID	INCINERATOR			OIL: CARCINOGEN	#32		
	USED ENGINE OIL							OIL SLUDGES				SLUDGE	INCINERATOR/ LAND SPREADING			OIL: CARCINOGEN			
	CHLORINATED HYDROCARBONS FROM DEGREASING OPERATIONS				2 3 4 1 1 3 1 1			METHYLENE CHLORIDE TRICHLOROETHYLENE		TOXIC HEAVY METALS (Pb, Cr, Cu, Cd, Zn)							924 p 13-14		
	ALKALINE STORING SOLUTION				2 2 2 2			NaOH (pH 10)											
METAL REFINING ALUMINUM PRODUCTION	SLUDGES			199,202	3 3 1 3			FLUORIDE	13	CYANIDE		SLUDGE	LAGOONS			COMPOUNDS OF FLOORING, CYANIDE	10 - 110 p 113		
	POLYMERS AND POTASH SKIMMING			212,250	3 3 1 3			FLUORIDE	19	CYANIDE	0.1	SOLID	OPEN DUMP			COMPOUNDS OF FLOORING, CYANIDE			
	DUSTS			19,313	3 3 1 3 1 2 1 1			FLUORIDE COPPER	2.0 1.0	LEAD	0.0015	SOLID	OPEN DUMP			COMPOUNDS OF FLOORING, COPPER, LEAD			
	COPPER			601 x 10 ⁶	1 2 1 1			Cu, Cu TAILINGS				SLUDGE	LAND DISPOSAL			OVER-SURFON, TAILINGS	#26, 64		
	LEAD - ZINC ORES			12 x 10 ⁶	2 2 2 2 2 2 2 2			Pb, Zn TAILINGS				SLUDGE	LAGOONS/DUMP				107		
	ZINC				1 3 2 1			LIMESTONE, DOLOMITE, Ca				SLUDGE	DUMPING			TOX: Cd; ENV: Cd	146		
	URANIUM, RADIUM, THORIUM			2 x 10 ⁶				U ₂ , RADIUM, THORIUM				SOLID	PILES			TOX: U ₂ - HIGHLY TOXIC RADIOACTIVE	149		
	IRON AND STEEL							U ₂ S, SCH, BENZENE, NAPHTHALENE				LIQUID	INCINERATION				#32, 337		
IRON AND STEEL	COKE OVEN WASTES							U ₂ S, SCH, BENZENE, NAPHTHALENE				LIQUID	INCINERATION				#32, 337		
	FERROUS MANGANESE BLAST FURNACE DUST							Mn, Fe, Zn	20, 5 3	Al, Pb, Cu, Cr, Zn	5	SOLID				TOXIC WASTE	REACTIVE DUE TO PYROPHORIC NATURE - TOXIC	352	
	FERROUS MANGANESE BLAST FURNACE SLUDGE							Mn, Fe, Zn		Al, Pb, Cu, Cr, Zn		SLUDGE				TOXIC WASTE	357		
	ELECTRIC ARC FURNACE DUST							Zn, Pb, Mn	24, 5	Cu, V, Cr						HIGHLY TOXIC DUST, TOX:	359		
	ELECTRIC ARC FURNACE SLUDGE							Mn	5	Ni, Zn, Cl, Se, As, Cu		SLUDGE					365		

INDUSTRY	WASTE STREAM	1	2	3	ANNUAL PRODUCTION OF HAZARDOUS WASTES (METRIC TONS)	TOTAL				MAJOR COMPONENT	7	HEAVY COMPONENTS	8	FORM	CURRENT DISPOSAL	WASTE CHARACTERISTICS	COMMENTS	FBI	
						AL	AS	CI	CS										
PAINT & ALLIED PRODUCTS	SOLVENT-THINNED TRADE SALES PAINT			X	101,366	3	3	12	3	CO, Se, Hg, Pb, Cr PIGMENTS		SOLVENTS			LANDFILL		TOX CO, Se VOLATILE BECAUSE OF SOLVENTS	P24	
	WATER-THINNED TRADE SALES PAINT			X	126,659	3	3	3	3	PENTHYLMERCURIC ACETATE CO, Se		Hg, Pb, Cr PIGMENTS					TOX PENTHYLMERCURIC ACETATE TOXICITY IN RATS LD ₅₀ 30 mg/kg		
	INDUSTRIAL & NON-INDUSTRIAL LAQUERS	X		X	20,919					VINYL ACETATE	38	TITANIUM OXIDE	21						
	FACTORY APPLIED COATINGS	X		X	126,482					TOLUENE, ACETATE, NITROCELLULOSE, METHYL ETHYL ACETATE, METHYL ISOBUTYL	33, 1 22, 6 6	ALKYD RESIN, BUTYL ALCOHOL, ISOPROPYL ALCOHOL	5, 3, 3						
	CLEANING SOLVENTS	X 70°F X 80-100°F		X		2	2	1	1	ACETONE		Pb	178 mg/l 1996 mg/l 390 mg/l						
				X		1	2	1	2	XYLENE		Pb - 342mg/l Zn Cr							
	PORCELAIN ENAMELING WASTE DECREASING SOLVENT			X		2	2	2	2	PERCHLOROTYLENE				LIQUID	LANDFILL				
	WASTE WATER TREATMENT SLUDGE									HEAVY METALS				SLUDGE	LANDFILL	TOXIC WASTE STREAM	NOT ENOUGH INFORMATION TO DETERMINE I, R, V WE FEEL THE WASTE STREAM IS VOLATILE DUE TO USE OF SOLVENTS IN PROCESSING	01 P-30 58950	
PHARMACEUTICAL	SYNTHETIC ORGANIC MEDICINAL CHEMICALS	X		X	527,100	1	2	2	2	TOLUENE- BENZENE	102, 20	Hg, Cl, Cu, As, Fe Fe OXIDE	11.6,	LIQUID/ SLUDGE	INCINERATED/ LANDFILL/ ENCAPSULATED				
	INORGANIC			X	200	1	2	2	2	MgOH, ALON		HgSiO ₃ , Se	.2		LANDFILL			#33 44	
	FERMENTATION PRODUCTS			X	662,000					SOLVENT WASTE CONCENTRATE	10	BUTYL ACETATE, ORGANIC	6.6					8: BECAUSE OF CORROSIVE NATURE OF A HYDROXIDE	48 49
	ALKALOID PRODUCTION			X	5,030					HALOGENATED SOLVENT		METHANOL, NORMAL SOLVENT						53	
PLASTICS AND RESINS	INSULIN			X	1,205,000					SOLVENT	1	Fe	.025						
	PLASTIC RESINS			X	2,335,284 TOTAL WASTES kg/yr	2	2	2	2	PHENOL RESINS, No. 58		ABS, POLYSTYRENES, POLYPROPYLENE, SiO ₂		SLUDGE	LANDFILL/ INCINERATION		TOX: Pb, Hg	04 137	
	SYNTHETIC RUBBER			X	2,335,284 TOTAL WASTES kg/yr					SOLVENTS		POLYBUTADIENE, NEOPRENE		LIQUID	LANDFILL/ INCINERATION			138	
	CELLULOSIC MANMADE FIBER	X 100°F		X	2,335,284 TOTAL WASTES kg/yr	2	2	2	2	DIAMINE, DITHIOCARBONATE		WASTEWATER TREATMENT SLUDGE		SLUDGE	LANDFILL/ INCINERATION		DIAMINE FLAMMABLE, SPONTANEOUS COMBUSTION WITH OXIDANTS	139	
	NON CELLULOSIC MANMADE	X			2,335,284 TOTAL WASTES kg/yr	2	2	2	2	Zn SLUDGES		ACRYLICS & MODACRYLICS		SLUDGE	LANDFILL/ INCINERATION		TOX Zn ZINC JUST TOXICABLE	139	
	URETHANE FOAM MANUFACTURE, WASTE SOLVENT	X		X						TOLUENE DI-ISOCYANATE				SLUDG	LA D'FILL				

INDUSTRY	WASTE STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000
ORGANIC CHEMICALS	HEAVY ENDS PURIFICATION	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																	

UNIT	NAME	Q	R	V	ACTUAL PRODUCTION OF HAZARDOUS WASTES (METRIC TONS)	AL	AR	AT	CH	HAZARDOUS COMPONENT	UNIT	CONCENTRATION	PHASE	TYPE OF DISPOSAL	ANALYTICAL CHARACTERISTICS	COMMENTS	LOC.
ORGANIC CHEMICALS CONT	DITHIOCARBONATE PRODUCTION WASTES	X		X	4/STRA	2	2	2	2	ETHYLENE DIAMINE ETHYLENE THIOUREA 2,3 DICHLOROPROPANE TRIOCARBONATES						ETHYLENE THIOUREA IS A SUSPECTED CARCINOGEN	274 269
	DIURON PRODUCTION WASTE WATER TREATMENT SLUDGE			X		2	3	3	3	DIURON 3,4 DICHLORODANILINE OR DICHLOROPENTYL- CARBONIC ACID DIOXANE						DIURON - TOXIC FUMES ON HEATING LD ₅₀ = 3.4g/kg	272
	PARATHION/ETHYL-PARATHION PRODUCTION TANK BOTTOMS	X		X		1	1	1	1	TRIALKYLTHIOPHOSPHATE DIALKYLDI- THIOPHOSPHONIC ACID P-NITROPHENOL ORGANOPHOSPHATES			SLUDGE	INCINERATE/ LANDFILL			282
	PENTACHLOROPHENOL PRODUCTION WASTES				40mm 22110g 1mm 9.760g 1mm 9.530g 1mm 9.440g	3	3	3	3	PENTACHLOROPHENOL TRICHLOROPHENOLS DICHLOROPHENOLS CHLOROPHENOLS							285
	PROBATE PRODUCTION WASTES	X		X		1	1	1	1	PROBATE ETHYLHECAPTAN FORMALDEHYDE DIETHYLTHIO- PHOSPHONIC ACID			LIQUID/ SLUDGE	OCEAN DUMPING/ LANDFILL		PROBATE - HIGHLY TOXIC	287
	2,4,5-T PRODUCTION WASHINGS/TRAFFIC SEPARATION BOTTOMS	X		X	440g 1mm	3	3	3	3	HCL PHENOL CHLOROPHENOL CHLOROPHENOL ACIDS	112mg/ 1 232mg/ 1		LIQUID/ SLUDGE	LAGOON/ LANDFILL		CHLOROPHENOL ACETIC ACID LD ₅₀ = 850mg/kg	291
	TOXAPHENE PRODUCTION EXCESS REAGENTS	X		X		1	1	1	1	TOXAPHENE CAUPHENE PHTHENE			LIQUID	BIOLOGICAL TREATMENT/ LAGOONS			293
	TRIFLURALIN PRODUCTION WASTES			X		10	10	10	10	CHLOROBENZO- TRIFLORIDES DICHLOROBENZO- TRIFLORIDES P-CHLOROBENZO- ATE BY SULFONES ETHYLENE			LIQUID/ SLUDGE				296
	VERMOLATE PRODUCTION WASTE WATER TREATMENT SLUDGE	X		X		6	6	6	6	VERMOLATE N-PROPYLHECAPTAN							298

ORGANIC CHEMICALS CMT	UNIT STEAM	I	P	V	APPROXIMATE PROPORTION OF HAZARDOUS (NETRIC TONS)	HAZARDOUS WASTE			HAZARDOUS WASTE	HAZARDOUS WASTE	HAZARDOUS WASTE	HAZARDOUS WASTE	HAZARDOUS WASTE	HAZARDOUS WASTE
						1	2	3						
ANILINE DISTILLATION STILL BOTTOMS						1	2	3	NITROBENZENE					
ACRYLONITRILE PRODUCTION - BOTTOM STREAM FROM QUENCH COLUMNS						2	3	4	BCN	7E	ACRYLAMIDE	1E		BCN FLAMMABLE AND EXPLOSIVE IF STORED FOR AN EXTENSIVE PERIOD
- BOTTOM STREAM WASTE WATER STRIPPER						2	3	1E	BCN 225 PPM BICOTIMONITRILE 500PPM					
- STILL BOTTOMS						1	2	3	METHACRYLONITRILE ACRYLAMIDE ACRYLIC ACID					
- SOLID WASTE						1	2	3	ACRYLONITRILE					
ALDRIN WASTE WATER						1	2	3	H ₂ SO ₄ ACETIC ACID ALDRIN/DIELDRIN					
CACODYLIC ACID PRODUCTION SOLID WASTE						1	2	3	H ₂ SO ₄	4D		.8PPM		DIELDRIN LD ₅₀ = 46 mg/kg H ₂ SO ₄ - MODERATELY TOXIC
CAPTAN PRODUCTION WASTE WATER TREATMENT SLUDGE						1	2	3	CAPTAN BUTADIENE CARBON DISULFIDE					CAPTAN - LOW TOXICITY CAPTAN AND CS ₂ - FLAMMABLE
CARBARYL PRODUCTION WASTE WATER						1	2	3	NAFTHALENE CARBARYL					CARBARYL IS A RECOGNIZED CARCINOGEN
CHLORDANE PRODUCTION WASTE WATER						1	2	3	CHLORDANE HEPTACHLOR CYCLOPENTADIENE HEXACHLOROCYCLOPENTADIENE					HEPTACHLOR IS HIGHLY TOXIC CYCLOPENTADIENE IS MODERATELY TOXIC HEPTACHLOROCYCLOPENTADIENE IS TOXIC AND READILY ABSORBED VIA SKIN VOLATILE
CHLOROXURON PRODUCTION PROCESS WASTES						1	2	3	CHLOROXURON p-CHLOROPHENOL p-CHLORANILINE					RECOGNIZED CARCINOGENS BENZOPIRENE IS HIGHLY TOXIC
CRESOTE PRODUCTION PROCESS WASTES						1	2	3	BENZANTHRACENE BENZOPIRENE					
2, 4-D PRODUCTION WASTES						1	2	3	HCl CHLOROPHENOLS PHENOLS CHLORACETIC ACID					
DIAZINON PRODUCTION WASTES						1	2	3	DIAZINON ORGANOPHOSPHATES					CHOLINESTERASE INHIBITOR DIAZINON IS HIGHLY TOXIC AND ABSORBED THROUGH THE SKIN

INDUSTRY	WASTE STREAM	1	2	3	ANNUAL PRODUCTION OF HAZARDOUS WASTES (METRIC TONS)	AL	AS	CS	MAJOR COMPONENT	2	MINOR COMPONENTS	1	FORM	CURRENT DISPOSAL	WASTE CHARACTERISTICS	COMMENTS	REF
ORGANIC CHEMICALS CONT	PRODUCTION OF CHLORINATED HYDROCARBON SOLVENTS (CH ₂ PERCHLOROETHYLENE) HEAVY ENDS FROM SOLVENT RECOVERY	X	X	X	3851 tons BCS	"	"	"	HEXACHLOROCYCLOTRISILANE HEXACHLOROCYCLOTRISILANE HEXACHLOROCYCLOTRISILANE	743 148 102				DRUMS/ LANDFILL, RECOVERY OF BCS		VARIOUS METHODS OF DISPOSAL USED INCLUDE LANDFILL, DEEP WELL DISPOSAL AND INCINERATION	#10 36
	STILL BOTTOMS, HEAVY ENDS	X	X	X		"	"	"	HEXACHLOROCYCLOTRISILANE HEXACHLOROCYCLOTRISILANE HEXACHLOROCYCLOTRISILANE	152 752 102			LIQUID	LAGOON	VISCOUS RED LIQUID W/WHITE SOLID	BCS HAS SUSPECTED LOW TOXICITY	39
	PESTICIDE PRODUCTION DISTILLATION RESIDUE	X	X	X	2633	"	"	"	HEXACHLOROCYCLOTRISILANE PRODUCT	752 252			SOLID		YELLOW CRYSTALLINE SOLID		41
	LIQUID STILL BOTTOMS	X	X	X		"	"	"	HEXACHLOROCYCLOTRISILANE LOWER C1 BENZENES	802 202							57
	SPENT ALKALI SCRUBBER ATRAZINE MANUFACTURE	X	X	X	353,960	1	1	0	LIQUIDABLE RESIDUE	8. 14	CAUSTIC CYANIC ACID	30 5	LIQUID	DEEP WELL INJECTION		REACTIVE DUE TO CAUSTIC MATERIAL	#3
	SPENT CARBON COLUMN TRIFLURALIN MANUFACTURE				1,150				UNREACTED INTERMEDIATES	40	TRIFLURALIN	8	SOLID	STORAGE CONTAINERS		TRIFLURALIN SLIGHTLY TOXIC LD ₅₀ IN RATS 500 mg/kg	v-21
	FILTER CAKE SOLIDS - MALATHION	X	X	X	(152) OF TOTAL PROD.	1	2	1	TOLUENE & INSOLUBLE REACTION PRODUCTS	41	DIMETHYL DITHIOPHOSPHORIC ACID	4	SOLID	LANDFILL		TOLUENE; VOLATILE	v-134
	LIQUID PROCESS WASTES - MALATHION	X	X	X		3	4	2	NaOH (2% SOLUTION)	97.6	MALATHION & TOLUENE	2 4	LIQUID	OCEAN DUMPING		NaOH; REACTIVE	v-144
	SULFUR SLUDGE FROM CHLORINATION - PARATHION MANUFACTURE				(10.3) OF TOTAL PROD.	0	0	0	ELEMENTAL SULFUR	93	ORGANOPHOSPHORUS	7	SLUDGE	INCINERATION		ORGANOPHOSPHATE HIGHLY TOXIC DUE TO ORGANIC ORGANIC PHOSPHATE, 8-10%IT-ABLE BUT FLASHPOINT > 140°F	v-153
	DIELDRIN PROCESS WASTES	X	X	X		5	3	"	CHLORINATED HEAVY ENDS, C ₁₂ H ₆ Cl ₆ O				LIQUID/ SLUDGE	LAGOONS/ LANDFILL		LD ₅₀ 46 mg/kg LIQUID ORGANIC; VOLATILE	v-137
	MALATHION PROCESS WASTES	X	X	X					C ₁₀ H ₁₁ O ₄ P ₂ ORGANIC PHOSPHATE ORGANIC SULFUR				LIQUID/ SLUDGE	OCEAN DUMPING /LANDFILL		LD ₅₀ 1 - 1.37 mg/kg LIQUID ORGANIC; VOLATILE	v-160
	ALDICARB PROCESS WASTES	X	X	X					C ₇ H ₁₄ N ₂ O ₂ S ORGANIC SULFUR				LIQUID/ SLUDGE	INCINERATION		LD ₅₀ 1mg/kg LIQUID ORGANIC; VOLATILE	v-163
	ATRAZINE PROCESS WASTES	X	X	X					CHLORINATED HYDROCARBON				LIQUID/ SLUDGE	LAGOONS/ LANDFILL		C ₈ H ₁₄ ClN ₃ LD ₅₀ 3 mg/kg V: GENERALIZATION FOR HYDROCARBONS	v-165
	WASTEWATER TREATMENT SLUDGE FROM POLYVINYL CHLORIDE PRODUCTION			X		3	3	3									
	ACID SCRUBBER EFFLUENT FROM NITROBENZENE PRODUCTION	X	X	X		"	3	"	NITROBENZENE								
	HEAVY ENDS FROM NITROBENZENE PRODUCTION	X	X	X		"	3	"	NITROBENZENE				LIQUID	LANDFILL		HIGHLY TOXIC, NITROBENZENE, ICHITABLE, FLASHPOINT IS 190°F	

INDUSTRY	WASTE STREAM	I	H	V	APPROXIMATE PROPORTION OF HAZARDOUS WASTES (HECTIC TONS)	AL			CL	CS	OTHER	TREATMENT	DISPOSITION	
						AL	AS	CL						
ORGANIC CHEMICALS UNIT	DICHLOROBENZENE PRODUCTION WASTE WATER SLUDGE	X 120° F X 1500 P X 85° F		X		2	2	0			BENZENE	LIQUID/SLUDGE	LANDFILL/INCINERATION	P21 761
				X		2	2	0			DICHLOROBENZENES			
				X		1	1	0			CHLOROBENZENE			263-264
	DISULFOTON WASTE WATER SLUDGE	X	X	X		3	3	0			HCl ETHANOL DISULFOTON	LIQUID/SLUDGE	STORAGE	DISULFOTON LD ₅₀ = 12.5mg/kg (CHOLINESTERASE INHIBITOR)
	PYRETHRIN PROCESS WASTES			X							HYDROCARBONS		INCINERATION	V; GENERALIZED HC ARE USUALLY VOLATILE.
	ZAMTRATE PRODUCTION WASTES	X 270° F		X							CARBON DISULFIDE		INCINERATION	P 40
	ACROLEIN PROCESS WASTE STREAM	X 150° F	X	X		3	3	3			ACROLEIN	LOW CONC. LIQUID	INCINERATION, DEEP WELL INJECTION	ACROLEIN IS A LACHRYMATOR, ONE OF THE MOST REACTIVE ORGANIC CHEMICALS AVAILABLE TO INDUSTRY. HIGHLY TOXIC BY SKIN CONTACT, INHALATION AND INGESTION
INDUSTRIAL ORGANIC CHEMICALS	TAR AND TAR OILS PROCESS WASTES		X	X		3	=	2	=		H ₂ SO ₄ , SULFONATE NON-AROMATIC	4,	TRIOPHERE DERIVATIVES	P29 A-3 - 19
	ANTILINE PROCESS WASTES		X	X		2	3	2	3		ANTILINE, NH ₄ Cl	5	NITROBENZENE	TOXIC
	ALKYLPHENOLS, COMEST, STYLAZENE PROCESS WASTES		X	X		=	2	=	2		H ₂ SO ₄ , OLEUM		ALUMINUM CHLORIDE	TOXIC; OLEUM IS POISONOUS H ₂ SO ₄
	CHLOROBENZENE PROCESS WASTES	X		X		1	2	0	3		CHLOROMATED BENZENES	11° 6		A-3 - 27
	CYCLOHEXANE PROCESS WASTES	X		X		3	2	=	1		SPENT CATALYST			A-3 - 30
	ISOCYANATES PROCESS WASTES		X	X		3	3	2	=		CARBONYL CHLORIDES, UREA		INCINERATION	TOXIC; CYCLOHEXANE
	PHENOL PROCESS WASTES	X		X		3	2	2	2		FENOL, FENOXIOW, FORMIC ACID TAR STILL BOTTOM	HCl BRINES		A-3 - 34
	BTHERAC - STILL BOTTOM	X		X		1	2	1	3		TOLUENE, BENZENE, STYLAZENE			CARBONYL Cl - EVOLVES TO HCl WHEN STARCHING
	DTES/CN BLUE BLACK B PROCESS WASTE	X	X	X		3	2	2	2		H ₂ SO ₄ , D-NAPHTHOL, NaOH	80, 3 3	HCl, NaNO ₂	TOXIC: Pb, FORMIC ACID FORMIC ACID IRRITABLE - 150°F ACUTE IRRITANT DUE TO IRRADIATION
	VINYL CL, SPENT CATALYST	X 70° F	X	X		3	2	2	3		CARBON WITH VINYL CHLORIDE			TOXIC: VINYL CHLORIDE FORMS EXPLOSIVE MIXTURE WITH AIR

[illegible]

INDUSTRY	WASTE STREAM	1	2	3	ANNUAL PRODUCTION OF HAZARDOUS WASTES (METRIC TONS)	TOX			MAJOR COMPONENT	8	MINOR COMPONENTS		9	FORM	CURRENT DISPOSAL	WASTE CHARACTERISTICS	COMMENTS	REF
						AL	AS	CS										
STEEL FINISHING	ALKALINE CLEANING WASTES			X		3	u	2	CAUSTIC, SULFIDE CM-					LIQUID	LANDFILL	HIGHLY CAUSTIC	TOXICITY DATA: ALKALINE CAUSTIC MATERIAL - REACTIVE CM- 1, 3, 2, 1 TOXICITY RATINGS Cr - KNOWN CARCINOGEN, MINOR COMPONENTS - TOXIC ACIDIC WASTES - 8 & 9	368
	WASTE PICKLE LIQUOR			X		148	148	148	Zn, Cr	13, 12	Cu, Pb, Cd, HCl, H ₂ SO ₄ , HNO ₃ , As			LIQUID		HIGHLY ACIDIC		370
	CM- SEARING WASTES FROM ELECTROPLATING COATING			X		3	3	3	Cd, CM-, Cu	1, 1, 1	Zn, Ni		1, 1	SLUDGE			TOXICITY: Cd/CM- CM- REACTIVE	376
	CHROMATES & DICROMATES FROM CHEMICAL TREATMENT FROM CHROMATING SOL., Cr, BIRSE			X		1	1	1	CrO ₃ , H ₂ SO ₄	5, 5	CrOM		5	LIQUID			Cr: CARCINOGEN CHROMIC AND SULFURIC ACID REACTIVE AND VOLATILE	381
	1° Cu, ELECTRIC FURNACE SLAG			X		1	1	1	Cu, Pb, Mn	4	Cd, Sb, Se, Zn, Ni			SOLID			TOXICITY: Cu & Pb Cu - MILDLY REACTIVE IN AIR WITH OTHER COMPOUNDS	383
	1° Cu CONVERTER DUST			X		1	1	1	Cu, Zn	28, 3	Pb, Cd, Sb, Ni, Se, Cr, Fe		8, 3	SOLID			TOXICITY: Cu & Zn Cu MILDLY REACTIVE IN AIR AND WITH OTHER COMPOUNDS	389
	1° Cu, ACID PLANT SLUDGE			X		1	1	1	Cu, Pb	38, 1	Pb, Zn, Cd, Mn, Se, Ni, Fe			SLUDGE			TOXICITY: Cu & Pb Cu MILDLY REACTIVE IN AIR WITH OTHER COMPOUNDS	393
	1° Cu, REVERTORY DUST			X		1	1	1	Cu, Zn, Pb	24, 4, 1	Cd, Cu, Mn, Sb, Se, Ni			SOLID			TOXICITY: Cu & Zn Cu MILDLY REACTIVE IN AIR AND WITH OTHER COMPOUNDS	397
	1° Pb, BLAST FURNACE DUST			X		10	10	10	Pb, Zn, Cd	14, 8, 1	Cr, Cu			SOLID			TOXICITY: Pb & Zn Pb REACTS WITH WATER AND ACIDS	400
	1° Pb, LADDER DREDGINGS (SLOTTOR)			X		10	10	10	Pb, Zn	14, 13				SLUDGE			TOXICITY: Pb & Zn Pb REACTS WITH WATER AND ACIDS	405
	1° ZINC SMELTING & FINISHING OTTUM CAKE			X		140	140	140	Pb, Cr, Cd	1				SOLID		HIGHLY ACIDIC	TOXICITY: Pb & Cr V & B - ACID	409
	SMELTING & REFINING ACID PLANT SLUDGE			X		3	3	3	As, Cd, Pb	7, 3 AS mg/l				SLUDGE		TOXIC	TOXICITY: As & Cd VOLATILE AND REACTIVE ACID	413
	1° ZINC SMELTING & REFINING ANODE SLUDGE			X		10	10	10	Pb, Cd	17				SLUDGE		HIGHLY ACIDIC	TOXICITY: Pb & Cd V & B - ACID	415
	1° TUNGSTON DICESTION RESIDUE			X		1	1	1	Cu, Zn	4	Pb, Sb			SOLID			TOXICITY: Cu & Zn Cu MILDLY REACTIVE IN AIR AND WITH OTHER COMPOUNDS	419
	1° SINTER SCRUBBER SLUDGE			X		10	10	10	Pb, Zn, Cu	16, 3, 1	Cd			SLUDGE			TOXICITY: Pb & Zn Pb REACTS WITH WATER AND ACIDS	423
	FERROCHROME SILICON FURNACE EMISSION CONTROL DUST/SLUDGE			X		10	10	10	Zn, Mn		Cu, Cr, Pb			SLUDGE			TOXICITY: Zn & Mn Zn REACTIVE WITH ACIDS	430

NOTE: 1° - PELDANT
2° - RECONDANT

INDUSTRY	WASTE STREAM	1	2	3	ANNUAL PRODUCTION OF HAZARDOUS WASTES (METRIC TONS)	TOX				MAJOR COMPONENT	4	MINOR COMPONENTS	5	FORM	CURRENT DISPOSAL	WASTE CHARACTERISTICS	COMMENTS	REF	
						AL	AS	CL	CS										
STEEL FINISHING CONT	2° Pb, SCRUBBER SLUDGE FROM SO ₂ EMISSION CONTROL BOFF Pb PRODUCTION					10	10	10	10	Pb, Sb, Cd		Pb		SLUDGE			TOXICITY: Pb & Sb Pb REACTIVE WITH WATER AND ACID	43	
	2° Pb, WHITE METAL PRODUCTION FURNACE DUST /					10	10	10	10	Pb, Zn, Sn	12, 12, 12	Sb, Cd, Cr, Cu		SOLID			TOXICITY: Pb & Zn Pb REACTIVE WITH WATER AND ACID	442	
	2° Cu, PYROMETALLURGICAL BLAST FURNACE SLAG					10	10	10	10	Cu, Mn, Zn	7, 7, 7	Cd, Cr, Pb, Sb, Ni		SOLID			TOXICITY: Cu & Zn Cu MILDLY REACTIVE IN AIR AND WITH OTHER COMPOUNDS	44	
	2° Cu, ELECTROLYTIC REFINING WASTE WATER SLUDGE					10	10	10	10	Cu, Cr, Sn, Ni	17, 9, 7, 2	Zn, Cd, Pb		SLUDGE			TOXICITY: Cu & Cr Cu MILDLY REACTIVE IN AIR AND WITH OTHER COMPOUNDS	450	
	2° Al, SMELTING & REFINING 2° Al DROSS SMELTING RE SALT SLAG					10	10	10	10	Se, As, CH		Cd, Cr, Pb		SOLID			TOXICITY: CH & Cd CH: R & U	455	
	1° Zn SMELTING & REFINING CA PLANT RESIDUE					10	10	10	10	Cd, Cr, Pb				SOLID			TOXICITY: Cd & Cr Cd - IN VAPOR FORM WHEN ROASTING Zn ORES	456	
	STILL BOTTOMS RECOVERY OF DRY CLEANING CHLORINATED SOLVENTS					2	2	2	2	VARIOUS ALIPHATIC & AROMATIC HYDROCARBONS (INCL TRICHLORO BENZENE)				LIQUID	LANDFILL		TOX: TRICHLOROBENZENE	49	
	ACETONE RECOVERY STILL BOTTOMS					2	2	2	2	ACETONE				LIQUID	INCINERATION				4 - 21
	PERCHLOROETHYLENE STILL BOTTOMS					2	2	2	2	PERCHLOROETHYLENE				LIQUID					4 - 21
	FABRIC DYEING AND FINISHING					1,676,000 kg/yr (WST)	3	2	1	1	HEAVY METALS, HYDROCARBONS				SLUDGE			TOX: RC	3 - 34, 3 - 39, 3 - 51
TEXTILES	CARPET DYEING				34,000 kg (WST)	3	2	1	1	HEAVY METALS, HYDROCARBONS				SLUDGE			TOXIC WASTE	3 - 63	
	WOOL SCOURING WASTES				255,000	3	2	1	1	HEAVY METALS, CHLORINATED ORGANICS	.5								1 - 10
	WASTE WATER TREATMENT, SLUDGE FROM COLORED DYEINGS				3,000	3	3	3	3	Cd	54	Hg, Zn	0.3, 0.5				CONSIDERED REACTIVE BECAUSE OF HIGH 2 OF Cd	3 - 76	

NOTE: 1° - PRIMARY
2° - SECONDARY

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APPENDIX C

SELECTION OF IGNITABLE, REACTIVE AND VOLATILE WASTE STREAMS

C. SELECTION OF IGNITABLE, REACTIVE AND VOLATILE WASTE STREAMS

Nearly 300 waste streams were identified from literature and roughly characterized by industry; whether the waste was ignitable, volatile or reactive; key component of the waste stream; toxicity of the key component; form for disposal, and disposal methods identified in literature.

The list was made as a starting point for choosing the 13 waste streams to be studied further. The initial list of waste streams, along with references and comments on each are included in Appendix B.

C.1 METHOD FOR SELECTION OF WASTE STREAMS

The methodology used for choosing waste streams from the list of approximately 300 is shown in Figure C.1. Ignitability, reactivity and volatility, and their possible combinations, were prime considerations and were the basis for initial grouping of the waste streams. A prioritized listing of selection criteria follows each heading. Representation of each group in the list of 13 waste streams was not a selection criteria.

Ignitable waste streams were evaluated based on the industry generating the waste, the quantity of waste stream generated, concentration of ignitable constituents, toxicity of the waste stream and its form for disposal. Efforts were made to minimize the number of waste streams from a particular industry and eliminate from consideration waste streams generated in very low quantities, and those with very low concentrations of ignitable constituents, or low toxicity. Efforts were also made to choose a variety of waste stream forms such as sludge, tar, liquid or solid. None of the 13 chosen waste streams were just ignitable. Criteria for ignitability were used to evaluate waste streams that are ignitable and volatile, ignitable and reactive, and ignitable, volatile and reactive.

Volatile waste streams, as defined in an earlier section, were evaluated based on their degree of volatility. Those with vapor pressures from 78 to 0.1 mm Hg at 40°C were given a set of criteria

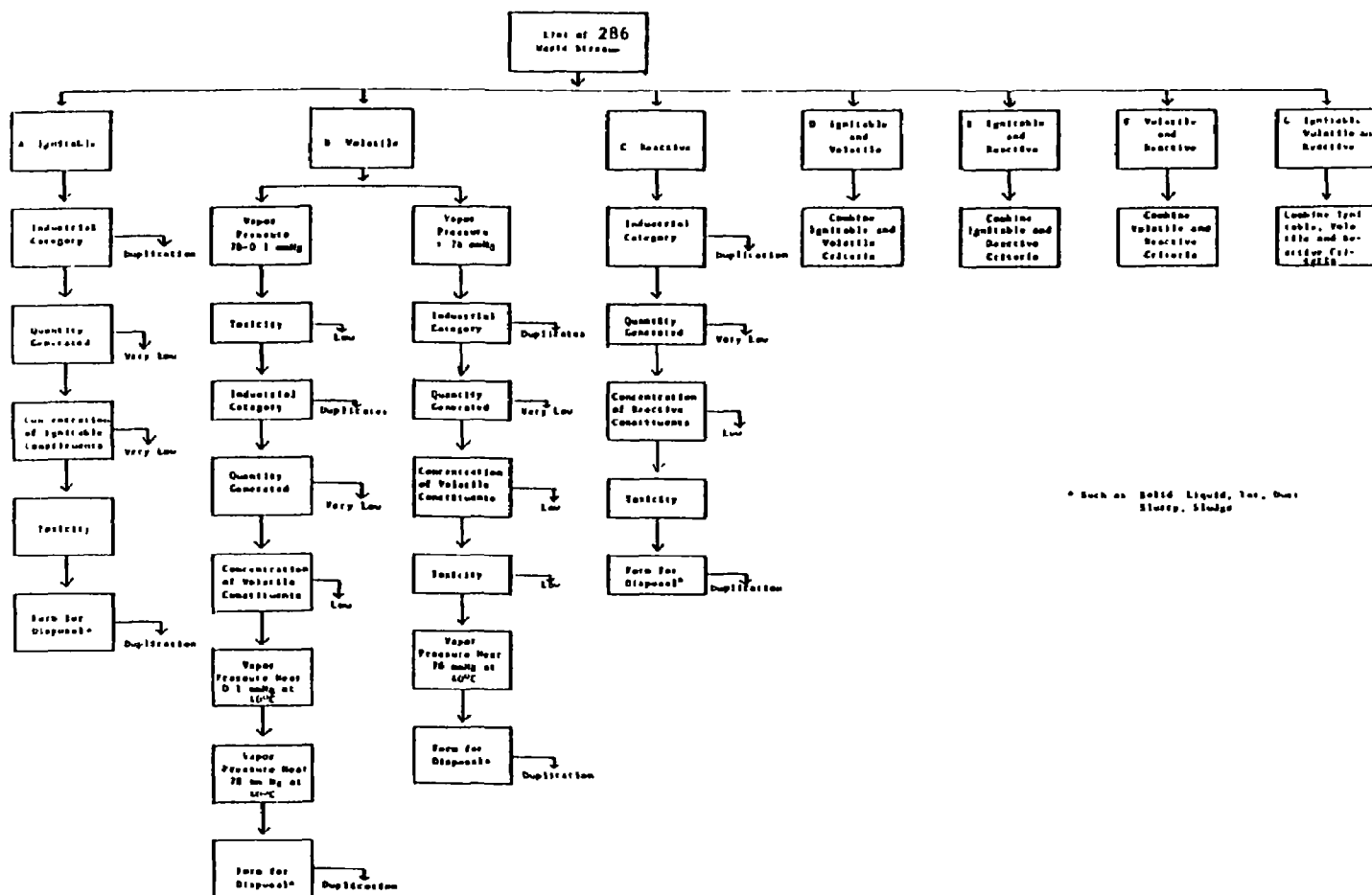


Figure C.1 - Methodology for Selection of 13 Waste Streams for Further Study

differing from those used to evaluate waste streams having vapor pressures greater than 78 mm Hg at 40°C.

Waste streams with volatilities from 78 to 0.1 mm Hg were evaluated for toxicity, industrial category, quantity of waste generated, concentration of volatile constituents in the waste stream, vapor pressure near 0.1 mm Hg at 40°C, vapor pressure near 78 mm Hg at 40°C and form for disposal. A toxicity rating of moderate or high qualified the waste stream as volatile in this vapor pressure range, according to the definition given in an earlier section. As before, duplicated industrial category, and generation of a very low quantity and low concentration of volatile constituents were reasons for eliminating waste streams from further consideration. Choosing waste streams with vapor pressures near 0.1 and near 78 mm Hg at 40°C will help verify these values as cutoff points. Form for disposal was the final criteria.

Waste streams with volatilities greater than 78 mm Hg at 40°C were evaluated for industrial category, quantity generated, concentration of volatile constituents, toxicity, vapor pressure near 78 mm Hg at 40°C and form for disposal. Choice of waste streams with vapor pressures near the cutoff point of 78 mm Hg at 40°C aided in evaluating the criteria.

Reactive waste streams were evaluated for industrial category, quantity generated, concentration of reactive constituents, toxicity and form for disposal.

Combinations of ignitable, reactive and volatile characteristics in a waste stream required use of criteria for each characteristic. Considerable judgment was necessary for conflicting priorities in the criteria.

C.2 WASTE STREAMS FOR FURTHER STUDY

Thirteen waste streams (Table C.1) were chosen for further study from an initial list of approximately 300, using the methodology described previously. A discussion of each waste stream follows.

TABLE C.1 Waste Streams Chosen for Study

INDUSTRY	PRODUCT	WASTE STREAM	IGNITABILITY	REACTIVITY	VOLATILITY	TOXICITY				COMMENTS
						AL	AS	LL	CS	
Organic Chemical Manufacturing	Pesticides	Sulfur Sludge from Chlorination - Parathion Production	Medium	Low	Medium	3	3	3	3	Toxic, Volatile, Ignitable
	Plastics	Wastewater Treatment Sludges from Polyvinyl Chloride Production	High	Low	High	3	3	3	3	Ignitable, Volatile, Toxic, Large Volume
	Aniline	Tars	High	High	Medium	3	3	3	3	Ignitable, Reactive, Toxic, Volatile, Tar
	Chlorobenzene	Distillation Residue	High	Low	Medium	2	2	2	2	Ignitable, Volatile, Toxic
	Nitrobenzene	Column Bottoms	Low	Low	Medium	u	3	u	3	Volatile, Toxic
Petroleum Refining	Petroleum Products	Dissolved Air Flotation Unit Skimmings	Medium	Low	Medium	3	3	3	3	Ignitable, Volatile, Toxic
Electroplating and Metal Finishing	Electroplated Metal Products and Finished Metal Products	Water Pollution Control Sludges	Low	Low	Medium	1	3	2	1	Volatile, Toxic
Textile Manufacturing	Textiles	Wastewater Treatment Sludges from Dyeing and Finishing	Medium	Low	Medium	3	3	3	3	Ignitable, Volatile, Toxic
Paint Manufacturing	Solvent-Thinned Trade Sales Paint	Process Liquid Wastes	High	Low	High	3	3	u	3	Ignitable, Volatile, Toxic Liquid
Battery Manufacturing	Lithium-Sulfur Dioxide Cells	Scrap Cells	Low	High	Medium	2	2	u	2	Reactive, Volatile, Toxic; Lithium reacts violently with moisture producing hydrogen gas
Commercial Explosives	TNT	Red Water	High	High	High	u	u	u	u	Ignitable, Reactive, Volatile Liquid
Military Explosives	Bulk PET Munitions	Bulk PPP	High	High	High	u	u	u	u	Ignitable, Reactive, Volatile Liquid
	IAP Operations including Manufacture of Composition A	Pink Water	High	Low	High	u	u	u	u	Ignitable, Volatile Liquid

C.2.1 Organic Chemicals and Plastics Manufacturing

Sulfur sludge from the chlorination step in parathion manufacture is generated in combination with organophosphate compounds. The vapor pressure is between 0.1 and 78 mm Hg, but, being toxic, is volatile by our definition. Sulfur has a flashpoint of 66°C. Disposal in landfills, ocean dumping, and incineration have been mentioned in the literature.

Polyvinyl chloride wastewater treatment sludges are one of several waste streams from polyvinyl chloride production. This waste stream is approximately 70 percent water and 30 percent vinyl chloride monomer, polyvinyl chloride, intermediate products and process additives. The waste is a sludge and is ignitable, volatile and toxic.

Tars from aniline manufacture contain as key components aniline and nitrobenzene. The waste is ignitable, reactive, volatile and toxic.

Distillation residues from chlorobenzene manufacture are ignitable, volatile and toxic, and are typically disposed on land. They are generated at the rate of 13,000 kkg/yr. (See Appendix B.)

Nitrobenzene column bottoms are volatile and toxic and are produced at an estimated 350 kkg of waste/per yr. (Appendix B) The composition of the waste streams is not known, although nitrobenzene, benzene, various sulfates and nitro-substituted aromatics are believed to be present.

C.2.2 Petroleum Refining

Top surface skimmings from dissolved air flotation (DAF) units are ignitable and volatile. Their estimated average oil content is 12.5 percent. The waste stream is considered toxic because of the trace metals and toxic organics present. An estimated 952,560 kkg of DAF skimmings were disposed in 1979 (Appendix B).

C.2.3 Electroplating and Metal Finishing

Wastewater treatment sludges from electroplating and metal finishing contain cyanide, alkalies, acids, chromium and heavy metals in

significant quantities. The generation rate estimated for 1979 is 56,398 kkg dry weight, and the waste is volatile and toxic.

C.2.4 Textile Manufacturing

Wastewater treatment sludges from woven fabric dyeing and finishing operations in the textile industry contain heavy metals, chlorinated organics and dyes in significant quantities. The sludge was generated at an estimated 13,700 kkg dry weight for 1977 (Appendix B) and is ignitable, volatile and toxic. Constituents and disposal methods for this waste stream are currently being investigated by the industry, but results were not available in time for inclusion in this study.

C.2.5 Paint Manufacturing

Liquid wastes from solvent-thinned trade sales paint production are generated at 101,366 kkg/yr (Appendix B). The waste stream is ignitable, volatile and toxic and is generally disposed on land. The waste stream contains pigments and solvents and may contain heavy metals such as cadmium, selenium, mercury, lead and chromium depending on type and color of paint produced.

C.2.6 Primary Batteries

Although a relatively new battery, the lithium-sulfur dioxide cell will present challenging treatment, storage and disposal problems as production increases. The quality control rejection rate for this battery is estimated at 1-3 percent by weight of plant production. Produced in steel containers, battery components include lithium metal (reactive with moisture) and volatile organic solvents. Some of the components are toxic.

C.2.7 Commercial Explosives

Red water from TNT manufacture is ignitable, reactive and volatile. A key component of this waste is TNT, which has a high inhalation toxicity. The waste is normally disposed as a liquid.

C.2.8 Military Explosives

Bulk propellants, explosives and pyrotechnic munitions exhibit high volatility, reactivity and ignitability. The waste stream is a liquid.

Pink water from LAP operations, including manufacture of Composition A, is ignitable and volatile. The key components are nitro compounds. Toxicity is not known. The literature cites carbon absorption and subsequent incineration or regeneration of the carbon for treatment of the waste stream as methods of disposal.

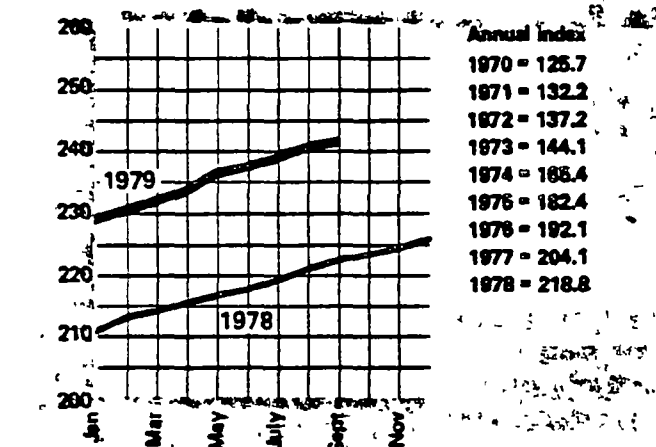
In summary, the steps followed in choosing waste streams for further study included developing a data base list of approximately 300 waste streams, developing a selection methodology and using the methodology to select 13 waste streams for study. Detailed study of waste streams provided information on treatment, storage and disposal techniques and allowed further evaluation of the cost and environmental impact of implementing these techniques.

APPENDIX D

UPDATING COSTS

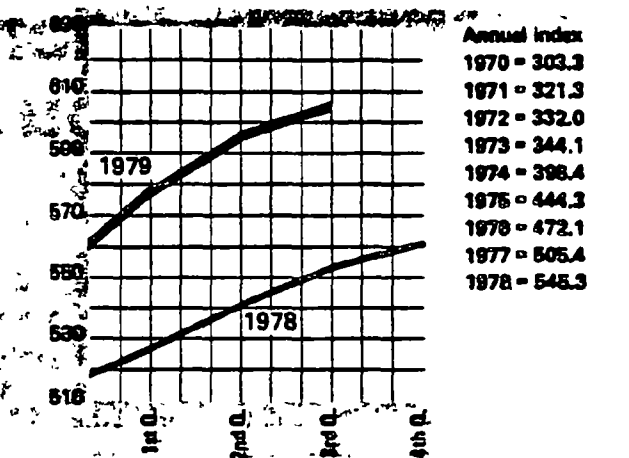
D. UPDATING COSTS

Cost information reported in literature varied in age from 1973 dollars to 1978 dollars. A means of converting cost is given in the accompanying chart. To obtain 1978 costs, a multiplier for the costs given in the report is obtained by first dividing the 1978 annual index by the index for the year given in the text. The multiplier is then applied to costs given in the text to update costs to 1978.



CE plant cost index	Sept. 79	Aug. 78	July 78	Sept. 78
(1957-59 = 100)	prelim.	rev.	final	final
Equipment, machinery, supports	263.1	240.7	239.2	221.8
Construction labor	194.3	195.9	194.7	188.2
Buildings	231.5	230.0	228.9	214.3
Engineering & supervision	193.4	190.2	187.5	162.0
Fabricated equipment	265.5	264.2	262.6	243.3
Process machinery	264.7	262.3	261.5	231.9
Pipe, valves & fittings	304.3	302.5	301.1	273.1
Process instruments	235.9	233.4	232.3	218.3
Pumps & compressors	285.4	284.5	281.2	258.8
Electrical equipment	185.4	184.2	182.5	169.5
Structural supports & misc.	275.0	274.5	273.4	253.5

NOTE: Details and subcomponents of the index are described in Chemical Engineering, Feb. 18, 1965, pp. 140-152. (Reprints are available No. 132 on the reprint order form in the back of each issue.) For reissuing and updating, see issues of Aug. 25, 1966, May 5, 1969, Nov. 23, 1972, Apr. 28, 1975 and May 8, 1978.



M&S equipment cost index	3rd Q. 1979	2nd Q. 1979	1st Q. 1979
(1929 = 100)	608.4	593.3	577.0
Process industries, average	615.4	601.5	585.9
Gases	620.6	606.6	591.9
Chemical	608.0	592.0	576.5
Clay products	602.2	587.5	573.7
Glass	578.7	565.6	550.1
Paper	617.2	603.9	586.7
Petroleum products	643.6	630.1	614.1
Rubber	642.3	627.4	610.8
Related industries, electrical power	583.3	570.7	550.7
Mining, milling	625.7	613.4	599.3
Refrigerating	710.8	693.8	675.8
Steam power	602.7	588.5	573.7

Figure D.1 Curves for Updating Costs for Treatment, Storage and Disposal